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Agricultural Biomass Based Potential Materials

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Editors are honoured to dedicate this book to the Universiti Putra Malaysia (UPM), the premier institute of higher learning and research.

Preface

Agricultural biomass is abundant worldwide and it can be considered as alternative source of renewable and sustainable materials which can be used as potential materials for different applications. Despite this enormous production of agricultural biomass, only a small fraction of the total biomass is utilized for different applications. Industry must be prepared to take advantage of the situation and utilize the available biomass in the best possible manner. Agricultural biomass such as natural fibres has been successfully investigated as a great potential to be used as a renewable and sustainable materials for the production of composite materials. Natural fibres offer excellent specific properties and have potential as outstanding reinforcing fillers in the matrix and can be used as an alternative material for biocomposites, hybrid composites and pulp and paper industries. Natural fibre based polymer composites made of jute, oil palm, flex, hemp, kenaf have a low market cost, are attractive with respect to global sustainability and find increasing commercial use in different applications. Agricultural biomass based composites find applications in a number of fields viz., automotive industry and construction industry such as for panels, frames, ceilings and partition boards, structural applications, aerospace, sports, recreation equipment, boats, office products, machinery, etc. Future research on agricultural biomass natural fibre-based composites is not only limited to its automotive applications but it also requires to explore its application in aircraft components, construction industry, rural housing and biomedical applications. In this book we will cover chemical, physical, mechanical, thermal, electrical, flame retardancy and biodegradability properties of agricultural biomass based composite materials and its different potential applications.

We wish to express our gratitude to all the contributors from all over the world for readily accepting our invitations for not only shearing their knowledge but also for admirably integrating their proficiency on scattered information from diverse fields in composing the chapters and enduring editorial suggestions to finally produce this venture that will hope be a success. We greatly appreciate their commitment.

We thank Springer team for their generous cooperation at every stage of the book production.

Khalid Rehman Hakeem
Mohammad Jawaid
Othman Y. Alothman

Foreword

Agricultural biomass has stirred much interest worldwide due to its tremendous availability; however, only a small fraction of the total biomass is utilized for different applications. The publication of the chapters appearing in this book represent a cooperative effort of various individuals from different background. The book reviews the multiple uses of agricultural biomass and reports on basic characteristics and performance in various potential applications such as construction materials, automotive parts, biomedical, bioresin and bioenergy.

This book will be very helpful not only to scientists and engineers who are interested in converting natural fibres and other biomass into higher value-added products but hopefully also to a variety of people in other disciplines either in the academic world, in industry or in the area of policy.

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Dr. Othman Y. Alothman PhD is currently an Associate Professor at the Department of Chemical Engineering, College of Engineering, King Saud University (KSU), Riyadh, Saudi Arabia. He is also the Dean of Graduate Studies, Saudi Electronic University, Riyadh since May 2014. Previously he also worked as Vice Director of the Translation Center, KSU, Riyadh. He has completed his PhD from University of Manchester, UK. He teaches Fluid Mechanics, FORTRAN Programming, and Polymer Properties and Rheology to undergraduate and postgraduate students. He has supervised three M.Sc students. Currently he is working on a number of research projects in the field of polymer blending and characterization. So far he has published more than 15 international ISI journal papers and 4 translated books and book chapters. He is also a reviewer of a number of journals. He is also a member of Polymer Processing Society (PPS) and the society of Plastics Engineering (SPE).

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Potential Utilization of Kenaf Biomass in Different Applications

N. Saba, M. T. Paridah, M. Jawaid, K. Abdan and N. A. Ibrahim

Abstract Kenaf is regarded as an industrial crop, and belongs to family Malvaceae along with hibiscus (*Hibiscus hibiscum* L.), hollyhock (*Althaea rosea*), cotton (*Gossypium hirsutum* L.), and okra (*Hibiscus esculentus*), and is grown commercially in different countries including Malaysia. It is undoubtedly the utmost important cultivated plant for fiber globally, next to cotton, a short day, herbaceous 4000 years old, original crop which is endemic to ancient Africa. It has a precise promising prospect because of its long fibers derived from outer fibrous bark, the bast with great potential in the biocomposite industry. The plants possess a wider range of adaptation to environments, climates, soils, and are rich sources of cellulose compared to any of other fiber plant in profitable manufacture industry. Kenaf reveals a virtuous source of high and improved quality cordage fiber which can be processed into a variety of goods such as fiber and particle boards, fiber-reinforced plastic components, pulp and paper, chemical absorbents, and many others. The tensile strength and modulus of solo kenaf fiber is found to be as high as 11.9 and 60 GPa, respectively. All the components of kenaf plant, leaves, seeds, bast fiber, and core, are of industrial importance. The countless variabilities in the utilization of kenaf only because of its appropriateness as construction material (such as boards of different densities, breadths, along with fire and insect resistance), adsorbent, textile, livestock feed, and fibers in original and reprocessed plastics are demonstrated by

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many recent studies and research efforts are increasing nowadays. Numerous other kenaf fiber products are also being developed and marketed. Thus, it is important to gather the information of its constituents and the matters governing the composition of the plant.

Keywords Kenaf (*Hibiscus cannabinus* L.) · Natural fibers · Composite · Antioxidant · Adsorption · Geotextiles

Introduction

In the global market, kenaf is regarded as an industrial crop. Kenaf (*Hibiscus cannabinus* L., Malvaceae) is an annual warm-season crop, relative to cotton, and from historic times has been suggested by many researchers for use as both fodder crop and fiber (Taylor 1992; Webber 1993). Kenaf is the traditional crop in Thailand, certain areas of Africa, India, and Bangladesh, and to a certain level in Southeast Europe. It has been grown for over 4000 years in Africa, and its parts have been used for animal diet, food, handicraft manufacture, and fuel by inherent communities (Dempsey 1975). However, numerous types of kenaf crops nowadays are found to be cultivated easily and widely in numerous countries. Moreover, the major farming areas are throughout India, China, and several new countries, including Texas, USA (seed farms), Tamaulipas, Mackay, Australia, and Mexico (Chan and Ismail 2009). Kenaf has a growing demand from Australia, Europe, Japan, and Korea. In the past decade, the crop has received an increased attention by EU as a high-yielding "non-food crop" for fiber production and particularly for the newsprint paper pulp and other paper products industry (Clark et al. 1962; White et al. 1970), as it is fast growing and high yielding and pulp can be obtained easily (Clark et al. 1962). Kenaf also gets more familiarized into arid regions (Francois et al. 1992) and is progressively getting mature in other dry, marginal soils, light-textured, under water-limited situations. It is regarded as a potential crop to substitute tobacco. Currently, about 95 % of total kenaf production belongs to India, Thailand, and China (Tahery et al. 2011). Based on research findings, kenaf is regarded as Malaysia's next industrial crop due to its technical, practical, and commercial potential. Figure 1 shows the kenaf plantation in Malaysia. In Malaysia, it was first presented in the early 1970s and was highlighted in the 1990s as the substitute and inexpensive important basis of material for manufacturing panel products such as particleboard, fiberboard, and textiles, and as a source of fuel (Abdul Khalil et al. 2010).

Kenaf is a dicot and has two different kinds of fibers—long bark fibers, constituting 35 % of its fibrous portion, and short core fibers, determining the rest (Manzanares et al. 1997). Kenaf has a straight, single, and branchless stem. Kenaf stalk is composed of an internal woody core and a superficial fibrous bark neighboring the core. Bast fiber is the fiber derived from the superficial fibrous bark (Edeerozey et al. 2007). Materially, their seeds are comparatively smaller (6 mm long × 4 mm wide), black or dark brown in color with a triangular shape in acute angles (Chan

Fig. 1 Showing the kenaf plantation in Malaysia

and Ismail 2009). Kenaf leaves are lobed or unlobed reliant on position and variety; flowers are usually monoecious and fruit is a capsule of 2 cm diameter containing numerous seeds and takes about 40–50 days for maturing (Monti and Zatta 2009). Moreover, kenaf plant has a long effective taproot system and a wide-ranging lateral root system which is moderately deep ensuring the plant to be drought tolerant. Greater moisture is the major requirement, thus about 23.6 in. of water is highly important during its growing period of about 120–150 days (Anonymous 2012). It is quite hard, thus it is unaffected to the effects of robust winds and drought. Like hemp, it is a diverse fiber; however, unlike hemp it does not possess the stigma of marijuana (Anonymous 2014). Kenaf does not require any chemical pest control, or toxic or synthetic products during its growing cycle, thus growing kenaf profits the ecosystem. Kenaf plant collects poisonous elements, such as heavy metals from the earthy soil. Kenaf plant shows absorption of CO_2 from the atmosphere compared to any other crop—about 1.5 t of CO_2 is needed for a production of 1 t of dry matter of kenaf (Fig. 2). Thus, every hectare of kenaf consumes 30–40 t of CO_2 for each growing cycle (Eshet 2014).

Kenaf is one of the significant fast-growing crops, producing two harvests annually and can yield a profit 15–20 t per hectare (dry-weight basis) with the appropriate seedlings and seeds. Reliant on the yield, 3–5 t (20 %) consist of fiber. Maturity is about 4–4.5 months (Chen et al. 2011). Compared to that of conventional trees, the photosynthesis rate of kenaf is considerably much greater. Kenaf's environmental sustainability is deceptively perfect related to other predictable annual crops such as sugar beet and maize (lesser amounts of fertilizers required) (Monti and Zatta 2009). It is considered as one of the pillars among export commodities for the country and a vital source for employment and foreign exchange earnings. Thus, it is an economically important crop of the country as it has a wide range of uses mostly in the fabrication of currency notes, bags, cigarette filter paper, meat casing, cable insulation, and a host of other industrial products. However, like every other crop, kenaf production requires some agronomic practices, especially soil nutrient amendment, to improve its productivity and biomass quality. Moreover, kenaf has

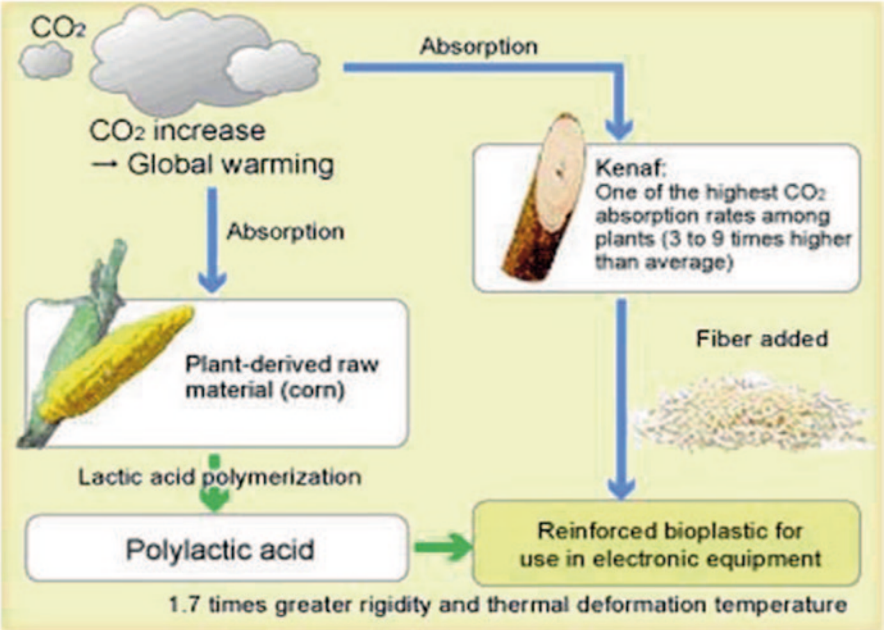
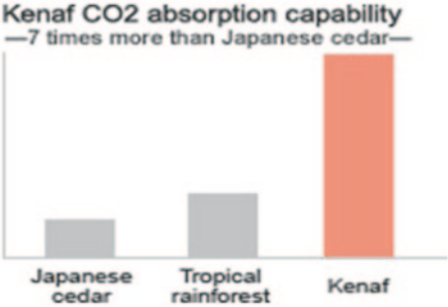


Fig. 2 Shows the absorption of CO_2 from atmosphere http://www.kenafibers.com/users_nec.html

been cultivated widely because of its tendency to captivate phosphorus and nitrogen present in the soil; it can accumulate carbon dioxide at a significantly high rate than that of Japanese cedar shown in Fig. 3. Natural fibers such as banana, hemp, flax, oil palm, kenaf, jute, sisal, etc. have gained significant attention in the past few years due to their environmentally green and renewable nature (Abdul Khalil et al. 2012). Natural fibers are primarily classified on the basis of their origin, either belonging from animals, minerals, or plant fibers. Natural fibers are renewable materials and also possess the ability to be reprocessed (Jawaid and Abdul Khalil 2011). Natural fiber itself consists of helically wound cellulose microfibrils, embedded in amorphous lignin matrix, and hence resembles that of naturally occurring composites. Cellulose (a-cellulose), lignin, pectins, hemicellulose, and waxes are the major

Fig. 3 Kenaf CO_2 absorption capability http://www.toyota-boshoku.com/global/about/development/eco/kenaf



components of natural fibers. Generally, these fibers are extremely hydrophilic in nature. This water-loving feature leads the water uptake and the formation of hydrogen bonds between water and fiber. The required stiffness and strength of the fibers are delivered by the hydrogen bonds and other similar linkages. Natural fiber properties mostly depend on conditions of plant growth, making them highly variable. A foremost disadvantage of natural (plant) fibers compared to synthetic fibers is a variety of dimensions, their nonuniformity, and mechanical properties; this is also in the case of individual natural (plant) fibers from the same cultivation (Bismarck et al. 2005). However, treatment with chemicals such as maleic anhydride, silane, and acetic anhydride improves the fiber dimensional stability properties (Wambua et al. 2003). Researchers found that these fibers are not applicable for aerospace applications and high-performance military due to their low strength, environmental sensitivity, and lower moisture resistance resulting in deprivation of stiffness and strength of natural fiber-reinforced composites. However, all these shortcomings can be overcome only by effective hybridization of lignocellulose fiber with perfectly proper synthetic fiber or natural fiber (Abdul Khalil et al. 2012).

Physicochemical Characteristics of Kenaf Fiber

Physical Properties of Kenaf Fiber

Kenaf is well recognized to have both ecological and economic advantages instead of cellulosic nature. It can grow in 3 months (after sowing the seeds), under an extensive range of climate conditions, up to a height of more than 3 m and a width diameter of 3–5 cm (Aziz et al. 2005). Kenaf (*H. cannabinus* L.) stem principally comprises two types of materials: the long fiber (bast) and the short, woody-like fiber (core), present at the innermost part of the kenaf stem. The bast to core ratio is almost 30:70 (w/w). These fibers are different considerably in anatomical structure, fiber, and their appearance (Voulgaridis et al. 2000). Fiber quality and its superiority are relevant with its characteristics like capability of uptaking humidity, biodegradability, no allergic and harmful substance effects, and good air permeability. Figure 4 shows transverse sections of kenaf cell wall fibers, showing hollow tube of cell wall with four different layers: one primary cell wall, three secondary cell walls, and a lumen which opens in the middle of the microfibril (Abdul Khalil et al. 2010). The microfibril size, chemical content, and extractive percent of kenaf stem are shown in Table 1.

Kenaf core fibers exhibited countless variability in size, shape, and structure of the cell wall fibers. Figures 4b, c are the transverse sections of kenaf bast fibers. The cell wall fibers are polygonal to round in shape. The kenaf core and bast fiber's average lumen diameter is 6.7 and 2.8 µm, respectively. This shows that kenaf core can be a potential fiber for pulp and paper industries, thus substituting wood and many other natural fibers as a raw material (Abdul Khalil et al. 2010). The pit structure can be observed undoubtedly in kenaf core fiber (Fig. 5). However, in other

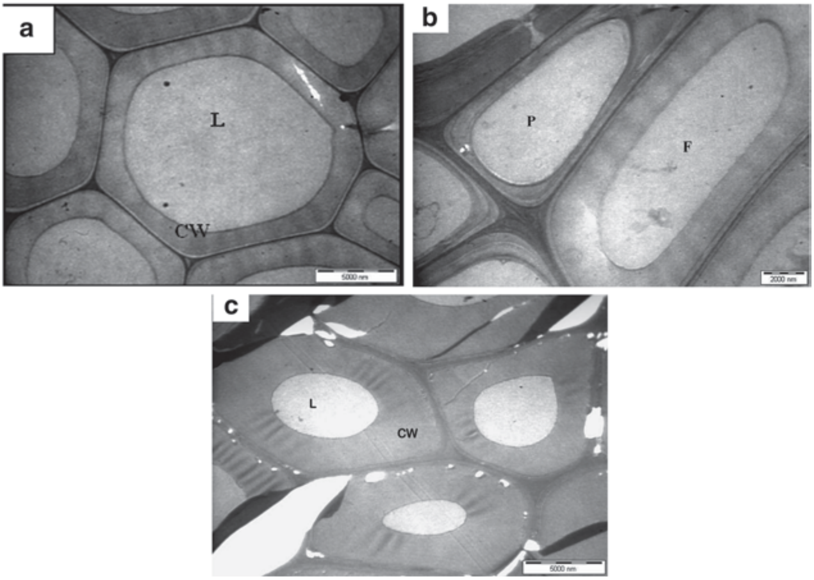


Fig. 4 Transmission electron micrograph of ultrathin section of kenaf fibers: **a** kenaf core fibers showing cell wall and lumen, **b** transverse section of core fibers, **c** transverse section of kenaf bast fibers. Cell wall structure stained with uranyl acetate and lead citrate. Scale bar = 5000 nm in. (**a**) and (**c**), 2000 nm in (**b**). *CW* cell wall, *L* lumen, *F* fiber, *P* parenchyma (with permission)

Table 1 Microfibril size, extractive percent, and chemical content of kenaf stem. (Source: Akil et al. 2011; Abdul Khalil et al. 2010)

Nonwood fibers	Style1 bark	Style4 core	Kenaf whole	Softwood	Hardwood
Fibril length, *L* (mm)	2.22	0.75	1.29	–	–
Fibril width, *W* (µm)	17.34	19.23	22.1	–	–
L/*W*	128	39	–	–	–
Lumen diameter (µm)	7.5	32	12.7	–	–
Cell wall thickness (µm)	3.6	1.5	4.3	–	–
Extractive (%)	5.5	4.7	6.4	0.2–8.5	0.1–7.7
Cellulose (%)	69.2	32.1	53.8	30–60	31–64
Lignin (%)	2.8	25.21	21.2	21–37	14–34
Hemicellulose (%)	27.2	41	87.7	60–80	71–89
Ash content (%)	0.8	1.8	4.0	< 1	< 1

fibers, pits are seldom realized, and they are variable in their dimension. Average bast fiber's length is 2.5 mm, comparable to different species of southern pine and the core length is 0.5 mm resembling hardwoods. This composition provides a required balance for several other pulp and paper applications, stimulating constant attention, research and development in the industries (Schroeter 1994).

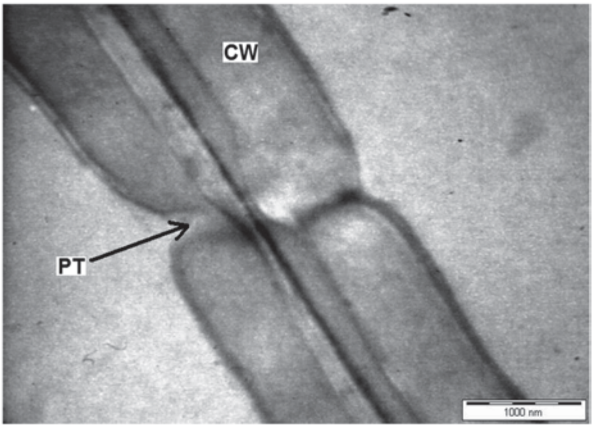


Fig. 5 Transmission electron micrograph of ultrathin section of kenaf fiber. Transverse section of pit fiber wall. Scale bar = 1000 nm. *CW* cell wall, *PT* pit. (With permission)

Chemical Composition

Kenaf Fiber

Generally, kenaf fibers like other natural fibers consist of 60–80 % cellulose, 5–20 % lignin (pectin), and up to 20 % moisture (Mohamed et al. 1995; Nishimura et al. 2002). The composition and products of kenaf constituents have been affected by several aspects including cultivar, planting date, plant populations, length of growing season, photosensitivity, and plant maturity (Ayerza and Coates 1996). Fiber is composed of cellulose entrenched in a matrix of hemicellulose and lignin, resembling the reinforced composites. Hemicellulose is accountable for biodegradation, moisture absorption, and thermal degradation of the fibers, whereas lignin (pectin) is quite thermally stable and responsible for the ultraviolet (UV) degradation of the fibers (Akil et al. 2011). Kenaf fibers were fairly dissimilar with respect to their chemical constituents (Abdul Khalil et al. 2010). Shorter and thicker core fibers are poor in slenderness ratio, thus reducing the tearing resistance intensely (Ververis et al. 2004). However, fibers of core are extremely flexible with a good Runkel ratio as shown in Table 2 and lower felting power thus can supplement the developed mechanical strength of the bark fibers (Khristova et al. 1998) and Table 3 shows the density and cost of glass fibers and natural/bio-fibers.

Kenaf Seed Oil

Oil composition of kenaf seed is alike to cottonseed apart from the existence of gossypol (a toxic phenolic pigment) in cottonseed oil (Bhattacharjee et al. 2007). Soxhlet extraction is most commonly used for the kenaf seed oil extraction, rich in unsaturated fatty acids (76.0–81.5 %) with linoleic acid being the major fatty acid (45.9 %) in the oil (Mohamed et al. 1995). Besides this, the oil is also rich in phytosterols and phospholipids (0.9 and 6.0 % of the oil, respectively).

Table 2 Fiber dimensions along the stalk/branch of the kenaf plant. (Source: 1998)

Fiber dimension	Stalk height/branch length (%)	Kenaf
Length (mm)	10	2.30[a]
	50	2.33
	90	2.37[b]
Diameter (Î¼m)	10	22.09
	50	21.65
	90	21.52
Lumen diameter (Î¼m)	10	11.03
	50	10.69
	90	10.9
Cell wall thickness (Î¼m)	10	4.53
	50	4.37
	90	4.32

[a] Bark
[b] Internodes

Table 3 Density and cost of glass fibers and natural/bio-fibers. (Zampaloni et al. 2007, with permission)

Fiber	Density (g/cm^3)	Cost (kg^{-1})
Flax	1.4–1.5	$ 0.40–0.55
Hemp	1.48	$ 0.40–0.55
Jute	1.3–1.45	$ 0.40–0.55
Cotton	1.5–1.6	$ 0.44–0.55
Kenaf	1.4	$ 0.40–0.55
Ramie	1.50	$ 0.44–0.55
E-glass	2.5	US $ 2
S-glass	2.5	US$ 2
Pineapple leaf	1.53	$ 0.40–0.55

Mechanical Properties

Most of the properties of natural fibers are extremely variable and governed by conditions and situations of growth. So it is quite challenging to get the similar mechanical properties even after repeat testing. Mechanical properties such as modulus and tensile strength are correlated to the internal structure and composition of the fibers (Abdul Khalil et al. 2012). Natural fibers' properties influenced by their cellulose and its crystalline association or organization determine the mechanical properties (Bledzki and Gassan 1999). Researchers also found that the tensile strength and Young's modulus of plant fiber rise with increasing cellulose content of the fibers (Aji et al. 2009). Table 4 shows the comparison of various mechanical and physical properties of natural and synthetic fiber. Moreover, like other natural fibers kenaf fibers have poorer thermal resistance and specific modulus and are cheaper

Table 4 Comparison of mechanical and physical properties of natural fibers versus synthetic fibers. (Source: Misnon et al. 2014, with permission)

Fiber	Density (g/cm^3)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Length (mm)	Diameter (μm)
Bamboo	0.6–1.1	140–800	11–32	2.5–3.7	1.5–4	25–40
Jute	1.3–1.49	320–800	8–78	1.5–1.8	1.5–200	20–200
Kenaf	1.4	223–930	14.5–53	1.5–2.7	–	–
Flax	1.4–1.5	345–2000	27.6–103	1.2–3.3	5–900	12–600
Sisal	1.33–1.5	363–700	9–38	2.0–7.0	900	8–200
Hemp	1.4–1.5	270–900	23.5–90	1.0–3.5	5–55	25–500
Coir	1.15–1.46	95–230	2.8–6	15–51.4	20–150	10–460
Ramie	1.0–1.55	400–1000	24.5–128	1.2–4.0	900–1200	20–80
Abaca	1.5	400–980	6.2–20	1–10	–	–
Cotton	1.5–1.6	287–800	5.5–12.6	3.0–10.0	10–60	10–45
Bagasse	1.25	222–290	17–27.1	1.1	10–300	10–34
E-glass	2.5–2.59	2000–3500	70	2.5	–	–
Aramid	1.4	3000–3150	63–67	3.3–3.7	–	–
Carbon	1.4	4000	230–240	1.4–1.8	–	–

as compared to synthetic fibers. Kenaf bast fiber has considerably higher flexural strength mutually associated with its outstanding tensile strength, making it perfect material for a variety of collection of extruded, molded, and nonwoven products. They are tough and hard enough to be a probable reinforcement fiber in polymer composites. It was concluded that kenaf fiber has a strong interfacial adhesion with polymers. All these properties make kenaf fibers superior over other natural fibers such as oil palm (Yousif and El-Tayeb 2007, 2008), sugarcane (El-Tayeb 2008) and jute (Chand and Dwivedi 2006). Furthermore, research shows that alkalizing the kenaf fibers offered improved flexural strength, impact strength, flexural modulus, and strength modulus for polymeric composites (Nishino et al. 2003; Liu et al. 2007; Huda et al. 2008). Chemical treatment through acetic anhydride, silane, and maleic anhydride also shows improvement in the properties of fibers such as dimensional instability. Table 5 shows the chemical composition of the kenaf fibers after different treatments (Karimi et al. 2014) (Table 3).

Integrated Industrial Applications of Kenaf

The consideration and utilization of kenaf have been the matter of many investigations, studies, and projects since the late 1950s to explore it as an industrial crop. Currently, the industrial use of kenaf fibers endures to expand its application from its ancient and historic appeal as a cordage crop (twine, rope, and sackcloth) to a variety of novel tenders including building materials, absorbents, paper products, and livestock feed, enabling it as a major industrial crop (Webber et al. 2002).

Table 5 Chemical composition, diameter, and average diameter range of the kenaf fibers after different treatments. (Source: Karimi et al. 2014)

Different treatments	Diameter range (µm)	Average diameter	Component (%)		
			Cellulose	Hemicelluloses	Lignin
RF/no method	15.5–148	55.18	61.2±0.8	18.5±1.5	12.9±0.7
	49.9–115.5	82.7	–	–	–
	10–80	–	–	–	–
UBP/method	2.09–22.9	11.37– 40.7	82.3±0.6	11.2±1.5	2.6±0.2
Alkali treatment	20–90	–	–	–	–
	20.7–60.7	–	–	–	–
BP/method	1.94–21.1	10.56	91.8±0.9	4.9±0.4	0.5±0.1
Bleaching process	8–14	11	–	–	–
	7.4–11	9.2	–	–	–
	8.58–12.68	10.63	–	–	–

BP Bleaching process; *RF* Water retted Kenaf bast fibers; *UBP* unbleached pulp

Figure 6 illustrated diverse application of kenaf in enhanced bio-composites and lignocellulosic materials (Chen 2011). Moreover, the residues from its different industrial processes can be utilized as energy sources. Kenaf's inner woody core fibers possess high absorbency and many researchers have investigated its uses in diverse fields such as seats for the automotive industry, sewage sludge composting as a bulking agent, particleboard in dashboards (Webber 1994), acting absorbent (Goforth 1994), as animal bedding and poultry litter (Tilmon et al. 1988), as a potting soil amendment (Webber et al. 1999), and effectively used for toxic discarded waste removal such as oil spills on water, waste cleanup, and the removal of chemically adulterated soil's composition (Webber and Bledsoe 2002). Kenaf bast fibers have noteworthy mechanical properties and are thus used in a variety of applications such as burlap bags, twine, sacks, ropes, canvas, cordage, carpets, industrial and commercial fabrics, and plastics (Cheng et al. 2004). Kenaf fiber is nowadays regarded as a standard and typical raw material in the production of particleboards, animal feeds, paper, textiles, and fuel; some varied applications of kenaf fiber are shown in Fig. 7 (Alexopoulou 2013). However, kenaf products' prices are influenced by the procedure, specifications, and conditions. Novel attractiveness of kenaf and its products aretheir eco-friendly, strong, and very light nature (Chen et al. 2011). Table 6 display different application of kenaf plant and its fibres in pulp paper, panels, traditional cottage, adsorption agent, packaging materials, natural fuels, and animal fodder and feeds.

Pulp and Paper

Kenaf is evidently a promising natural fiber, basic source for both, textiles and attire and industrial applications. Kenaf shows significant advantages, having small

Fig. 6 Diverse and multiple uses of kenaf across industries (New Lightweight and Nanotechnology Enhanced Bio-composites from Lignocellulosic Materials, http://www.greenprospectsasia.com/content/fibrous-kenaf, Accessed on 24 June 2014)

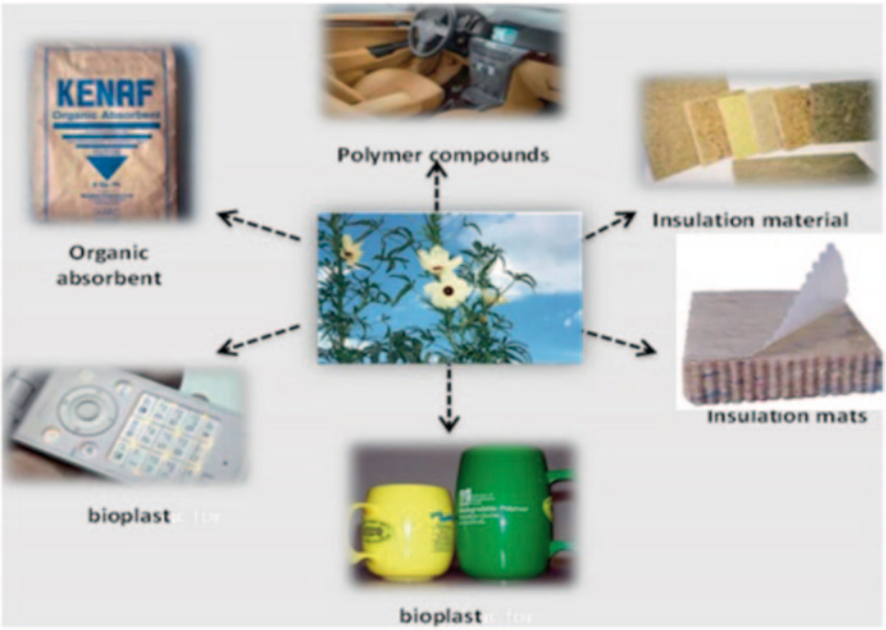


Fig. 7 Versatile kenaf applications. KENAF (*Hibiscus cannabinus* L.) agronomy and crop management http://www.fibrafp7.net/Portals/0/05_Alexopoulou.pdf

Table 6 Varied applications of kenaf plant and its fibers. (Source: http://www.kenaf-fiber.com/en/infotec-tabella4.asp. Accessed on 15th Sept, 2014)

Pulp paper and cardboard	Panels	Traditional cordage	Adsorbent agent	Packing material	Natural fuels	Animal fodder and feed
Variety of writing and printing paper	Variety of decorative wall panels	As padding material	For animal litter	For wrapping gifts and handicraft products	Kenaf biomass used for burning	Green plants used as fodder
Used to prepare fine coated paper	Used to make Pressed board	To make string, rope, and cord	For making filtering products	To make inert, natural, biodegradable filler	Production of ethyl alcohol	Production of alcohol from the byproducts of animal litter
Variety of tissue paper, handmade art paper	Compressed insulating panels	Materials for mattresses and furniture	To make compost from sullage	Bags and fabrics	Production of other chemical products by lingocellulosic conversion technologies	For wood fungus inoculation
Linen for roofs in felt paper	Interior panels for cars and planes	For instant lawns	To clean industrial flooring	For hamburger wrapper	Production of ethyl alcohol from animal litter	For the production of edible mushrooms
Wafer board, flakeboard, particleboard, fiberboard	Fine moldable fiber mattresses	For controlling terrain erosion	Cleaning of liquid leakages from industrial plants	–	Used to derive cellulose kenaf fibers	Use of seeds for the production of oil and extraction panels, for reducing cholesterol and heart diseases
Super –calendered writing and printing paper	To make rigid molded products for industrial applications	–	Used in horticulture and for flower growing products	–	Black liquor, a by-product of making paper from kenaf	To prepare the middlings for bird feeds
To make coarse cloth (similar to that made from jute)	–	–	Core used for soil remediation (natural bioremedation)	–	Used for both electricity/heat and second-generation biofuels	For poultry and cat litter

harvestable period and nonchlorinated bleaching techniques employed for its diverse applications. Kenaf has been regarded as an ultimate source of fiber for paper and pulp industries because of its suitable and sufficient physical strength properties. Unlike hemp, whose longer fibers are most commonly used in textiles and ropes, kenaf's outer stalk has shorter fibers similar to the best softwood fibers and thus its applications are limited in making papers and composites (Loynd 2010; Ververis et al. 2004). The kenaf core particles are also explored as absorbents in paper products like wipes, tissues, and hygienic products (Zaveri 2004). Kenaf fibers' pulping (bast and core) also benefits the atmosphere as this procedure requires smaller amount of energy and chemicals compared to the other typical pulping procedures employed for woody fibers. The makeable greater lumen diameter and negligible fiber thickness provide better pulp mat formation in the paper making process; kenaf cell wall lumen is the best in pulp and paper processing techniques (Abdul Khalil et al. 2010). Compared to hardwood, core pulp has a greater tensile and burst strength but lower tear strength (Kaldor et al. 1990). Bark fibers deliver good slenderness ratio compared to those softwoods and undoubtedly to most hardwoods (Ververis et al. 2004). Kenaf bark fiber papers have improved mechanical strength and thus are appropriate for writing, printing, wrapping, and for packaging material (Saikia et al. 1997; Neto et al. 1996). Nowadays, the whole stems are being used to produce a pulp of high strength and better quality. Much more significant practical and economic advantages appeared by using the whole stem as it is simple, easy to process, and devoid of the supplementary separation expenses. Kenaf paper is longer lasting, whiter, stronger, resistant to staining, and has better ink adherence compared to conventional tree paper (Han et al. 1995; Kaldor et al. 1990). The kenaf virgin fiber is also applied for increasing reprocessed paper excellence and paper power or strength (Webber et al. 2002). Excellent quality of newsprint paper could be made from whole kenaf stalks and kenaf pulp by mixing with conventional or traditional softwood pulps producing a wide range of paper grades (Kugler 1988). Furthermore, kenaf also reduces the cost and labor compared to the process of making pulp from wood. Thus, the growing industry of kenaf paper leaves forests undamaged while dropping energy consumption and industrial pollution, leading to both ecological and commercial benefits (Anonymous 1994).

Magnetic Paper

Recently, researchers demonstrated the use of unbleached kenaf fibers for making magnetic paper using chemical co-precipitation method through ferrous and ferric compounds. It involves the precipitation and stacking of nano-sized ferrite particles into the lumen of the kenaf fibers. Kenaf fibers with large lumen get integrated with magnetic constituents apt for making paper for multiple printing papers, information storage, electromagnetic shielding, etc. The cobalt compound for this type of co-precipitation is also being observed. Degree of loading of the kenaf fibers increases the magnetic properties of the papers, which in turn increases with temperature and stirring speed. Moreover, these fibers form good fiber–fiber bonding and the chance of loss of paper strength owing to the filler is reasonable (Chia et al. 2008).

Medium Density Fibreboard (MDF) Panels

MDF manufacturing from Kenaf bast fibres have several application in non-structural products. MDF panels are influenced by different factors including resin content, resin type, and moisture content on their physic mechanical properties are well established. Research shows that resin type and moisture content have noteworthy effect on the mechanical properties while resin content is the least significant (Ali et al. 2014). These panels are often used in a variety of nonstructural applications such as furniture, laminated floors, paneling, cabinet doors, and underlay of carpet floors (Bowyer et al. 2007).

Animal Bedding and Poultry Litter

The use of waste core particles as absorbents in animal bedding material is their most important and explored possibility. Kenaf core fibers are extensively used as bedding material for horses, cattle, poultry, and rodents (Lips et al. 2009). These absorbent materials fulfill some requirements of animals such as perfect absorption features for urine, low dust content, nonedible, and nonirritating particles for their hoofs and skin (K.E.F.I. 2006). Absorption values and water-retention characteristics for kenaf core particles are found to be up to 12 g water/g of small milled particles (38–1000 µm) and it competes with other natural absorbents and commercial bedding materials like flax shaves, wood shavings, straw, and hemp core. Superior water-retention values are shown by the bigger kenaf core particles; however, this product contains higher amount of bast and coarse fibers found to be a perfect animal bedding material. Moreover, bigger kenaf core particles have the significant water-retention properties compared to the marketable materials at both high and low centrifugal forces. According to Lips et al. (2009), wood shavings absorb water 2.4 times of its own weight whereas kenaf core shows absorbency more than wood shavings. Under high pressure, kenaf possesses higher water holding or retaining capacity than wood shavings (Lips et al. 2009). Kenaf pith shows high water absorption features due to its cushioned structures and absorbs 20 times more water than its own weight. Water-retention value even after high centrifugal forces is five times (Lips et al. 2009). Kenaf bedding is carried in masses to ranch stock stores and farm providing in wholesale to large consumers such as zoos, poultry, and farm stables (Zhang 2003). In the USA, straw and wood shavings are regarded as inferior bedding absorbing materials than kenaf core (Lips et al. 2009).

Microfiltration Membranes

The possibility of using kenaf (*H. cannabinus* L.) nonwoody plant as the elementary and alternative material for making cellulose acetate membranes applied in pressure-driven processes used in microfiltration processes is being studied nowadays (Radiman et al. 2008). Hardwood is usually used for making cellulose acetate membranes, but the consideration of using kenaf provides another alternative resource from nonwood plants. The acetylated kenaf membrane displays a more spongy arrangement and higher Young's modulus value compared to that obtained from commercial cellulose acetate because of its lower molecular weight. Kenaf (nonwoods) is lesser in lignin and higher in silica and ash than the hardwoods with comparable cellulose content (Barba et al. 2002). Thus, fewer chemicals are involved in bleaching and cooking processes. Nonwoody kenaf plants require only a few months to attain full growth compared to hardwood trees which take years (Radiman et al. 2008). As shown in Table 7, the Young's moduli of commercial ones are lower than the kenaf membranes in all compositions. So, recently kenaf applications in membrane technology (Radiman et al. 2008) received much attention (Table 6).

Adsorption Material

Recently, the use of raw natural agricultural and forest by-products as cheap adsorbent materials, to eliminate contaminated and heavy metals from wastewater, is extensively studied as the unconventional manner of dealing with that of existing expensive methods (Aydin et al. 2008; Demirbas 2008). Recent research studies confirmed prospective use of core and bast fibers of kenaf to improve bioremediation (Borazjani and Diehl 1994), adsorption (Sajab et al. 2010, 2011), sound absorption, and thermal insulation (Sellers et al. 1994). Besides kenaf, several agricultural by-products were previously used to confiscate heavy metals such as eucalyptus, mushroom biomass, wheat bran, bark, rice husk, sunflower stalks, *Ficus religiosa* leaves, fruit peel of orange, and waste tea leaves. Kenaf possesses decent tendency to eliminate heavy metals from aqueous solution in batch studies (Hasfalina et al. 2010; Sajab et al. 2010).

Adsorption of Copper (II)

Cu (II) is toxic at high concentration but is vital for certain biosyntheses in human body as micronutrient for both plants and animals but it could cause anemia and

Table 7 Young's modulus of acetylated kenaf and commercial cellulose acetate membranes. (Radiman et al. 2008, with permission)

Type of cellulose acetate membrane	Cellulose acetate concentration (wt. %)	Young's modulus (107 N/m^2)
Kenaf	14	5.38
	16	6.78
	18	6.85
Commercial	14	5.17
	16	5.40
	18	5.60

stomach intestinal distress (Hasfalina et al. 2012), and might increase the risk of cancer (Aydin et al. 2008) after exceeding normal standard level. Research works investigated the successful use of kenaf in fixed-bed column for the adsorption of copper (II) from aqueous solution (Hasfalina et al. 2012).

Adsorption of Hazardous Dye

Further, probable application of kenaf core fibers is the removal of hazardous dye from wastewater. Citric acid (CA)-treated kenaf core fibers prepared via esterification in the presence of CA display greater adsorption proficiency towards methylene blue (MB). About 131.6 mg/g of maximum adsorption capacity was achieved for the CA-treated kenaf core fibers. The study also cleared that treated kenaf core fibers have higher adsorption capacity towards MB, compared to untreated kenaf core fibers. Table 8 summarizes the maximum capacity of adsorption (Q_0) of the CA-treated kenaf core fibers with different adsorbent materials. CA-treated kenaf core fibers' heavy metal ions uptake or adsorption capacity is equivalent to that of other bio-adsorbents (Sajab et al. 2011).

Oil and Chemical Absorbents

The kenaf core is a perfect absorbent to clean up oil spills and chemicals alike. Kenaf absorbs oil before taking on water making the product to float on the surface enabling easier assembly. The obtained product is nonabrasive, more effective, nontoxic than conventional remedies like clay and silica. In Texas oil fields,

Table 8 Comparison of maximum adsorption capacity (Q_0) of the kenaf core fibres with other materials towards methylene blue (MB). (Source: Sajab et al., 2011)

Bio-adsorbent	Maximum adsorption capacity, Q_0 (mg/g)
Peanut hull	161.3
Poplar sawdust	153
Rejected tea	156
Mango seed kernel powder	153.846
Jute processing waste	22.47
Wheat shells	16.56
Rice husk	40.6
Garlic peel	142.86
Meranti sawdust	158.73
Hazelnut	76.9
Cherry sawdust	39.84
Oak sawdust	29.94
Kenaf core fibres	131.6

this product absorbs coolant spills, gasoline, diesel, and transmission fluid. In some places, it is used for personal garages along with bulk applications such as oil rigs, clean-up operations in land, sea spills, and refineries, utility companies, storage terminal industries, and for refueling applications in military field (Sellers et al. 1993).

Biologically Active Acidic Oligosaccharides

The major hemicellulose (hemicellulose A and hemicellulose B) from kenaf consists of a β-(1 → 4)-D-xylopyranose backbone with 4-O-methyl-glucuronic acid side chains at the two-position of many xylose units (Duckart et al. 1988; Neto et al. 1996) obtained by a series of sequential extractions. It has 92–94 % xylose content and analogous spectral profile to a classic hardwood birch wood xylan (Nacos et al. 2006). Neutral and acidic xylo oligosaccharide results from hydrolysis of xylan with suitable enzymes. Achieved xylooligosaccharides are used as constituent elements in pharmaceuticals, cosmetics, food, or agricultural products (Vasquez et al. 2000). Acidic xylooligosaccharides also display exciting functions as growth regulators in plants, acclimatization bioregulators (Katapodis et al. 2003), regulating certain biological activities, and as antibacterial sterile agents (Christakopoulos et al. 2003).

Geotextiles

Geotextiles are textile-like materials used to improve soil structural performance used for short term (6 months to 10 year) for mulching, absorption, as soil filters, and for erosion control. Kenaf fiber-based geotextiles compete with polymeric geotextiles on both technical and commercial grounds; only the need is to increase their competitiveness, with the biggest market share mainly focused on jute, coir, and sisal fibers (Leão et al. 2012). Forest Products Laboratory's (FPL) initial effort is to use kenaf as a staple fiber in nonwoven geotextiles.

Reinforcements in Composite

The natural fiber polymer composites have become the attractive centers for the research community since the past few decades (John and Thomas 2008). Natural fiber-reinforced composites are proposed to substitute synthetic fiber-based composites due to several advantages such as renewability, less abrasiveness to equipment, high specific properties, biodegradability, and low weight and cost (Frone et al. 2013; El-Shekeil et al. 2012), thereby creating a positive environmental impact (John et al. 2010). Kenaf fiber is regarded as one of the most important natural fibers, and is getting much attention from the composite industry as the potential polymer reinforcement fiber. Kenaf fibers have lower thermal resistance as compared to synthetic fibers, similar to other natural fibers. The application of mature kenaf bast fibers in fiber-reinforced thermoplastic composites involves separation of the core from the bast fibers (Lips et al. 2009). Compared to other parts of the kenaf plant, its bast fiber has enhanced mechanical properties. The addition of kenaf fibers improved the mechanical properties of neat polymers considerably. A study by researchers indicated enhancement in flexural and impact strength, tensile as well as stiffness of the composites when reinforced with kenaf fibers (Anuar and Zuraida 2011). In another research it was also observed that composite kenaf sheets/poly-L-lactic acid (PLLA) obtained has large mechanical anisotropies such as Young's modulus and tensile strength (Nishino et al. 2003). In another research work, addition of kenaf fibers into the epoxy, thermal study results showed that it slightly improved both the thermal and charring stability of the samples. Alkalization also causes declination in the properties for the kenaf/epoxy composite (Azwa and Yousif 2013). Kenaf bast fiber-reinforced poly(vinyl chloride) (PVC)/thermoplastic polyurethane (TPU) poly-blend (PVC/TPU/KF) composites have shown lower tensile strength and strain with increase in fiber content whereas impact strength and thermal stability were decreasing with increase in fiber content (El-Shekeil et al. 2014). Kenaf fiber-reinforced composites show wide feasible applications for cell phone shells comprising 15–20 % kenaf fibers (Aji 2008). Another illustration is in the automobile parts industry like Toyota RAUM, equipped with a spare tire cover composed of kenaf fiber composites (Anonymous 2007). Some of the important reported works on the kenaf fiber as a reinforcement and filler in the various composites are tabulated in Table 9.

Automobile Industries

The rising efforts, awareness, and recent trend towards sustainable product design, enable natural fiber materials to substitute synthetic-based fiber in the preparation of composites exclusively for automotive organizational and semi-structural applications. Several locomotive parts and their components prepared formerly by glass fiber composites are recently being mass-produced using environmentally friendly composites (Dahlke et al. 1998; Leao et al. 1997). Among the natural fibers, kenaf received greater attention from the scientists and auto-industries as all its parts could be perfectly applicable by forming composites with a variety of resins or polymeric matrices. Figure 8 shows the pathway of using kenaf components but their lower mechanical strength and hydrophilic nature restricted their submission particularly for aesthetically associated locomotive components such as interior accessories, floor pan, and dashboard. Natural-based fiber is combined with synthetic-based fiber such as glass fiber within the same matrix, to develop hybrid polymer composites, to overcome this problem (Davoodi et al. 2010; Kumar et al. 2010; Rao et al. 2011). Kenaf bast fiber scored the highest priority value of 0.129 or 12.9 %, followed by pineapple leaf fiber (0.114), oil palm empty fruit bunch (EFB) fiber (0.097), and many other types of natural fibers based on the overall design analysis (Mansor et al. 2013). Thus, analytical hierarchy process (AHP) method

Table 9 Reported work on kenaf fiber as reinforcement in composite

Reinforcement	Matrix	Reference
Kenaf fiber	HDPE	Salleh et al. 2014
Treated and untreated kenaf	Epoxy	Yousif et al. 2012
Kenaf fiber	Poly(furfuryl alcohol) bioresin	Dekaa et al. 2013
Kenaf/fiberglass	Polyester	Ghani et al. 2012
Short fibers nonwoven kenaf	Polypropylene	Asumani et al. 2012
Long kenaf/woven glass	Unsaturated polyester	Salleh et al. 2012
Kenaf bast fibers	Polypropylene (PP) blended with (TPNR) and (PP/EPDM).	Anuar and Zuraida 2011
Kenaf fibers	Polyurethane	Batouli et al. 2014
Kenaf fibers in polylactide	Polylactide	Lee et al. 2009
Kenaf–polypropylene	Kenaf–polypropylene	Johna et al. 2010
Kenaf	PLA	Ochi 2008
Kenaf-glass	Unsaturated polyester	Atiqah et al. 2014
Kenaf fibers and corn husk flour	Poly(lactic acid)	Kwon et al. 2014
Nonwoven kenaf	Polypropylene	Hao et al. 2013
Kenaf fibers	Polypropylene	Shibata et al. 2006
Alkali-treated kenaf fibers	PLA	Shukor et al. 2014
Kenaf fibers	Cassava starch	Zainuddin et al. 2013
Kenaf/glass	Epoxy	Davoodi et al. 2012
Kenaf/glass	Epoxy	Davoodi et al. 2010
Kenaf sheets	PLLA	Nishino et al. 2003
Kenaf fibers	Polyurethane	El-Shekeil et al. 2012
Kenaf fiber	Polypropylene	John et al. 2010

TPNR thermoplastic natural rubber, *EPDM* ethylene propylene diene terpolymer, *PLA* poly (lactic acid), *PLLA* poly-L-lactic acid

and sensitivity analysis recommended kenaf bast fiber as the perfect and most suitable applicant material to prepare the hybridized glass fiber polymer composites for the automotive component construction such as the design of center lever parking brake component. Figure 9 shows the three-dimensional (3D) computer-aided design (CAD) model of a commercial passenger vehicle center lever parking brake design from kenaf glass fiber hybridized composite (Mansor et al. 2013). In the other study, hybrid kenaf/glass epoxy composites are utilized in locomotive operational components such as bumper beam by improving the impact property (Davoodi et al. 2010). Bumper system is shown in Fig. 10a with its three main elements, fascia, energy absorber, and bumper beam (Sapuan et al. 2005). Harusmas Agro Sdn. Bhd. (HASB) based in Sabah, Malaysia, initiated a kenaf project back in the year 2000. HASB is currently developing kenaf fibers to replace glass fibers in exterior automotive parts such as front and back bumpers (Khan 2011). Figure 10b shows the kenaf bumper. In another important study, commercialization of door trims using

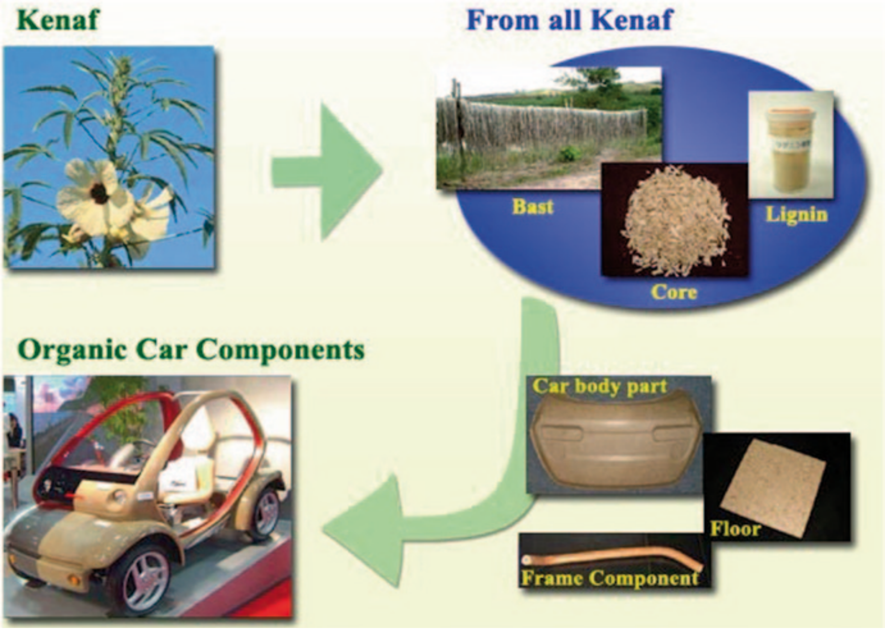
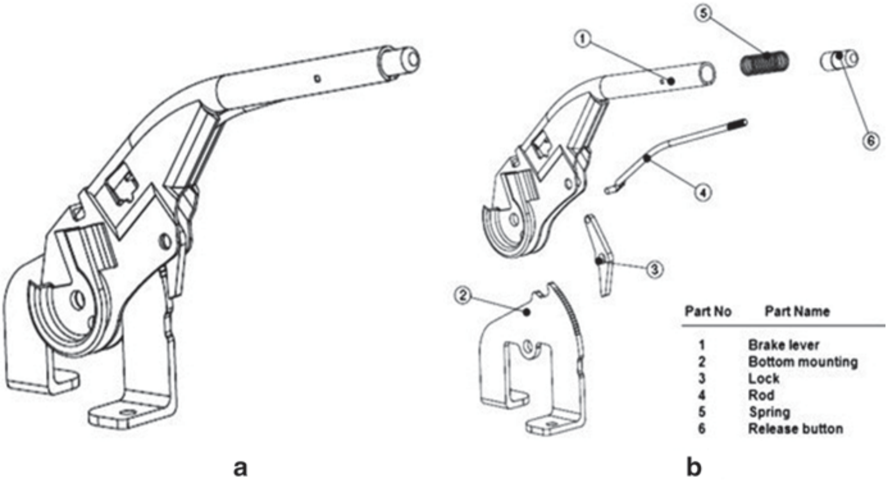


Fig. 8 Toyota's organic car from Kenaf http://www.kenafibers.com/users_toyota.html (Accessed on 29th August)



Part No	Part Name
1	Brake lever
2	Bottom mounting
3	Lock
4	Rod
5	Spring
6	Release button

Fig. 9 3D CAD model of a commercial passenger vehicle center lever parking brake design in **a** assembly view, and **b** exploded view. CAD Computer-aided design. (Mansor et al. 2013, with permission)

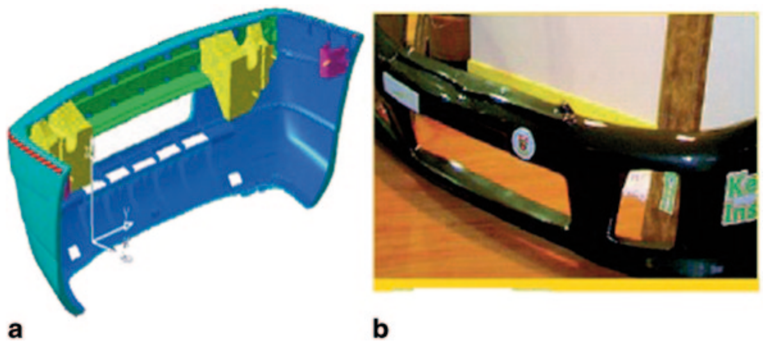


Fig. 10 **a** Bumper system components (Davoodi et al. 2011, with permission); **b** Kenaf bumper. (Source: Kenaf, a fibre for the future: the Harusmas experience. http://www.jeccomposites.com/news/composites-news/kenaf-fibre-future-harusmas-experience)

kenaf and petroleum-derived polypropylene (PP) resin is made and Fig. 11 shows the door trim using kenaf base material. This combination reduced the weight while retaining the same level of durability as conventional products although achieved by establishing a unique technology to realize a high level of shock resistance and heat resistance (Toyoto 2014). Another research involves the formulation of biodegradable composite using kenaf base material with biodegradable polylactic acid (PLA) resin to develop spare tire covers and deck board (Fig. 12) which is more environmentally friendly (Fig. 7).

Preparation of Activated Carbon

Recently, agricultural and forest by-products are drawing great contemplation as unconventional feedstock for fabrication of activated carbons (ACs) due to their

Fig. 11 The door trim using kenaf base material. (Source: Commercialization of door trims using kenaf and polypropylene (PP). http://www.toyota-boshoku.com/global/about/development/eco/kenaf/)

Fig. 12 Deck board using kenaf base material, spare tire cover base material made from kenaf and PLA. *PLA* Poly(lactic acid) http://www.toyota-boshoku.com/global/about/development/eco/kenaf/

easy availability, sustainability, and low cost (Thio et al. 2009, Hameed et al. 2009 and Chen et al. 2011). Kenaf core fiber has comparatively higher lignin content and low ashes (Akil et al. 2011), making it a favorable feedstock for fabrication of superior quality of AC on a commercial scale for cost-effective value. Aber et al. (2009) defined the activated carbon fiber (ACF) preparation from kenaf cloth (i.e., kenaf bark fibers) by carbonization trailed by K_2HPO_4 activation to attain highest specific surface area of 493 m^2/g. Recently potassium oxalate ($K_2C_2O_4$) was also recommended as an effective and promising activating agent for preparing high-surface-area ACs from kenaf core with perfect dye removal capacity (Chen et al. 2013).

Construction and Housing Industry

Wood and wood-based products can be replaced by kenaf/plastic compounds which are molded into lightweight panels in several applications. This is the first and economically priced plastic lumber for use as constructing materials in housing industry as an engineered material**.** Moreover, it is also used to make a strong, lightweight, cement block with great insulation and effective fireproof properties. Kenaf core blocks are nowadays used to construct multistory and solitary family homes, deprived of power tools.

Stoves in Cooking Mode

Kenaf Stove is premeditated for high-proficiency cooking and biochar (a form of charcoal) production as it is low cost, smokeless, and safe. The Kenaf Stove burns kenaf in an oxygen-poor atmosphere, thereby in a cleaner condition, with longer existence and certainly smoke-free fire.

Food Packaging Industry

Kenaf/plastic compound pellets are casted into a variety of commercial food storage containers—non-food-related packaging, including bulk pharmaceutical drugs and chemical packaging, disposable packaging, and packaging parts of the electronics and electrical industries for large consumer appliances (Zhang 2003).

High-Protein Source Feed

Livestock Feed

Although kenaf is a fiber crop and used by the fiber industry, the whole immature kenaf plant, stalk (core and bark), and leaves could be considered as high-quality livestock feed (Phillips et al. 1996). Crude protein in kenaf leaves, stalk crude, and whole plant ranged from 14 to 34 %, 2 to 12 %, and 6 to 23 %, respectively (Killinger 1969; Suriyajantratong et al. 1973; Swingle et al. 1978). Kenaf leaves consist higher quantity of nitrogen compared to stalk, during the growing season (Phillips et al. 2002). Kenaf has reasonable digestibility with great percentage of digestible protein and hence can be ensilaged efficiently. Dried kenaf leaves are turned into different-sized pellets as high-protein feed source for chickens, rabbits, fish, and goats. Chopped kenaf meal is also used for sheep and Spanish goats as a supplement. Alfalfa hay in the finishing diets of lambs can be replaced by kenaf hay without affecting lamb routine or feed intake. Kenaf provides more flexibility than perennial crops to fabricators in managing integrated livestock-cropping enterprises (Phillips et al. 2002). Another study has demonstrated that the apical part of the kenaf plant that is harvested at full bloom can be ensiled and silage of satisfactory quality with good fermentation characteristics could improve the nutritional characteristics of the forage obtained, leaving the lower part for use by the paper industry (Xiccato et al. 1998).

Human Feed

Whitten variety of kenaf leaves are edible within 10 days of planting, are rich in protein, that is, about 34 %, and are delicious. Kenaf leaf recipes are important edible items in Haiti and used extensively in salads, soups, boiled like spinach, or added to rice, and can also be used for baking (Cross 2014). Kenaf seed oils displayed greater antioxidant activity compared to all traditional edible oils ($P<0.05$) because of the considerable unique composition and oil content of kenaf seed oil. Thus, it becomes an unconventional, cost-effective, and tremendous source of solvent-free vegetable cooking oil with extraordinary antioxidant properties for human consumption (Chan and Ismail 2009).

Medical Application

Kenaf from historic times is recommended in customary folk medicine in India and Africa (Agbor et al. 2005; Kobaisy et al. 2001). Kenaf consists of several active components including polyphenolics, tannins, saponins, alkaloids, essential oils, and steroids (Yazan et al. 2011). From the very past it is used to treat bilious conditions, bruises, puerperium, and fever. Kenaf seeds contain phytosterols such as β-sitosterol, alpha-linolenic acid (ALA), vitamin E, and other antioxidants with chemopreventive properties. The oils obtained by Soxhlet, sonication, and supercritical carbon dioxide fluid extraction (SFE) processes are found to be cytotoxic towards ovarian cancer (CaOV3) and colon cancer (HT29) cell lines via the induction of apoptosis. They are recently being used to detect the early colon carcinogenesis in vivo by virtue of their bioactive compounds (Yazan et al. 2011; Ghafar et al. 2012). The seed oil of kenaf contains ALA, an originator of eicosanoids that have antithrombotic activity, and are anti-inflammatory (Ruiz et al. 2002) and chemopreventive agents (Williams et al. 2007). Moreover, kenaf seed oil also consists of phytosterol showing antioxidant, anticancer, and lipid-lowering cholesterol properties (Kritchevsky and Chen 2005; Berger et al. 2004). A noteworthy ($P < 0.05$) increase in the red blood cell count, packed cell volume, and hemoglobin concentration against anemic condition is observed by the kenaf leaf extract (Agbor et al. 2005). This study shows the antioxidant properties of crude ethanolic extract (CEE) of defatted kenaf seed meal (DKSM) and its derived n-butanol (BF) and aqueous fractions (AqF). High-antioxidative phenolic compounds and saponins could be extracted from DKSM which is a prospective active ingredient that is multifunctional and applied in functional foods, nutraceuticals as well as natural food stabilizers recently (Chan et al. 2014).

Essential Oils and Volatiles from Leaves

Researchers explored that kenaf plant is a vital source of naturally occurring allelopathic chemicals having the tendency to inhibit weed seed germination and their growth, thus providing a harmless and profitable method of hindering weed rivalry in both vegetables and agronomic crops. The kenaf leaf essential oil is found to be phytotoxic to bent grass (*Agrostis stolonifera* L., Poaceae) and lettuce (*Lactuca sativa* L., Asteraceae), and it also showed antifungal activity against *Colletotrichum* species (*Colletotrichum fragariae, C. gloeosporioides,* and *C. accutatum*) which can cause anthracnose symptoms (Webber and Bledsoe 2002). Extracts from kenaf (stalks and leaves) abridged germination of redroot pigweed (*Amaranthus retroflexus* L., Amarathaceae) by more than 50% and to a smaller extent for tomato (*Lycopersicon esculentum* Mill., Solanaceae) and Italian ryegrass (*Lolium multiflorum* Lam., Poaceae) (Russo et al. 1997). The filtration characteristics of ground, inert, loose particles of identical size and structure of kenaf core formed during the fabrication of kenaf bast fibers for paper are investigated for certain leaching and filtration applications towards dissolved solids (Lee and Eiteman 2001). Moreover, a study also found that kenaf and commercial diatomaceous earth (DE) possess similar filtration characteristics. Prospective application of ground kenaf core due to its inertness, insolubility, light density, low expenditure, and homogeneity includes the aid in filtration of swimming pool water, drinking water, or in sugar refineries, breweries, and other industrial settings (Dickey 1961).

Fuel and Bioenergy Production

Biomass is abundant and it can be considered as an alternative source of renewable and sustainable energy, which promises to fulfill continuous supply of energy. Agricultural biomass such as industrial kenaf (*H. cannabinus* L.) has been successfully investigated as a great potential to be used as a renewable and sustainable feedstock for the production of bioenergy. High-capacity processes for the conversion of plentifully available biomass into liquid biofuels are needed for lowering reliance on petroleum sources.

Biofuel Production

Biomass as an entirely renewable and extensively distributed resource is being progressively used for the production of biofuels, chemicals, and many materials (Klass 1998; Huber et al. 2006). In another research work, liquefaction of kenaf biomass and its dried subcritical water hydrolysate and subcritical water non-hydrolyzed residue fractions were investigated in the presence of tetralin solvent under hydrogen pressure (Meryemoglu et al. 2014) (Fig. 13). The results of the present study show that kenaf can be a good alternative source for fuel production by liquefaction. Liquefaction of kenaf biomass, its dried hydrolysate, and non-hydrolyzed kenaf residue produced same compositions of the oils but in different amounts. The oils consisted of fuel-related compounds (Meryemoglu et al. 2014).

Anaerobic Digestion

Kenaf may be subjected to anaerobic digestion to produce methane even though hemp and kenaf produced the same amount of methane yield per hectare. It is estimated that higher cellulose and less lignin content in kenaf biomass make it an advantageous feedstock for biogas production (Muhammad et al. 2013).

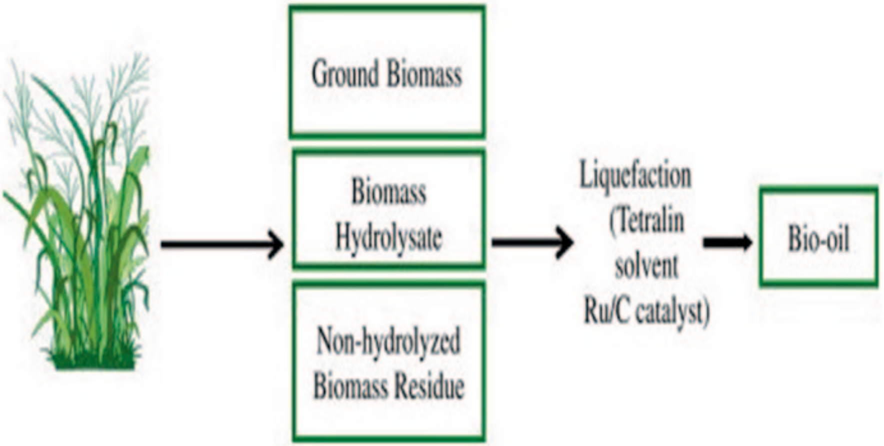


Fig. 13 Bio-oil from kenaf biomass (Meryemoglu et al. 2014, with permission)

Biohydrogen

The emergence of biohydrogen as a substitute fuel has now attained growing acceptance and attractions (Koroneos et al. 2008). Being the member of bioenergy, biohydrogen fuel is another important source of energy. Several feedstocks, such as lignocellulosic biomass, are used to produce biohydrogen. Kenaf produces considerably higher biomass but not explored as a potential feedstock for biohydrogen production as compared to maize and rice (Pakarinen et al. 2011). Hydrogen-rich gas mixture production from solubilized lignocellulosic biomass of kenaf in subcritical water and aqueous phase in the presence of Pt (platinum) on activated carbon are well-defined methods. Kenaf biomass produced small quantities of gas mixture by thermo-catalytic conversion. However, it is found to be very suitable for thermo-catalytic decomposition for the hydrogen production (Irmak and Öztürk 2010).

Solid Fuel

Kenaf biomass is used as a solid residue through pretreatment and hydrolysis. Kenaf can also be used as a fuel for combustion in boilers as a cheap bioresource biomass (Abbasi and Abbasi 2010; Tock et al. 2010; Sami et al. 2001; Kamm 2004). Kenaf biomass fuel offers significant advantages as a combustion feedstock because of its high volatility and high reactivity even of the resulting char (Demirbas 2005). The strength and tenacity of the biomass combustion deposits are more than the deposits of coal, thus making it more difficult to remove (Sami et al. 2001).

New Application of Kenaf Fiber

A new high-end use for kenaf was discovered when it was blended with cotton to convert them into fabric and yarn. These lightweight blend fabrics are appealingly attractive, having a linen look, pleasing, and soft to touch (Anonymous 2014). LG and Samsung employ kenaf powder for investigating as alternative materials for laptop covers and mobile phones. An armor factory in Malacca province of Malaysia is engaged in performing research work on blending kenaf with Kevlar to create a sort of brighter bulletproof vest. In another project, manufacturers are willing to use kenaf fibers for geotextiles applied for erosion control. Kenaf core is also being useful for soil remediation for hydrocarbonate infestations.

An industrial unit in Sabah, Malaysia, is organizing to intermix the kenaf with EFB fiber for forthcoming fabrication. The Malaysian Timber Industry Board (MTIB) of Malaysia reported that kenaf is being used for making pulp and paper in the USA, jeans in Mexico, China, and Thailand, indoor panels and other interior components for high-end cars like BMW and Mercedes Benz, and in composite materials for the building or construction industry (Chen et al. 2011). Recently, business corporations like Sony, Apple, The Nature Co., Warner Bros., Recreational Equipment Inc. (REI), J.C. Penny, The Gap, Esprit International, and Birkenstock are under way to consume kenaf paper for catalogs and many other related purposes. Major printing and graphics firms such as Anderson Lithographics, Kinkos, George Rice and Sons, and Ventura Printing are ready to offer printing services on kenaf paper. Kenaf paper is recently being utilized by major publisher companies, industries, corporations, and printing and graphics firms.

Conclusions

The crop has instigated to fascinate much interest and attention in the last decade, attributed to the growing concerns of global warming and the rising price of petroleum-based products. Kenaf, regarded as the fiber crop of the twenty-first century, is a renewable and sustainable alternative with a short gestation period of only 4 months, is exploding commercially for industrial products. The manifold beneficial components (e.g., stalks, leaves, seeds, fibers and fiber strands, oils, allelopathic chemicals, and proteins) of kenaf core are well established. Kenaf matures only within 5 months, is eco-friendly, tolerant of environmental and drought stress, making it a versatile encouraging and economic crop for industrial applications in the upcoming years. The commercial and profitable achievement of kenaf crop reflects prospective economic and environmental benefits in the different sectors of lethal toxic waste cleanup, removal of oil spills from water, and soil remediation. Besides these, successful efforts are also made towards the amounts of chemical and energy used in soil erosion due to wind and water and in paper production. Moreover, the potential of replacing synthetic polymers to reduced use of fiberglass, greater recycled paper quality, and timber in industrial products, along with the increased use of recycled plastics, are its additional applications. The versatile and diverse applications of kenaf plants and their different portions in varied sectors require a superior considerate of its components and the various issues influencing the plant composition. The activities of several isolated and private industries amplified by agrarian research and studies endured to offer a different variety of innovative kenaf products. These are used to encourage in highlighting the flourishing and bright future for the persistent extension of kenaf as a commercially profitable industrial crop.

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Natural Fiber-Reinforced Polymer for Structural Application

Juliano Fiorelli, Nolan Rempe, Julio Cesar Molina and Antonio Alves Dias

Abstract The glued laminated lumber (glulam) beams technique is an efficient process for making sustainable use of wood. Fiber-reinforced polymers (FRPs) associated with glulam provide significant gains in terms of strength and stiffness, as well as modify the rupture mode of these structural elements. Certain natural fibers display sufficient mechanical properties to reinforce the polymer used in the glulam technique. This chapter presents a theoretical analysis considering the behavior of stressed lumber and fibers in glulam beam of *Pinus* sp. and *Eucalyptus* sp. with and without natural fiber-reinforced polymer (NFRP), and a numerical analysis evaluating the stresses and displacements in glulam beams using the finite element method. Curauá, bamboo, and jute fibers were used for reinforcement. NFRP introduced in the tensioned section of glulam beams guaranteed a gain of strength and stiffness in function of the thickness percentage of NFRP used. In terms of maximum stresses and vertical displacement, theoretical and numerical analyses provided analogous results.

Keywords Glulam · Fibers · Polymer · Structural applications

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Introduction

The reduced availability of native woods has spurred the development of new techniques for the use of wood from managed forests (Segundinho et al. 2013). Currently, it is not economically viable to use wood from older trees. The use of wood from managed forests is contributing to the spread of the glued laminated timber technique. When used for structural elements, glued laminated lumber (glulam) refers to the material produced by gluing the edges and faces of wood chips together, in flat or curved shapes, with the grains of the sheets parallel to the axis of the larger piece. Longer sheets are obtained by joining boards together longitudinally, gluing them face to face and edge to edge to obtain the desired height and width. The sheets can also be bent to produce a curved shape during gluing. All these factors permit a wide variety of design choices, constrained only by production and/or application costs.

Fiorelli and Dias (2011) evaluated the rupture mode of glulam beams produced with *Pinus* sp. wood and phenol–formaldehyde resin with and without glue-laminated fiber-reinforced polymer (GFRP). The results indicated that beams without reinforcement presented tensile failure beginning in the lower sheet of lumber and spreading to the finger joint. Beams with GFRP reinforcement presented two observed failure stages. The first was a tensile failure in the sheet positioned under the reinforcement layer, while the second occurred as a result of preliminary compression yielding in the upper face of the lumber, followed by both a shear failure at the fiber–lumber interface and a tensile failure in the wood. The use of fiber-reinforced polymers (FRP) to reinforce the underside of beams (last line of glue) ensures improvements in structural strength and stiffness of the element, and alters its mode of rupture.

The use of synthetic FRP to reinforce glulam beams was studied by Triantafillou and Deskovic (1992), Dagher (1999), Lindyberg (2000), Tingley and Kent (2001), Bergmeister and Luggin (2001), Fiorelli and Dias (2006), Kim and Harries (2010), Gentry (2011), Fiorelli and Dias (2011), Garcia et al. (2013), and Yeou-Fong et al. (2014). In recent years, natural fiber-reinforced composites have received significant attention because of their lightweight, nonabrasive, combustible, nontoxic, low-cost, and biodegradable properties. Among the various natural fibers, flax, bamboo, sisal, hemp, ramie, jute, and wood fibers are of particular interest (Kalia et al. 2009).

Composites reinforced with natural fibers are commercially viable only if they have a higher value-in-use in the same application as the incumbent materials which they are going to replace. A new composite part has a better value-in-use than its incumbent counterpart if it has the same functionality but is less costly and more environmentally friendly (Wallenberger 2002). Carvalho (2005) studied the use of sisal fiber-reinforced plastic (SFRP), as an alternative to carbon and glass fibers, for repairing and reinforcing wood structural elements. The results showed that the new SFRP can be used to reinforce timber structures. Kalia et al. (2009) presented a review of pretreated natural fibers for use in polymer matrix-based composites. The effect of surface modification of natural fibers on the properties of fibers and fiber-reinforced polymer composites has also been discussed.

Lee et al. (2005) conducted a study to estimate the strength and elasticity of glued laminated timber beams, considering the modulus of elasticity (MOE) and modulus of rupture (MOR) in bending, obtained in specimens free from defects. The model showed results in accordance with those from tests in rafters performed in this work. Johnsson et al. (2006) studied the reinforcement of glulam beams with pultruded blades made of carbon fiber by analyzing the optimal anchorage length needed. This study concluded that the flexural strength can be modeled similarly to that of reinforced concrete. Plasticizing the compressed region of the beam serves as ductile compression reinforcement in the structural element; the use of reinforcement also alters the mode of rupture, which usually occurs in the region pulled weakly on beams without reinforcement.

Frese et al. (2010) conducted a numerical study to assess the strength of glued wood beams that were tested experimentally. Their model considers the tensile strength of the blades and the tensile strength of the toothed amendments, for slides visually or mechanically sorted. They concluded that these two resistance parameters are not sufficient to ensure the planned mechanical resistance.

Kim and Harries (2010) present a numerical study of three-dimensional finite element modeling, considering the orthotropic properties of wood but not considering the lamination in compression, in order to predict the behavior of glued laminated timber beams reinforced with carbon fibers. In the model, rupture of the wood was considered when the longitudinal strain calculated exceeded the ratio between the MOR and modulus of longitudinal elasticity. The model provides the relative force versus displacement, stress concentrations, and failure modes, allowing for a comparison between the theoretical results and experimental values. The strengthened beams showed an increase in load capacity and energy absorption compared to the beams without reinforcement. According to their findings, with the additional 1.9 % of cross-sectional area from reinforcement, the maximum value of force that the beam supports is reached.

This chapter examines the theoretical strength and stiffness, and provides a numerical evaluation of the stresses and displacements, based on the finite element method, of the natural fiber-reinforced polymer (NFRP)-reinforced glulam beams, where established *Pinus* sp. *and Eucalyptus* sp. sheets reinforced with curauá, bamboo, and jute fibers were fixed along the last line of glue in the tensioned section.

Theoretical Model to Estimate Strength and Stiffness of Glulam Beam

The theoretical deterministic model used in this study considers a realistic behavior for the stressed lumber and fibers. The lumber subjected to compressive loading parallel to its grains exhibits an initial linear elastic behavior, reaching compressive strength parallel to the grains (f_c), followed by decreasing levels of stress as the strain increases, until the material breaks (Buchanan 1990). The lumber subjected to tensile loading parallel to the grains displays a linear elastic behavior until it approaches the rupture point (Fiorelli and Dias 2006). To calculate the bending moment at failure for the timber beams, an elastic–linear model in tension and an elastic–plastic with softening model in compression were considered (Fig. 1). Related to FRP in tension, an elastic–linear model is considered until the point of failure. The bending stiffness was calculated by the transformed section method, in the elastic–linear range, using MOE and thickness of each lumber and fiber reinforcement layer.

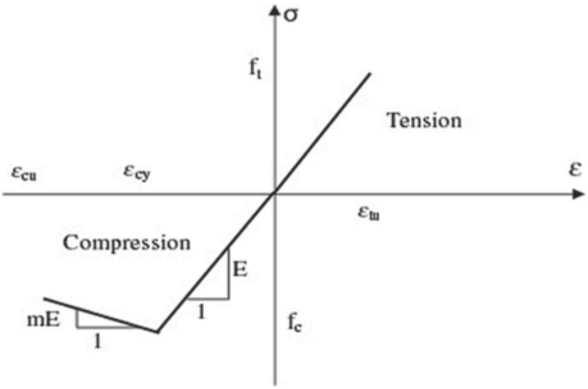


Fig. 1 Stress–strain relation of lumber under compression and tension parallel to the grain. (Source: Fiorelli and Dias 2011)

Software was developed to calculate the bending moment at failure. The position of the neutral axis line (NA) is determined by means of resultant loads of tension and compression equilibrium. By increasing the strain, it is possible to calculate the load on each sheet of lumber on the transversal section of the glulam beam and on the FRP layer, until failure occurs. Failure by tension can occur when the stress reaches the tensile strength, of timber or FRP. In the case of failure by compression, after the stress reaches the value of compressive strength, the section undergoes gradual plastic deformation, reaching the maximum bending moment.

Evaluation of NFRP in Glulam Beam Strength and Stiffness

This section presents information on the theoretical evaluation and numerical simulation performed on glulam beams reinforced with NFRP.

Mechanical Properties

To analyze the efficacy of natural fiber reinforcement in glulam beams, curauá, bamboo, and jute fibers were evaluated. The strength (bending moment failure) and stiffness (moment of inertia) of the glulam beam with NFRP were evaluated. Table 1 indicates the input parameters for analysis of strength and stiffness. Two species of wood were considered for theoretical analysis of reinforced glulam beams (*Pinus* sp. and *Eucalyptus* sp.) as well as three different types of fiber (curauá, bamboo, and jute fiber).

Theoretical Evaluation

For theoretical evaluation of the strength and stiffness of the NFRP-reinforced glulam beams, *Pinus* sp. *and Eucalyptus* sp. sheets were made with curauá, bamboo,

Table 1 Mechanical properties: wood and fiber

	Pinus sp.	*Eucalyptus* sp.	Curauá-fiber-reinforced plastic (CFRP)[a]	Bamboo-fiber-reinforced plastic (BFRP)[b]	Jute-fiber-reinforced plastic (JFRP)[c]
E (MPa)	9868	12,513	31,232	28,200	32,000
f_{c0} (MPa)	42.3	40.3	–	–	–
f_{t0} (MPa)	50.3	70.2	519	564	350

[a] Amaya (2013)

[b] Guimarães (1984)

[c] Beaudoin (1990)

and jute fiber reinforcement fixed along the last line of glue of the tensioned section. The percentage of fiber used was 1–7% of the height of the beam. The beams had ten 3-cm-thick layers of lumber, for a total nominal section of 7 × 30 × 400 cm.

Tables 2 and 3 show values of bending moment obtained in two ways: considering an elastic–perfectly plastic model ($m = 0$) of timber in compression, and an elastic–plastic model with softening ($m = 0.3$), according to Fig. 1.

Numerical Simulation

The numerical evaluation of the stresses and displacements in the glulam beams was performed using the ANSYS commercial software, version 10.0, which is based on the finite element method. For the proposed simulation, the tensile and compressive stresses in the outer grains of the wood (*Pinus* sp.) were evaluated as well as the values of tensile stress in the reinforcement layer (curauá fiber), which was considered in this case with a thickness of 7% (equal to 2.1 cm). The stress results

Table 2 Theoretical bending moment (M)—$m = 0$

	Bending moment (kN.cm)					
Reinforcement (%)	Pinus CFRP	Pinus BFRP	Pinus JFRP	*Eucalyptus* CFRP	*Eucalyptus* BFRP	*Eucalyptus* JFRP
0	5180	5180	5180	6492	6492	6492
1	5514	5488	5520	6787	6766	6798
2	5931	5810	5961	7150	7075	7159
3	6268	6185	6285	7425	7371	7439
4	6572	6485	6616	7735	7626	7788
5	6946	6764	7005	8036	7878	8055
6	7277	7038	7305	8295	8132	8317
7	7556	7350	7595	8568	8421	8642

BFRP bamboo-fiber-reinforced plastic, *CFRP* curauá-fiber-reinforced plastic, *JFRP* jute-fiber-reinforced plastic

Table 3 Theoretical bending moment (M)—m = 0.3

	Bending moment (kN.cm)					
Reinforcement (%)	Pinus CFRP	Pinus BFRP	Pinus JFRP	*Eucalyptus* CFRP	*Eucalyptus* BFRP	*Eucalyptus* JFRP
0	5146	5146	5146	5902	5902	5902
1	5478	5440	5494	6100	6087	6103
2	5871	5803	5883	6290	6266	6296
3	6161	6098	6176	6474	6442	6482
4	6517	6360	6548	6653	6613	6662
5	6791	6646	6813	6828	6781	6839
6	7064	6946	7124	6998	6945	7011
7	7357	7183	7382	7165	7109	7179

BFRP bamboo-fiber-reinforced plastic, *CFRP* curauá-fiber-reinforced plastic, *JFRP* jute-fiber-reinforced plastic

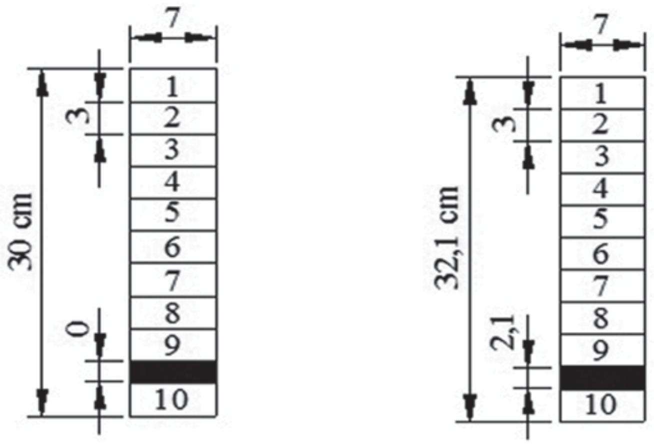
obtained for the reinforced beam were compared with those of the beam without reinforcement, as shown in Fig. 2. The stresses were obtained for values of applied load at the thirds of span of the beams (four-point flexural testing) which resulted in values for the theoretical bending moment (M) presented in Table 2. For the beam without reinforcement, a theoretical moment (M) of 5180 kN.cm was evaluated, corresponding to an applied force of 38.85 kN, whereas for the reinforced beam (7 %) with curauá a theoretical moment (M) equal to 7556 kN.cm was evaluated, corresponding to an applied force of 56.67 kN.

For the discretization of wood layers as well as the curauá fiber layer, the SOLID 45 tool was used, which allows consideration of plasticity effects of the materials. Materials were considered with an isotropic behavior. The constitutive model used for the wood in compression simulates an elastic–perfectly plastic behavior by using a bilinear curve as shown in Fig. 3. To avoid numerical problems in the portion of the curve between ε_y and ε_u, a small slope of E/1000 was considered. In tension, the model adopted for wood as well as curauá fiber simulates an elastic behavior. The mechanical properties of the wood were obtained through experimental tests performed on beams with structural dimensions and properties presented in Table 1.

Results and Discussion

Theoretical Values

Tables 2 and 3 indicated that theoretical model results showed approximately a 5 % reduction in value for the elastic–plastic model with softening (m = 0.3) when compared to those of the elastic–perfectly plastic model (m = 0), for timber in compression. Subsequently, an elastic–perfectly plastic model (m = 0) was used for



a MLC beam (*Pinus sp*) without reinforcement.

b MLC beam with reinforcement of 7% (caraua fiber)

Fig. 2 Configurations of beams evaluated in numerical simulations

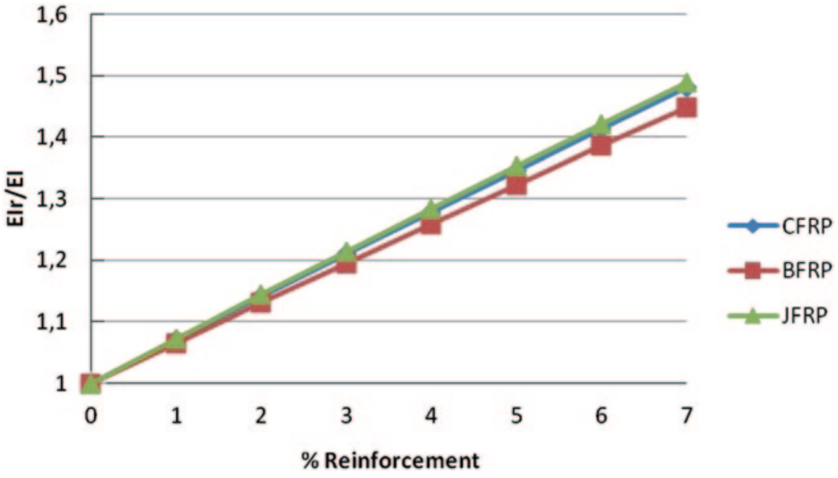


Fig. 3 EI_r/EI versus fiber reinforcement (%)—*Pinus* sp.

the numerical simulation. Table 4 presents the values of bending stiffness calculated on the linear portion of stress × strain curves for various materials.

Figures 3, 4, 5, and 6 present theoretical values of bending stiffness and bending moment of glulam beams (*Pinus* sp. *and Eucalyptus* sp.) reinforced with curauá (CFRP), bamboo (BFRP), and jute (JFRP), obtained according to the sections “Theoretical model to estimate strength and stiffness of glulam beam” and

Table 4 Theoretical bending stiffness (EI)

	EI (10^6 kN.cm^2)					
Reinforcement (%)	*Pinus* CFRP	Pinus BFRP	Pinus JFRP	*Eucalyptus* CFRP	*Eucalyptus* BFRP	*Eucalyptus* JFRP
0	15.54	15.54	15.54	19.71	19.71	19.71
1	16.64	16.56	16.67	20.86	20.77	20.88
2	17.73	17.56	17.77	22.01	21.84	22.06
3	18.81	18.56	18.87	23.16	22.90	23.23
4	19.87	19.55	19.95	24.31	23.98	24.39
5	20.92	20.54	21.02	25.46	25.05	25.56
6	21.97	21.53	22.08	26.61	26.13	26.73
7	23.01	22.51	23.13	27.76	27.22	27.90

BFRP bamboo-fiber-reinforced plastic, *CFRP* curauá-fiber-reinforced plastic, *JFRP* jute-fiber-reinforced plastic

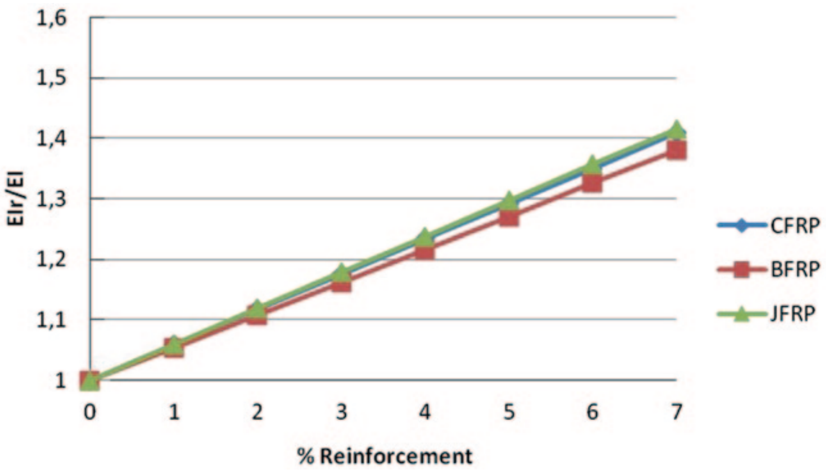


Fig. 4 EI_r/EI versus fiber reinforcement (%)—*Eucalyptus* sp.

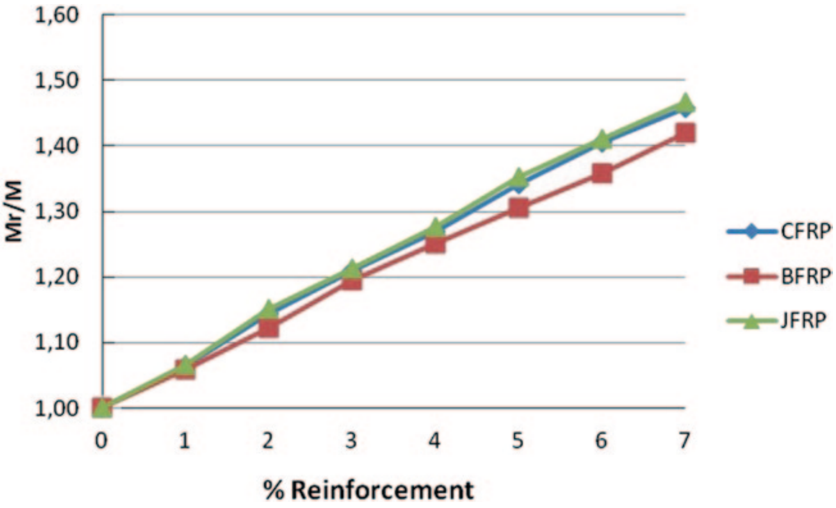


Fig. 5 M_r/M versus fiber reinforcement (%)—*Pinus* sp.

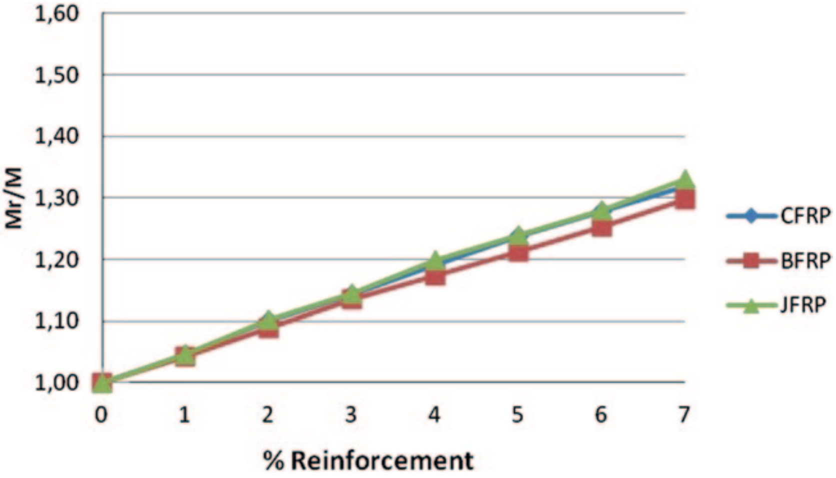
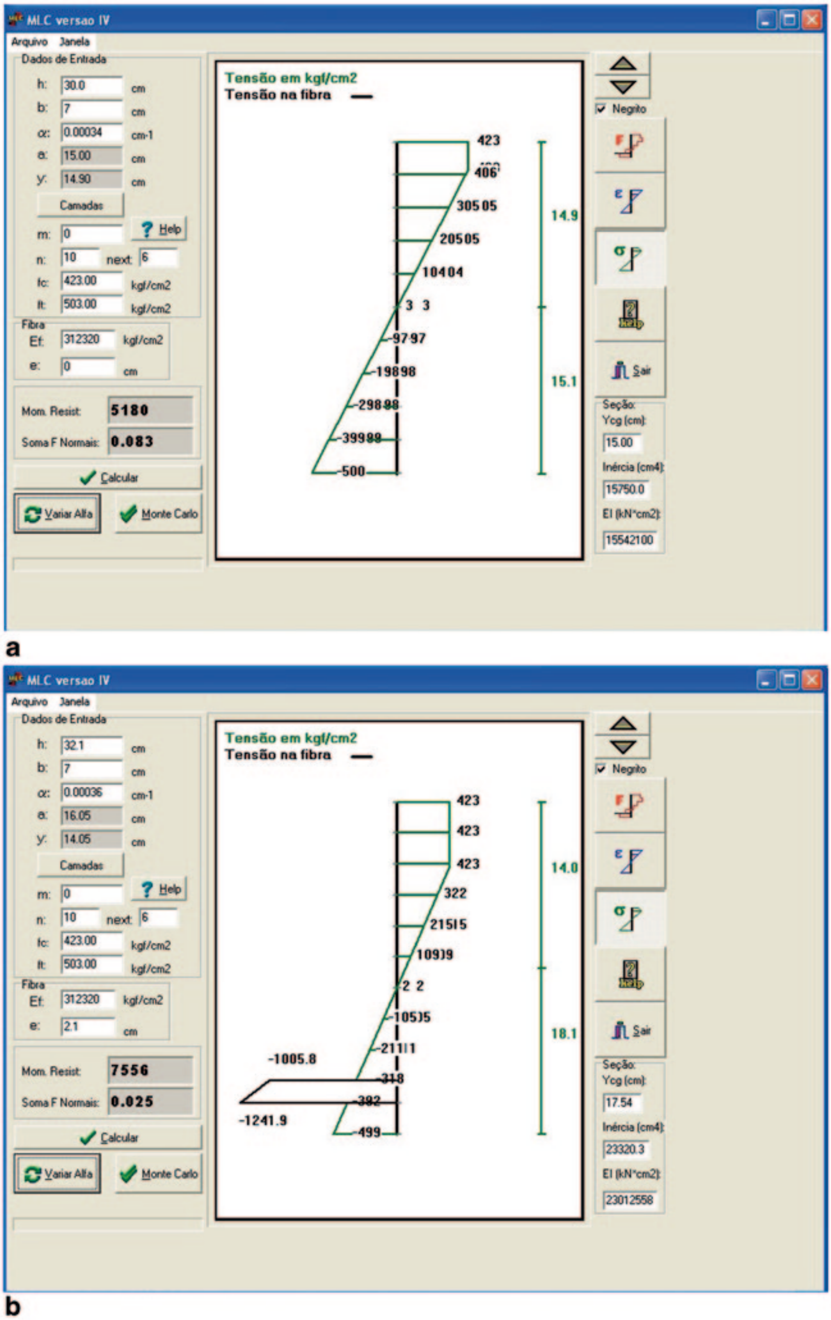


Fig. 6 M_r/M versus fiber reinforcement (%)—(*Eucalyptus* sp.)

"Theoretical evaluation," considering $m=0.0$. The increase in strength and stiffness is approximately linear until 7% of fiber reinforcement. As a continuation of this work, experimental tests will be conducted to check the validity of the theoretical data obtained by the theoretical model.

Figure 7 presents stress diagrams created with software for beams without reinforcement, and beams with 7% of fiber reinforcement (curauá, bamboo, and jute) to $m=0.0$. The curauá, jute, and bamboo fibers acted as efficient reinforcement for glulam beams, and presented analogous results because of similar values for MOE.



MLC versao IV

Dados de Entrada
h: 30.0 cm
b: 7 cm
α: 0.00034 cm-1
a: 15.00 cm
y: 14.90 cm
m: 0
n: 10 next: 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Fibra
Ef: 312320 kgf/cm2
e: 0 cm
Mom. Resist: 5180
Soma F Normais: 0.083
☑ Negrito
Seção:
Ycg (cm): 15.00
Inércia (cm4): 15750.0
EI (kN*cm2): 15542100

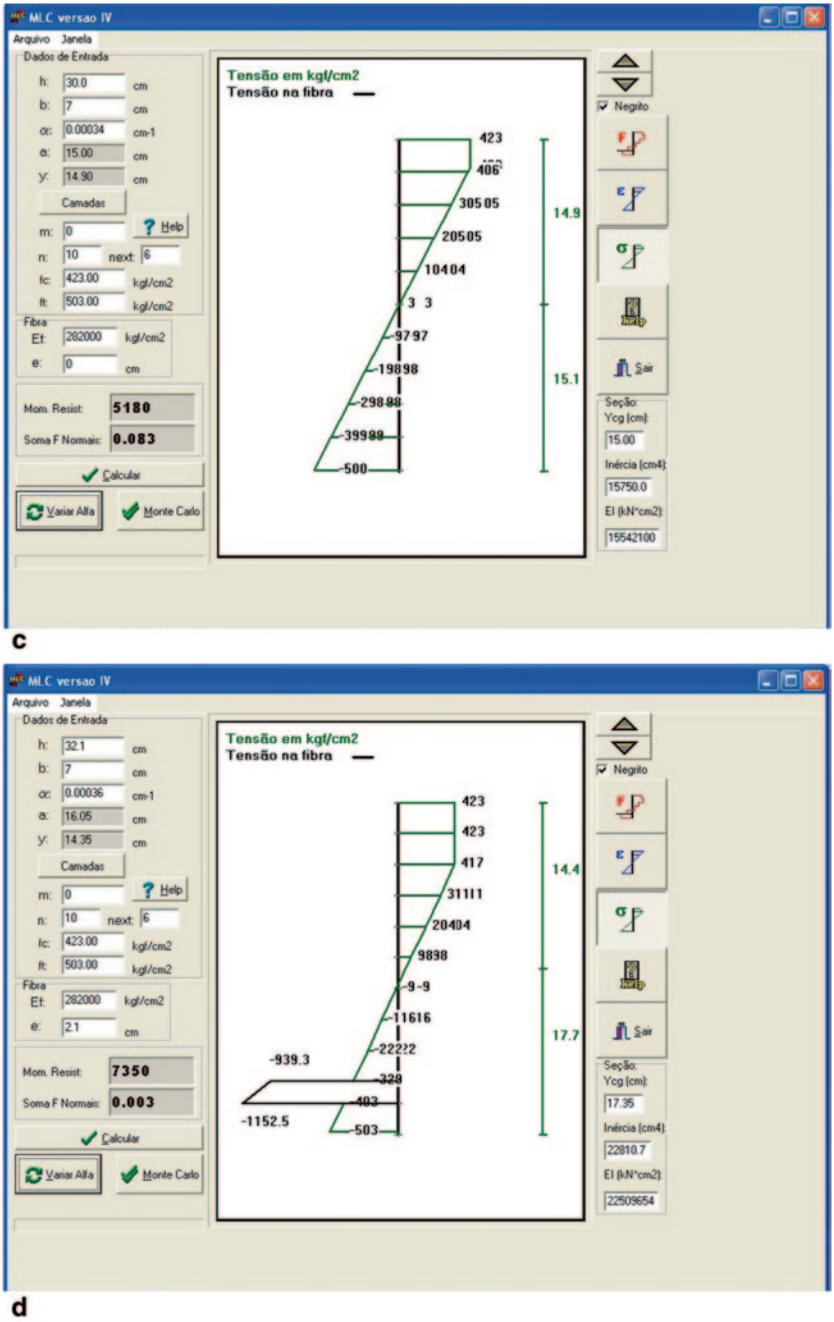
a

MLC versao IV

Dados de Entrada
h: 32.1 cm
b: 7 cm
α: 0.00036 cm-1
a: 16.05 cm
y: 14.05 cm
m: 0
n: 10 next: 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Fibra
Ef: 312320 kgf/cm2
e: 2.1 cm
Mom. Resist: 7556
Soma F Normais: 0.025
☑ Negrito
Seção:
Ycg (cm): 17.54
Inércia (cm4): 23320.3
EI (kN*cm2): 23012558

b

Fig. 7 Glulam beam program—stress diagram: curauá fiber (**a** and **b**), bamboo fiber (**c** and **d**), and jute fiber (**e** and **f**) to *Pinus* sp. glulam beams



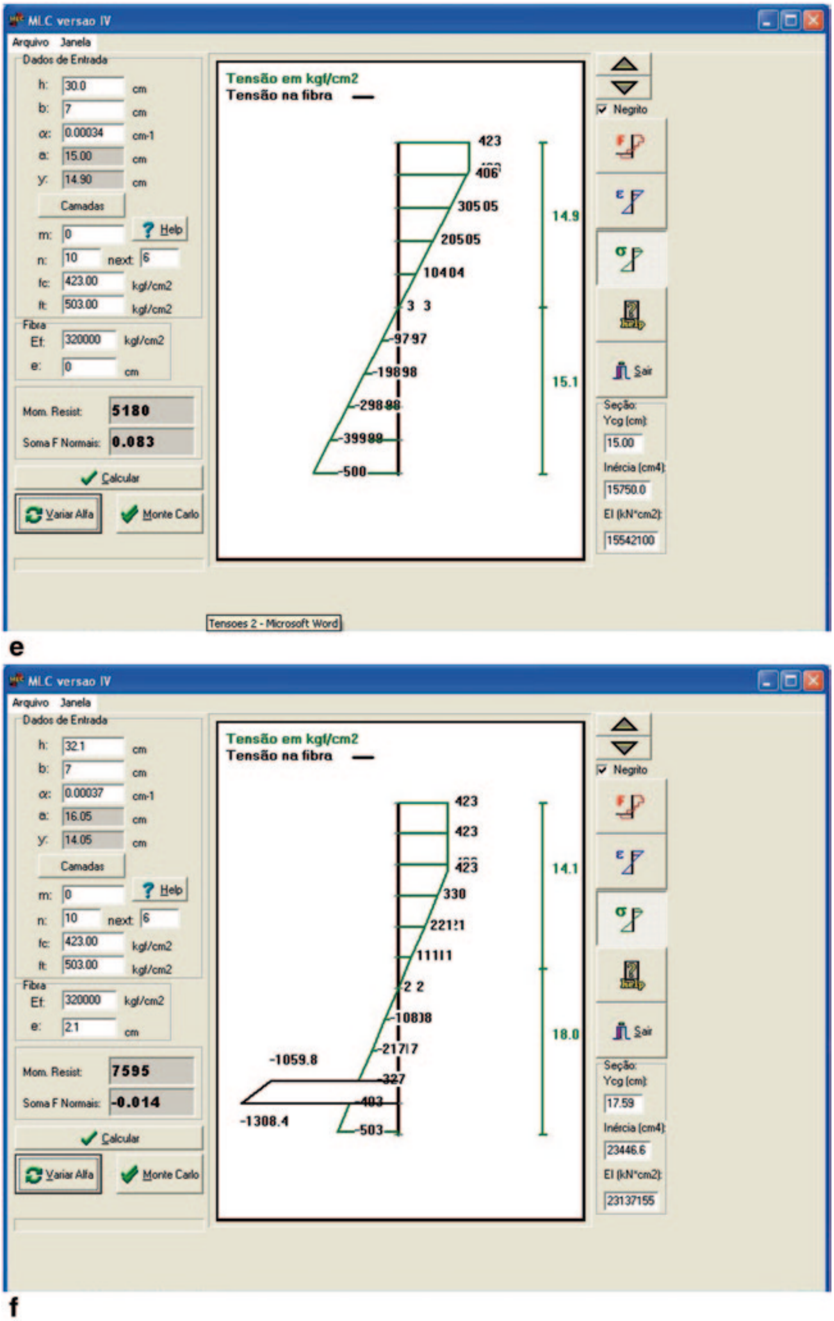
h: 30.0 cm
b: 7 cm
α: 0.00034 cm-1
a: 15.00 cm
y: 14.90 cm
m: 0
n: 10 next 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Ef: 282000 kgf/cm2
e: 0 cm
Mom. Resist: 5180
Soma F Normais: 0.083
☑ Negrito
Ycg (cm): 15.00
Inércia (cm4): 15750.0
EI (kN*cm2): 15542100

c

h: 32.1 cm
b: 7 cm
α: 0.00036 cm-1
a: 16.05 cm
y: 14.35 cm
m: 0
n: 10 next 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Ef: 282000 kgf/cm2
e: 2.1 cm
Mom. Resist: 7350
Soma F Normais: 0.003
☑ Negrito
Ycg (cm): 17.35
Inércia (cm4): 22810.7
EI (kN*cm2): 22509654

d

Fig. 7 (continued)



e

h: 30.0 cm
b: 7 cm
α: 0.00034 cm-1
a: 15.00 cm
y: 14.90 cm
m: 0
n: 10 next: 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Ef: 320000 kgf/cm2
e: 0 cm
Mom. Resist: 5180
Soma F Normais: 0.083
☑ Negrito
Ycg (cm): 15.00
Inércia (cm4): 15750.0
EI (kN*cm2): 15542100

f

h: 32.1 cm
b: 7 cm
α: 0.00037 cm-1
a: 16.05 cm
y: 14.05 cm
m: 0
n: 10 next: 6
fc: 423.00 kgf/cm2
ft: 503.00 kgf/cm2
Ef: 320000 kgf/cm2
e: 2.1 cm
Mom. Resist: 7595
Soma F Normais: -0.014
☑ Negrito
Ycg (cm): 17.59
Inércia (cm4): 23446.6
EI (kN*cm2): 23137155

Fig. 7 (continued)

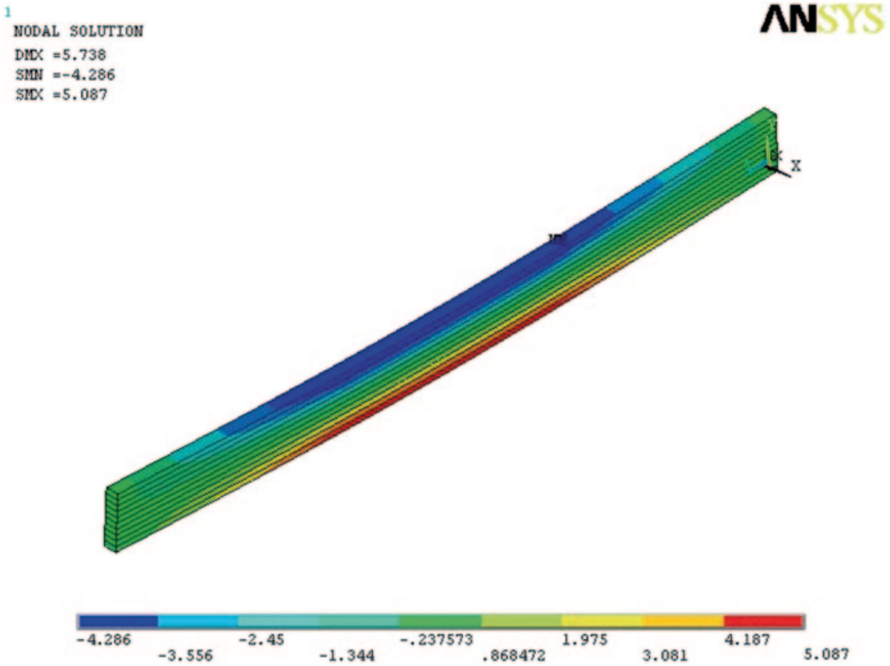


Fig. 8 Stresses (kN/cm2) in the beam (*Pinus* sp.) without reinforcement

The efficacy of these fibers as reinforcement is a result of their stiffness, with values for MOE approximately three times that of wood. The increase in stiffness was of 45–50 % for *Pinus* sp. beams and 40 % for *Eucalyptus* sp. beams, with 7 % of reinforcing fibers. The increase in strength was 40 % for *Pinus* sp. beams and 20 % for *Eucalyptus* sp. beams, with 7 % of reinforcing fibers.

Numerical Values

Figures 8 and 9 show a comparison of the stress values in the z direction obtained for beams with and without reinforcement. The numerical results for stresses and displacement were in accordance with the theoretical results. For the beam without reinforcement, the maximum tensile stress was 5.09 kN/cm^2 and the maximum compressive stress was 4.29 kN/cm^2. The theoretical analysis predicted 5.00 kN/cm^2 as the maximum tensile stress and 4.23 kN/cm^2 as the maximum compressive stress (Fig. 7a). The value of vertical displacement at mid-span corresponding to 40 % of the maximum applied load at the thirds of span was 2.28 cm. Theoretical analysis, using values of bending stiffness from Table 4, predicted a displacement of 2.23 cm.

For the beam with a reinforcement of 7 % (curauá fiber), the maximum tensile stress in the wood was 5.15 kN/cm^2 and the maximum compressive stress was 4.36 kN/cm^2. The maximum tensile stress in the curauá fiber layer was 12.76 kN/

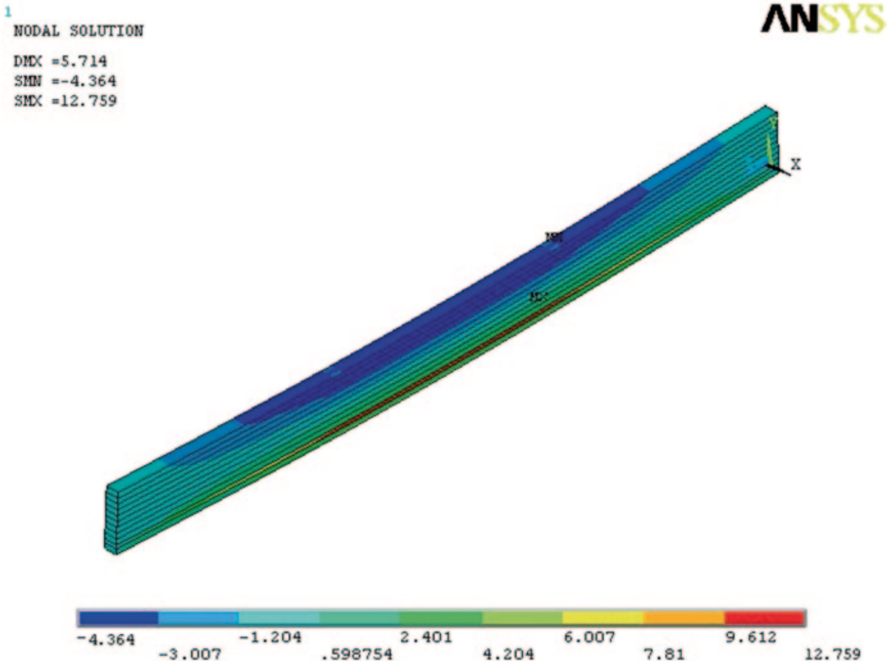


Fig. 9 Stresses (kN/cm2) in the beam (*Pinus* sp.) with reinforcement of 7 % (curauá)

cm^2. The theoretical analysis predicted 4.99 kN/cm^2 as the maximum tensile stress and 4.23 kN/cm^2 as the maximum compressive stress in wood, and 12.42 kN/cm^2 as the maximum tensile stress in the layer of curauá fiber (Fig. 7b). The value of vertical displacement at mid-span corresponding to 40 % of the applied load at the thirds of span was 2.25 cm. Theoretical analysis, using values of bending stiffness from Table 4, predicted a displacement of 2.24 cm.

Conclusion

Based on the current results, it is possible to conclude that the method used to produce glulam beams led to a higher efficiency of the structural elements. The FRP introduced in the tensioned side of glulam beams improved strength and stiffness as the percentage of reinforcement increased.

Reinforced beams have presented two failure stages. The first one was caused by tension in the sheet positioned under the reinforcement layer, while the second occurred as a result of a compression yielding on the upper side of the beam, followed by both a shear failure on the fiber–lumber interface and a tensile failure on the wood.

The maximum stress and vertical displacement calculated by numerical analysis were in good agreement with the values obtained from theoretical analysis.

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Natural Fiber-Reinforced Composites: Potential, Applications, and Properties

Piyush P. Gohil, Vijay Chaudhary and A. A. Shaikh

Abstract The majority of the mounting countries are extremely rich in agricultural biomass such as natural fiber. Apart from a few exceptions, a huge part of agricultural biomass wastes is used as a substitute for different applications. India only produces more than 400 million tonnes of agricultural dissipate yearly. A huge fraction of agricultural biomass wastes comprises various natural fibers. All these natural fibers have brilliant properties and could be exploited successfully in the development of composite materials for a variety of structural and nonstructural applications. This chapter focuses on the prospective use of natural fibers in composite materials, their availability, importance, mechanical and physical properties, and their applications.

Keywords Natural fiber composites · Mechanical properties · Physical properties · Applications

Introduction to Composite Materials

A composite is a mixture of more than two materials, i.e., reinforcement and resin (Schwartz 1992), which differs in structure or composition on a macroscale. This structure results in a material that increases specific performance properties. The components do not disband completely and as a result normally show an interface

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between one another. Both reinforcing and matrix keep their physical and chemical identities; however, constituents make a combination of properties that cannot be attained with either of the constituents acting alone.

Composites are generally classified based on polymer matrix, ceramic matrix, and metallic matrix. Fibers are load-carrying members, and matrix keeps them at desired location and orientation in fiber-reinforced composites. The load is transferred between fibers via matrix, which also guard the composites from harmful effects of the environment.

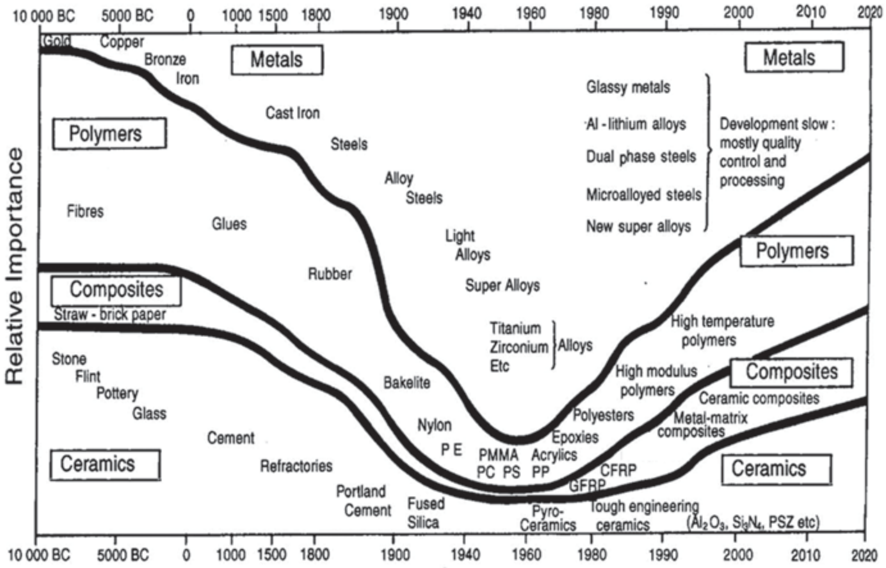
Glass, carbon, and Kevlar are the principal fibers for conventional composites. These fibers can be incorporated into a matrix either in continuous or discontinuous form (Mukhopadhyay 2005). Over the past three decades, composites have progressed from a laboratory curiosity to a production reality; the composites are extremely attractive in various applications.

Importance of Composites

It can be seen that composites can help to improve the quality of life so they are becoming more and more important. Composites are used in various services like aerospace, automobile, marine, pipings, and infrastructure. Researchers and scientists are defining ways to get better qualities of composites so it may be tough, lightweight, long-standing, and cheap to produce. The relative importance is shown in Fig. 1.

Applications of Composites

Various saleable and industrial applications of PMCs are aircrafts and spacecrafts, ship and submarines, trucks and railways, automobiles, structures and prosthetics. Due to their high-specific stiffness and strength, fiber-reinforced polymer composite materials have long been used in the aerospace industry and, with increasing focus on lightweight vehicle manufactures due to environmental legislation, automotive applications are becoming more widespread. Other notable engineering applications include pressure vessels and wastewater pipes and fittings. The need to utilize the mechanical performance of materials and to avoid unreasonable over-specification for aerospace applications was highlighted by Boeing, who estimated that it cost US$ 10,000 per pound (approximately UK£ 12,500/kg) to launch a satellite into orbit (Boeing Press Release 1996). Also of significance, when considered in terms of the levels of production and use, is that up to 40 % of the fuel consumption of a road vehicle is considered to be attributable to its inertia; the effects of inertia are particularly significant on the urban test cycle. With increasing environmental pressure, some vehicle manufacturers look towards an increased use of polymer composite materials for weight savings. Another driving force for efficient



The relative importance of metals, polymers, composites and ceramics as a function of time. The scale is not linear. (After Ashby, 1987)

Fig. 1 Importance of composites

design with composites in high-volume production industries is the cost of the basic material (Mayer and Seeds 1994). Because of the fact that composite material has characteristics that are as good as conventional materials, the use of natural fiber composites has begun gaining attractiveness in engineering applications. Properties like low density, lower material cost, renewability, and environmental friendliness are most important. In the past, various studies on natural fiber composites are carried out (Sapuan and Malique 2005). Thus, the design of product using composites is extremely essential issue and it is imperative to know of various property predicting factors for the design of composites.

Natural Fiber Reinforcement

Natural fiber reinforcement have had the attention of scientists and technologists due to environmental advantages that these fibers present above conventional reinforcement materials, and the development of natural fiber composites has been a subject of interest for the past 20 years. Natural fibers are low-cost fibers having low density and high specific properties. Natural fiber reinforcement is biodegradable and nonabrasive, unlike other manmade reinforcing fibers. Specific properties of some natural fibers are comparable to those of synthetic fibers used as reinforcements in composites (Bledzki and Faruk 2004; Gayer and Schuh 1996).

Classification of Natural Fibers

There are three types of natural fibers: plant fibers, animal fibers, and mineral fibers (Fig. 2; (FAO 2010).

Plant Fiber and Their Sources

Plant fibers normally consist of lignin, cellulose, hemicellulose, and pectin. Cotton, jute, flax, ramie, sisal, and hemp are famous examples. To develop paper and cloth, cellulose fibers are used. This fiber is categorized into leaf fibers, seed fibers, fruit fiber, bast fiber/stem fiber, and stalk fiber.

Animal Fiber and Their Sources

Animal fibers usually consist of proteins. Wool, silk, human hair, feathers, etc., are well-known examples. There are quite a few behaviors that differentiate wool from hair. Wool grows in staples and it is elastic (D'Arcy 1986).

Mineral Fibers and Their Sources

Mineral fibers occur in nature and a slightly modified fiber developed from minerals that may have distinct appearances. Asbestos arises naturally in the environment,

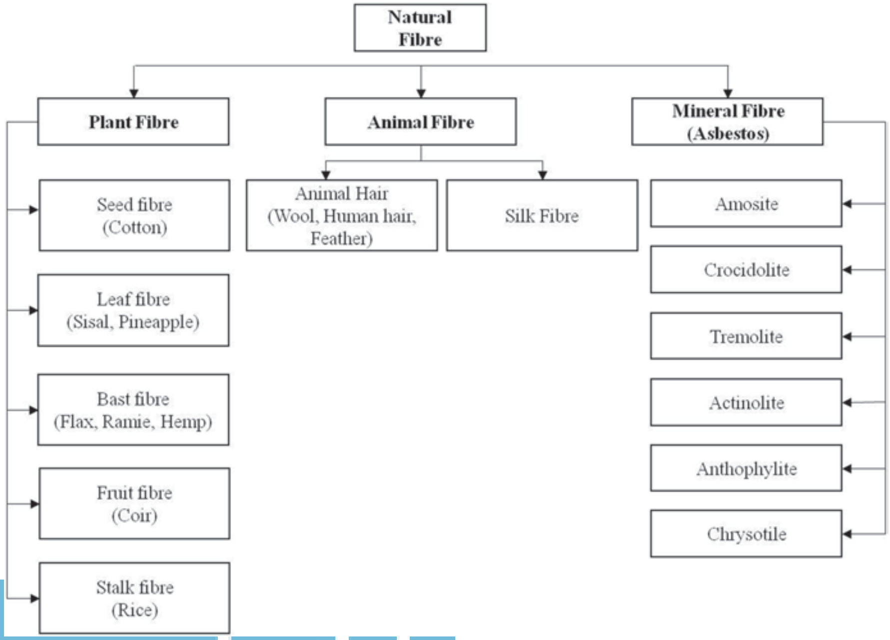


Fig. 2 Classification of natural fiber. (Saxena et al. 2011)

which has good heat and fire resistance but bad electrical conductivity. The two major groups of asbestos minerals are serpentine asbestos and amphibole asbestos (ATSDR 2011). Asbestos is mainly divided into six fibrous minerals: (1) amosite, (2) crocidolite, (3) tremolite, (4) actinolite, (5) anthophyllite, and (6) chrysotile asbestos.

All abovementioned types of natural fibers are available. For example, sisal fibers are widely cultivated in Tanzania and Brazil, and in tropical and subtropical North and South America. Sisal is also widely grown in Africa, West Indies, and the Far East (Bisanda and Ansell 1992). The largest producers of jute are India, China, and Bangladesh.

Presently, the annual production of natural fibers in India is about 6 million tonnes as compared to worldwide production of about 25 million tonnes (Mohanty et al. 2005). Flax and hemp are largely being cultivated in Europe, Russia, Canada, Argentina, and India. Kenaf is a crop grown commercially in the USA (Sanadi et al. 1995). India also produces 20 % of world production of coir (Satyanarayana et al. 1982).

Table 1 shows the fiber and countries of origin (Mohanty et al. 2005), and the composition of different natural fibers are shown in Table 2 (Bledzki and Gassan 1999).

According to the data collected from other scientific publications, the strength of natural fibers is lower than that of glass fibers (Table 3), while the specific stiffness is on the same level. However, taking into consideration low density of natural fibers, which are up to two times lighter than glass, the resulting specific stiffness of natural fibers is substantially higher than the same parameter of glass fibers.

Natural Fiber Composite Potential

In the plastics industry, tonnes of reinforcements are used per annum, and there is a vast possible market for environment-friendly composite materials using natural fiber reinforcement.

Table 1 Fibers and countries of origin. (Source: Amar et al. 2005)

Fiber	Country of origin
Flax	Borneo
Hemp	Yugoslavia, China
Sun hemp	Nigeria, Guyana, Sierra Leone, India
Ramie	Honduras, Mauritius
Jute	India, Egypt, Guyana, Jamaica, Ghana, Malawi, Sudan, Tanzania
Kenaf	Iraq, tanzania, Jamaica, South Africa, Cuba, Togo
Roselle	Borneo, Guyana, Malaysia, Sri Lanka, Togo, Indonesia, Tanzania
Sisal	East Africa, Bahamas, Antigua, Kenya, Tanzania, India
Abaca	Malaysia, Uganda, Philippines, Bolivia
Coir	India, Sri Lanka, Philippines, Malaysia

Table 2 Composition of different natural fibers. (Source: Bledzki and Gassan 1999)

Component	Cotton	Jute	Flax	Hemp	Sisal
Cellulose, wt.%	82.7	61–71.5	64.1–71	70.2–74.4	65.7–78
Hemicellulose, wt.%	5.7	13.6–20.4	16.7–20.6	17.9–22.4	10.0–14.2
Pectin, wt.%	–	0.2	1.8–2.3	0.9	10
Lignin, wt.%	–	12–13	1.7–2.0	3.7–5.7	9.9
Wax, wt.%	0.6	0.5	1.5–1.7	0.8	2.0
Moisture wt.%	10.0	10.0–12.6	10.0	10.8	11.0
Microfibrillar spiral angle (degree)	–	8.0	10.0	6.2	20.0
Component	*Kenaf*	*Coir*	*Ramie*	*Palm*	*Henequen*
Cellulose, wt.%	31–39	36–43	68.6–76.2	70–82	77.6
Hemicellulose, wt.%	21.5	0.15–0.25	13.1–16.7	–	4–8
Pectin, wt.%	–	3–4	1.9	–	–
Lignin, wt.%	–	41–45	0.6–0.7	5–12	13.1
Wax, wt.%	–	–	0.3	–	–
Moisture wt.%	–	8.0	8.0	11.8	–
Microfibrillar spiral angle (degree)	–	41–45	7.5	14.0	–

Table 3 Properties of some synthetic and natural fibers. (Source: Saeb and Jog 1999)

Fibers	Tensile strength (MPa)	Tensile modulus (GPa)	Specific gravity	Specific strength	Specific stiffness
E-glass	2500–3500	70–73	2.56	27	29
Carbon	2500–6000	220–700	1.75–1.9	116	400
Flax	500–900	50–70	1.4–1.5	33	50
Sisal	80–840	9–22	1.3–1.45	6	17
Jute	200–450	20–55	1.3–1.4	14	42
Hemp	310–750	30–60	1.48	20	41
Banana	530–750	7–20	1.4	5	14
Coir	130–175	4–6	1.15	3	5
Cotton	300–600	6–10	1.5	4	7
Silk	–	–	1.34	–	–
Wool	125–200	–	1.31	–	–

Major source of natural fibers like sisal, jute, banana, and coir is grown in many parts of India and many of them have greater than 65 % aspect ratio. Sisal and banana fibers have greater than 65 % cellulose and give comparable tensile strength, modulus, and failure strain with other cellulose rich fibers. These fibers are widely used for fishnets, matting, cordage, sacks, and rope, and as filling for cushions (e.g., rubberized coir). Cellulosed fibers are achieved from different parts of plants.

In polymer composites, plant-based natural fibers can be replaced to some level by more expensive and nonrenewable synthetic fibers like glass. Nangia and Biswas

(2009) showed that the maximum tensile strength (jute–epoxy), impact strength (jute–polyester), and flexural strength (banana–polyester) is 104.0 MN/m^2, 22.0 kJ/m^2, and 64.0 MN/m^2, respectively.

Several countries have devoted themselves to the Kyoto protocol, whereby a reduction in greenhouse gas emissions (mostly CO_2) have to be compacted to levels under that of 1990 among the years 2008 and 2012. Pervaiz and Sain (2003) illustrated that, by using hemp fiber and other natural fiber in place of glass fiber in composites, 3 t CO_2 per tonne of product can be saved (Fig. 3).

The mechanical properties of natural fiber composites depend on parameters like fiber strength, modulus, fiber length, and orientation in addition to the interface strength. In the natural fiber composite properties, fiber–matrix interface plays an important role. For effective load transfer, a good interfacial bond is required. In addition, it improves moisture resistance and the composite properties. The modulus of elasticity of the fiber should be higher than matrix for effective reinforcement. The mechanical properties of unidirectionally aligned continuous fiber composite with polyester resin along with randomly oriented short fiber composites are given in Table 4. Sisal fibers show a very good impact performance with specific impact strength similar to fiber-reinforced composites and show the most balanced mechanical properties. Coir presents as high a strength as jute and banana fibers with respect to tensile and impact strength of composites. Table 5 shows different properties of cotton fabric–polyester composite (Wiley 1955)

Gohil and Shaikh (2007) developed cylinders of varying thickness (3, 5, and 7 mm) with cotton fiber and polyester resin using the filament winding technique on lathe machine which are shown in Fig. 4. The hydro test and some weight study were also carried out. At the same time, the polyvinyl chloride (PVC) shell of the same dimension was also tested and a comparative study was carried out.

Mussig (2008) compared the cotton fibers in composites to ramie fibers. By using a Dia-Stron device, the strength of fiber was tested and the testing of fineness was carried out with fiber shape. Cotton- and ramie-based composites were prepared with epoxy resin and a bio-based resin. The results of tensile and impact tests show that mechanical properties of the composites strongly depend on fiber properties. Cotton with its morphological and mechanical properties can play a more vital role to optimize products with a view to improve the impact properties.

Fig. 3 CO_2 emissions per tonne of composite, and reduction in emissions by substituting glass fibers with hemp fibers. (Pervaiz and Sain 2003)

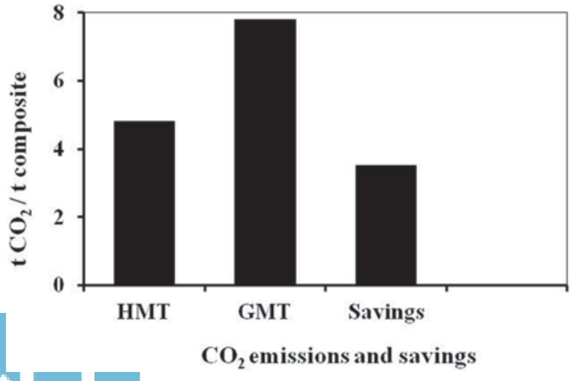


Table 4 Mechanical properties of unidirectionally aligned continuous fiber composite with polyester matrix along with that of randomly oriented short fiber composites. (Sangeeta Nangia and Soumitra Biswas, TIFAC)

Fiber (wt.%)	Tensile strength (MPa)	Modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m2)
Unidirectional					
Sisal (40)	129	8.5	192	7.5	98
Banana (30)	121	8.0	–	–	52
Coir (30)	45	4	56	4	44
Chopped random					
Sisal (25)	34.5	1.9	86.4	–	30
Banana (25)	43.5	2.3	92	–	10
Coir (25)	14.0	1.4	31.2	–	11
Fabric					
Banana–cotton	27.9–35.9	3.3	50.6–64	–	3.1–7.5

Table 5 Properties of cotton fabric–polyester composite. (Source: Wiley 1955)

Property	Value
Density (kg/m^3)	1400
Tensile strength (MPa)	34.5–68.96
Flexural strength (MPa)	62.1–124.1
Modulus (GPa)	2.76–4.14
Impact resistance (kg m/m^2)	253.3–428.8

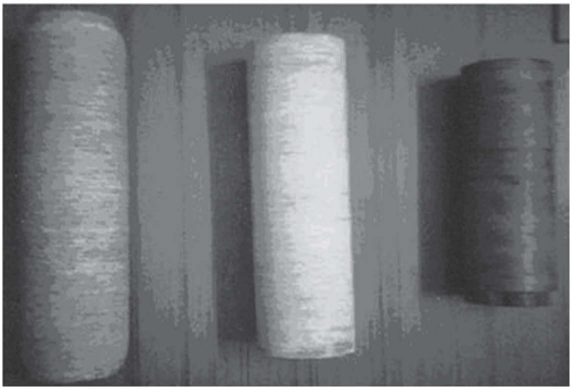


Fig. 4 Cotton–polyester cylinders (Gohil and Shaikh 2007)

In India, approximately 1.5 million acres of land is cultivated with banana plantations, which yield about 3 × 10^5 t of fiber (Kulkarni et al. 1983). It has been noted that banana fiber has been substituted for asbestos in bitumen and can be used for roofing (Satyanarayana et al. 1990); also, banana fiber/polymer composites and cotton fabric/polyester have been used in cars and for bearings, respectively (Satyanarayana et al. 1990).

Satyanarayana et al. (1984) prepared banana fiber composites with 25 % wt fraction by hand lay-up method and weathering tests (ASTM D570) were carried out. It was observed that the specific modulus was around 2.39 GPa and impact strength was about 10×10^3 J/m^2. After weathering tests, reduction was observed in modulus, ultimate tensile strength, and flexural strength around 8, 13, and 26 %, respectively.

Satyanarayana et al. (1981,1983, 1986) included banana fiber in the weft direction and cotton in the warp direction with polyester resin in different weight fractions (9– 25 wt.%). It was observed that up to 14 wt.% fabric can be included by way of a hand lay-up practice with no pressure. Mechanical properties of these composites have been estimated and are shown in Table 6 (Mohan et al. 1983). Geethamma et al. (1998) anticipated the persistence and modulus of elasticity of banana fiber within the range 529–759 MPa, and 8–20 GPa, correspondingly. The percentage elongation at break of fiber varied from 1.0 to 3.5. Banana fibers are stiffer and stronger than sisal fibers (Fig. 5).

Sapuan et al. (2006) carried out the tensile and flexural tests. They prepared three samples from woven banana fiber composites with different geometries. It was found that the maximum value of stress in *x*-direction and *y*-direction is 14.14 and 3.398 MN/m^2, respectively. The elastic modulus was 0.976 GN/m^2 in *x*-direction and 0.863 GN/m^2 in *y*-direction. To get the deflection of woven banana fiber specimen beam of 0.5 mm in flexural test, a load of 36.25 N was applied. The maximum stress and elastic modulus in *x*-direction was recorded to be 26.181 MN/m^2 and 2.685 GN/m^2, respectively. They used one-way analysis of variance (ANOVA) for statistical analysis and showed the variations of results obtained from samples are insignificant. Sapuan et al. (2001, 2003) have also performed an experimental study for epoxy/coconut shell fiber composite.

Properties of Composite

Properties of Plant Fiber Composites

Natural fibers like jute, sisal, flax, cotton, etc., require a shift in application; additionally, advantages such as biodegradability, lightweight, noise absorption, strength, etc., are present.

Jute Composites

Jute fibers have reasonably elevated stiffness and definite strength. Development of jute composite has constantly been a most important anxiety area because of low cost, easy availability, and high tensile strength. A variety of composites were prepared with various thermoset polymers and thermoplastic.

The mechanical properties of bleached and control jute composite at different fiber loadings were evaluated by Dash et al. (1999). The maximum tensile strength

Table 6 Properties of various fiber–polyester resin composites. (Source: Mohan et al. 1983)

Property	Polyester resin	Glass fiber-reinforced polyester resin, fabric content not mentioned	Cotton fabric-reinforced polyester resin, fabric content not mentioned	Banana fiber fabric-reinforced polyester resin, 11 wt.% fabric, cotton in the weft direction	Banana fiber fabric-reinforced polyester resin, 11 wt.% cotton in the weft direction	Coir-reinforced polyester resin, 9% fiber	Banana–cotton fabric-incorporated polyester		
							9 wt.%	14 wt.%	18 wt.%
Density (kg/m^3)	1300	1500–1900	1400	1215	1215	1160	–	–	–
Strength (MPa)									
Tensile	41.38	241.4–689.6	34.5–689.6	35.92	27.96	18.61	25.86	30.96	29.50
Flexural	89.69	344.8–862.1	62.1–124.1	50.60	64.00	38.15	52.38	61.24	60.40
Modulus of elasticity (GPa)	2.06	6.9–41.38	2.76–4.14	3.33	3.34	4.045	1.36	2.03	1.90
Impact resistance (kg m/m^2)	77.5	3116–8476	257.3–428	748.5	329.2	391	–	–	–
Water absorption (24-h room temp), %	0.21–0.40	0.2–1.0	0.8	1.93	1.36	1.36	–	–	–
Volume resistivity at 100-V DC, (ohm-cm)	1000	–	–	400	400	–	–	–	–
Dielectric strength in 2.5-mm thickness, (kV/min)	10	–	–	10	10	–	–	–	–
Dielectric constant at 1.5 (MHz)	3.04	–	–	3.5	3.5	3.14	–	–	–

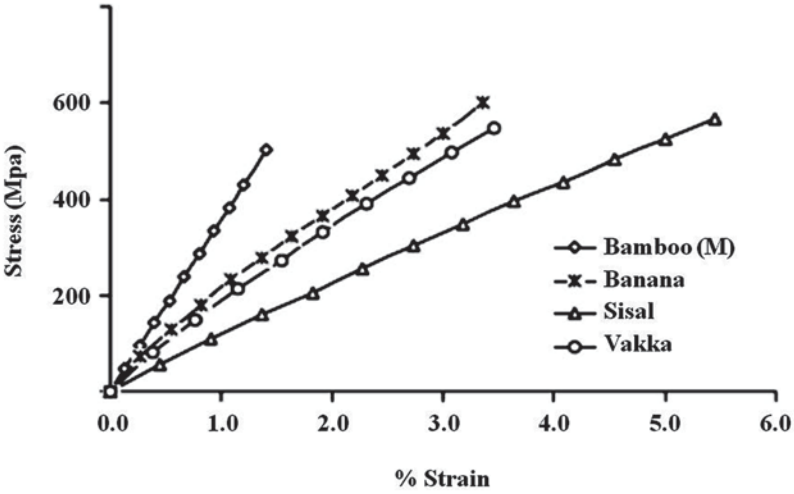


Fig. 5 Stress versus percentage strain of various natural fibers (Geethamma et al. 1998)

was found at 60% fiber loading which is shown in Table 7. Control jute–polyester composite shows maximum tensile strength while bleached jute–polyester composite shows maximum flexural strength.

Ray et al. (2001) had treated the jute fiber for 0, 2, 4, 6, and 8 h at 30 °C by using NaOH (5%) solution. They used 35 wt.% jute fiber treated for 4 h and observed that the flexural strength, flexural modulus, and laminar shear strength was improved by 20, 23, and 19, respectively, which is shown in Table 8.

Mishra et al. (2000) developed and evaluated the mechanical properties of bleached and control jute–epoxy composite and the result showed improved flexural strength and impact strength for bleached jute composite while tensile strength was higher at 50% fiber loading for controlled jute–epoxy composite which is shown in Table 9.

Table 7 Mechanical properties of jute–polyester composite. (Source: Dash et al. 1999)

Composite	Fiber volume (%)	Tensile strength (MPa)	Ult strain (%)	Tensile modulus (MPa)
Jute–polyester hot curing (Control)	60	132±6.33	5.83±0.68	2956±774
Jute–polyester hot curing (Bleached)	60	117±21.32	6.687±0.82	2106±229
Jute–polyester hot curing	55	78.15±7.45	5.04±0.72	2535±884
Jute–polyester hot curing	60	90.52±8.83	3.82±0.12	4189±403
Jute–polyester hot curing	66	80.6±12.5	3.27±.40	4072±402
Jute–polyester hot curing	71	70.31±6.89	2.85±0.25	4328±358

Table 8 Flexural properties of jute–vinyl ester composite. (Source: Ray et al. 2001)

% Fiber volume	Flexural strength (MPa)	Flexural modulus (GPa)	Breaking energy (J)
0	2.120	2.951	0.8227
8	106.30	4.220	0.2948
15	128.60	5.544	0.3399
23	145.70	7.355	0.3531
30	180.60	10.030	0.4799
35	199.10	11.890	0.5543

Hatta and Akmar (2008) investigated the mechanical properties of polystyrene/polypropylene ((PS/PP)-reinforced coconut and jute fibers and showed that there is an increment from 24.73 to 30.99 MPa in tensile strength of PP/PS blend after jute fiber loading which is shown in Table 10. It was also concluded that Young's modulus of composite increases with 10% fiber loading but the Charpy impact strength decreases.

Cotton Composites

Gohil and Shaikh (2010) prepared the setup of mold punch for the experiments to study the effect on unidirectional modulus of cotton–polyester composites at various fiber volume fractions. It was found that the strength for longitudinally placed cotton fiber with 10.41–35.27% varies from 27.94 to 71.16 MPa. It was also concluded that the strength in addition to longitudinal modulus of elasticity increases linearly with increase in fiber volume fraction (Table 11).

Chaudhary and Gohil (2013) characterized mechanical properties of unidirectional cotton–polyester composites (Uni-CPC). They compared experimental data with finite element analysis (FEA) data. Experimental tensile and flexure strength was 86.47 and 108.95 MPa, respectively, while FEA tensile and flexure strength was 102.96 and 111.061 MPa.

Kim et al. (2008) compared cotton fiber with wood fiber. They found that with increase in weight percentage of the PP/wood fiber composites, the tensile strength was decreased while the PP/cotton fiber composites showed unusual behavior. They also found that the tensile strength decreases with the addition of 10 wt.% cotton fiber but it increases with the addition of 20 and 30 wt.% cotton fiber.

Sisal Composites

The majority of the mechanical properties of sisal–polyester composite are shown in Table 12. It was indicated that density was not changed relating to the surface-modifying agents. Fonseca et al. (2004) carried out work on silane-treated sisal–polyester composites and concluded that the elongation at break (1.7%) is greater than that of the related composites which is explained by Singh et al. (1996). It was

Table 9 Mechanical properties of jute–epoxy composite. (Source: Mishra et al. 2000)

Composite	Fiber vol. (%)	Ult. strength (MPa)	Ult. strain (%)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact strength (J/K)	Charpy impact strength (J/K)
Jute–epoxy (control)	50	148.3±6.94	6.29±0.93	3184±620	155.82±13.59	14232±2216	94.46	11482.14
Jute–epoxy (bleached)	50	131.09±23.563	7.41±0.90	2348±261	196.12±18.99	20445±2240	107.94	14701.38
Jute–epoxy	40	139.8±4.59	7.32±0.69	2826±146	–	–	–	–
Jute–epoxy	50	148.3±6.94	6.29±0.93	3184±185	–	–	–	–
Jute–epoxy	57	143.36±4.06	5.98±0.92	3060±185	–	–	–	–

Table 10 Mechanical properties of jute–polypropylene/polystyrene composite. (Source: Hatta and Akmar 2008)

Type of composite	Fiber volume (%)	Tensile strength (MPa)	Young's modulus (GPa)	Impact strength	Flexural strength (MPa)
Jute fiber mat polypropylene composite	–	28.4±0.90	–	65±3.2 J/m	35.1±1.2
Pure polypropylene +pure polystyrene (50/50)	0	24.73±0.99	1.1745	3.89 kJ/m^2	–
Pure polypropylene +pure polystyrene (50/50)+10% fiber	10	30.99±0.85	1.2163	3.11 kJ/m^2	–

Table 11 Tensile properties of cotton–polyester composite. (Source: Gohil and Shaikh 2010)

S. No.	% Fiber volume	Tensile strength (MPa)	Elastic modulus (GPa)
1	10	28	2.8
2	20	45	3
3	25	53	3.4
4	28	62	3.6
5	35	72	4

Table 12 Physico-mechanical properties of sisal–polyester composite

Composite	Fiber volume (%)	Density g/cm^3	Tensile strength (MPa)	Elongation (%)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Ref
Sisal–polyester composite	50	0.99	29.66	9.52	1.15	59.57	11.94	Singh et al. (1996)
Polyester neat composite	–	–	22.5	1.8	1.39	–	–	Fonseca et al. (2004)

also observed that, with addition of sisal for polyester–sisal composites, the tensile strength and elongation at break decrease 69 and 46 %, respectively.

Oksman et al. (2002) studied the mechanical properties of unidirectional sisal–epoxy composites prepared by resin transfer molding. It was concluded that the sisal–epoxy composites (46 % (v/v)) have considerably higher tensile strength (210 MPa) and Young's modulus (20 GPa) which are summarized in Table 13.

Zhong and Wei (2007) investigated the mechanical properties of sisal-fiber-reinforced composites and concluded that the best Charpy impact strength (9.5 kJ/m^2) was achieved with 50 % (w/w) sisal fiber which is shown in Table 14, whereas the composite with 30 % (w/w) sisal fiber gave excellent wear resistance, flexural strength, and water absorption properties.

Nair and Thomas (2003) investigated the effect of interface modification on the mechanical properties of polystyrene–sisal fiber composites. It was observed that the greatest improvement in tensile and impact strength was with polystyrene with maleic anhydride (PSMA) coating (Table 15). It was also observed that there was

Table 13 Mechanical properties of sisal–epoxy composite. (Source: Oksman et al. 2002)

S. No.	Composite	Fiber volume (%)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
1	Epoxy	0	76	7.3	3.1–3.2
2	Sisal–epoxy composite	28	169 ± 23	2.3	14.2 ± 1.6
3	Sisal–epoxy composite	35	183 ± 16	2.2	14.5 ± 1.6
4	Sisal–epoxy composite	46	211 ± 12	1.9	19.7 ± 1.5

Table 14 Mechanical properties of sisal–urea formaldehyde composite. (Source: Zhong and Wei 2007)

S. No.	Fiber volume (%)	Charpy impact strength (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)	Density (g/cm^3)
1	30	5.75	58.58	7.63	1.53
2	40	6.5	55.80	5.27	1.52
3	50	9.5	53.07	4.93	1.48
4	60	7	37.73	4.09	1.44
5	70	6.8	15.28	1.59	1.22

no significant difference in flexural modulus and flexural strain with fiber modification.

Mohanty et al. (2004) investigated the dynamic and mechanical properties of PP–sisal fiber composites which are summarized in Table 15. It was shown that the greatest mechanical strength was obtained with 21 % fiber content and 1 % methylacetylene–propadiene propane (MAPP) concentration. It was also observed that with increase in the fiber and MAPP the damping properties decrease.

Flax Composites

Baiardo et al. (2004) investigated the effect of processing conditions on fiber length distribution and the dependence of the mechanical properties on fiber content. It was observed that the tensile modulus increases with increase in fiber percentage. It was also observed that at 12.5 % flax loading the tensile strength was around 20 MPa and decreases at 37.5 % flax loading (Table 16).

The flax fiber has low modulus compared to epoxy resin modulus. Lamy and Pomel (2002) investigated the modulus for unidirectional flax epoxy composite with 40 % fiber volume fraction and compared with experimental results (Table 17). It was observed that the longitudinal flexural modulus for unidirectional composite

Table 15 Mechanical properties of sisal–polypropylene (PP)/polystyrene (PS) composite

Composite	Fiber volume (%)	Tensile strength (MPa) approx	Flexural strength (MPa)	Impact strength (J/m)	Reference
Polystyrene	0	35	48	–	Nair and Thomas (2003)
Untreated sisal–PS composite	0	43	72	–	
Sisal–PP	0	17.80	19.60	23.25	Mohanty et al. (2004)
Sisal–PP	6.8	24.17	34.83	40.50	
Sisal–PP	10.3	26.11	46.35	46.10	
Sisal–PP	21.0	29.25	48.96	51.79	
Sisal––PP	31.0	23.21	43.41	39.83	

Table 16 Mechanical properties of flax–polyester composite. (Source: Baiardo et al. 2004)

S. No.	Composite	Fiber volume (%)	Breaking strength (MPa)	Breaking strain (%)	Young's modulus(MPa)
1	Polyester	0	20.0	19.6	435
2	Flax–polyester	12.5	21.7	14.1	760
3	Flax–polyester	25	19.4	6.1	1112
4	UPR	–	70	2.2	3.7
5	Flax composite	–	1150	3	70

Table 17 Flexural strength of flax–epoxy composite. (Source: Lamy and Pomel 2002)

S. No.	Composite	% Fiber	Thickness (mm)	Flexural stiffness (J)	Flexural modulus
1	Flax–epoxy	34	2.28 ± 0.01	82,900 ± 1800	3500 ± 150
2	Glass–epoxy	50	1.03 ± 0.01	41,800 ± 900	19,000 ± 1000

is 12000 MPa, and determined modulus of the woven-flax-reinforced composite is 3500 MPa.

Kaith et al. (2008) evaluated the mechanical behavior of mercerized flax, raw flax, and methylmethacrylate-grafted mercerized flax (MFx-g-MMA) fiber-reinforced polystyrene composites. It was found that polystyrene blend gave tensile property of 125 N/mm^2 which becomes 175 N/mm^2 after loading raw flax fiber. The properties are shown in Table 18.

Cantero et al. (2003) carried out a maleic anhydride polypropylene treatment and found that the flax and fiber PP composite gave greater flexural strength than the neat PP blend. They also found that the composite with 10 wt.% MAPP-treated fiber gave maximum tensile and flexural strength which are shown in Table 19.

Table 18 Mechanical properties of flax–polystyrene (PS) composite. (Source: Kaith et al. 2008)

Composite	Compressive strength (N/mm^2)	Compression	Tensile strength (N/mm^2)	Extension
PS	100 ± 5.5	00.27 ± 0.02	125 ± 3.6	0.42 ± 0.05
Flax–PS composite	400 ± 3.6	0.9 ± 0.04	175 ± 4.6	4.3 ± 0.01

Table 19 Mechanical properties of flax–polypropylene (PP) composite

Composite	Tensile strength (MPa)	Tensile modulus (MPa)	Charpy impact strength (MJ/mm^2)	Flexural strength (MPa)	Flexural modulus (MPa)	Reference
PP	27	700	–	35	1400	Cantero et al. (2003)
Flax PP	19	17,500	–	48	3400	
Flax PP	39	4200	19	56	3800	Bledzki et al. (2008)

Properties of Animal Fiber Composite

Wool Composites

Blicblau (1997) investigated the mechanical properties of wool-based polyester composite. The properties are summarized in Table 20. It was observed that with increase in fraction of wool content, the elastic modulus and tensile strength are influenced a little. It was also observed that the tensile strength was increased when the fibers were placed in a crosswise position to the load.

Silk Composites

Composite materials reinforced with silk fiber are comparatively light despite having a high impact resistance. *Bombyx mori*-woven natural silk gives greater specific strength and specific stiffness (Bledzki and Gassan 1999). Perez-Rigueriro et al. (2000) observed that *Bombyx mori* natural silk is superior in terms of elongation at failure than Kevlar or steel.

Dasgupta and Agarwal (1992) investigated the tensile and bending strength of the composite through varying silk content. It was found that with increase in fiber content the tensile as well as bending strength increase and it is maximum for 30 % fiber. It was also observed that with increase in the silk content the tensile modulus and bending modulus increase.

Human Hair Composites

There are not enough investigations on mechanical properties of human hair. Elasticity is the important property of human hair. Bleaching varies the hair elasticity and also decreases up to 25 % of its tensile properties (Dawber and Messenger 1997). Berivan et al. (2008) carried out tensile tests with a 50-N load cell device and observed that there is no effect on mechanical property of human hair whether they were dyed or not.

Table 20 Mechanical properties of raw wool–polyester resin composites. (Source: Quazi et al. 2010)

S. No.	Wool (wt.%)	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Izod impact toughness
1	0	33.7 ± 4.2	0.7 ± 0.2	–	–
2	22	35.9 ± 3.3	3.2 ± 0.2	76.2 ± 6.3	9.2 ± 1.3
3	37	34.6 ± 2.6	2.7 ± 0.3	72.1 ± 6.2	46.7 ± 15.8
4	51	39.1 ± 1.7	1.6 ± 0.2	75.4 ± 6.3	49.9 ± 10.4
5	54	40.7 ± 1.2	1.8 ± 0.1	7.5.1 ± 1.3	58.1 ± 9.3
6	54	17.1 ± 1.2	1.3 ± 0.1	54.7 ± 0.9	25.1 ± 0.6

Feather Fiber Composites

Hong and Wool (2005) developed bio-based composite material from soybean oils and keratin feather fibers (KF). It was found that at 30 wt.% feather fiber the bulk density was 1.08 g/cm^3. However, up till now, very narrow work has been reported on feather fiber composites. Acda (2010) prepared composite boards comprising different proportions of cement, waste feather, sand, and chemical combinations. It was observed that with increase in the feather proportion from 5 to 20 % workability was decreased considerably. It was also observed that higher feather proportion reduces the modulus of elasticity.

Properties of Mineral Fiber Composites

There is 8–16 % of asbestos fiber by volume in asbestos cement products. Shah (1981) compared strength of chrysotile and crocidolite fiber and found that the strength of crocidolite asbestos–cement composites was greater than chrysotile–cement composites. Mechanical properties of asbestos–cement composites are shown in Table 21. Sung et al. (1975) studied the mechanical properties of asbestos reinforced with phenolic resin and found that the flexural strength, flexural modulus, and impact strength were 93.76 MPa, 159.96 GPa, and 64.08 J/m, respectively. Lee and Kim 2004) showed the maximum tensile strength in axial fiber composites and maximum compressive strength in the radial position (Table 22). Mechanical properties of asbestos–cement composites are shown in Tables 23 and 24. Akers and Garrett (1983) investigated the failure process of asbestos–cement composites and calculated the flexural strength (35–37 MPa). Akers and Garrett (1986) also showed that modulus of rapture increases up to 15 % with increase in fiber mass fraction. It was also observed that the density decreases from 1.65 to 1.23 g/cm^3 when 35 % fiber was added.

Table 21 Physico-mechanical properties of asbestos–cement composites. (Source: Shah 1981)

S. No.	Type of composites	Tensile strength (MPa)	Young's modulus of elasticity (GPa)	Density	Elongation of break (%)
1	Chrysotile asbestos–cement composites	3100	16.4	2.55	2–3
2	Crocidolite asbestos–cement composites	3500	19.6	3.37	2–3

Table 22 Mechanical properties of asbestos–phenolic composite. (Source: Lee and Kim 2004)

S. No.	Orientation of fiber	Tensile strength (MPa)	Tensile modulus (GPa)	Compressive strength (MPa)
1	Hoop	82	13.3	86.2
2	Radial (orientation of fiber)	11.1	3.0	105.3
3	Axial (orientation of fiber)	15.6	3.5	75.3

Table 23 Physico-mechanical properties of asbestos fiber–cement composites (different percentage fiber content). (Source: Akers and Garrett 1986)

S. No.	% Fiber mass fraction	Modulus of rapture (N/mm^2) (no pressure)	Impact resistance (kJ/m^2)	Density (g/cm^3)
1	5	20–24	0.6–1.4	1.65
2	10	35–40	2.0–2.4	1.55
3	15	37–42	2.2–3.0	1.45
4	20	33–37	3.0–3.5	1.3
5	25	25–30	3.5–3.8	1.25
6	30	25–30	3.5–3.8	1.23

Table 24 Physico-mechanical properties of asbestos fiber–cement composites (variation in water–cement ratio). (Source: Akers and Garrett 1986)

S. No.	Water–cement ratio	Modulus of rapture (N/mm^2) (no pressure)	Impact resistance (kJ/m^2)	Density (g/cm^3)
1	0.30	30–32	0.8–1.2	1.65
2	0.33	32–35	1.2–1.4	1.55
3	0.35	25–30	1.0–1.3	1.45
4	0.37	23–25	1.2–1.4	1.3
5	0.40	20–25	0.8–1.2	1.25
6	0.45	15–20	0.4–0.8	1.23
7	0.50	10–15	0.2–0.06	–

Conclusion

This work has examined the different types of natural fiber available for the development of potential composites. Classification, courtiers of origin, chemical composition, mechanical properties of the natural fiber derived from various references has been cited. This chapter also discusses the properties of various natural fiber-reinforced composites.

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Effects of Nanotechnology on Fluid Flow in Agricultural and Wood-Based Composite Materials

Hamid Reza Taghiyari, Ali Karimi, Paridah MD Tahir and Adrian Cheng Yong Choo

Abstract Wood is a natural renewable material with continuous porous structure. Density in each wood species significantly depends on its porosity. The continuous porosity in wood provides easy transfer of different fluids through it. Wood is mainly composed of three polymers, including cellulose, hemicellulose, and lignin. The hydroxyl groups (–OH) in cellulose and hemicellulose are mostly free, providing opportunity for water molecules to easily make bonds with them. This is the root cause for shrinkage and swelling phenomena in wood and wood-composite materials. In wood composites, constant and repeated shrinkage and swelling result in breakdown of the resin bonds in the composite matrix, eventually weakening the whole structure. Moreover, water molecules interact with resin polymer, significantly weakening its strength. Easy transfer of water vapor and liquid through composite matrix speeds up this process. It is therefore necessary to monitor, and if possible to decrease, flow of water vapor and droplets into the wood-composite matrix, increasing its service life. A brief overview of the research project carried out on the utilization of nanomaterials in the wood-composite manufacturing industry proved numerous potential applications of nanotechnology in this industry. The use of metal and mineral nanomaterials with high thermal conductivity coefficient helps to improve thermal conductivity and better cure of the resin, resulting in a significant decrease in gas and liquid permeability. Improved thermal conductivity also helped to decrease press time to a considerable extent, lowering production costs, as well as accelerating the production rate. The water-repellent property of some nanoparticles (nanozycosil) can also hinder penetration of water and vapor

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into wood-composite matrix; ultimately, the service life of the parts used in the furniture or structure would significantly increase.

Keywords Fluid flow · Nanotechnology · Penetration · Permeability · Wood composites

Introduction

Understanding fluid flow in wood is of vital importance as it has great impact on its utilization in different industries (such as wood preservation, wood drying, pulp, and paper; Chen et al. 1998). The way gases and liquids flow through wood cells in solid woods, and the matrix in wood-composite materials, also affects their properties, and ultimately it influences their applications (Taghiyari 2013a; Taghiyari et al. 2014a). Interaction between wood components as the fluid passes through the complicated network of pores and cavities would also have significant effects on the physical and mechanical properties as well as applications. Moreover, as aerobic organisms, wood fungi produce CO_2, water, and energy by respiration and need therefore air oxygen. Fungi activity is, therefore, affected by the flow of gases through wood. There are various reactions occurring in wood fungi that require oxygen, such as degradation of lignin, oxidative polymerization of phenols, and melanin synthesis in blue-stain fungi and other fungi (Schmidt 2006).

The total area of the world's forests is decreasing in an alarming manner while the consumption of wood in the world is progressively increasing along with the exponential growth of the world population and the rising prosperity in several continents. It was estimated that the total area of the world's forests was under 4 billion hectares (Kues 2007). Shortage of wood resources and natural regeneration of forests necessitate the use of fast-growing trees as well as harvesting them at short rotations (Ruprecht et al. 2012). The harvested wood of these trees usually are not suitable for furniture industry; however, they provide a sustainable source for paper- and composite-manufacturing industries. For many centuries, the size of wooden structures made by man was limited by the natural dimensions of trees and the wood produced (Kues 2007). Moreover, solid woods had an inherent disadvantage; their strength properties were significantly different in different directions. In fact, the strength across the fiber in solid woods is about 1/20–1/10 of that in the longitudinal direction (Nowak and Drach 1949). The orientation of cells is also characteristically different, leading to a swelling and shrinking anisotropy. Therefore, the necessity of a more uniform material with no limitation to the natural dimensions of trees was brought up. The term wood-composite panels (or wood composites, panels boards, etc.) refers to any product, which is manufactured on the basis of mechanically chopped, milled, and grinded or refined wood (such as veneers, strands, particles, fibers, etc.) that are bonded by adhesives usually through a process at high temperature and pressure (Youngquist et al. 1997; Kharazipour 2004). During the production of wood composites, the homogenized raw materials can be formed in the desired shape, size, dimension, and amount. Current important wood-composite panels are particleboards, medium-density fiberboards (MDF), oriented strandboards (OSB), and plywood. The term particleboard refers to a wood-based panel manufactured under pressure and heat from wood particles (wood chips), usually by addition of adhesives and under hot press. MDF is made from lignocellulosic fibers mixed with a resin and under hot press. OSB is manufactured from shredded into small rectangular strips, layered across each other in the direction of their grain, and bonded together by a resin under hot press. Plywood is produced by wood veneer being stacked crosswise onto each other (Kues 2007).

Wood-composite materials have the advantage of offering a homogeneous structure which may be important for many design purposes (Doost-hoseini et al. 2013). Wood-composite materials also have the advantage of in-process treatments (IPT); this particular property is quite useful when the end uses necessitate treatment of wood chips and fibers with nanomaterials during the process of wood-composite production (Manning 2002; Gardner et al. 2003; Taghiyari 2014a). In wood-composite materials, the passing fluid may even affect other components, such as resin and paraffin used in their production. A better knowledge of the porous structure in woods and wood-composite materials would therefore provide us with useful information on how they would react under different conditions; these conditions include the relative humidity in which the wood-composite materials are installed because wood has a thermohygromechanical behavior and its properties depend on the combined action of temperature, relative humidity, and mechanical load variations (Figueroa et al. 2012; Taghiyari and Moradi Malek 2014), the temperature of the surrounding environment, exposure to sunlight and ultraviolet (UV) radiation, exposure to high temperature and possibly fire, the possibility of biological wood-deteriorating agents (Schmidt and Moreth 2003; Schmidt 2007; Karimi et al. 2013; Taghiyari et al. 2014b, 2014c) such as fungi, wood-boring beetles, and termites, as well as exposure to special bacteria and microorganism to gain biofuels, bioincising, etc.

Many methods have so far been introduced to measure permeability in wood and wood-composite materials with different precision, as porous media, over the past few decades (Siau 1995; Shi 2007). In the recent years, there was a possibility to measure gas permeability values in solid woods as well as composite materials due to the invention of a gas permeability measurement apparatus with 0.001-s precision (Taghiyari et al. 2010; Taghiyari and Sarvari Samadi 2010). The high precision, as well as the easiness for operation, made the results obtained through this apparatus credit-worthy for scientific and industrial purposes. The point is that gases usually do not interact with wood material components while liquids may come to chemically and physically interact with it, mostly with its hydroxyl groups (Taghiyari 2013a). Besides, most industries in which permeability is important deal with impregnation of solid woods with liquid or extraction liquids from them. Therefore, in the first place, liquid permeability measurement seems to be of great importance too, in order to have a better scope and understanding of practical behavior of wood structure towards penetration of liquids. In the second place, finding a correlation between gas and liquid permeability is important for industrial decision-making processes.

From another perspective, wood is considered a biological material that is greatly affected by its moisture content (MC; Schmidt 2006). Different modification methods have therefore been tried to ameliorate the effects, such as acetylation, and thermal modification (Hill 2006; Borrega and Karenlampi 2010). The thermal modification of wood has long been recognized as a potentially useful method to improve the dimensional stabilization of wood and increase its decay resistance (Hill 2006; Taghiyari 2011a). Although it has negative effects on the strength properties of wood, there are some techniques for mitigating these effects (Awoyemi and Westermark 2005; Awoyemi 2007). However, the thermal conductivity coefficient of wood is quite low (Taghiyari et al. 2012; Taghiyari et al. 2013a). The thermal conductivity of nanofluids containing dispersed metallic nanoparticles has been studied in research projects (Ayesh and Awwad 2012; Taghiyari 2012a). Enhancement in the thermal conductivity of common heat transfer fluids when small amounts of metallic and other nanoparticles were dispersed in these fluids has been reported by many researchers (Yu et al. 2010, 2012; Saber et al. 2013). The possibility of using an enhanced thermal conductivity in the structure of woods and wood-composite materials occurs to mind.

In this chapter, the potentiality of using different nanomaterials (metal nanoparticles, mineral nanofibers, mineral nanosheets, etc.) in wood-composite materials is discussed. The simplicity of using nanomaterials, using the IPT process, has made it quite attractive for the industry (Taghiyari 2014a). Their effects on fluid flow of gases and liquids are further explained in details.

Gas Permeability Measurement

Gas permeability measurement apparatus can measure permeability values in porous media (including solid woods, wood-composite materials, carton and paper, lightweight cement, etc.) with millisecond precision (Taghiyari 2012b; Taghiyari and Efhami 2011; Fig. 1); it is equipped with a seven-storey automatic-time-measurement device (USPTO No. US 8,079,249, B2). The falling-water volume-displacement method is used to calculate specific longitudinal gas permeability values based on the microstructure porosity of wood (Siau 1995; Taghiyari 2013b). Specimens can be prepared by a lathe machine (turning machine), or by a hole saw (a hollow saw). The optimum diameter of specimens was 17.5 mm. For each specimen, gas permeability values can be measured at seven different water-column heights, that is seven different vacuum pressures, in a single run. The internal diameter of the glass tube was 13 mm. The water level should be 15 cm above the starting sensor of the first time-measurement device (gas 1). The connection between the specimen and holder was made fully airtight. A pressure gauge with millibar precision was connected to the whole structure to monitor pressure gradient (ΔP) and vacuum pressure at any particular time as well as height of water column. Vacuum pressures

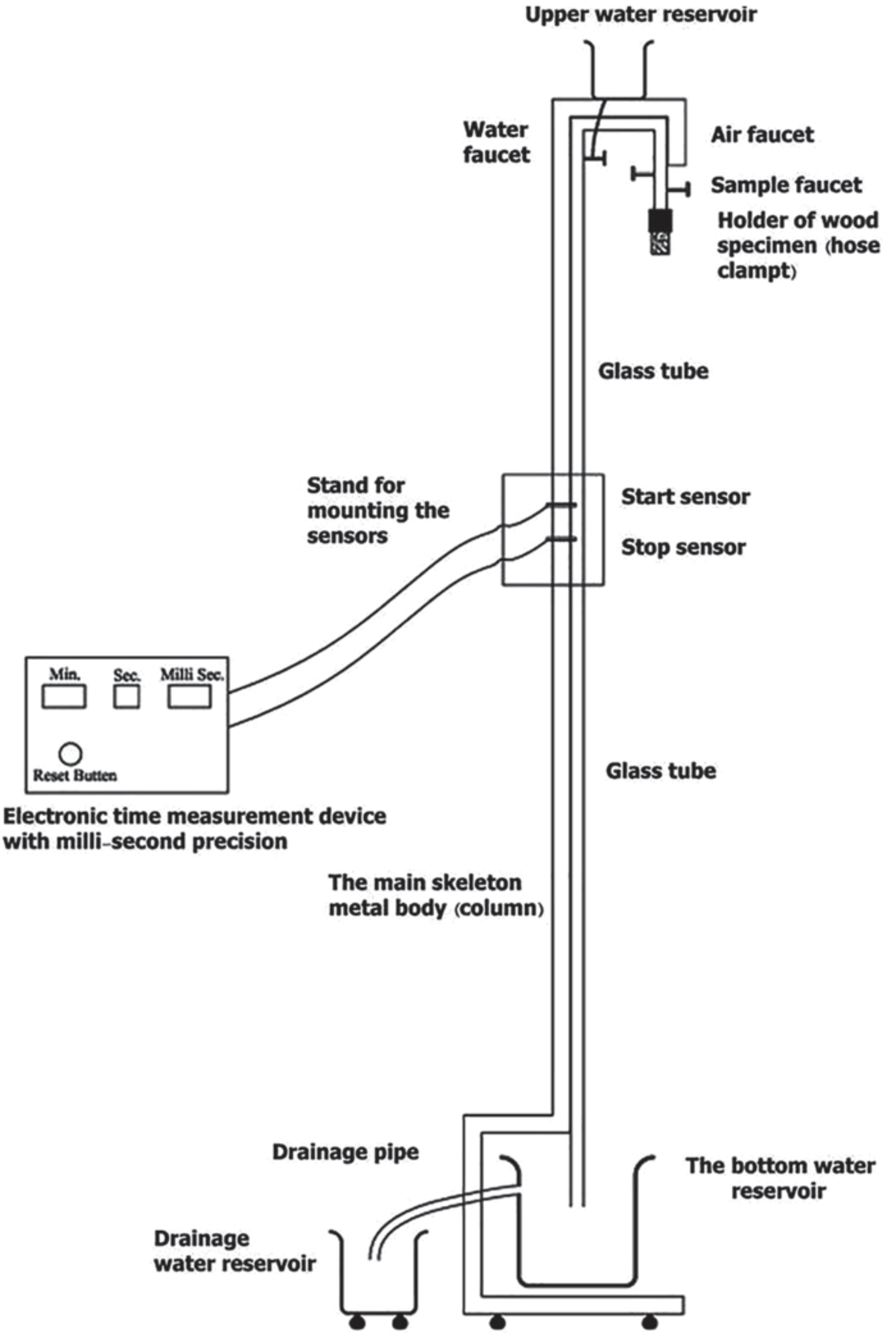

Fig. 1 The overview of the gas permeability apparatus (USPTO No. US 8,079,249, B2) equipped with single-storey millisecond precision electronic time-measurement device (approved by The Iranian Research Organization for Scientific and Technology under certificate No. 47022). (Source: Taghiyari and Efhami 2011; Taghiyari 2012b)

Table 1 Vacuum pressures at starting and stopping points for each of the seven water column heights. (Source: Taghiyari 2013a)

Code of the seven water columns	Height of the seven water columns at starting point (cm)	Height of the seven water columns at stopping point (cm)	Starting-point vacuum pressure (minus millibar)	Stopping-point vacuum pressure (minus millibar)
Gas 1	149.5	139.5	155	146.5
Gas 2	134.5	124.5	141.5	132
Gas 3	119.5	109.5	126.5	117
Gas 4	104.5	94.5	112	101.5
Gas 5	89.5	79.5	97.5	86.5
Gas 6	74.5	64.5	82	72
Gas 7	59.5	49.5	66.5	56

at starting and stopping points for each of the seven different heights are listed in Table 1.

Three measurements are to be taken for each specimen in order to obtain a trustworthy mean value for each specimen. The superficial permeability coefficient was then calculated using Siau's equations (Siau 1995; Eqs. 1 and 2). The superficial permeability coefficients were then multiplied by the viscosity of air ($\mu = 1.81 \times 10^{-5}$ Pa s) for the calculation of the specific permeability ($K = k_g \mu$):

$$k_{\mathrm{g}} = \frac{V_{\mathrm{d}} C L (P_{\mathrm{atm}} - 0.074\bar{z})}{t A (0.074\bar{z})(P_{\mathrm{atm}} - 0.037\bar{z})} \times \frac{0.760\ \mathrm{mmHg}}{1.013 \times 10^{6}\mathrm{Pa}} \tag{1}$$

$$C = 1 + \frac{V_{\mathrm{r}}(0.074\Delta z)}{V_{\mathrm{d}}(P_{\mathrm{atm}} - 0.074\bar{z})}, \tag{2}$$

where

k_g	longitudinal specific permeability ($\mathrm{m}^3\ \mathrm{m}^{-1}$)
V_d	$\pi r^2\ \Delta z$ [r=radius of measuring tube (m)] (m^3)
C	correction factor for gas expansion as a result of change in static head and viscosity of water
L	length of wood specimen (m)
P_{atm}	atmospheric pressure (m Hg)
$\bar{z}$	average height of water over surface of reservoir during period of measurement (m)
t	time (s)
A	cross-sectional area of wood specimen (m^2)
Δz	change in height of water during time t (m)
V_r	total volume of apparatus above point 1 (including volume of hoses; m^3)

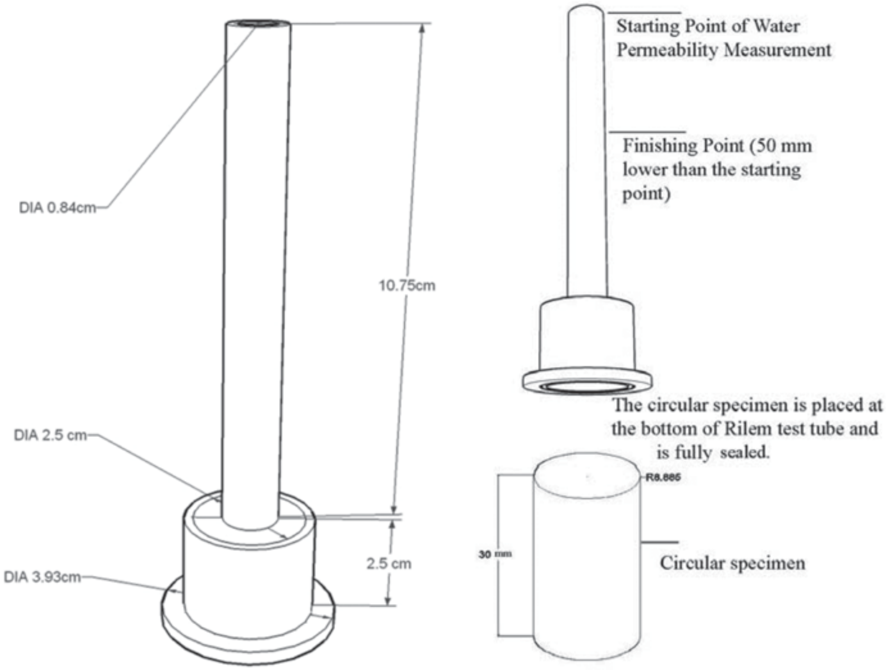

Fig. 2 Liquid permeability measurement apparatus (*Rilem*). (Source: Taghiyari 2012b)

Liquid Permeability Measurement

Liquid permeability was measured using Rilem test method II.4 (Fig. 2) according to Rilem Commission 25, PEM, Test Method 1154 by International Union of Laboratories and Experts in Construction Materials, Systems, and Structures; penetration tests were conducted under laboratory conditions according to ASTM E-514. Two times were measured: (1) the time the first drop of water falls off the bottom surface of the specimens and (2) the time the level of water in the Rilem tube lowers by 50 mm in the tube (that is, 6.6 CC of water). Correlations between each of the seven gas permeability times were separately calculated with the first-drop time, as well as the 50-mm-lowering time.

Permeability in Nanomaterial-Treated Wood Composites

One of the characteristics of wood is its water-absorbing potentiality when placed in water or even moist areas. The easy transfer of water vapor and liquid through it is due to its continuous porous structure. This affects wood-composite materials from different aspects. First, the dimensions of wood-composite panels and parts alter

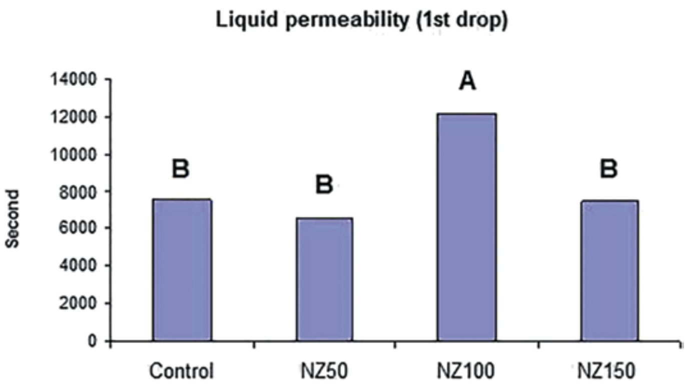

Fig. 3 The liquid permeability of the first drop for the four treatments of control, NZ-50, NZ-100, and NZ-150 treatments (s). *NZ* nanozycosil. (Source: Taghiyari 2013)

due to the phenomenon called swelling. The swelling not only has undesirable side effects on the design and dimensions of the wood-composite part that is used in the structure but also the wood chips and fibers lose their integrity by micromovements due to swelling. Second, water breaks down the resin bonds that have stuck wood chips or fibers together in the matrix, again decreasing the overall strength of the composite matrix.

In order to decrease water absorption in MDF, water-repellent property of nanozycosil (NZ) was used (Taghiyari 2013a). The NZ liquid (NZ-liquid) used was the resultant product of organo silane reacted with an organic reactant. Its color was pale yellow, with the flash point at more than 85 °C and autoignition temperature at more than 200 °C, specific gravity of 1.05 g/mL (at 25 °C), and viscosity of 500–1000 cps (at 25 °C). The NZ-liquid was composed of hydroxyalkyl–alkoxy–alkylsilyl compounds (38–42 %), and the solvent was ethylene glycol (58–62 %). NZ was used at four consumption levels of 0, 50, 100, and 150 g/kg dry wood fibers. The NZ-liquid was smoothly mixed with the resin. NZ content was based on the solid parts in the NA suspension. For each treatment, the weight of NZ solids was deducted from the fiber used; this way, the density of panels in different treatments with different fiber contents was managed to be kept constant. The final mixture of NZ + resin was smoothly sprayed on the fibers. The pH and viscosity of the resin were kept constant for all treatments in this study. Density of all treatments was kept constant at 0.67 g/cm^3. The cited author reported that NZ significantly decreased liquid permeability in MDF (Fig. 3) although the amount of wood fibers was lower in NZ-treated panels and microcavities formed in the composite matrix (Fig. 4). This resulted in NZ100 treatment to be clustered with the control panels (Fig. 5). In another study, NZ was reported to decrease water absorption and thickness swelling in MDF (Taghiyari et al. 2013b). NZ treatment affected the wood composite in two ways. First, the water-repellant property of NZ nanoparticles acted as a physical barrier towards penetration of liquid (water in this case). And second, NZ contributed in the process of sticking wood fibers together; that is, NZ

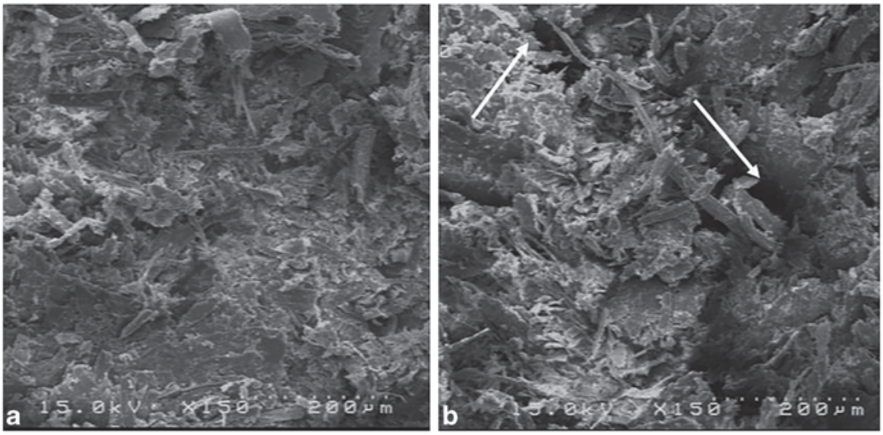

Fig. 4 MDF texture **a** control specimen: fibers are integrated more intensely; **b** NZ-150: some void spaces (↓) are observed in the texture leading air to pass through much easier. (Source: Taghiyari 2013)

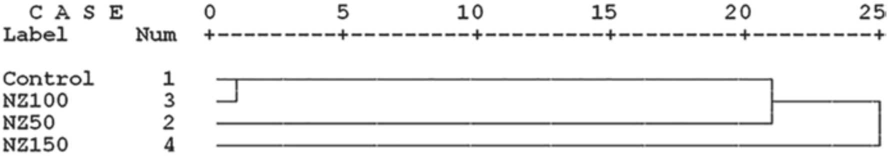

Fig. 5 Cluster analysis based on gas permeability value, as well as the two liquid permeability times for the four treatments of control, NZ-50, NZ-100, and NZ-150. *NZ* nanozycosil. (Source: Taghiyari 2013)

acted as an additional resin, although not as strong as the urea–formaldehyde (UF) resin used in the process. However, it was reported that silane-treated panels were susceptible to molds and therefore they were not recommended for moist climates (Taghiyari 2014b). The molds and fungi were mainly *Aspergillus niger, Penicillium* spp., and the Phycomycetes group. Therefore, in order to prohibit wood-deteriorating fungal attack, wollastonite nanofibers can be recommended to improve durability (Taghiyari et al. 2014b).

Silver and copper nanoparticles were also reported to significantly decrease both gas and liquid permeability in particleboards produced at industrial scale (Taghiyari 2011b; Taghiyari and Farajpour Bibalan 2013). NS and NC suspensions were added to the mat at two levels of 100 and 150 mL/kg dry weight wood particles and compared with control boards. Permeability values were significantly decreased in all nanotreated composite panels. The decrease was due to the high thermal conductivity coefficient of metal nanoparticles, resulting in better heat transfer to the mat, eventually causing better cure of the resin. However, the optimum consumption levels of nanosilver (NS) and nanocopper (NC) were reported to be different. This was explained to be due to the significant difference in the thermal conductivity coefficients of silver and copper. In fact, in the case of silver nanoparticles, overheating of the surface layer of the composite mat resulted in depolymerization of resin in the surface layer; eventually, the lower consumption level of 100 mL was recommended. In the case of copper with lower thermal conductivity coefficient, though, it was reported that the optimum NC-consumption level was 150 mL/kg. Water absorption and thickness swelling were also reported to significantly decrease after addition of NS and NC to particleboard matrix (Taghiyari et al. 2011; Taghiyari and Farajpour Bibalan 2013). The high thermal conductivity coefficient of metal nanoparticles helped UF resin cure more effectively; ultimately, wood chips were better integrated in the composite matrix, resulting in the decreased gas and liquid permeability values. As to the close relation between permeability versus water absorption and thickness swelling, the nondestructive nature of air permeability (gas permeability) can be very helpful for industrial purposes.

Accelerated heat transfer in NS- and NC-treated composite panels can influence permeability from another point of view. Heat treatment was reported to have significant effects on fluctuations of permeability in different woods (Taghiyari 2013b). In this connection, structural modifications and chemical changes of lignin occur while heating woods (Repellin and Guyonnet 2005). Moreover, the irreversible hydrogen bonding in the course of water movements within the pore system also affects the fluid transfer process (Borrega and Karenlampi 2010). These processes caused permeability to increase when woods are heated from about 75 up to 150 °C. In these steps, higher temperatures increase high internal stresses that are released as cracks (Oltean et al. 2007). These microcracks facilitate the process of fluid transfer through the porous material causing the gradual increase in permeability. Heat treatment at 185 °C caused permeability values to decrease. In fact, these processes are present during hot pressing in wood-composite panels too. The fluctuations in permeability alter behavior to the release of evaporation during hot-press time.

Nanoclay was reported to have no significant effects on permeability in plywood; however, moisture diffusion decreased significantly (Dashti et al. 2012). The cited authors used nanoclay at two levels of 3 and 5 %; hot-press time was also studied at two levels of 4 and 5 min. It was concluded that due to the hydrophobic property of clay nanoparticles, an increase in the level of consumption of filler resulted in reduction in thickness swelling and diffusion coefficient.

Thermal Conductivity in Wood-Composite Mat

The thermal conductivity of wood is rather low (0.055–0.17 W/mK depending on the direction of wood texture, in comparison to 429 in silver). In a study on MDF, thermal conductivity coefficient of control MDF boards was measured to be 0.099 (W/mK). Addition of 10 % of wollastonite nanofiber (NW) to the MDF matrix

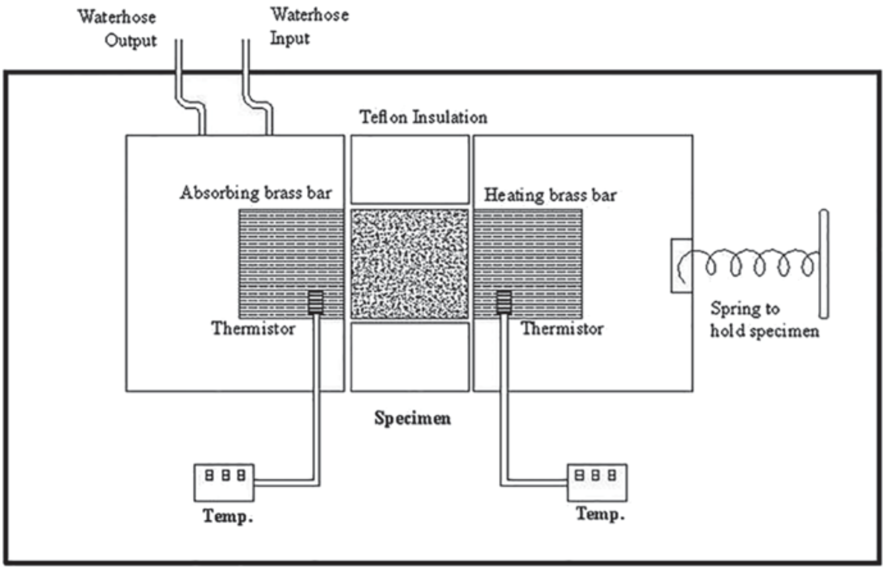

Fig. 6 Schematic drawing of the thermal conductivity measurement apparatus in this study. (Source: Taghiyari et al. 2013a)

(based on the dry wood fibers) increased thermal conductivity coefficient to 0.110 (W/mK); that is an increase of about 11.5 % (Taghiyari et al. 2013a). Addition of NW was further reported to decrease standard deviation in thermal conductivity among the replications of NW-treated MDF panels. This means that NW resulted in more homogeneity in the composite matrix.

Thermal conductivity was measured based on Fourier's law for heat conduction (Fig. 6). Circular specimens were prepared, 30 mm in diameter and 16 mm in length; all around, the specimens were covered with silicone adhesive for better insulation. Thermal conductivity was calculated using Eqs. (3) and (4). Temperatures were measured with 0.1 °C precision:

$$Q = KA\frac{\Delta T}{L} \tag{3}$$

$$\mathrm{K}=\frac{Q \times L}{A \times \Delta T}, \tag{4}$$

where

K	thermal conductivity (W/mK)
Q	heat transfer (W)
L	specimen thickness (m)
A	cross-sectional area of specimens (m^2)
ΔT	temperature difference ($T_1 - T_2$; °K)

The results of the cited authors clearly proved the better cure of the resin in the core section of the MDF mat, resulting in an increase in the physical and mechanical properties (Taghiyari et al. 2013c).

Moreover, hot-press time is dependent on many factors, including the thickness of the composite mat, press temperature, closing rate, and, most importantly, moisture distribution throughout the mat (Taghiyari et al. 2011). Moisture of the mat cannot always be increased as it in turn increases the hot-press time; hot presses are usually considered the bottleneck in wood-composite manufacturing factories. It is therefore necessary to try to decrease the time of hot pressing of wood-composite mat; however, higher MCs increase the time significantly. Increase in the MC also causes blows in wood-composite panels; high volume of vapor should be withdrawn from the mat to the surrounding atmosphere. If the volume is too high, permeability in the composite matrix would not be enough to have a timely withdrawal of vapor. Accumulated vapor within the composite matrix would eventually blow, once the hot-press plates open. Furthermore, for UF resin, there is a limitation of MC level (Papadopoulos 2006); that is, higher MCs than standard level for UF resin would eventually weaken the strength of resin. Finding new ways to increase the heat-transferring rate to the core section of the composite mat has always been a challenge before the wood-composite manufacturing industry. Silver nanoparticles were reported to decrease hot-press time by 10.9 % when 100 mL of NS suspension was used for each kilogram of wood particles. Copper nanoparticles were also reported to decrease hot-press time. It was reported that NC decreased hot-press time by 5.7 % when 100 mL of NC suspension was used. With due consideration to the lower thermal conductivity coefficient of copper in comparison to silver, this was reasoned.

The heat-transferring property of metal (Khojier et al. 2012; Sadeghi and Rastgo 2012) and mineral nanomaterials (Haghighi Poshtiri et al. 2013) was reported to improve some properties in solid woods as well as wood-composite materials. In a recent study, effects of a 400-ppm aqueous suspension of silver nanoparticles on the heat-transferring rate from the hot-press plates to the core section of MDF was studied (Taghiyari et al. 2013d). NS suspension was sprayed on the mat at three consumption levels of 100, 150, and 200 mL/kg based on the dry weight of wood fibers. Scanning electron microscope (SEM) micrographs showed uniform spread of silver nanoparticles over wood fibers (Fig. 7). A digital thermometer with temperature sensor probe was used to measure the temperature at the core section of the mat at 5-s intervals (Fig. 8). The probe of the thermometer was directly inserted for about 50 mm into the core of the mat (from the edge boarder of the mat), in the horizontal direction. Temperature measurement was started immediately after the two hot plates reached the stop bars. Measurement of temperature at the core section of the mat (immediately after the upper plate of the hot press reached the stop-bars) indicated significant difference between the temperatures of the four treatments of control, NS100, NS150, and NS200 (Fig. 9). The cited authors reported that temperatures at the core section of NS150 and NS200 were both higher than both NS100 and control treatments. The depolymerization of the surface resin bonds in the surface layers of panels with high metal nanoparticle content can be related

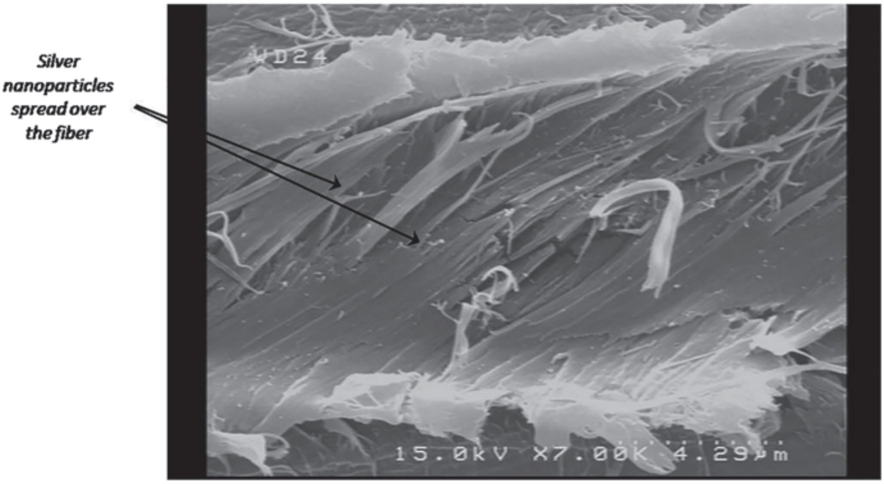

Fig. 7 Scanning electron microscope (SEM) micrograph showing silver nanoparticles (↓) scattered all over the fibers. (Source: Taghiyari et al. 2013d)

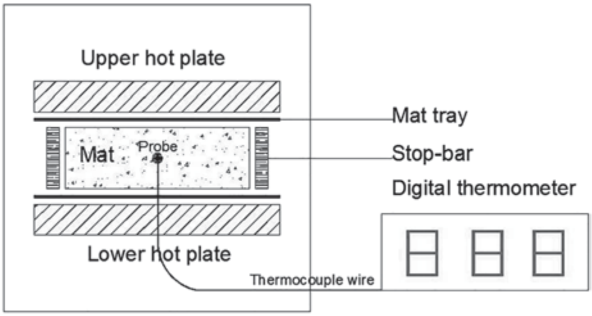

Fig. 8 Temperature measurement using a digital thermometer with its sensor probe inserted into the core section of the composite-board mat. (Source: Taghiyari et al. 2013d)

to the increasing trend in the final minutes of the hot pressing; that is, in the final minutes when all MC was nearly evaporated in the surface layers, the heat resulted in the depolymerization and breaking down of resin bonds. The depolymerization increased the fluid flow in the composite matrix. As to the fact that rapid transfer of heat to the surface layers of the mat would eventually result in the depolymerization of resin, ending up in decrease in some of the physical and mechanical properties, further studies should be carried out on possible spread of metal nanoparticles or mineral nanofibers in only the core section of composite mats to facilitate the heat transfer to this part; this would also prevent overheating of the surface layers and the consequent resin breakdown.

It may, therefore, be concluded that addition of metal nanoparticles to increase the heat-transferring rate to the core section of composite mats should not necessarily improve all physical and mechanical properties. Furthermore, the optimum

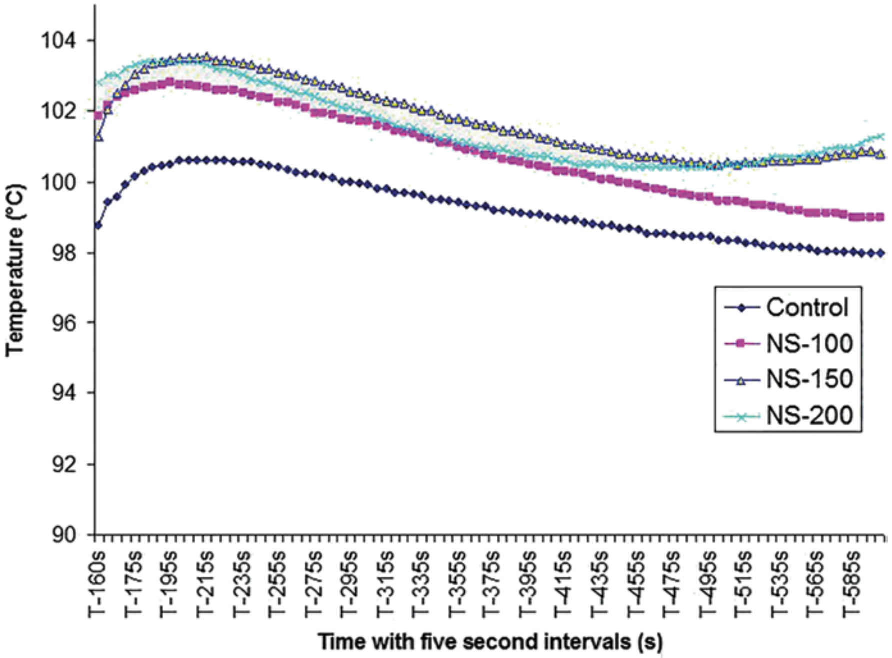

Fig. 9 Temperature at the core section of the medium-density fiberboard (MDF) mat after the third minute of hot pressing with 5-s intervals. (NS=Nanosilver content mL/kg). (Source: Taghiyari et al. 2013d)

consumption level for metal nanoparticles is dependent on many factors, including the hot-press temperature, hot-press duration, thermal conductivity coefficient of metal nanoparticles, and the type and density of composite panels.

Conclusions

Wood-composite materials offer the advantage of providing a homogeneous structure to be used in many applications. However, its biological nature causes it to suffer from several shortcomings, such as susceptibility to biological wood-deteriorating agents, water absorption and thickness swelling, fire, etc. A brief overview of the research project carried out on utilization of nanomaterials in the wood-composite manufacturing industry proved numerous potential applications of nanotechnology in this industry. The use of metal and mineral nanomaterials with high thermal conductivity coefficient helps in improved thermal conductivity and better cure of the resin, resulting in a significant decrease in gas and liquid permeability. The water-repellent property of some mineral nanoparticles (NZ) can also hinder penetration of water and vapor into wood-composite matrix; ultimately, the service life of the parts used in the furniture or structure would significantly increase.

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Composites from Bagasse Fibers, Its Characterization and Applications

Deepak Verma, P.C. Gope, Inderdeep Singh and Siddharth Jain

Abstract As an important branch of the composite materials field, natural fiber-reinforced polymer composites have been studied for decades. Natural fibers are originated from several sources such as cotton, nut, shells, bagasse, corncobs, bamboo, and vegetable. This work aims to discuss the different surface modification techniques of bagasse fibers including alkaline, silane, acetylation, and benzoylation treatments. The chapter also deals with the discussion on processing techniques of bagasse fiber-reinforced composite manufacturing and its mechanical and morphological properties. It also covers advantages of bagasse fiber reinforcement in composites and future trends and applications.

Keywords Bagasse fiber · Processing techniques · Surface treatment · Scanning electron microscopy (SEM)

Introduction

Cellulose-based natural fibers are achieving increasing consideration for their applications in engineering and their uses in general applications like building resources and structural parts for the automotive purpose, where lightweight is requisite. Environmental awareness motivates the researchers worldwide on the application of natural fibers as strengthening/reinforcement and an alternative to synthetic fibers

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in polymer matrix composite. By taking into account the importance of polymer composites, lot of work has been reported by various scientists/researchers to assess the mechanical characteristics of different types of polymers and their composites. Highly developed composite materials have been employed to construct a good number of structural parts in engineering purposes. This is because of their striking properties such as high strength with lightweight and high stiffness as well as good fatigue and corrosion resistance. Also, the capability to manufacture parts with complicated geometry using lesser components permits manufacturers to save cost as compared to other conventional metallic materials fabrication techniques. The composite processing includes the best use of available materials through the understanding of chemical interaction of ingredients, structural changes during processing, suitable processing methods for desired product shapes, and the resultant consequence on the mechanical and physical properties. Various chemical treatment methods of bagasse fibers have been reported by different researchers. A morphological study of composites by the use of scanning electron microscopy (SEM) is carried out to recognize why the mechanical characteristics of the composites prepared from treated and untreated bagasse are dissimilar and also to know the effect of fiber handling or treatment on the interfacial adhesion of filler–matrix. This chapter also reported the consequence of the filler material on the reflex characteristics of the composites materials. The composition, surface chemistry, and Fourier transform infrared (FT-IR) spectra of the bagasse fiber composites have also been discussed. In addition, various literatures related to polymer composites have been cited in this chapter.

Surface Modification Methods (Chemical Treatment) of Bagasse Fibers

Alkaline-Based Treatment

Treatment of natural fiber using sodium hydroxide (NaOH) is broadly applied for composites. This handling alters the direction of extremely packed crystalline cellulose arrangement and creates an unstructured region by enlargement of fiber cell wall. This process offers more access to penetration of chemicals. Alkali-sensitive hydrogen bonds existing among the fibers are agitated, and new hydrogen bonds form between the chains of cellulose molecules and increase surface roughness. This treatment removed the waxy substances on the surface of the fiber, thereby improving the close contact of matrix of fibers. This treatment was performed using saturating 5 g of fibers in 100 mL of NaOCl 4–6 % (v/v):H_2O (1:1) for 2 h at 300 °C and, thereafter, the fibers were rinsed with water and soaked in 100 mL of 10 % NaOH for 1 h at 300 C (Brigida et al. 2010). Acharya et al. (2011) performed chemical treatment of bagasse fibers by soaking in a "0, 1, 3, and 5 % (w/w) NaOH" solution at atmospheric temperature. The bagasse fibers were kept plunged in the solution for 2, 4, and 6 h, respectively, and thereafter the fibers were cleaned by the fresh clean water for several times for the removal of the NaOH contents from the fibers.

Silane Treatment

Coupling mediators generally recover the degree of cross-linking in the region of interface and provide a great bonding. Silane coupling mediators were found to be successful in adjusting the fiber–matrix interface. It goes through several stages such as hydrolysis, condensation, and bond formation throughout the treatment process with the fiber. This process also forms Silanols in the presence of moisture and hydrolysable alkoxy groups. Silanols retort with the cellulose hydroxyl group of the fiber and ultimately improves adhesion between fiber and the matrix to stabilize the properties of composites (Bledzki et al. 2010). Coupling agents such as toluene dissocyanate and triethoxyvinylsilane were tested in fiber treatment in order to enhance the interface properties. Silanols can create polysiloxane structures by reacting with hydroxyl group of the fibers. Arsene et al. (2008) reported the effect of combining pyrolysis and silane treatment. They used fibers of unpyrolyzed and pyrolyzed sugarcane bagasse and treated with the help of an alkyltrialkoxysilane ($RSi(OR')_3$), S_1 or a dialkyldialkoxysilane ($R2Si(OR'')_2$), S_2 silane solutions. The range of silane solutions used varies from 0.5 to 8 % (v/v). By combining the pyrolysis with silane treatment in composites, the water resistance capacity increases and a hydrophobic character is shown.

Acetylation Treatment

Plasticization of cellulose fibers can only be achieved by the esterification method which is also known as acetylation treatment. This method involves the rejoinder which causes the production of acetic acid as a derivative and that must be eradicated from the lignocellulosic material. Sreekala et al. (2002) have reported that acetic anhydride that is used for chemical alteration replaces the polymer hydroxyl groups of the cell wall by acetyl groups and then enhances the properties of these polymers so that they will turn into hydrophobic materials. Rowell and Keany (1991) treated the bagasse fiber by acetic anhydride to various levels of acetyl weight gain. This treatment (acetylation) causes the bagasse fiber to become more hydrophobic by lowering the equilibrium moisture content as the level of acetylation increased.

Benzoylation Treatment

Benzoyl chloride is used in benzoylation treatment to decrease the hydrophobicity of the fiber and improve fiber–matrix adhesion, and ultimately lead to increase the composite strength. In benzoylation treatment, the alkali pretreatment is used to activate the hydroxyl groups of the fiber. Then the fiber is soaked in benzoyl chloride solution for 15 min. Benzoyl chloride which adheres to the fiber surface is removed by ethanol solution followed by washing using water and is then dried in the oven. Benzoyl chloride processing on alkali-treated sisal fiber results in higher thermal stability than untreated fiber composites (Joseph and Mathew 2007).

Processing Techniques for Composite Manufacturing

There are various methods available for the processing and manufacturing of the composite materials some of which are discussed below.

Hand Laminating (or Wet Layup)

The hand/wet layup method is a very simple and effective method for the fabrication of composite material. As a part requirement for the hand layup process, a mold must be used unless the composite has to be fixed right to the next structure. The mold should not be complicated and can be a flat sheet or have unlimited curves and edges. For few typical sizes/shapes, molds should be joined in sections/parts so that after curing they can be separated. A release agent can be used and applied on the surfaces of the molds so that the part will not be able to stick to the mold surfaces. The fibers (for reinforcement) can also be laid in the mold as desired by the designer. After that, resin should be added to the fibers. Figure 1 shows the hand layup process.

Filament Winding

Filament winding is another method for the preparation of composite. Process parameters necessary to complete these tasks include exact filament tow, longitudinal placement, and mandrel winding speed. Filament winding advantages include low material and labor costs and precision of product dimensions. Cost and design constraints of removable mandrels and concave surfaces are some disadvantages of filament winding. The filament winding process is shown in Fig. 2.

Pultrusion

Pultrusion is a composite manufacturing process used for structural shapes. The pultrusion process is only suitable for mass production. First, the fibers are passed

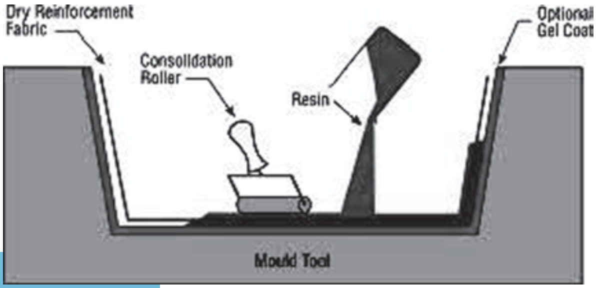
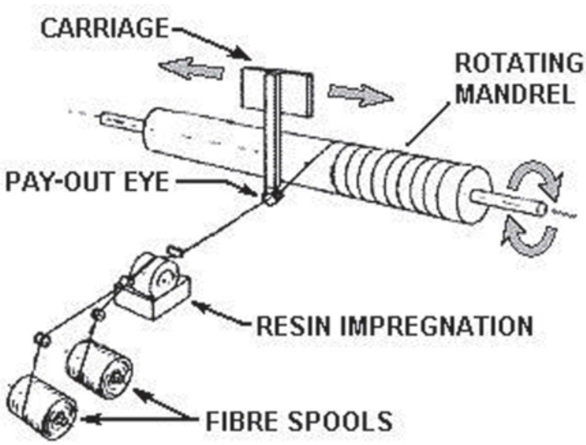


Fig. 1 The hand Layup method (http://www.net-composites.com/education.asp?sequence=65)

Fig. 2 Filament winding



through a resin bath and then through a forming block. Heaters are generally used to insure fast curing through steel dies and then the part is cut to ensure proper length. Because of the orientation of fibers, the pultruded parts are stronger in the longitudinal direction. The main purpose of the fiber orientation is to increase strength in other directions. By using the pultrusion process, solid shapes and open-sided, hollow shapes can be produced. Cores such as foam and wood can be built inside of the pultruded shapes. Due to the pressure and designs of production, protruded production can be up to 95 % effective in material utilization. Figure 3 shows the pultrusion process.

Compression Molding

The compression molding technique for composite manufacturing requires designing for the proper routing of the excess resin. Figure 4 shows the compression molding process. Compression molding generally follows the first steps of the hand layup process. In the process, the mold for a compression-molded part is designed

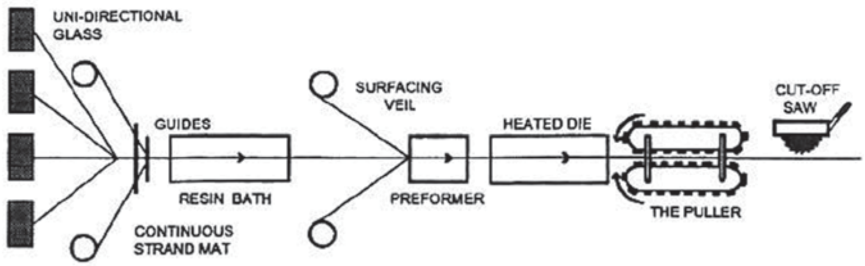


Fig. 3 Pultrusion process (http://www.amgrating.com/pultrusionprocess.aspx)

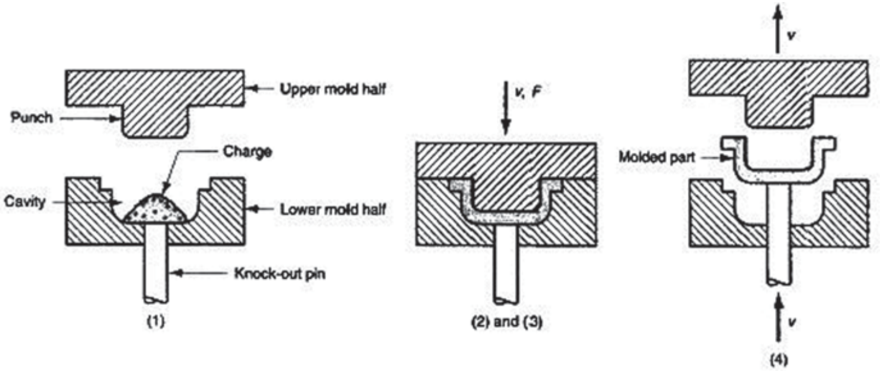


Fig. 4 Compression molding (http://www.sinotech.com/compressionAndTransferMolding.html)

for proper routing of excess resin. In compression, molding a male and female mold will be required. In the composite production method, a release agent must be applied on the mold surfaces. After that, the fibers must be slashed accordingly and placed on the surface of the molds. Then catalyzed resin must be applied onto the fibers in excess. After joining the two molds, an adequate pressure is applied pneumatically/mechanically. After the mold is set up in a proper manner, the desired amount of resin is applied/distributed throughout the fibers and then allowed to come out through the exit channels.

Injection Molding

Injection molding (Fig. 5) is a pure plastic injection process without any fibers and has been used to make injection molded parts. The resin generally used in this process is mainly engineering thermoplastics such as polypropylene, polystyrene, polymethylmethacrylate (PMMA), etc. Sometimes short fibers (such as short glass or carbon fibers) can be incorporated into the thermoplastics to make reinforced plastic components. In this case, the fibers are mixed with the resin and injected together, rather than in the form of fiber preform.

Integration into Matrix and Mechanical Properties of Polymer Composites

Integration into Thermoset Polymer

Mariatti et al. (2008) proposed the utilization of reinforcing part of unsaturated polyester (USP) resin for more opportunities in the waste management sector. To

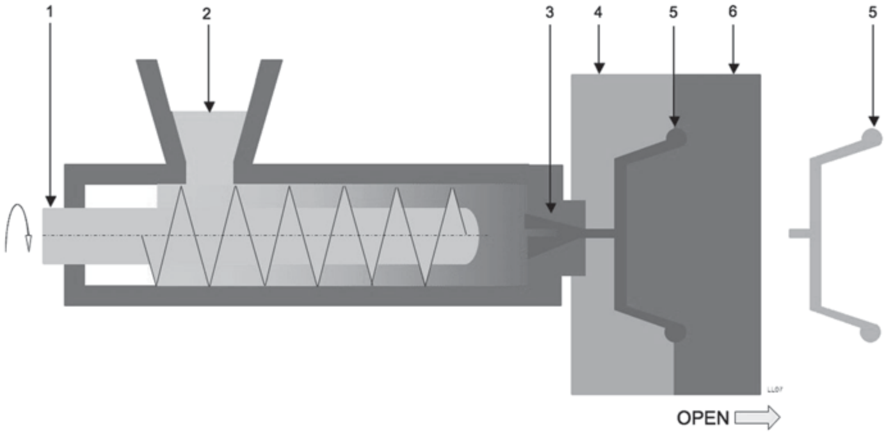


Fig. 5 Injection molding

modify the fiber properties, chemical treatments processes were carried out by using NaOH and acrylic acid. The result showed that by, selecting different fiber weights, acrylic-acid-treated fiber composites demonstrated improved mechanical characteristics than sodium-hydroxide-treated fiber composites. Dynamic mechanical analysis (DMA) shows that the treatment of fibers by sodium-hydroxide- and acrylic-acid-reinforced composites improves the storage properties of composites; however, from water absorption study, it has been found that processed fiber composites are better in terms of "lower water absorption properties" than unprocessed fiber composites.

From study, it has been found that on the one hand surface modification of bagasse decreases the moisture absorption, and on the other hand it improves the damp ability and hence ultimately improves the mechanical characteristics of composites.

The tensile and flexural properties of the composites, as shown in Figs. 6 and 7, represent the response of treated and untreated bagasse content. It has been found that the most favorable value of treated bagasse fiber for improving the tensile and flexural strength of the polyester composites is from 10 to 20 % (v/v). The increase in mechanical properties of sodium-hydroxide- and acrylic-acid-treated bagasse-based composites is due to increase in fiber surface adhesives characteristics by the fibrillation process as mentioned by Mariatti et al. (2008).

De Sousa et al. (2004) have mentioned the effect of three operating parameters on the mechanical properties of chopped bagasse–polyester-based composites. From the analysis, it has been found that composites made from bagasse with size under mesh #20 sieve pretreated for sugar and alcohol extraction were optimum and have the best mechanical characteristics. This is due to the fact that treatment increases the surface area and the complete sterilization of the bagasse surface. The molding pressure made a closer contact between the bagasse and the resin matrix, which condenses the snare voids. The weight fractions of the chopped bagasse are shown in Table 1. Sieving provides a very uniform size distribution of particulate

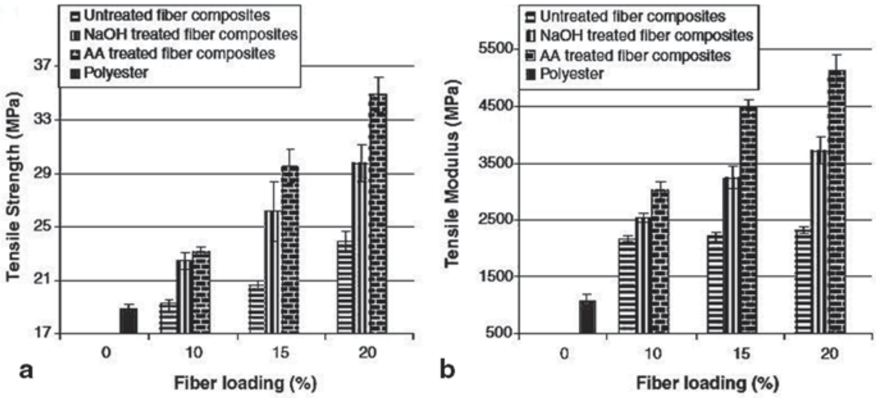


Fig. 6 The **a** tensile strength and **b** tensile modulus of treated and untreated fiber composites at different fiber loadings. Unfilled polyester resin is used as a control. (Reproduced with permission from Elsevier (Mariatti et al. 2008))

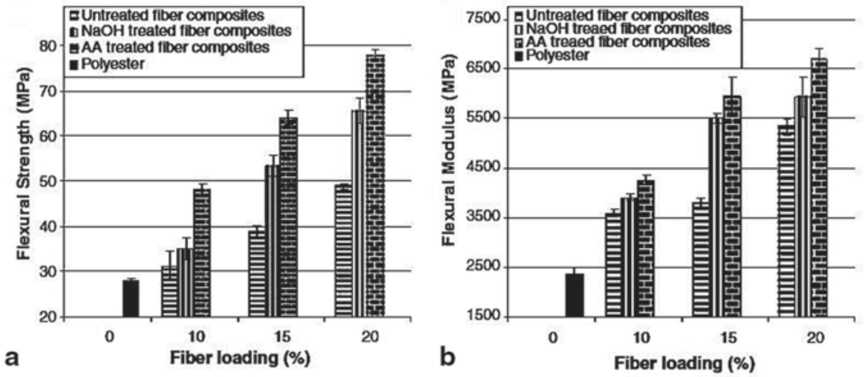


Fig. 7 **a** Flexural strength and **b** flexural modulus of treated and untreated fiber composites at different fiber loadings. (Reproduced with permission from Elsevier (Mariatti et al. 2008))

Table 1 Weight factions of the chopped bagasse. (Reproduced with permission from Elsevier Ltd. (Sousa et al. 2004))

Sieve (mesh)	Size of retained material (mm)	Weight fraction (%)
4	>4.7	0.6
10	4.7–2.0	31.7
20	2.0–0.85	35.8
Bottom	<0.85	31.9

Table 2 Flexural properties as a function of the bagasse size. Untreated bagasse. Molding pressure: 0.3 MPa. (Reproduced with permission from Elsevier Ltd. (Sousa et al. 2004))

Sieve (mesh)	σ_r (MPa)	ε_r (%)
10	7.6 ± 1.4	1.60 ± 0.14
20	19.5 ± 1.1	1.65 ± 0.10
Bottom	21.6 ± 1.6	1.84 ± 0.14

material ranging from 4.7 to under 0.85 mm. Three different meshes were used in the present investigation to analyze the effect of the size of bagasse on the mechanical properties of the composites. Table 2 shows the flexural stress (σ_r) and the deformation at rupture (ε) of the composites.

Balakrishna et al. (2013) prepared and tested Asian palmyra which is a natural fiber-reinforced composites (NFRC). The experiments were designed in accordance with a factorial design (three level) and determined the deviation of tensile strength of short and randomly oriented NFRC under the condition of control parameters. A thriving mixture of process parameters showed an improvement in the mechanical characteristics of the composite. The developed model was able to explain the influence of a design alter on each one of the operating parameters. Response surface methodology (RSM) is used in this study to model the influence of operating parameter on tensile strength. The mathematical model which is developed to predict tensile strength is found statistically suitable within the operating range of the designed parameters.

Tables 3, 4, and 5 show distinctive experiment values of tensile strength (related to output responses) and are used to put into practice the proposed tactic. The developed mathematical relationships are used to develop a correlation for tensile strength with the range of process parameters which will ultimately result in the

Table 3 Mechanical properties of the composite of fiber length 3 mm. (Reproduced with permission from Elsevier Ltd. (Balakrishna et al. 2013))

Specimen ID	Percent of fiber	Alkali treatment time (2, 4, 6 h)	Tensile load (N)	Tensile strength (MPa)	Elongation (%)
Sp301	20	2	549.653	13.741	2.51
Sp302	30	2	631.846	15.796	6.66
Sp303	40	2	674.846	16.857	4.78
Sp304	20	4	594.653	14.866	10.47
Sp305	30	4	658.076	16.451	3.57
Sp306	40	4	687.493	17.187	6.09
Sp307	20	6	696.653	17.416	2.42
Sp308	30	6	727.134	18.178	5.32
Sp309	40	6	789.652	19.742	4.27

Table 4 Mechanical properties of the composite of fiber length 5 mm. (Reproduced with permission from Elsevier Ltd. (Balakrishna et al. 2013))

Specimen ID	Percent of fiber	Alkali treatment time (2, 4, 6 h)	Tensile load (N)	Tensile strength (MPa)	Elongation (%)
Sp501	20	2	824.519	20.612	4.06
Sp502	30	2	766.615	19.165	12.17
Sp503	40	2	819.980	20.499	15.89
Sp504	20	4	834.134	20.853	5.35
Sp505	30	4	799.210	19.980	3.27
Sp506	40	4	846.346	21.158	6.42
Sp507	20	6	823.442	20.585	9.56
Sp508	30	6	864.115	21.602	13.79
Sp509	40	6	891.846	22.296	8.60

Table 5 Mechanical properties of the composite of fiber length 7 mm. (Reproduced with permission from Elsevier Ltd. (Balakrishna et al. 2013))

Specimen ID	Percent of fiber	Alkali treatment time (2, 4, 6 h)	Tensile load (N)	Tensile strength (MPa)	Elongation (%)
Sp701	20	2	864.423	19.116	2.50
Sp702	30	2	864.136	21.604	4.65
Sp703	40	2	875.961	21.899	1.84
Sp704	20	4	869.346	21.733	17.37
Sp705	30	4	898.856	22.471	19.40
Sp706	40	4	926.960	23.174	11.45
Sp707	20	6	910.653	22.766	3.70
Sp708	30	6	920.340	23.008	3.24
Sp709	40	6	1091.34	27.283	10.23

optimization of the operating parameters. For the computation of the regression coefficients, design expert 8.0 as statistical analysis software is used. The interaction effects between the process parameters and tensile strength was also found suitable, and based on analysis and results, a second-order quadratic mathematical model is suggested.

Choudhury et al. (2011) prepared epoxy novolac hybrid composites reinforced with the help of short bagasse and coir fibers. The dynamic mechanical properties and the mechanical properties of the composite were determined and reported for different layering patterns of the composites. It is found that the tensile strength of the three-layer composites is maximum as compared to the two-layer composites; on the other hand, it is observed that the flexural performance of the three-layer composites is lesser as compared to two-layer composites. The tensile strength of the mixed composite is similar to that of three-layer composites having bagasse as covering material. The temperature and frequency functions were used to study the effect of different pattern of layers on damping behavior (tan δ), storage modulus (E'), and loss modulus (E''). It is found that the modulus value of the two layers composite is lesser than that of three layers as bagasse–coir–bagasse composites. The composite made with the coir as covering layer shows minimum E'. The two-layer composite shows the best damping property. The theoretical modeling represents a suitable relation with experimental outputs above glass transition temperature (T_g) while the theoretical model departs experimental data at lesser T_g. The activation energy of the glass transition was calculated by Arrhenius correlation.

Choudhury et al. (2011) also reported and found diameter of fiber (bagasse based) to be higher as compared to coir fiber. The tensile characteristics of various sheeting orders of hybrid composites consisting of three-layer/sheets, two-layer, and mix composites are reported in Fig. 8a, b. It has been noticed that the tensile strength was maximum when bagasse was used as the covering material and coir as the core material. This is due to the fact that the use of high-strength material

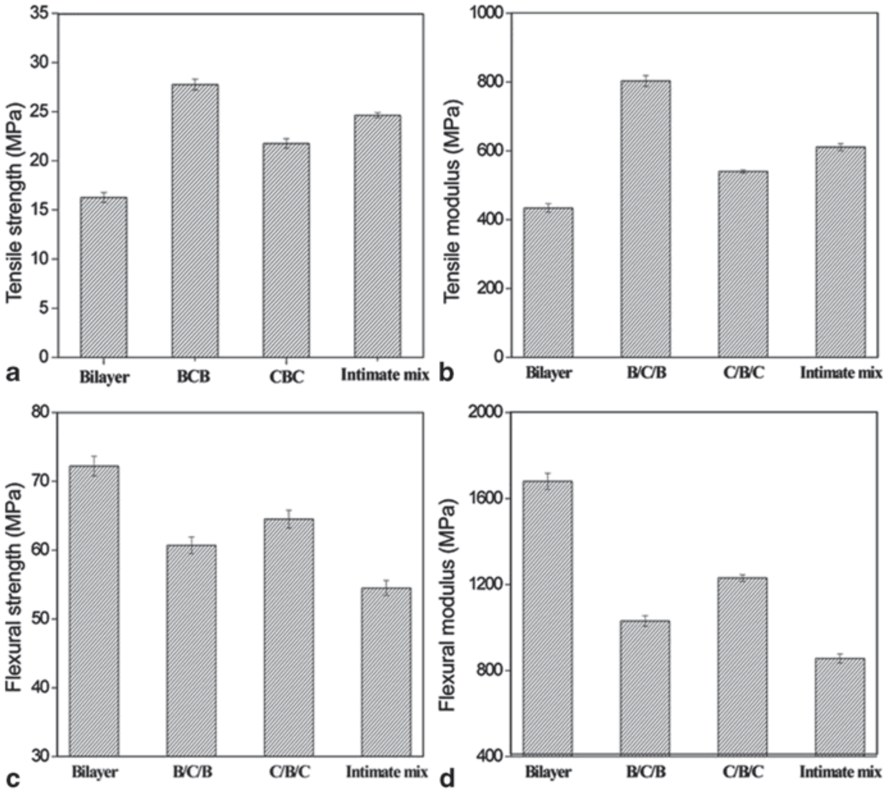


Fig. 8 Comparison of mechanical properties of different layering pattern hybrid composites. (Reproduced with permission from Elsevier Ltd. (Choudhury et al. 2011))

which is the prime load-bearing component for tensile value computation. In other composites of coir–bagasse–coir, the value is minutely lesser because of the low-strength coir fiber. In the bilayer, the tensile strength is found to be again lesser. The tensile modulus for the trilayer (bagasse/coir/bagasse) composite is found to be higher and the same in all other patterns.

Monteiro et al. (1998) studied the possible uses of bagasse waste as reinforcement material in composites of polyester matrix. Preliminary results have attested this possibility. Homogeneous microstructures composites could be fabricated and the levels of their mechanical properties enable them to have practical applications similar to the ones normally associated with wooden agglomerates. Future developments are expected to increase the performance and competitiveness of these composites as compared to those of other materials in the same structural class.

De Sousa et al. (2004) reported the effect of operating parameters on the mechanical performance of polyester composites (chopped bagasse based). The parameters to be evaluated were the “size of the material” and “molding pressure.” It has been noticed that composites made with bagasse fiber of #20 sieve size pretreated for sugar and alcohol extraction had good mechanical properties. Acharya et al. (2010) conducted experiments to determine the abrasive wear behavior of reinforced epoxy composite (bagasse fiber-based) in different directions which are named parallel orientation (PO), antiparallel orientation (APO), and normal orientation (NO) by using a abrasion wear tester (two body). Three different types of abrasives wear behavior have been observed in the composite in three directions and follow the following trends: $WNO < WAPO < WPO$, where WNO, WAPO, and WPO are the wear in normal, antiparallel, and parallel directions of fibers orientation, respectively.

Satyanarayana et al. (2011) described an option for pretreatment of sugarcane-based bagasse fibers for fabrication of USP composite. Bagasse fibers were treated by different methods, namely, steam explosion and alkali washing. From the experiments, it is found that the hemicellulose amount and bagasse fiber acid-soluble lignin were reduced by steam explosion method significantly, while acid-insoluble lignin increased in equal proportion.

Satyanarayana et al. (2011) reported that the DMA shows that the application of a small oscillatory mechanical tension leads to the deformation in solid environment under a variation of frequency. The DMA curves of the PPC and the fiber composites are represented in Fig. 10. From the figure it is observed that in all developed specimens a sudden decrease in the modulus is noticed (as shown in Fig. 10), under the temperatures above 0 °C. The T_g displacement (as shown in Fig. 9) is noticed at higher temperature ranges for pretreated fiber composite as compared to the neat matrix or bagasse-fiber-reinforced composites without pretreatment. This performance is because of the good interfacial adhesion of the treated fibers with the matrix.

Lignocellulosic fibers have good water absorption capacity which is also observed in composites reinforced with lignocellulosic fibers. Figure 10 represents the curve for water absorption.

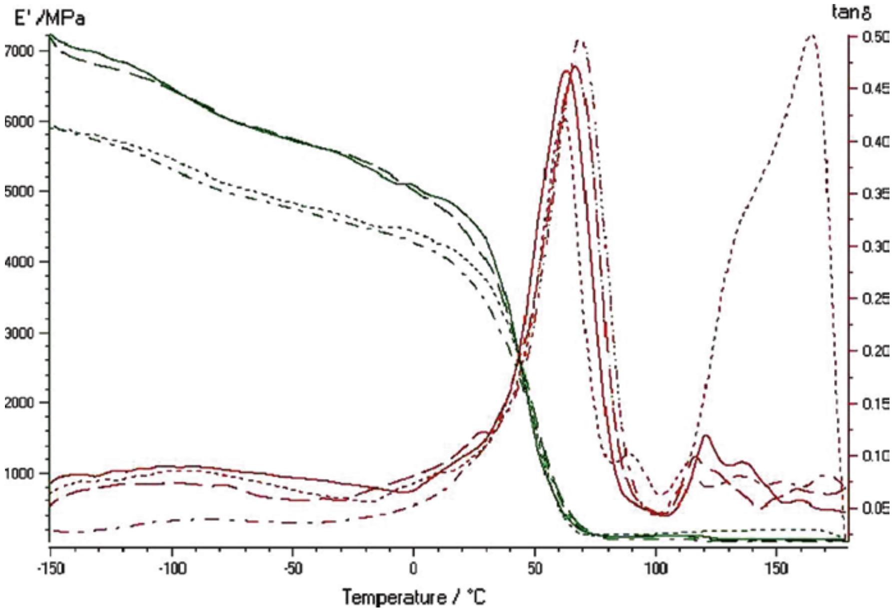


Fig. 9 Dynamic mechanical analysis (DMA) curves of polyester matrix and its composites **a** polyester matrix (PPC);**b** polyester-as-received bagasse (AR-PC); and **c** polyester-surface treated bagasse (STB-WI and WIPC). (Reproduced with permission from Elsevier Ltd. Satyanarayana et al. (2011))

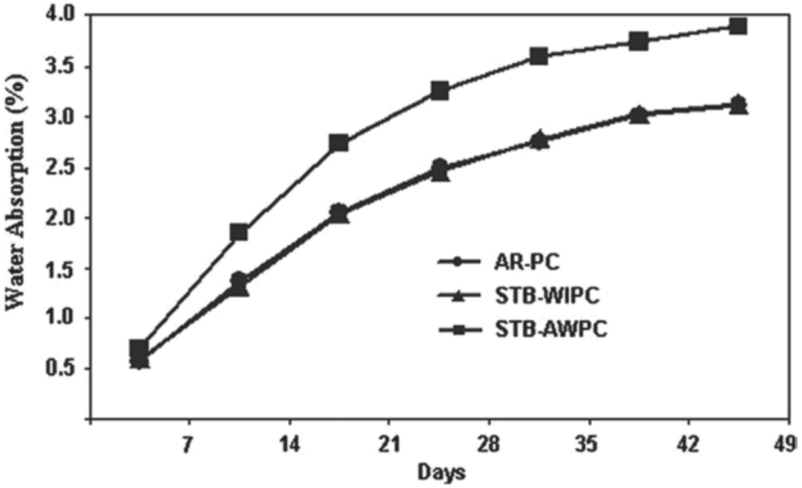


Fig. 10 Moisture absorption of polyester–bagasse composites containing **a** as-received bagasse (AR-PC); **b** steam-exploded and washed bagasse (STB-WIPC); **c** steam-exploded + alkali-washed bagasse (STB-WIPC). (Reproduced with permission from Elsevier Ltd. (Satyanarayana et al. 2011))

Verma et al. (2012) investigated and developed fly ash–bagasse fiber composite material which has been discussed. The bagasse fiber has been used in two different sizes for the developed material. In two developed composites, the diameter of bagasse fiber was varied between 13–16 and 83–95 µm in length. Correspondingly, in the other two developed composites, the length of bagasse fiber was varied from 1 to 5 mm. It was observed that the density decreases by mixing the fiber was more as compared to the composite having both bagasse fiber and fly ash. A bagasse fiber composite with size in the range of µm exhibited better tensile strength than the composite having bagasse fiber size in millimeter. The compressive strength of the material increases, if fly ash alone is used for the composite material but, when bagasse fiber was mixed with the fly ash, it was found that there was a decrease in the compressive strength. It was also observed that there was a reduction in the flexural strength of the material by mixing the bagasse fiber in the matrix.

Integration into Thermoplastic Polymer

Vazquez et al. (1999) developed bagasse-fiber-reinforced polypropylene composites. Different chemical treatments like isocyanate, acrylic acid, mercerization, and washing with alkaline solution of the vegetal fibers were performed to enhance the interface adhesion with the thermoplastic matrix. The effects of the treatment reactions on the chemical structure of the fibers were analyzed by infrared spectroscopy. Optical photomicrographs indicate that a highly fibrillated surface is achieved when fibers are mercerized. The effects of the fiber chemical treatment on the tensile properties of the composite were also analyzed and it was found that the tensile strength of the untreated bagasse-fiber-reinforced polypropylene composite decreases. On the other hand, isocyanate and mercerization treatments improve the tensile properties of the composite. Creep measurements were also carried out on the various composites studied. The best results were reported by the author with treated fibers.

Thwe and Liao (2003) reported the consequences of environmental and accelerated aging on tensile and flexural characteristics of bamboo-fiber-reinforced polypropylene composite (BFRP) and bamboo–glass-fiber-reinforced polypropylene hybrid composite (BGRP). Reduction in tensile strength for BFRP and BGRP was reported as 12.2 and 7.5 %, respectively, after aging at 25 °C for about 1200 h however, tensile and flexural strength of BFRP and BGRP were reduced by 32, 11.7 and 27, 7.5 %, respectively, after aging at 75 °C for 600 h. On the other hand, the strengths of the bamboo-fiber-reinforced composites reduces with sorption time and temperature.

De Silva et al. (2009) used pretreated and reform residues from sugarcane bagasse natural fibers. High-density polyethylene (HDPE) was used as matrix for composite. Composites were made by mixing cellulose (10 %) with HDPE and Cell/$ZrO_2 \cdot nH_2O$ (10 %). Extruder and hydraulic press were used for the development of composites. Results showed that the Cell/$ZrO_2 \cdot nH_2O$ (10 %)/HDPE composites represent good tensile strength as compared to cellulose (10 %)/HDPE composites.

This is because of agglomerations of cellulose which results in poor adhesion between fiber and matrix in cellulose (10 %)/HDPE composites. As compared to polymer, HDPE/natural fibers composites have lower tensile strength. The fiber reinforcement in the matrix also improves Young's modulus of composites.

Ashori and Nourbakhsh (2010) reinforced agricultural residues such as sunflower stalk, corn stalk, and bagasse fibers in thermoplastic matrix. The two grades (Eastman G-3003 and G-3216) of coupling agents were used and their effects on mechanical properties were also studied. The amount of fiber loading was kept 30 wt.% and also three percentages of coupling agent content (0, 1.5, and 2.5 wt.%) were used for making composite. As compared to the untreated samples, it has been observed that addition of both grades of the coupling agents results in an improvement in various mechanical properties such as tensile, flexural, and impact strength of the composites. It is also found that the composite made with coupling agent G-3216 gave better results as compared to the G-3003 coupling agent. The high melt viscosity of G-3003 may be one of the reasons for this.

The tensile strength and tensile modulus of fiber/PP composites reinforced with different fiber types are shown in Figs. 11 and 12. From the figure, it can be observed that the range of maximum tensile modulus of elasticity for bagasse composites varies from 2150 to 2190 MPa, while the maximum tensile strength is about 33 MPa. That means the addition of bagasse increases the modulus of elasticity of pure PP by 1.7 times. Different factors such as fiber aspect ratio, fiber–matrix interfacial adhesion, and also the fiber orientation in the composites improve the tensile properties of composites (Sameni et al. 2002). The fiber aspect ratio (length/width) is an important parameter which controls the mechanical properties of short fibers composite. A high aspect ratio indicates potential strength properties (Ashori and Nourbakhsh 2010).

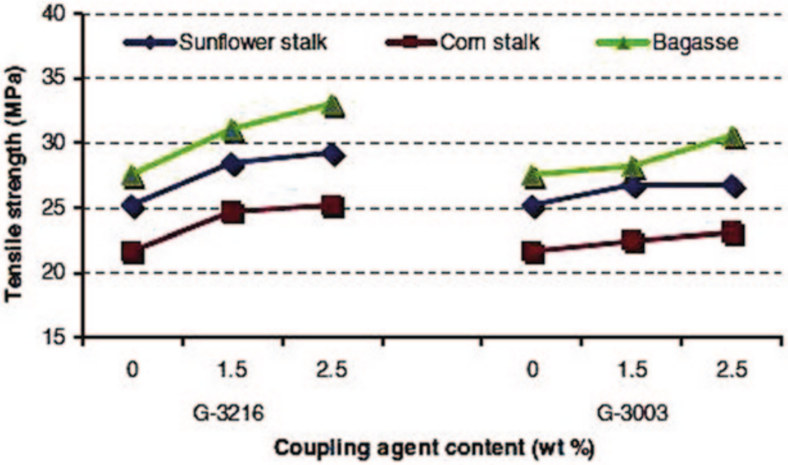


Fig. 11 Comparison of tensile strength of composites as function of the coupling agent content and grade. (Reproduced with permission from Elsevier Ltd. (Ashori and Nourbakhsh 2010))

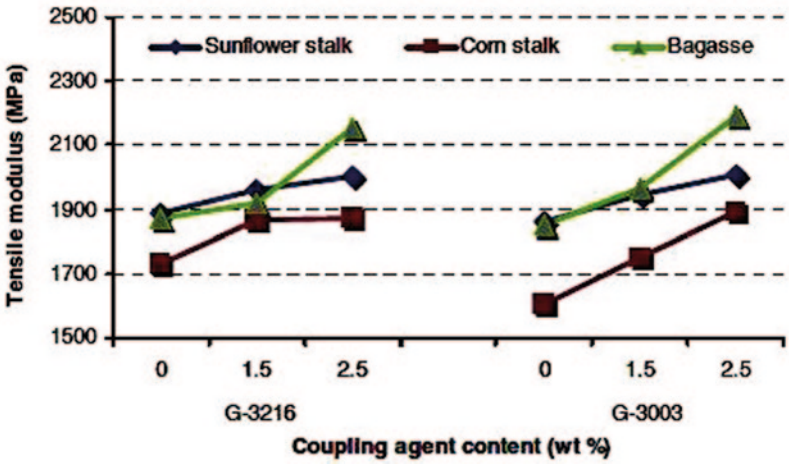


Fig. 12 Comparison of tensile modulus of composites as function of the coupling agent content and grade. (Reproduced with permission from Elsevier Ltd. (Ashori and Nourbakhsh 2010))

Table 6 Mechanical properties of the materials obtained by injection molding (reinforcement in wt.%). (Reproduced with permission from Elsevier Ltd. (Mulinari et al. 2009))

Materials	Elongation at break (%)	Tensile strength (MPa)	Tensile modulus (MPa)
High-density polyethylene (HDPE)	2.20 ± 0.2	1.54 ± 0.13	732 ± 90.6
Cellulose (10 %)/ HDPE composite	1.74 ± 0.04	1.54 ± 0.13	897 ± 27.5
Cell/ZrO2.nH2O (10 %)/HDPE composite	1.54 ± 0.13	18.2 ± 1.06	1233.1 ± 118.4

Mulinari et al. (2009) reported mechanical and morphological properties of high-density polyethylene/pretreated and reform residues from sugarcane bagasse cellulose composites. The modification of bagasse cellulose with zirconium oxychloride with HDPE showed higher tensile strength than unmodified bagasse cellulose. Mechanical properties of composites are reported in Table 6.

Experimental results in Table 8 may be summarized by analyzing interaction between fiber and matrix during mixing. From Fig. 13, the modified cellulose represents good tensile strength and adhesion properties between fiber and matrix as compared to the unmodified cellulose and thereby confirmed that modification of cellulose with zirconium oxychloride enhances the fiber–matrix adhesion. It is also found that the composites have lower elongation as compared to HDPE (Fig. 14) due to the reinforcement in the matrix. The modified cellulose reinforcement in matrix results in lower elongation as compared to unmodified cellulose and confirmed that fiber modification enhances fiber–matrix adhesion (Mulinari et al. 2009).

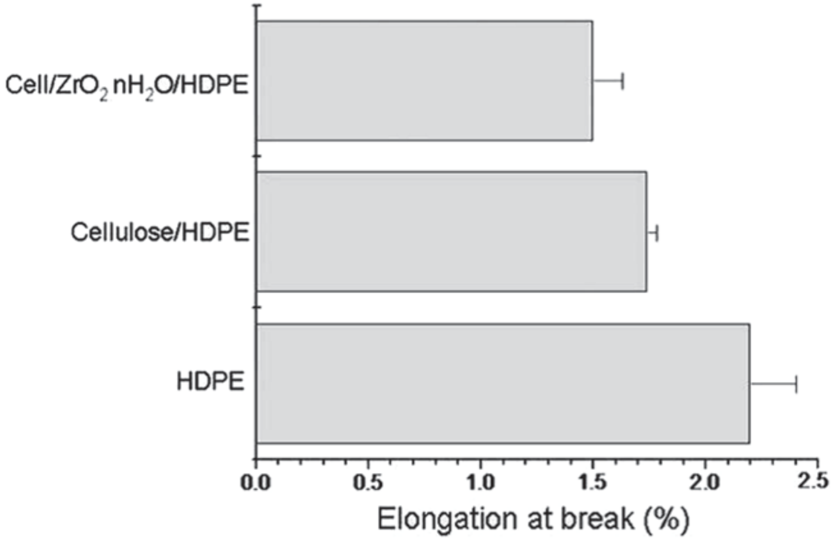


Fig. 13 Elongation at break (%) of composites specimens. (Reproduced with permission from Elsevier Ltd. (Mulinari et al. 2009))

Ashori et al. (2013) showed effects of multiwalled carbon nanotubes (MWCNTs) on the mechanical and physical characteristics of bagasse as HDPE composites. MWCNTs and maleic anhydride grafted polyethylene (MAPE) were used for the composite sample preparation. The morphological study of the specimens was studied with the help of SEM technique. From the experiments, it was found that the tensile and flexural strength increases when 1.5% (w/w) of MWCNTs was added in the matrix; however, at high amounts, which is about 3–4 wt.%, it was observed that an increased amount of MWCNTs results in agglomeration and ultimately blocks the stress transfer. The impact strength of composites decreased slightly by the addition of MWCNTs filler. When 4 wt.% of MAPE was added then both mechanical and physical characteristics of the composites were better. MWCNTs have found as a good reinforce material for the enhancement of physical–mechanical properties of composites. Statistical analysis exhibit that the mechanical properties such as tensile strength and tensile modulus were considerably affected by reinforcing MWCNTs and MAPE as shown in Table 7.

Figure 14a represents the tensile performance of composites prepared with different MWCNTs and coupling agent MAPE contents. MAPE was used to ameliorate the adhesion properties. Tensile strength of 1.5 wt.% of MWCNTs and 0 wt.% of MAPE composite was found to be 26.4 MPa. Composites made from 1.5% of MWCNTs and 4 wt.% of MAPE exhibit improved tensile strength and found to be 27.7 MPa. So, addition of MAPE increases the tensile properties of pure HDPE by 3–5%. In a broad way, by increasing the value of MAPE from 0 to 4% (w/w) ultimately improves the tensile strength and tensile modulus value as shown in Fig. 14a.

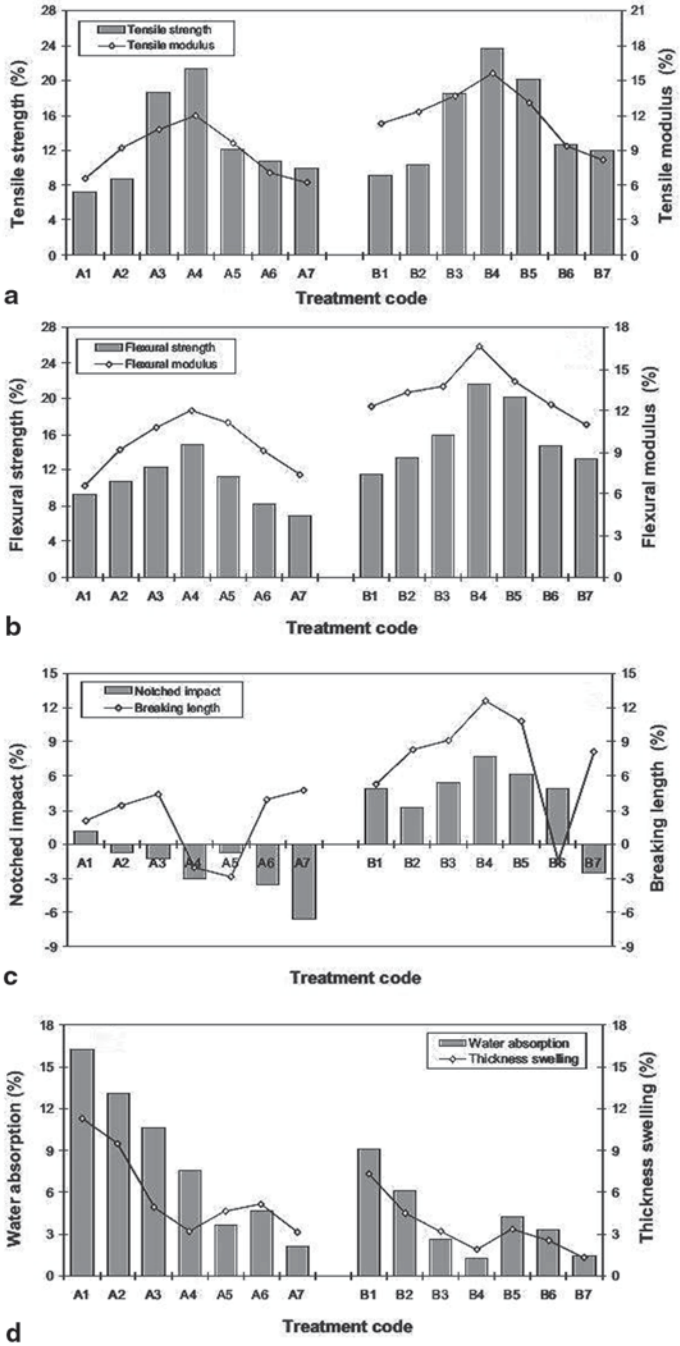


Fig. 14 Percentage of changes in the mechanical and physical properties of treated samples compared to the neat high-density polyethylene (HDPE). (Reproduced with permission from Elsevier Ltd. (Ashori et al. 2013))

Table 7 Composition of the studied treatments. (Reproduced with permission from Elsevier Ltd. (Ashori et al. 2013))

Treatment code	BP (wt%)	HDPE (wt%)	MAPE (wt%)	MWCNT (wt%)
A1	30	70	0	0
A2	30	69.5	0	0.5
A3	30	69	0	1
A4	30	68.5	0	1.5
A5	30	68	0	2
A6	30	67	0	3
A7	30	66	0	4
B1	30	66	4	0
B2	30	65.5	4	0.5
B3	30	65	4	1
B4	30	64.5	4	1.5
B5	30	64	4	2
B6	30	63	4	3
B7	30	62	4	4

From Fig. 14a, the tensile characteristics were increased by the addition of MWCNTs. Hussain et al. (2006) suggests that the inclusion of nanosized particles improves tensile properties of polymer matrix composites. The increment in tensile strength is because of the filler in MWCNTs form. The MWCNT were rigid as compared to polymer matrix, resulting provides rigidness to the composites. The phenomenon seen was stronger when using 4 wt.% MAPE.

Figure 14b shows the flexural strength and modulus of the developed composites. Composites prepared from 1.5 wt.% of MWCNTs and 4 wt.% of MAPE showed the utmost flexural strength and modulus, however, without MWCNTs and MAPE composites displayed least mechanical values. It has been also noticed that composites prepared from 4 wt.% of MAPE offered significantly greater flexural strength and modulus than untreated samples. Flexural modulus of MWCNTs is found significantly greater as compared to BP and HDPE, respectively. As it is clear from Fig. 14b, with an increase of MWCNTs amount from 1.5 to 3% (w/w), the flexural properties were greatly reduced. Farsheh et al. (.2011) examined composites at larger CNT loading and suggested that the modulus might not be amplified because of the agglomeration of CNT. Figure 14c represents the steady decline in the notched impact strength values by reinforcing MWCNT filler. The largest reduction in impact strength value was observed with the addition of 3 wt.% of MWCNTs and reported to be reduced by 6.6% than that of pure HDPE (Eitan et al. 2003).

In general, thermoplastic polymers, like HDPE, show moisture resistant property due to hydrophobic character and thereby indicates that moisture is absorbed by the hydrophilic wood component and voids found in the composite. Increasing the percentage of MAPE and MWCNT results less water absorption by the composites.

Table 8 Results of wear characterization of the materials. (Reproduced with permission from Elsevier Ltd. (Aigbodion et al. 2012))

S. No	Speed (m/s)	Load (N)	Distance (m)	Wear rate (g) at 0 % Bap	Wear rate (g) at 10 % Bap	Wear rate (g) at 30 % Bap
1	1	10	1000	0.40	0.36	0.30
2	1	10	2000	0.55	0.49	0.35
3	1	20	1000	0.60	0.54	0.44
4	1	20	2000	1.10	0.84	0.75
5	3	10	1000	1.00	0.77	0.70
6	3	10	2000	1.15	1.07	0.95
7	3	20	1000	1.27	1.12	1.08
8	3	20	2000	1.67	1.51	1.49

Sheshmani (2013) studied and examined the two variable parameters, namely the extractives and filler loading level. Injection molding method was used to make HDPE composites by reinforcing agricultural waste bagasse flour (BF) as filler. For increasing the adhesion between matrix and flour, MAPE was used as a coupling agent. For extraction three solvents, such as ethanol–benzene, 1 % NaOH, and hot water, were used. Composites made by extracted bagasse showed improvement in water absorption and tensile strength values (TSVs).

Aigbodion et al. (2012) studied the tribological nature of recycled low-density polyethylene (RLDPE) polymer composites with bagasse ash particles as a reinforce material using a pin-on-disc wear rig under dry sliding environments. The effect of wear factors, e.g., applied load, sliding speed, sliding distance, and percentage of bagasse ash fillers, on the wear rate were examined. SEM study was undertaken to examine the microstructure of the fractured surface of different samples. The effect of operating parameters on wear properties of the samples were experimented by the regression analysis and analysis of variance (ANOVA). The envisaged wear rate of the RLDPE and its composites showed the range nearer to the experimental values.

Experimental results obtained for the wear properties of the bagasse as particles-based RLDPE and RLDPE are reported in Table 8 and Fig. 15. From the analysis, it is found that addition of bagasse ash particles in to the matrix results in reduction in the wear rate of the developed composites.

Moubarik et al. (2013) examined three distinct stages to isolate the cellulose fibers from Moroccan sugar cane bagasse. In this process, a hot water treatment process (70 °C) is used to remove the hemicellulose from the bagasse, then the lignin content was removed by the alkalization process, and the bleaching process is used as final step of the chemical treatment. The extracted fibers from the sugarcane bagasse were reinforced into LDPE matrix. From the experiment, it was found that due to good interfacial adhesion between matrix and fibers results increase in mechanical properties of composites. Table 9 shows the mechanical characteristics of the composites before and after water absorption.

Natural fibers reinforcement in thermoplastics has given good importance due to the low cost and high specific characteristics (Souza et al. 2009). Souza et al.

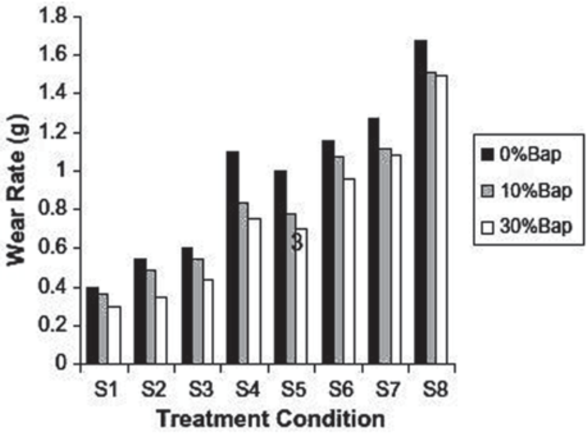


Fig. 15 Variation of wear rate with treatment condition. (Reproduced with permission from Elsevier Ltd. (Aigbodion et al. 2012))

has studied the mechanical properties of high-density polyethylene/textile fibers residues composites. Effect of pretreatment of textile fibers with sulfuric acid to prepare composites was prepared to provide an enhancement in mechanical characteristics of these materials.

Mechanical characteristics/properties of composites are reported in Table 10. Composites resulted good mechanical properties as compared to the neat pure HDPE.

Table 9 Mechanical properties of the composites before and after water absorption. Fifty replicates of each composites. S.D. standard deviation. (Reproduced with permission from Elsevier Ltd. (Moubarik et al. 2013))

Materials	Before water absorption			After water absorption		
	Tensile strength (MPa) Mean ± S.D	Young's modulus (MPa) Mean ± SD	Flexural modulus (MPa) Mean ± SD	Tensile strength (MPa) Mean ± SD	Young's modulus (MPa) Mean ± SD	Flexural modulus (MPa) Mean ± SD
Low-density polyethylene (LDPE)	14 ± 0.9^{a}	236 ± 21^{a}	194 ± 12^{a}	13 ± 0.7^{a}	207 ± 11^{a}	186 ± 10^{a}
Cellulose (10 %)/LDPE composites	10 ± 0.4^{b}	263 ± 11^{b}	230 ± 8^{b}	9 ± 0.9^{b}	249 ± 14^{b}	214 ± 13^{b}
Cellulose (15 %)/LDPE composites	9 ± 0.2^{c}	310 ± 9^{c}	260 ± 15^{c}	9 ± 0.5^{b}	289 ± 10^{c}	233 ± 11^{c}
Cellulose (20 %)/LDPE composites	11 ± 1.5^{d}	360 ± 17^{d}	310 ± 16^{d}	8 ± 1^{c}	333 ± 12^{d}	286 ± 20^{d}
Cellulose (25 %)/LDPE composites	7 ± 1.8^{e}	407 ± 12^{e}	360 ± 11^{e}	6 ± 1.1^{e}	378 ± 18^{e}	308 ± 18^{e}

Table 10 Mechanical properties of the materials. (Reproduced with permission from Elsevier Ltd. (Souza et al. 2009))

Samples	Tensile strength (MPa)	Tensile modulus (MPa)
HDPE	15.7 ± 1.1	732.5 ± 90.6
HDPE/FT5 %	22.8 ± 0.7	1239.6 ± 72.2
HDPE/FT10 %	24.1 ± 0.6	1557.3 ± 88.8

Luz et al. (2007) have done work on injection and compression molding processes and evaluated a mixer method for fiber and matrix. The samples were slice in accordance order to the measurement of the suggested mechanical properties (flexural and tensile). The injection molding process (under vacuum) is found to be the best process for composite making with homogeneous distribution of fibers.

A comparison has been made between the composites made by injection molding and compression molding process with respect to the mechanical (tensile and flexural strength) properties. From elongation point of view, the obtained composites showed less elongation as compared to the polypropylene. Two points can be undertaken as: (1) fibers are points of failure that can produce a crack and (2) there is a sliding of the fibers with respect to the matrix (Fig. 16).

Morphological Studies of Bagasse Fibers in Polymer Composites

SEM can be used for the morphological characterization of coconut/coir fiber-reinforced composites. This is most widely used method for the surface analysis of the composite materials.

Figure 17a reports the composite with 4 wt.% of MAPE and without MWCNTs. It is clear from the figure that there is very good contact between the fibers and the matrix because of the inclusion of the coupling agent, responsible for strong bonding. Figure 17b reports WPC without MAPE and MWCNTs, shows some cavities and can absorb water and/or reduce mechanical characteristics. (Ashori et al. 2013)

In another investigation, Aigbodion et al. (2012) report the SEM study of the fractured or wear out surfaces (Figs. 18 and 19 of plates 4 and 5) of RLDPE and its composites at 20 N load, 3 m/s speed and 3000 m sliding distance, for RLDPE matrix and RLDPE + 30 wt.% Bap. From plates 4 and 5, it can be noticed that the RLDPE without bagasse ash particles reinforcement form a good thin and uniform film (plate 4). In the case of RLDPE with bagasse, ash particle filler (see plate 5) have some disruption of transfer film (Fig. 19).

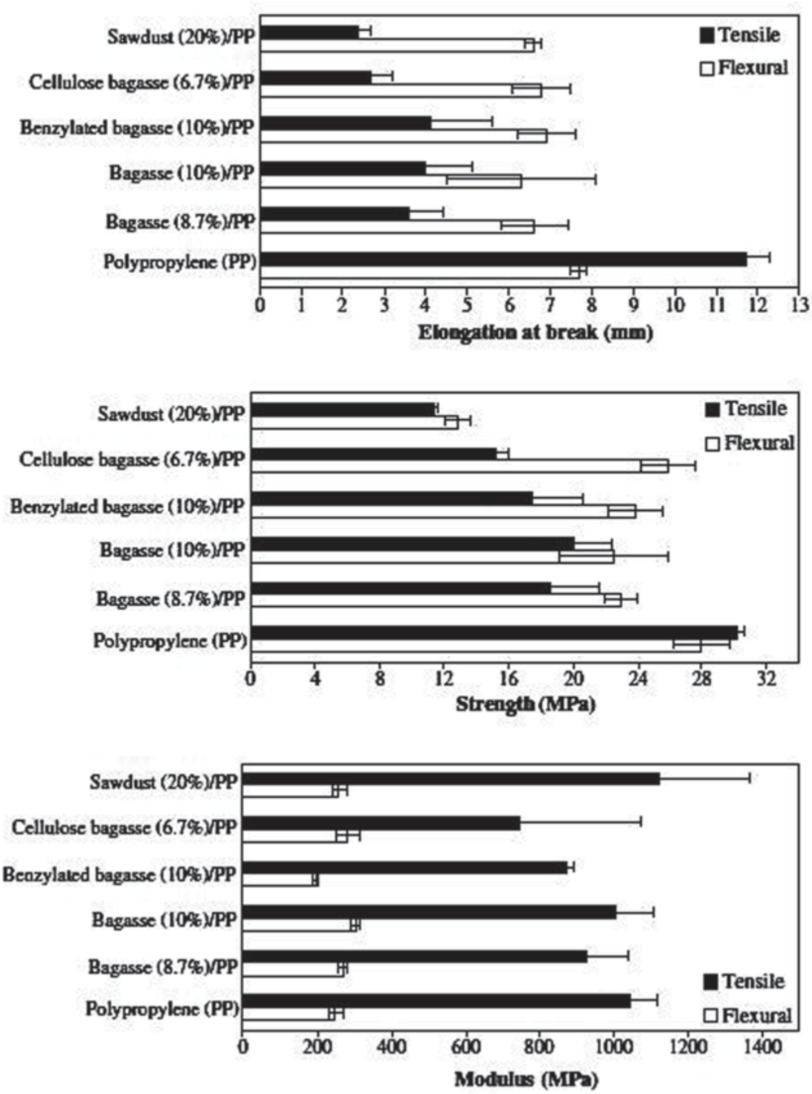


Fig. 16 Mechanical properties of composites materials obtained by injection molding. The amount of reinforcement is expressed in weight percentage. (Reproduced with permission from Elsevier Ltd. (Luz et al. 2007))

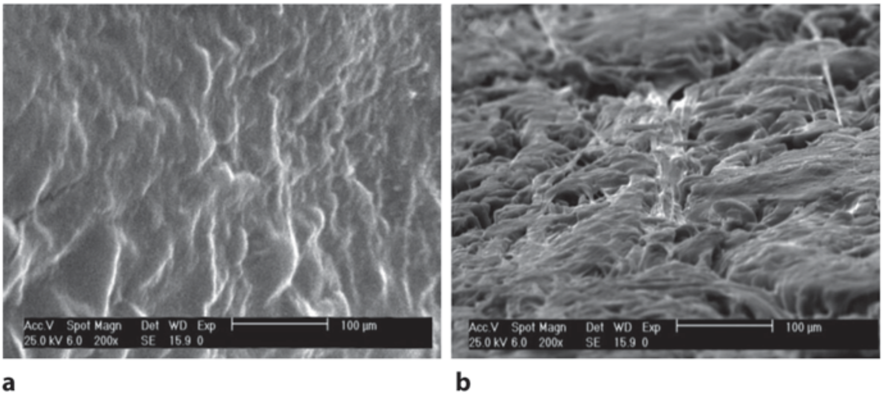


Fig. 17 SEM micrographs of **a** the surfaces of samples with 4 wt.% maleic anhydride grafted polyethylene (MAPE) (B1) and **b** without MAPE (A1). (Reproduced with permission from Elsevier Ltd. MAPE maleic anhydride grafted polyethylene (Ashori et al. 2013))

Fig. 18 Plate 4. Scanning electron microscopy (SEM) morphology of the worn surface for recycled low-density polyethylene (RLDPE) matrix. (Reproduced with permission from Elsevier Ltd. (Aigbodion et al. 2012))

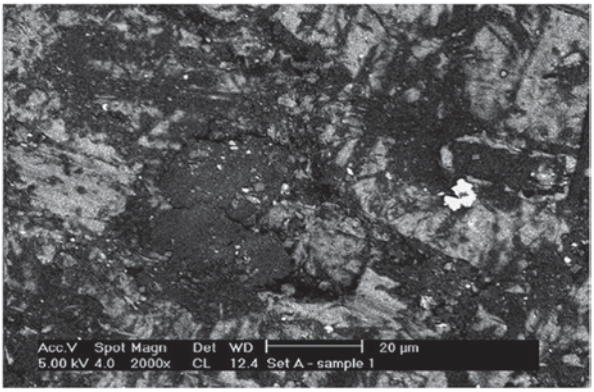
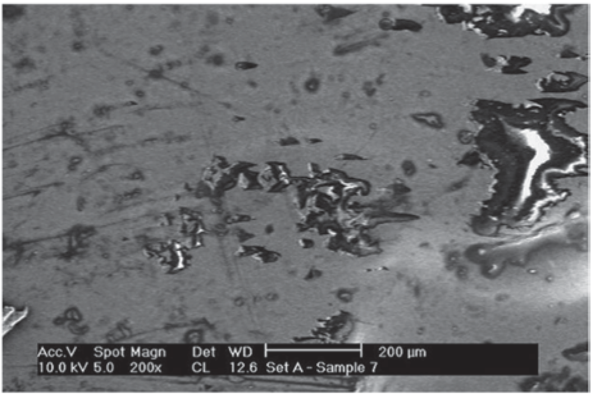


Fig. 19 Plate 5. Scanning electron microscopy (SEM) morphology of the worn surface for RLDPE + 30 wt.% Bap composite. (Reproduced with permission from Elsevier Ltd. (Aigbodion et al. 2012)). *RLDPE* recycled low density polyethylene



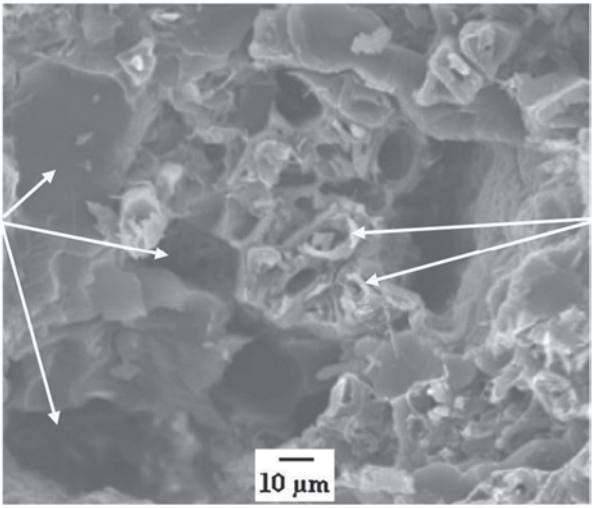


Fig. 20 Scanning electron microscopy (SEM) images of the tensile fractured surface of optimal cellulose fibers (20 %)/LDPE composites. (Reproduced with permission from Elsevier Ltd. (Moubarik et al. 2013)). *LDPE* low-density polyethylene

In another investigation, Moubarik et al. (2013) reported that the fibers were shielded with the LDPE to a maximum degree (Fig. 20). In addition, it has been found that there were no signs of fiber pullouts and most of the fibers were fractured from the surface. Figure 21 represents the SEM image of the treated and untreated bagasse fiber. Figure 21a reports the fiber with cellular structure. The NaOH and AA treatments showed a compressed cellular structure as shown in Fig. 21b, c. In other words, the cellular structure of the fiber is destroyed by the treatment and hence decreases the void content of the fiber. (Vilay et al. 2008).

Luz et al. (2007) examined SEM tests on developed composites and observed the morphological properties of lignocellulosics as shown in Fig. 22a. The polypropylene represented a brittle fracture around the fibers. Figure 22b reports the bagasse/matrix interface. Figure 22c and d represents the higher magnified micrograph of fiber and matrix interface. The optical micrograph (Fig. 23a) displays the bagasse outline shape

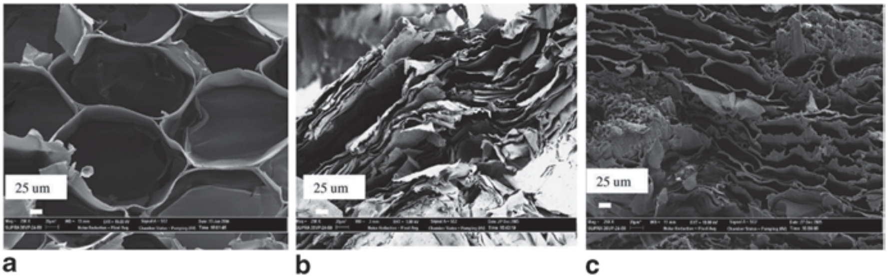


Fig. 21 Scanning electron microscopy (SEM) micrograph of the cross section of: **a** untreated bagasse fiber, **b** NaOH-treated fiber, and **c** AA-treated bagasse fiber (magnification 250×). (Reproduced with permission from Elsevier Ltd. (Vilay et al. 2008))

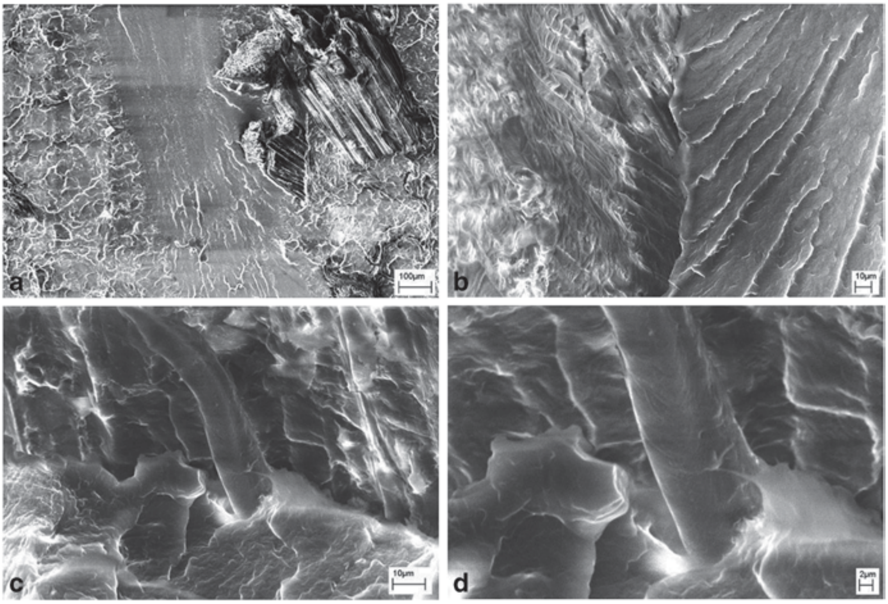


Fig. 22 Scanning electron microscopy (SEM) of fracture surfaces of bagasse/polypropylene composite injected under vacuum. **a** Morphology of composite fracture surfaces towards the bagasse, the presence exhibits of brittle fracture. **b** Morphology of composite fracture surfaces exhibits the limit region between fiber and matrix (brittle fracture). **c** and **d** Higher magnification of limit region between fiber and matrix. (Reproduced with permission from Elsevier Ltd. (Luz et al. 2007))

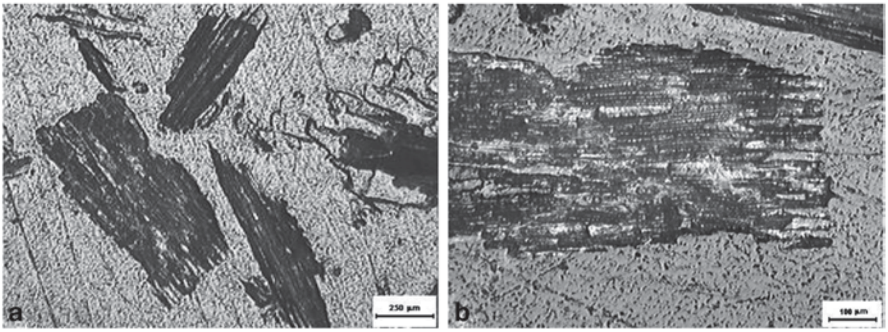


Fig. 23 Optical micrograph with reflected light of composite polished surface (bagasse/polypropylene). **a** Fifty Magnified micrograph exhibits the bagasse forms and distribution within the matrix. **b** Hundred magnified micrograph shows the detail of limit region between fiber and matrix. (Reproduced with permission from Elsevier Ltd. (Luz et al. 2007))

within matrix and a random allocation. The highly magnified micrograph of bagasse and polypropylene interface showed a major diffusion of polypropylene into fiber which results in good adhesion between fiber and matrix as shown in Fig. 23b.

Advantages of Bagasse Fiber Reinforcements in Polymer Composites

Following are the advantages of the bagasse fiber-reinforced polymer composites:

1. Bagasse fiber preparation from sugarcane results lesser environment related issues.
2. The composites reinforced with bagasse are lighter in weight and have equivalent performance with regard to aesthetic point of view.
3. In growing stage (during cultivation) sugarcane consumes carbon which can be directly linked to the carbon credits.
4. The economic reutilization of the end of life of composite material is the better option to reduce environment related issues.
5. The utilization of natural fibers-reinforced composite also add up to a great chance for economic progress of developing countries (Luz et al. 2007).

Summary/Conclusion

From this chapter, it can be concluded that bagasse fiber can be used as a filler in composite material, which ultimately helps to resolve the environmental issues generally arises from bagasse. The chapter explored the potential use of bagasse fiber in composites specifically polymer composites and also studied and showed the mechanical and morphological properties of developed composites. This chapter also discussed the surface modification (chemical modification) of fibers which is utmost important and provides good interfacial adhesion between the fiber and matrix. Wide variety of application of bagasse fiber composites can also be found like packaging, doors, furniture, etc. The influence of bagasse fibers on the mechanical properties of bio composites has also been reported.

Future Trends/Applications

The following application of the bagasse fiber composites can be observed based on different areas:

1. Building component

(a) Doors
(b) Window
(c) Wall partition
(d) Ceiling

2. Transport sector (railway coach and Vehicle)

(a) Flooring
(b) Ceiling
(c) Seat and backrest

3. Furniture

(a) Tables
(b) Chairs
(c) Kitchen cabinet, etc.

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Life Cycle Assessment of Natural Fiber Polymer Composites

Muhd Ridzuan Mansor, Mohd Sapuan Salit, Edi Syam Zainudin, Nuraini Abdul Aziz and Hambali Ariff

Abstract Widespread environmental awareness towards achieving product sustainability has spurred great efforts in using more environmental-friendly materials in product design. Among the most promising solutions to address the needs is by using natural fibers to reduce the dependence on synthetic fibers as reinforcement and filler materials for polymer composites' construction. Many efforts have been made to fully quantify the advantages of natural fiber composites (NFC) for diverse applications such as automotive, building materials, and household appliances. Life cycle assessment (LCA) is among the efforts being undertaken related to NFC with the primary aim to determine the overall potential environmental impact of using such materials on the surroundings. Among the major advantages of performing LCA is its capability to provide a more holistic overview of the environmental impact whereby it covers the whole product life cycles from raw material extraction to end-of-life stages, hence enabling justified decisions on the suitability of using NFC for specific applications to be made scientifically. In this chapter, an overview of the LCA method is explained and subsequently followed by description of its applications involving NFC in different applications. The advantages and limitations of the LCA method related to the NFCs are also discussed as well as a final conclusion on the future directions of LCA application for NFC.

Keywords Life cycle assessment · Natural fiber composites · Environmental impact

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Introduction

Widespread environmental awareness towards achieving product sustainability has spurred great efforts in using more environmental-friendly materials in product design. Among the most promising solutions to address the needs is by using natural fibers to reduce the dependency on synthetic fibers as reinforcement and filler materials for polymer composites' construction. The introduction of natural fiber composites (NFC) has grown tremendously over the years. Lucintel, one of the main players in global market research and management consulting firms, reported that in 2010, the world market on NFC reached US$ 2.1 billion with compound annual growth rate of 15 % in the past 5 years. Furthermore, they also revealed that NFC market is predicted to reach US$ 3.8 billion by 2016 with compound annual growth rate of 10 %, highlighting positive growth of the materials by consumers globally (Anonymous 2011). Elsewhere, based on the report from the Technology Road Map for Plant/Crop-Based Renewable Resources 2020 which was funded by the US Department of Energy (DOE) stated that up to 10 % increase in the basic chemical building block is expected from the renewable resources application derived from plants by year 2020 and further predicted to rise up to 50 % in year 2050. Apart from that, over the past 10 years similar positive growth rate up to 13 % was also observed in the application of natural fibers for building, industrial, and commercial market sectors (Pandey et al. 2010). As for the automotive industry, based on the UK Department for Environment Food & Rural Affairs (DEFRA) report, the use of natural fibers in automotive components is also expected to grow approximately 54 % per annum contributed by the consumption of the material for car production to achieve environmental directives by European and American automotive companies. It is revealed that nearly 1.5 million vehicles produced by American carmakers have already incorporated natural fibers such as kenaf, hemp, and jute for producing both thermoset and thermoplastic polymer composites to be used in the car component construction especially in automotive textiles application. The growing demand was also supported by record of the NFCs market for European and North American regions which was revealed to reach 685,000 t worth nearly US$ 775 million (Alves et al. 2010).

The increasing trend on the application of NFCs is contributed to its lightweight, environmental and cost superiority especially compared to synthetic-based composites (El-Shekeil et al. 2012; Holbery and Houston 2006; Sapuan et al. 2011). Other advantages associated with the use of NFC especially for automotive applications include improved lightweight and thermal property, enhanced acoustic insulation performance as well as enabling CO_2 neutrality originated by the consumption of the greenhouse gas during the plant cultivation process (Brosius 2006). The automotive industry, for instance, has embraced NFC to achieve better environmental performance of vehicles attributed to its renewable property, lower energy consumption, hence promoting cleaner manufacturing processes and highly recyclable material during the component disposal phase which also further promotes the implementation of ecodesign during the component initial product development stage (Luz et al. 2010). The recyclability advantage also enables the development of environmental-friendly marketing strategy of NFC-based products. As for other sectors, additional benefits are also materialize through the utilization of NFC such as reducing processing temperatures, minimizing energy consumption, reducing process cycle times by up to 25 %, reducing composite reinforcement material consumption per unit volume due to the natural fiber lower specific weight, cheaper shipping costs due to better lightweight property, and longer mold life in composites' manufacturing owing to the natural fiber minimal abrasive nature (Luz et al. 2010; Rowell 1998).

In conjunction with the global acceptance, one of the research areas regarding NFC, which is also gaining high interest currently, is life cycle assessment (LCA) whereby researchers are interested to determine the actual environmental impact of NFC applications. The main intention is to quantitatively analyze the environmental performance of NFC throughout its complete life cycle which later can be compared to its competitors. In this chapter, an overview of the LCA method is explained and subsequently followed by description of its application involving NFC in different applications. The advantages and limitations of the LCA method related to the NFC are also discussed as well as a final conclusion on the future directions of LCA application for natural fiber polymer composites.

The Life Cycle Assessment Method

The use of various products in daily applications consequently contribute to some portion of environmental damage throughout the product's lifetime. Due to that reason, understanding the resulting effect of the product as well as differing environmental performance between products are crucial and invoke much interest by various stakeholders in improving the situation towards achieving sustainability. Currently, LCA is among the popular methods applied in analyzing and quantifying the effect of not only products but also services and materials to the surrounding environment during their total lifetime. LCA is also gaining recognition as among the key factors in environmental management, most notably involving corporate and public decision making (Song et al. 2009). The methodology is considered to be a young and evolving application, with its roots in research related to energy requirements in the 1960s and pollution prevention, which was formally initiated in the 1970s. Since its establishment, apart from end product assessment objective, the LCA method has expanded into a wide range of applications both at the downstream and upstream activities such as ecolabeling, energy systems, product designs, transportation, and food production, which further highlight its functionality and effectiveness (Goedkoop et al. 2009).

In general, LCA is the method available to study the environmental aspects and potential environmental impacts (e.g., use of resources and the environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling, and final disposal, termed as cradle-to-grave approach. The distinguish advantage of LCA lies on its ability to consider the product's entire life cycle stages, which include raw material extraction and acquisition, material production and manufacturing, product use, packaging and transportation, end-of-life treatment, and final disposal. The overall overviews of the products help us especially to identify the potential environmental burden shifting between individual life cycle stages and minimize its possible occurrence, thus making the whole analysis more comprehensive and consequently enable holistic view of the results to be obtained (Finnveden et al. 2009). Figure 1 shows an example of the overall life cycle phases for NFC from during natural fiber production up to final composite application.

In terms of focus, LCA only addresses the product system environmental aspects and impacts thus excluding its scope on the impact from the economic and social aspects (Hunkeler and Rebitzer 2005). Nevertheless, LCA still permits integration with other tools to attain further extensive assessments. With the structure based on functional unit, the LCA approach is considered relative whereby the functional unit defines the attribute of the study being carried out. All defined inputs and outputs of the system inventory, the impact assessment approach, and the analyses are also

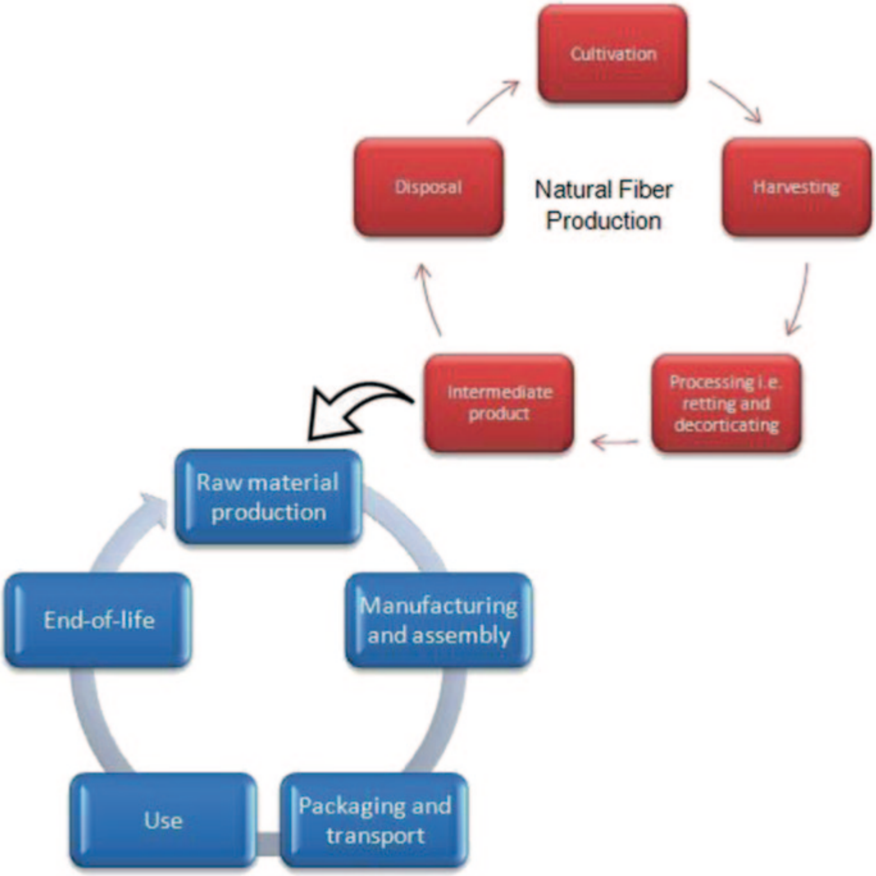

Fig. 1 Example of the overall life cycle phases for natural fiber composites (NFC)

related to the functional unit. The method is also iterative in nature, whereby results from individual phases are forwarded and shared within and between other phases. This enables comprehensive and consistent results to be obtained from the study. Moreover, to obtain proper results' interpretation, transparency is crucial as it acts as the guiding principle to cater to the inherent complexity which may arise during execution of any LCA studies. Through the inclusion and consideration of natural environment, resources, and human health aspects in a single analysis, the LCA method is considered very comprehensive, enabling the identification as well as assessment of emerging potential trade-offs (Anonymous 2006a).

Since 2006, the LCA methodology is currently governed by two international standards and is implemented in LCA-related works. The two standards are ISO 14040 (principles and framework) and ISO 14044 (requirements and guidelines), which are based on revision from the former LCA standards, namely, ISO 14040, ISO 14041, ISO 14042, and ISO 14043. The revisions were made in order to remove the errors and inconsistencies as well as to improve the readability of the former standards. The new standards also highlight that apart from the cradle-to-grave approach, other techniques such as cradle-to-gate studies, gate-to-gate studies, and specific part of the life cycle phase may also be applied in LCA studies with proper justification (Finkbeiner et al. 2006).

For implementations with regard to NFCs, among the advantages of LCA is the possibility for comparison purpose, such as to determine if from an ecological point of view, the use of natural fibers is more advantageous compared to synthetic fibers as reinforcement in composites. In addition, LCA also enables the identification of key environmental parameters and phases in the whole life cycle of products as well as permitting study on disposal scenarios of the NFC in order to improve the environmental performance for the specific life cycle phase. Furthermore, through the implementation of LCA, the investigation on the effect of different factors on the sensitivity of the LCA results such as resin fiber content, product lifetime, and total transport distance can also be performed (Corbière-Nicollier et al. 2001; Luz et al. 2010). Apart from that, LCA also enables specific view to focused stage in the whole product life cycle and subsequently their relation in terms of environmental performance to the whole product life cycle such as analyzing the significance of the disposal phase relative to other life cycle phases and identifying various disposal technology impacts to the overall environmental profile (Schmidt et al. 2004). Businesses related to NFC applications also may benefit from LCA implementation in reducing the product cost in several ways such as reducing operating costs via supply chain coordination of transports to reduce the fraction of vehicles traveling with light or empty loads, new product introduction by considering unused raw materials as a marketable asset rather than a cost-centered waste stream, reducing disposal cost and improved relations with authorities, linked with the installation of near-zero discharge facilities, which are much easier to implement for small scales if planned from the outset, reducing cost to certify to ISO 9001 and ISO 14001, which also brings indirect benefits via stakeholder coordination (requirements from industrial customers) and reducing overhead by having in place an environmental management system, which permits the small- and medium-sized enterprises (SMEs) in question to correspond to clients and suppliers programs. Besides that, LCA can also act to support NFC-related businesses by creating a favorable image to local and regional politicians which can further provide loan guarantees for promising firms without any significant operational or environmental risks and improved credit terms with major financial institutions (Rebitzer et al. 2004).

On the other hand, there are also several challenges reported to the successful implementation of LCA. Among them is the need for consistent commitment by the organization embracing the methodology in the products and services, especially by the top management (Rebitzer et al. 2004). In addition, considering the vast amount of LCA specific methodologies related to life cycle impact assessment (LCIA) methods available, international harmonization of methodologies and data to reduce the problem of potentially divergent conclusions obtained from the LCA exercise are required while allowing flexibility with respect to the main principles. There are many ongoing efforts to address the challenge and close the gap through the development of several new methodologies such as ReCiPe 2008 (Goedkoop et al. 2009), the LCIA method based on endpoint modeling (LIME) (Itsubo and Inaba 2003), and IMPACT 2002+(Jolliet et al. 2003).

There are four main stages in the LCA process which are identifying the goal and scope definition, inventory analysis, LCIA, and interpretation (Anonymous 2006b). The first phase in LCA implementation involves defining the goal of the project such as the reason of the study and the intended application, defining the scope of the study such as the system boundary and the functional unit. In this phase, normally a cradle-to-grave approach is applied in assessing the environmental impact, which includes all life cycle phases, namely production that includes material and component productions, use phase up to end-of-life processing of the product. However, partial LCA or cradle-to-gate approach is also used for similar purposes whereby a selected portion of the total life cycle is analyzed. The system unit processes are defined by the system boundary which covers the input and output of the system such as life cycle stages, resources, and by-products associated with the product of interest. In the first phase, the functional unit of the product is also defined where it is used as the reference unit in the LCA where a system performance is quantified. The reference unit is essential to enable producing comparable LCA results on a common basis which is critical especially when assessing varying systems. The second phase in LCA is inventory analysis to quantify inputs and outputs relevant to the product system involving collection of data and calculation procedures.

The next phase in LCA is LCIA that provides further information that permits results obtained from the inventory to be interpreted. In this phase, the significance of potential environmental impacts are evaluated and inventory data are related to the specific environmental impact categories and category indicators, thus allowing more accurate improvement decision to be made (Saur et al. 2000). In general, there are two types of LCIA models used in LCA studies which are the midpoint damage model and endpoint damage model. In the midpoint damage model, the environmental impacts such as hazardous elements' production and natural resources' extraction are converted into impact category indicators such as acidification, eutrophication, and global warming. Examples of commonly used midpoint impact categories in LCA research are shown in Table 1.

Table 1 Commonly used impact categories in life cycle assessment (LCA) research. (Pelletier et al. 2007)

Impact category	Description of impacts
Global warming	Contributes to atmospheric absorption of infrared radiation
Acidification	Contributes to acid deposition
Eutrophication	Provision of nutrients contributes to biological oxygen demand
Photochemical oxidant formation	Contributes to photochemical smog
Aquatic/terrestrial ecotoxicity	Contributes to conditions toxic to flora and fauna
Human toxicity	Contributes to conditions toxic to humans
Energy use	Contributes to depletion of nonrenewable energy resources
Abiotic resource use	Contributes to depletion of nonrenewable resources
Biotic resource use	Contributes to depletion of renewable resources
Ozone depletion	Contributes to depletion of stratospheric ozone

In the endpoint damage model, the midpoint impact categories are further classified into three broad groups which are damage to human health, damage to ecosystem quality, and damage to resources (Pennington et al. 2004). Midpoint LCIA approach was reported to better support more scientifically based decision analysis whereas endpoint damage model provides additional support when a smaller or single environmental indicator is desired (Bare 2010). Because of the invariable presence of value judgments in any LCIA, there is no unique, best method for conducting an impact assessment (Hertwich et al. 2000). Therefore, method developers have to determine certain criteria which they judge to be the most important in order to select a characterization model (Toffoletto et al. 2007). A detailed summary of existing LCIA methods such as Eco-indicator 99, Center of Environmental Science of Leiden University (CML) 2002, and ReCiPe was reported in the EU International Reference Life Cycle Data System (ILCD) report (Anonymous 2010).

The final phase in LCA involves interpretation of the results obtained from the LCIA phase. Currently, there are many commercial LCA software available for modeling subsystems and unit processes in order to help hasten the analyzing time to secure the results apart from systematic data management especially for the inventory analysis phase. Among them are SimaPro, Umberto, and GaBi (Consultants 2008; Stylos and Koroneos 2014; Willers and Rodrigues 2014). Based on the defined goal and scope, the results obtained are interpreted to obtain conclusions, clarify limitations, and offer recommendations. Furthermore, the interpretation phase also provides decision makers the ability to compare between alternatives and impact categories especially with the existence of trade-off between product alternatives or desirability to prioritize areas of concern within a single life cycle study (Rebitzer et al. 2004).

Application of LCA for Natural Fiber Polymer Composites

The earliest reported comparative LCA study for automotive parts was performed between hemp/epoxy composites and acrylonitrile butadiene styrene (ABS) materials for the production of automotive side panel component of passenger cars (Wötzel et al. 1999). Cradle-to-grave life cycle approach was implemented in this study to determine the environmental impact between both candidate materials. The study was aimed to support automotive engineers in the decision-making process by providing the data on the potential environmental benefits that can be gained through substituting ABS by hemp fibers in producing the component. The Eco-indicator 95 impact assessment method was applied in the assessment process due to its good handling and transparency with the assistance of Umberto LCA software. Lower total eco-indicator score has been achieved by using hemp/epoxy material compared to ABS. The cumulative energy demand results showed that natural fiber required lower energy (73 MJ) compared to ABS (132 MJ) for the production of a single basic component. Further ecological advantage is also provided due to lower component weight by using NFC compared to ABS especially during the use phase of the passenger car. Nevertheless, the substitution of hemp nearly doubles the eutrophication effect compared to ABS which is caused by the use of fertilizer during hemp cultivation process and the score can be found higher if pesticides are also employed during the cultivation phase of the natural fiber crops.

An exhaustive LCA study of a whole vehicle was reported involving Mercedes-Benz S-class passenger vehicle model, which also included the application of coconut, wood, flax, and cotton fiber in combination with different polymers in the new component construction (Finkbeiner and Hoffmann 2006). Cradle-to-grave approach was also selected for the LCA involving design, production, use, recycling, and disposal. In their report, results obtained from LCA which were analyzed using GaBi LCA software revealed that approximately 85 GJ reductions in the overall energy demand compared to the preceding model were achieved, corresponding to the energy content of approximately 2500 L of fuel. Over the life cycle, emissions of the carbon dioxide greenhouse gas also were predicted to reduce by 7 %, with a 14 % reduction in nitrogen oxide emissions compared to the previous S-class model. In the analysis, the contributing factors to the improved environmental performance of the vehicle were found due to the new introduction of 27 components with a total weight of nearly 43 kg which were produced from NFC to the overall vehicle buildup. The total weight of components made from renewable raw materials also increased nearly 73 % compared to the previous model which also highlights the success of the design for environment (DfE) initiative taken for the vehicle design.

The importance of renewable resources in technical applications especially in vehicle design was also reported through LCA by Mussig et al. (2006). Comparative LCA study was made using two types of matrix materials reinforced with hemp natural fibers, which are Polymer material made from Triglycerides and Polycarbon acid anhydrides (PTP) vegetable-based thermoset resin and polyester resin, while a bus body component produced from sheet-molding-compound (SMC) technology was selected as the reference component. For both materials, the cradle-to-grave LCA approach was implemented covering materials flow and energy usage across the entire life cycle. The Umberto LCA software was used as the tool for the modeling composites' product system and environmental impact calculations. Environmental impact assessment results based on seven major indicators which are resources used, cumulative energy demand, human toxicity, eutrophication, acidification, summer smog, and greenhouse effect show positive effect on the use of natural-based polyester resin for nearly all environmental impact categories expect eutrophication due to high agricultural prechain portion involving a vegetable-based thermoset resin at the raw material extraction phase in the product life cycle.

In another report, Schmehl et al. (2008) published LCA results on the application of hemp natural fiber and PTP vegetable-based thermoset resin for passenger bus body component casing. Their work was an extension of the previous report on similar project reported by Mussig et al. (2006) but has been extended into more detail by comparing four different variants of the hemp/PTP composites to the glass fiber/unsaturated polyester composites used in the existing component. Eco-indicator 99 and cumulative energy demand life impact assessment method were both employed for the analysis with the assistance of Umberto LCA software which covers the whole product life cycle starting with acquisition of raw materials, semifinished parts (prepregs) and body components' production, the use phase, and finally end of life. In the results obtained, the material system using hemp/PTP composites at 66 wt% with optimized production conditions (natural fiber and vegetable-based thermoset resin (NFK) optimized) scored the lowest environmental impact based on the total eco-indicator method compared to other listed alternatives while the existing synthetic-based glass fiber/unsaturated polyester composites scored the highest environmental impact. Apart from that, similar environmental impact trend was also observed through the cumulative energy demand indicator whereby NFK optimized composites required less energy throughout their total life cycle especially compared to glass fiber/unsaturated polyester composites. The performance of NFK optimized composites in their report was contributed by lower overall weight of the component which further brought benefits in eco-balancing through lower material input and emissions in the production phase as well as lower fuel consumption required in the product use phase.

Zah et al. (2007) investigated the use of curaua-reinforced polypropylene (PP) NFC for automotive interior component production compared to glass fiber-reinforced PP composites in terms of their environmental impacts using LCA. CML impact assessment method was applied to analyze the related ecological impact of both composite materials based on the cradle-to-grave approach for a better overview of the component performance. Final results show that overall, lower environmental impact performance was obtained by using curaua/PP composites compared to glass fiber/PP composites. Apart from that, results from the exercise also highlight that lower fuel consumption obtained through lightweight curaua composites significantly affect the environmental impact for the component. On the other hand, they also stated from the economical and sociological point of view, that the use of curaua composites over glass fiber composites will be able to present further positive advantages such as low cost, amplifying more agricultural business, and eco-marketing works as well as increasing jobs for less developing countries and reducing health risks during the component manufacturing process.

Alves et al. (2010) performed LCA on buggy enclosure component made from three types of jute fiber composites which are produced in dried, untreated, and dried and bleached-treated conditions. In their study, the jute fiber composite (JFRP) alternative materials are also compared with glass fiber composites (GFRP) to determine the difference in environmental performance for the same application. Cradle-to-grave approach and Eco-indicator 99 LCIA method were both chosen in the analysis and the LCA modeling was made using SimaPro software whereby for the end-of-life phase, three types of disposal methods were also included in the investigation namely recycling, incineration, and landfilling. Results for overall life cycle show that GFRP produced higher environmental damage compared to JFRP, caused by heavier GFRP weight which further caused higher fuel consumption for the vehicle. Besides that, similar high-fuel consumption which relied on nonrenewable fossil fuel resource was also the reason found to cause the use phase of the product to create highest environmental damage compared to the other life cycle stages, and they suggested that future improvement actions should be focused on the use stage to minimize the environmental damage. On the other hand, for components made from three types of jute fiber composites (untreated, dried, and dried/bleached-treated conditions), results also show that treated jute bonnet composites are more pollutant compared to nontreated jute bonnets until the production phase. They also added that through qualitative analysis made on the social and economic impacts of using jute composites compared to glass fiber composites, they found that jute fiber composites performed better in both categories compared to glass fiber composites despite their lower technical performance.

In another automotive application, Luz et al. (2010) studied the environmental performance of an aesthetic covering component of a vehicle made from hybrid sugarcane/bagasse-reinforced PP composites using LCA. The environmental performance of hybrid NFC was also compared with talc-reinforced PP composites for similar application. The study was focused on a Brazilian setting which included data gathering and component usage. Cradle-to-grave approach was adapted in defining the LCA boundary condition and modeling of the system was made using GaBi LCA software. Apart from that, three different product end-of-life methods were also investigated in the study to simulate and compare their effect on the environmental performance and results obtained showed that recycling disposal method caused the lowest environmental damage compared to incineration and landfilling methods. From the comparative LCA analysis results, it was observed that hybrid sugarcane/bagasse composites produced lower environmental damage compared to talc-reinforced PP composites throughout the component life cycle, with added advantage of comparable mechanical properties between both composite materials for the intended application. They also concluded that lower hybrid sugarcane/bagasse composites environmental damage was influenced by several factors such as lower global warming impact especially during cultivation stage of the raw materials, cleaner raw material production process, lower materials weight which causes lower-fuel consumption during use stage of the component, and the availability of implementing recycling method to dispose the material at the end-of-life stage.

LCA analysis related to the application of NFC in packaging for transportation application was also investigated by Duigou et al. (2011). They performed simplified LCA of flax mat/poly-L-lactic acid (PLLA) biocomposites and flax mat/PLLA/balsa bio-sandwich composites and later compared the environmental performance to synthetic-based glass mat/unsaturated polyester composites and glass mat/unsaturated polyester/balsa sandwich composites. Cradle-to-gate approach was selected for their study which covers raw material extraction up to composites' production stages. The CML 2000 and cumulative energy demand impact assessment methods were applied to quantify the environmental effect of the composite materials using SimaPro LCA software. From the analysis, results show that lower environmental damage can be achieved using NFC (flax/PLLA composites and flax/PLLA/balsa bio-sandwich composites) instead of synthetic glass fiber/polyester composites. Furthermore, they also found that a larger weight of flax NFC is required compared to glass fiber/polyester composites in order to provide comparable mechanical performance for the intended application which influenced the overall environmental performance. Thus, they suggested that weight reduction initiatives to be taken to reduce the effect especially towards the intended application.

LCA study was also made to investigate the environmental impact of using natural fiber as alternative materials in paper pulp production (González-García et al. 2010). Two different types of natural fibers, namely, flax and hemp, were chosen as the candidate materials and LCA analysis was carried out to predict and compare the environmental impact associated with the use of both natural fibers. In their study, cradle-to-gate approach was selected in the study which covers the raw material cultivation up to the production of the paper pulp product (pulp mill gate). SimaPro LCA software was also used in the LCA modeling based on CML baseline 2000 LCIA method. The environmental impact obtained by the use of natural fibers was later categorized in terms of global warming potential, acidification, eutrophication, photochemical oxidant formation, energy usage, and pesticide usage. Overall results gained from the analysis showed that the potential use of flax fiber as a raw material for the paper pulp production is more environmentally friendly compared to hemp fiber. Despite the overall environmental advantage, flax fiber however showed lack in irrigation and pesticide use environmental performance compared to flax fiber and future improvement were later suggested to be focus in both of the identified areas to further strengthened the final decision in applying hemp fiber as the new raw materials for paper pulp product.

LCA was also implemented in determining the building materials' environmental impact performance involving the use of kenaf-reinforced polyester composites for thermal insulation board component (Ardente et al. 2008). A cradle-to-grave approach was selected for the LCA analysis which included kenaf raw material cultivation, transportation, manufacturing, use, and disposal stages of the product. The environmental impacts were assessed in three major categories which are energy consumption, waste product, and environmental impact indexes such as global warming potential and water consumption. The analysis results showed that significant reduction of the environmental impact was obtained through the use of NFC compared to synthetic composites for the insulation board application while maintaining the required thermophysical and noise-abatement properties. The comparative LCA results involving six other alternative candidate materials for thermal insulation board component, namely, polyurethane, glass wool, flax rolls, stone wool, mineral wool, and paper wool with kenaf composites, showed that highest environmental impact was contributed by synthetic materials and improved environmental impact score was due to mineral wools. It was shown that kenaf-based composites' environmental impact performance is situated between both material categories and its performance can be further improved by adopting other disposal scenario in the end-of-life stage of the product such as through the use of incineration method with energy recovery and energy production. Elsewhere, LCA results also point out that the use of kenaf-based composites as thermal insulation materials will be able to provide higher energy, saving gain during the whole building operation time compared to the material calculated total energy consumption throughout its life cycle which further highlights the advantage of using NFC for the intended application.

Xu et al. (2008) also studied environmental performance of NFC particularly involving the use of wood fiber-reinforced PP composites for the production of preforms which are intermediate materials for producing other final composite products. In the study, wood polymer composites were compared with PP material for the production of preforms product and Eco-indicator 99 impact assessment method was employed to determine the materials environmental burden based on cradle-to-gate approach by assuming that the production phase dominates the environmental standing of the product throughout its total life cycle stages. The processes involved in the analysis using SimaPro LCA software were limited from raw material extraction up to the product production. Analysis results showed that the use of wood fiber-reinforced PP composites was able to contribute to lower environmental impact compared to PP materials for the production of preforms and the environmental performance is directly linked to the amount of wood fiber used as the reinforcement. Moreover, at similar volume conditions, preforms made from wood fiber-reinforced PP composites also possessed better environmental standing due to lower density, and subsequently better lightweight property of the composite material compared to PP material. Apart from that, in terms of material's service density index which was also proposed in their study to determine the equivalent materials strength required to withstand the operational load, the environmental performance of wood fiber-reinforced PP composites was also found to be consistent with the previous results in comparison with PP materials due to less volume of material required by wood fiber-reinforced PP composites. This is contributed by the higher wood fiber tensile strength compared to PP.

Vidal et al. (2009) studied environmental burden of NFC made from cotton linters and rice husks as the reinforcement materials and aggregated in recycled thermoplastic PP and high-density polyethylene (HDPE) matrices. The cotton liner/PP composites, rice husks/PP composites, and cotton liner/HDPE composites environmental impacts were later compared to virgin PP and virgin HDPE resins based on a similar functional unit. Cradle-to-grave life cycle approach was selected in their analysis and the results were displayed in four main categories, namely, greenhouse effect, nonrenewable energy depletion, eutrophication, and acidification which were all simulated using SimaPro LCA software. Apart from that, two disposal scenarios were also studied for the selected materials which are incineration and landfilling. For all impact categories, LCA results show that NFCs were able to reduce the environmental burden compared to virgin thermoplastics. Moreover, for both incineration and landfilling disposal process, all NFC also yielded lower greenhouse gas effect impact as high as 40 % lower for cotton linters/HDPE compared to virgin thermoplastic. Another interesting finding was also observed between the simulated disposal scenarios whereby disposal of NFC through landfilling process was able to provide higher greenhouse gas savings compared to incineration process, thus providing a useful insight for selection of disposal method involving NFC.

Corbière-Nicollier et al. (2001) studied comparative LCA of transport pallet product made by using China reed biofibers and glass fibers, both reinforced in PP matrix. Their study used the cradle-to-grave approach where the life cycle of product was assessed from the raw material production, transport, use, and disposal stages. For natural fiber production, it also includes the plant cultivation stages up to fiber processing. Critical surface-time method (CST95) was employed as the impact assessment method due to its ability to include the effect of heavy metals in the soil, and the final results were later checked for reliability using CML 95 and Eco-indicator 99 methods. Apart from that, during the functional unit definition process, due to lack of actual data, rules of mixture composites' micromechanical model were employed to determine the China reed composite's fiber weight fraction information. LCA results showed that the use of China reed composites for the production of transport pallet product is more environmental-friendly compared to glass fiber composites for minimum pallet service time of 3 years. Moreover, life cycle emissions (air, water, and soil emissions) and primary nonrenewable energy usage are both higher using glass fiber compared to China reed fiber, while natural fiber lacks in terms of higher land-use requirement for China reed pallet production. In addition, they also stated that the potential of natural fiber to be implemented in product design application is greater compared to biofuel production and direct biomass heat production.

Apart from single system composites, LCA was also utilized in the environmental impact assessment analysis of hybrid thermoset NFC (LaRosa et al. 2013). Hybrid thermoset composites made from hemp/glass fiber were compared with conventional glass fiber thermoset composites for the production of elbow-fitting component designed for chemical plant cooling pipeline application. Cradle-to-grave approach was applied in the study and the environmental damages were analyzed based on ReCiPe, cumulative energy demand, and Intergovernmental Panel on Climate Change (IPCC) 2007 100a method LCIA methods. The comparative

LCA study indicated that overall, the use of hemp fiber in the hybrid thermoset NFC formulation has enabled better environmental performance compared to conventional glass fiber thermoset composites due to lower petroleum-based synthetic glass fiber and thermoset resin quantity needed for the hybrid composites production. Besides that, hemp fiber was also found to significantly reduce the environmental damage in the production phase of the product life cycle due to the natural fiber's inherent ecofriendly attributes. Moreover, in a similar study, life cycle costing (LCC) was also performed to evaluate the economic advantages between the hybrid thermoset NFC and the conventional glass fiber composites. The economic analysis results showed that the hybrid hemp/glass fiber thermoset composites were able to reduce the raw material, labor, and waste costs for the elbow-fitting component production compared to conventional glass fiber thermoset composites. The overall results showed that the introduction of hemp natural fiber into the hybrid thermoset NFC formulation was able to provide improvement in both environmental and economic aspects for the elbow-fitting product.

Wang et al. (2012) performed comparative LCA of three fiber-reinforced SMCs made from kenaf fiber, glass fiber, and soy-based resin, respectively. SMCs for automotive applications are typically made of unsaturated polyesters and glass fibers and used for the production of automobile interior parts. Kenaf fiber and soy-based resin application were selected to partially replace the glass fiber and polyester resin due to their potential environmental benefits. In their study, a soy-based resin, maleated acrylated epoxidized soybean oil (MAESO), was synthesized from refined soybean oil. SMC1 composite was made from kenaf fiber and polyester resin while SMC2 composite was made from kenaf fiber and a resin blend of 20 % MAESO and 80 % unsaturated polyester. The cradle-to-gate LCA using Eco-indicator 99 and cumulative energy demand methods was conducted for three composites, namely, SMC1, SMC2, and the glass fiber-reinforced SMC using SimaPro LCA software. The materials and energy input/output data for the production of one functional unit of three composites were collected from laboratory experiments and literature. The results showed that both kenaf fiber-reinforced SMCs perform better than glass fiber SMC in every environmental category and the effect of global warming potential of kenaf fiber SMC (SMC1) and kenaf soy resin-based SMC (SMC2) was only about 45 and 58 % of that for glass fiber SMC, respectively. Their findings demonstrated that using soy-based resin and kenaf natural fiber for SMC would have a great ecological benefit for the SMC product.

A summary of several comparative LCA studies was also reported in determining NFC environmental performance compared to specific glass fiber composites (Joshi et al. 2004). Based on the cradle-to-grave approach, in general, the review performed showed that NFC has better environmental performance compared to glass fiber composites. The study also points out four main factors which contribute to the ecofriendly advantages of NFCs which are lower energy requirement during raw fiber materials and final composite materials' production, higher fiber contents in producing the final composites which reduced the petroleum-based resin requirement, lower final composites weight due to the natural fiber's low density which affects lower fuel consumption and lesser release of emission during use stage particularly for automotive application, and finally higher energy recovery and lower carbon emission during the end-of-life stage of the product life cycle. Moreover, based on the four primary life cycle stages, NFCs actively contribute to better environmental performance in the production, use, and disposal life cycle stages with the exception of raw material acquisition/extraction stage due to the reported possibility of higher eutrophication effect from NFC. It is primarily caused by the use of fertilizers as well as pesticides during the cultivation of natural fibers. Nevertheless, in general, the overall findings strengthened the advantages of using NFC in terms of ecological contributions apart from cost and lightweight attributes especially for material substitution purpose in new product development. Table 2 summarizes examples of LCA application involving NFC.

Table 2 Examples of life cycle assessment (LCA) application involving natural fiber composites (NFC)

NFC	Application	Life cycle approach	Impact assessment method use	References
Hemp/epoxy vs. ABS	Side panel component for passenger car (Audi A3)	Cradle-to-grave	Eco-indicator 95	(Wötzel et al. 1999)
Coconut, wood, flax, and cotton fiber	Interior components	Cradle-to-grave	Not specified	(Finkbeiner and Hoffmann 2006)
PTP vegetable resin vs. polyester resin, hemp as the reinforcement material	Bus body component	Cradle-to-grave	Not specified	(Mussig et al. 2006)
Hemp/PTP vs. glass fiber/polyester	Bus body component	Cradle-to-grave	Eco-indicator 99 and cumulative energy demand	(Schmehl et al. 2008)
Curaua/PP vs. glass fiber/PP	Automotive interior component	Cradle-to-grave	CML	(Zah et al. 2007)
Jute fibers (untreated, dried, and bleached/dried) vs. glass fiber-reinforced plastics	Buggy vehicle enclosure component	Cradle-to-grave	Eco-indicator 99	(Alves et al. 2010)
Sugarcane bagasse/PP vs. talc/PP	Vehicle interior aesthetic coverings component	Cradle-to-grave	Not specified	(Luz et al. 2010)
Flax mat/PLLA vs. glass fiber/polyester and, flax mat/balsa/PLLA vs. glass fiber/balsa/polyester	Packaging for transportation	Cradle-to-gate	Eco-indicator 99 and cumulative energy demand	(Duigou et al. 2011)

Table 2 (continued)

NFC	Application	Life cycle approach	Impact assessment method use	References
Hemp fiber vs. flax fiber	Paper pulp product	Cradle-to-gate	CML baseline 2000	(González-García et al. 2010)
Kenaf/PP vs. polyurethane, glass wool, flax rolls, stone wool, mineral wool, and paper wool	Building thermal insulation board material	Cradle-to-grave	Not specified	(Ardente et al. 2008)
Wood fiber/PP vs. PP	Preform material	Cradle-to-gate	Eco-indicator 99	(Xu et al. 2008)
Cotton liner/PP, rice husks/PP, cotton liner/HDPE vs. virgin PP and virgin HDPE	Not specified	Cradle-to-grave	Not specified	(Vidal et al. 2009)
China reed fiber/PP vs. glass fiber/PP	Transport pallet	Cradle-to-grave	Critical surface-time method (CST95)	(Corbière-Nicollier et al. 2001)
Hybrid glass fiber-hemp/thermoset vs. glass fiber/thermoset	Elbow-fittings for the sea water cooling pipeline	Cradle-to-grave	ReCipe method, cumulative energy demand, and IPCC 2007 100a	(LaRosa et al. 2013)
Kenaf/soy-based resin, kenaf/soy resin with polyester blend, glass fiber/polyester	Sheet molding compound material	Cradle-to-gate	Eco-indicator 99 and cumulative energy demand	(Wang et al. 2012)

NFC natural fiber composite, *ABS* acrylonitrile butadiene styrene, *PP* polypropylene, *PLLA* poly-L-lactic acid, *HDPE* high-density polyethylene, *CML* Center of Environmental Science of Leiden University, *IPCC* Intergovernmental Panel on Climate Change

Conclusion and Future Perspectives

The increase of LCA-related activities in NFC applications as summarized in the previous section show a promising future for the area. Moreover, new trends of LCA in NFC research and applications are also expected in the future which will cover several areas involving product design, inventory data, scopes of assessment, and legislations as shown in Fig. 2.

In terms of product development aspect, LCA information is increasingly being incorporated into the conceptual design stage of the product especially during

Fig. 2 Future trends of life cycle assessment (LCA) related to natural fiber composites (NFC) application

the design and materials selection process. Traditionally, in the decision-making process, designers only consider technical and economic criteria in selecting the NFC materials for their intended application, but with growing requirements of environmental performance by regulatory bodies and customers, the information provided through LCA complements the requirement and aids designers to arrive at a more holistic and optimized decision with balance between all the three aspects (technical, cost, and environment), thus enabling a more sustainable product to be materialized. Among the examples of the incorporation of LCA works in the product design area are material selection of sandwich panels for car floor component, gear component, and automotive body-in-white structure (Ermolaeva et al. 2004; Mayyas et al. 2013; Milani et al. 2011). This is in agreement with Finkbeiner and Hoffmann (2006), who highlighted that information of LCAs for parts can provide support decisions between different technological or material concepts for new product development apart from conventional requirements such as technical performance, design, vehicle production, cost, quality, etc.

Current indicators also show that improved LCA methodology will be implemented in the future through the incorporation of social and economic impact into the current environment-based LCA analysis for various applications including NFC. It is argued that current practice of concentrating solely on environmental impact will induce some degree of inconsistency with the defined areas of protection in LCA, for example, social impact will also affect the human health damage categories (Jørgensen et al. 2008). Among them, proposed solution is life cycle sustainability assessment (LCSA) which incorporates traditional LCA with social life cycle ssessment (SLCA) and life cycle costing (LCC) methodologies (Finkbeiner et al. 2010; Kloepffer 2008; Zamagni 2012). The new approach brings together all the three domains of sustainability (environment, economic, and social aspects) into a single assessment method, thus it is able to provide more accurate insight on the impact of products or processes to all stakeholders which are currently being analyzed independently (Foolmaun and Ramjeawon 2013; Vinyes et al. 2013).

Another area that also generates much interest in LCA is on the inventory data which is crucial to secure accurate assessment results at the end of the analysis. It is acknowledged that the research efforts on NFC are tremendously increasing as new classes of NFC such as new reinforcement materials, fully biodegradable matrices, and hybrid natural fiber/synthetic fiber composites are developed and available for various applications, thus concurrently requiring the same amount of effort to quantify them in LCA perspective at various life cycle phases to add to the current available LCA inventory data (Ishak et al. 2013; Sahari and Salit 2012; Sahari et al. 2013). Apart from that, future directions also point out the importance of enhanced quality and reliable data especially on natural fibers to be present and be made more available for application in LCA process so that the higher degree of confidence and credibility for final results can be obtained and better accepted by all stakeholders.

Finally, as the current LCA methodology is being widely established and accepted, it is also expected that LCA will be made as compulsory tool for green certification of products and services in the future especially involving NFC. Thus, the perceived green technology can be verified to be really green which means to be able to provide positive influence to the environment (bring improvement in terms of environmental effects) compared to the current products and services or to its intended applications as LCA enables quantitative data such as cumulative energy demand of products to be determined and assessed by consumers. Up to date, LCA methodology has been steadily implemented to complement green certification process such as in the European energy performance of buildings directive (Directive 2002/91/EC), certification of buildings in Spain, and Leadership in Energy and Environmental Design (LEED) certification for green buildings in the USA (Trusty and Horst 2003; Zabalza Bribián et al. 2009).

Overall, it is shown that the implementation of LCA brings more benefits especially to the current and prospective user of NFC in applying the material in newer applications. LCA has untapped potential that still has to be exploited and increasing relevance of LCA is expected in the future.

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Tensile, Oxygen Barrier and Biodegradation Properties of Rice Husk-Reinforced Polyethylene Blown Films

Khaliq Majeed, Azman Hassan and Aznizam Abu Bakar

Abstract The past few years have witnessed a renewed interest in developing new ecofriendly materials, sparked mostly by the nonbiodegradability of most of the polymeric materials. In this context, incorporation of biofibres as load-bearing constituents in polymeric composites is a highly attractive research line for the development of ecofriendly composites. An experimental study, with the overall aim of making environmentally compatible packaging film, was conducted to investigate the influence of rice husk (RH) loading on morphological, tensile, oxygen barrier and biodegradation properties of low-density polyethylene (LDPE)-based extrusion blown films. Various compositions were prepared with varying contents of RH and the properties were correlated with the loading of RH. Morphological observations revealed that there were micro-voids at interface and the RH particles start agglomerating beyond 5 wt%. The tensile, tear and oxygen barrier properties decreased as the loading of RH increased. Soil burial tests revealed that the composite films are biodegradable and RH loading has significant impact on rate of biodegradation.

Keywords Composite film · Blow film · Tensile strength · Oxygen barrier · Biodegradability

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Introduction

Film is the largest market segment for polyolefin and is extensively used for foodstuff and goods packaging, agriculture and merchandising (Mezghani and Furquan 2012; Zhong et al. 2007a). Among other polyolefin, low-density polyethylene (LDPE) is a high-performance thermoplastic having good film-forming properties. It has a prominence over other polyolefin in flexible films because of its high flexibility, easy processability, extensibility, easy-to-seal ability, impact toughness, stress crack resistance, microwavability, recyclability, high resistance to moisture and fair gas barrier properties (Zhong et al. 2007b). In fact, exploitation of these unique properties has made LDPE extremely useful to mankind, and it is the widely used polymer for film packaging. Like most of the other petroleum-based plastics, LDPE is also nondegradable and this nonbiodegradability is the cause of many environmental problems associated with its disposal, including damage to the environment and ecosystem, water supplies, sewer systems as well as to the rivers and streams.

Environmental concerns related to the use of nonbiodegradable fossil fuel-based plastics and their increasing costs have propelled interest in the development of biocomposites (Ahmad Thirmizir et al. 2013; Butylina et al. 2013; Nahar et al. 2012). Composite materials composed of one or more phase(s) derived from a biological origin are considered as biocomposites (Fowler et al. 2006; Haq et al. 2008). The prospective benefits of biocomposites are derived from the properties of the natural fibres. Natural fibres are susceptible to microorganisms and their biodegradability is one of the most promising aspects of their incorporation in polymeric materials. Among others, their renewability, abundance, lower cost, environmental friendliness and relative non-abrasiveness for the processing machinery have made natural fibres an attractive candidate for reinforcement of polymers (Ahmad Thirmizir et al. 2013; Ismail et al. 2013). These biocomposites are being used in large number of applications, including but not limited to automotive, building and furniture industries (Butylina et al. 2013; Ihamouchen et al. 2012). However, their strong hydrophilic behaviour made using natural fibre-reinforced composites is less attractive. Moisture ingress may impair mechanical properties as well as facilitate fungus growth that can assist the degradation of composites (Ahmad Thirmizir et al. 2013). Most of the renewable materials are based on the agricultural residues as a source of raw material, particularly to plastic industries. Development and progression in these bio-based materials will not only benefit ecosystem but also would lead to economic development for farming and rural areas in developing countries, owing to non-food commercial applications of these underutilized renewable materials.

Rice husk (RH) is one of the widely available agricultural industrial residue materials. It would always be removed and separated from rice grain during the rice milling. The main components of RH are cellulose (25–35 %), hemicellulose (18–21 %), lignin (26–31 %) and silica (15–17 %). Cellulose is found in the cell wall of lignocellulose materials as microfibrils embedded in the non-cellulosic matrix, which is mainly formed by hemicellulose and lignin (Luduena et al. 2011). Besides these structured main components, some other nonstructural components, like waxes, pectin, inorganic salts and nitrogenous salts, are also present (Fowler et al. 2006). Like many other agricultural by-products, the industrial applications of this biomass are very limited with little economic value. It is reported that for every ton of rice produced, about 0.23 tons of RH is formed. As a consequence of large production of rice, millions of tons of RH are produced every year. The continuous generation of the RH may present a major disposal problem because of its limited commercial applications. Currently, this mass is being used as bedding material for animals and burned for power generation. Literature review indicated that there is a lack of investigations on the effect of natural fibres-reinforced polymeric composite films and their durability against moisture exposure. Moreover, the performance properties of LDPE/RH biocomposite films have seldom been reported. Therefore, this study focuses on the fabrication of RH/LDPE composite films using extrusion blown film machine.

The objectives of this study are to explore the possibility of incorporating RH as biodegradable filler in manufacturing composite films based on LDPE matrix. The resulting films were characterized by tensile, barrier and biodegradation properties. One of the main concerns of using natural fibres is their high hydrophilic behaviour which ultimately affects the overall properties of the composites. Thus, the effect of prolonged moisture exposure on the tensile properties was also investigated. An attempt has been made to correlate the results of performance properties of the films with RH loading.

Materials and Methods

Materials

LDPE (LDF 200 GG) having density of 0.922 g/cm^3 and melt flow index of 2 g/10 min was supplied by Titan chemicals, Malaysia. RH was obtained from BERNAS (Padiberas Nasional Berhad), Malaysia. The supplied RH was washed extensively with distilled water at room temperature to remove dust or other debris materials and dried in an air circulating oven at 100 °C for 24 h to reduce moisture content to less than 4 %. Prewashed and dried RH was ground using grinder and used for composites manufacturing.

Film Blowing

The RH was dried in an oven at 100 °C overnight prior to processing. The pre-dried RH was melt compounded with LDPE at different loadings (0, 3, 5 and 7 wt%) in a co-rotating Brabender twin-screw extruder. The extruded strands were air-dried in a cool air stream and pelletized. Finally, the resulting biocomposites pellets as well as the neat LDPE were blown into films using extrusion blown film machine (Tai King, model: TK/HD, Tai King Machinery Factory Co. Ltd., Taiwan).

Experimental Techniques

Morphological Analysis

The morphology of biocomposite films surface was evaluated using scanning electron microscope (SEM, Philips XL 40). The biocomposites film samples were frozen in liquid nitrogen and broken into pieces to make interface study. The fractured film samples were mounted onto copper stubs using double-sided sticky tapes and sputter coated with gold to provide enhanced conductivity. Finally, the SEM micrographs were taken under different magnifications.

Mechanical Measurements

The neat LDPE and the composite blown films were cut into rectangular-shaped specimen (102 × 15 mm) along their longitudinal direction. Micrometre (Mitutoyo, Japan) with precision of ±0.001 mm was used to measure thickness of the film samples. The mechanical measurements, including tensile strength, tensile modulus and tear strength, were carried out by using Lloyd's universal testing machine following the procedures described in ASTM D882 and D1938 standards, respectively. At least five different samples were tested for each sample composition and the mean values were reported.

To investigate the effect of prolonged moisture exposure on the tensile properties of composite films, the samples were submerged in distilled water and soaked for 7 and 14 days at room temperature. After soaking for a specific time, the test samples were wiped gently with tissue paper and tensile properties measured.

Permeability Measurements

The oxygen (O_2) permeability coefficient measurements for the films were carried out at room temperature in a constant pressure/variable volume type permeation cell designed according to ASTM D1434–82 (Reapproved 2009). Circular film samples of uniform thickness and 4.4 cm diameter were used to measure O_2 transmission rate (OTR, $\mathrm{mL(STP)/m^2/24\ h}$). Micrometre (Mitutoyo, Japan) with precision of ±0.001 mm was used to measure thickness of the film samples, and permeability coefficient was calculated by using the relation given below:

$$P = t\frac{\mathrm{OTR}}{\Delta p}$$

,where P is the permeability coefficient, mL(STP)-mm/m^2/24 h/atm, t is the thickness of the film under investigation, mm and Δp is the difference in partial pressure of O_2 on two sides of the film, atm.

Biodegradability Test

The biodegradability test has been developed for the investigation and comparative evaluation of degradability of different materials. In this study, biocomposite samples have been subjected to soil burial test for 6 months and the rate of biodegradation/disintegration of the buried samples of various compositions was studied as a function for number of days, with the help of SEM micrographs.

Results and Discussion

Morphological Analysis

Simple naked eye examination of the LDPE/RH biocomposites films prepared by extrusion blown film method indicated that good RH dispersion was achieved in the low fibre content materials. On the other hand, composite films with fibre content beyond 5 wt% showed fibre agglomeration in the matrix. Interface morphology of the RH-reinforced LDPE biocomposites films at micron and submicron levels was studied by examining the fractured surfaces with SEM. SEM micrographs of the biocomposites films containing 3 and 7 wt% of RH loadings and the representative micrographs showing the presence of voids and fibre pull-outs can be seen in Fig. 1.

Examination of these fractured surfaces indicates that the RH particles are well dispersed in the films prepared by adding 3 wt% of the fibre. Increasing the fibre content beyond 5 wt% started agglomeration (Fig. 1b) owing to the presence of hydroxyl groups. The presence of RH aggregates provides an evidence of low compatibility and poor dispersion (Ihamouchen et al. 2012). This agglomeration decreases homogeneity of the film and, in consequence, its performance properties. Furthermore, there are voids between biofibre and thermoplastic matrix (Fig. 1c). The voids play a crucial role in physical properties of the composites (Gwon et al. 2012; Nahar et al. 2012). Presence of these voids can act as stress concentrators, leading to failure of composite samples. Moreover, the fibres are pulled out from the LDPE matrix without their breakage depicting poor adherence of RH with LDPE. Holes can be readily seen owing to fibre pull-outs which result from the fibre pull-out due to poor interactions at the interface (Fig. 1d) (Zabihzadeh et al. 2011). These observations clearly indicate that the interfacial adhesion between the filler and the matrix is poor, and fracture seems to be dominated by the matrix failure since no fibre breakage can be observed. Poor interfacial adhesion results in a poor stress transfer between the matrix and the filler. The lack of compatibility and interfacial bonding

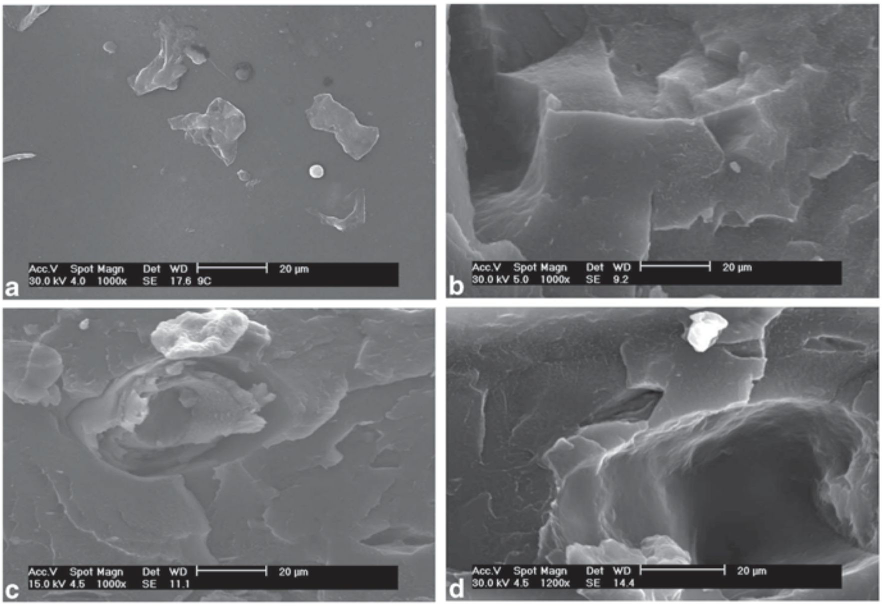

Fig. 1 Scanning electron microscope (SEM) micrographs of cryo-fractured surfaces of LDPE/RH biocomposites having **a** 3, and **b** 7 wt% of rice husk (RH); and the representative micrograph showing **c** presence of voids, and **d** pull-outs of RH fibre. *LDPE* low-density polyethylene

between RH and polyolefin matrix can be attributed to low polarity of polyolefin and the high surface energy of the cellulosic fibres (Bendahou et al. 2008). These observations are in agreement with the low strength values reported for these composites. Similar observation have been reported by Zhong et al. (2007a) for natural fibre-reinforced polyethylene composites.

Mechanical Measurements

Mechanical measurements were conducted to understand the effects of RH loadings on tensile and tear properties of the composites. These tests were carried out at ambient conditions. The influence of RH loadings on the matrix properties can be assessed by comparing the results of the composites with the virgin matrix. Figure 2 depicts the tensile modulus of RH-reinforced LDPE composite films as a function of fibre loadings under dry and wet conditions. A significant increase in tensile modulus was observed with both dry and wet composites at various loadings of RH. However, the ranges of increase in modulus values at various RH loadings were low in the case of water-soaked samples. The tensile modulus of neat LDPE was 163.4 MPa. About 42 and 47% increase was observed with the addition of 5 and 7 wt% RH, respectively. Nahar et al. (2012) have also reported a similar behaviour for natural fibre-reinforced polypropylene composites. It is also observed

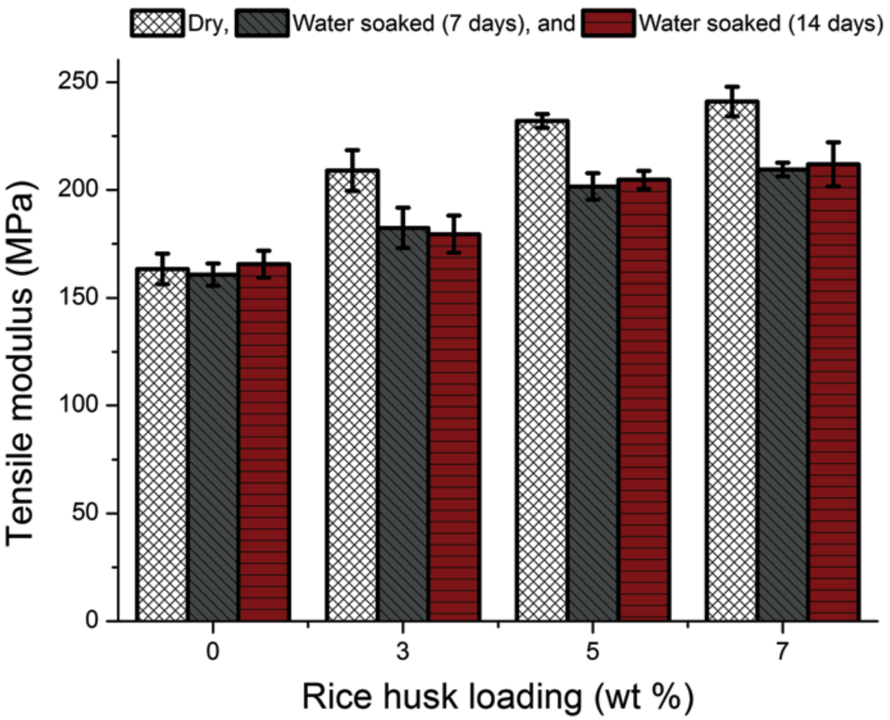

Fig. 2 Tensile modulus LDPE/RH biocomposite films as a function of rich husk (RH) loadings under dry and wet conditions. *LDPE* low-density polyethylene

that higher fibre loaded composite samples, as would be expected, showed higher improvement in comparison to neat LDPE. The effect of water absorption and time of exposure was also significant on all the studied composites except neat LDPE which hardly absorbed any water. The absorption of water decreased the modulus, and the magnitude was dependent on the RH loadings. The decrease in modulus upon exposure of the samples to wet environment can be attributed to decreased stiffness of the material components from absorbed moisture. This decrease in modulus might also be because of the damage of fibre interface from differential swelling. When the composite is exposed to moisture, hydrophilic RH fibre swells. As a result of fibre swelling, debonding occurs. This could be due the fact that immersion of composite samples at water affected the interfacial adhesion between the fibre and matrix (Athijayamani et al. 2009).

Figure 3 shows the effect of RH content on tensile strength of LDPE/RH composites under dry and wet conditions. It was observed that the tensile strength of the composites decreased with the RH loadings under both dry and wet conditions. The tensile strengths of the composites of 3 and 5 wt% RH are 9.9 and 8.1 MPa, respectively, at dry conditions. This decrease in the tensile strength may probably be due to incompatibility of RH with thermoplastic matrix that leads to poor interfacial adhesion, which would have caused discontinuity in the matrix material, resulting

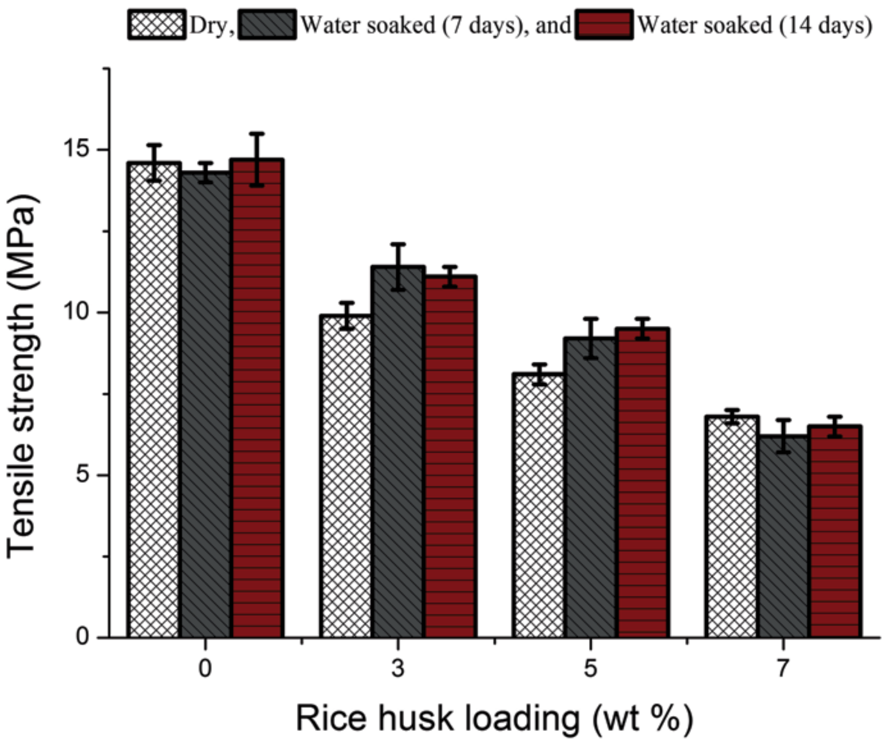

Fig. 3 Tensile strength of LDPE/RH biocomposite films as a function of rice husk (RH) loadings under dry and wet conditions. *LDPE* low-density polyethylene

in reduction in tensile strength (George et al. 2006). These findings further support the findings of Bendahou et al. (2008). This loss of tensile strength is in good agreement with microscopic analysis which showed a lack of adhesion between RH and LDPE. As the minimum acceptable tensile strength level for food packaging is 4 MPa (Tajeddin et al. 2010), it is worth noting that the incorporation of RH with the overall aim of making ecofriendly composites has produced composites with reasonable tensile properties.

The effect of moisture on composite tensile strength was also significant, and the percentage of improvement decreased with increase in RH content. The tensile strengths of the composites of 3 and 5 wt% RH are 11.4 and 9.2 MPa, respectively, after immersion in water for 7 days. The percentages of improvement when compared with dry samples are 15 and 13 %. The tensile strength, however, decreased by 9 %, for 7 wt% RH composites after water soaking for 7 days. Generally, for natural fibre-reinforced biocomposites immersed in water, it was expected that the relative extent of decrease in tensile strength was greater compared to dry samples for various fibre loadings. It is interesting to note that for 3 and 5 % RH composite samples, the tensile strength of wet samples was higher when compared with dry

Table 1 Effect of rice husk (RH) loading on tear strength and oxygen permeability of low-density polyethylene (LDPE)-based films

Sample LDPE/RH (wt %)	Tearing force (g)	Permeability $\left(\frac{mL(\mathrm{STP})-mm}{m^2-24hr-atm}\right)$
100/0	138.4 (6.4)	224 (27)
97/3	131.3 (4.2)	572 (45)
95/5	123.9 (5.2)	1450 (81)
93/7	105.7 (5.8)	3572 (221)

samples. This could be due to the fact that high amounts of water causes swelling of the fibres, which could fill the gaps between the fibre and the polymer matrix and eventually could lead to an increase in the strength of the composites. Dhakal et al. (2007) have also reported the similar observation for hemp fibre-reinforced polymer composites where ultimate tensile stress of wet samples was higher than that for dry samples.

Tear strength, resistance to the growth of a cut or nick in a specimen when tension is applied, is another significant property for the determination of suitability and effectiveness of a material for packaging. Table 1 displays the tear propagation strength of all the studied samples. These results suggest a decrease in the tear propagation strength with the addition of RH in LDPE matrix. This decrease in tear strength can be attributed to the poor interfacial bonding between filler and the matrix material that facilitate for tear propagation.

Permeability Measurements

Presence of oxygen (O_2) is a major detrimental factor for food deterioration, and a further part of our study was oriented to evaluate the O_2 permeance through the biodegradable films. The oxygen permeabilities for different loading of RH in LDPE matrix are reported in Table 1. It is worth mentioning that these results are in consistent with the mechanical measurements, and the trend of O_2 permeation through the biocomposite films is almost similar to that of changes in tensile properties with different amounts of RH.

The oxygen permeability of neat LDPE film is 224 mL-mm/m^2/24 h/atm. As seen in Table 1, adding 3 wt% of the fibre to the LDPE matrix advanced the permeation of O_2 through the biocomposite film, indicating that the barrier properties of the LDPE film deteriorates in the presence of RH. The permeability values of RH-filled films increased further to higher amount in the same manner, by the increase in RH loading. The similar behaviour have also been reported by George et al. (2006) in the LDPE/rice bran composite films where oxygen barrier was deteriorated by adding rice bran.

Biodegradability Studies

Biomaterials are susceptible to microorganisms and their incorporation into nondegradable polymeric materials promotes degradation and disintegration of the resulting composites as various microorganisms consume this biomaterial. Moreover, the incorporation of lignocellulosic material to the polymer increases the surface area available to oxygen that accelerates oxidation of the composite. Figure 4 shows SEM micrographs of the 5 wt% RH-reinforced LDPE-based biocomposite films samples after 2, 4, and 6 months of the soil burial. Before the biodegradability test, the samples surface was comparatively smoother and clear while, on the other hand, buried composite film samples appeared to be heterogeneously eroded depicting an irregular surface. Moreover, many holes of different sizes and depths are seen in the samples under investigation showing the disintegration and breakup of the samples, indicating microorganisms attack. These numerous surface irregularities and the disintegration of the samples following the incorporation of RH can be attributed to biodegradability of the bio flour. It is worth mentioning that the biodegradation effect was more obvious with increased filler loading and enhanced time of burial under the soil environment.

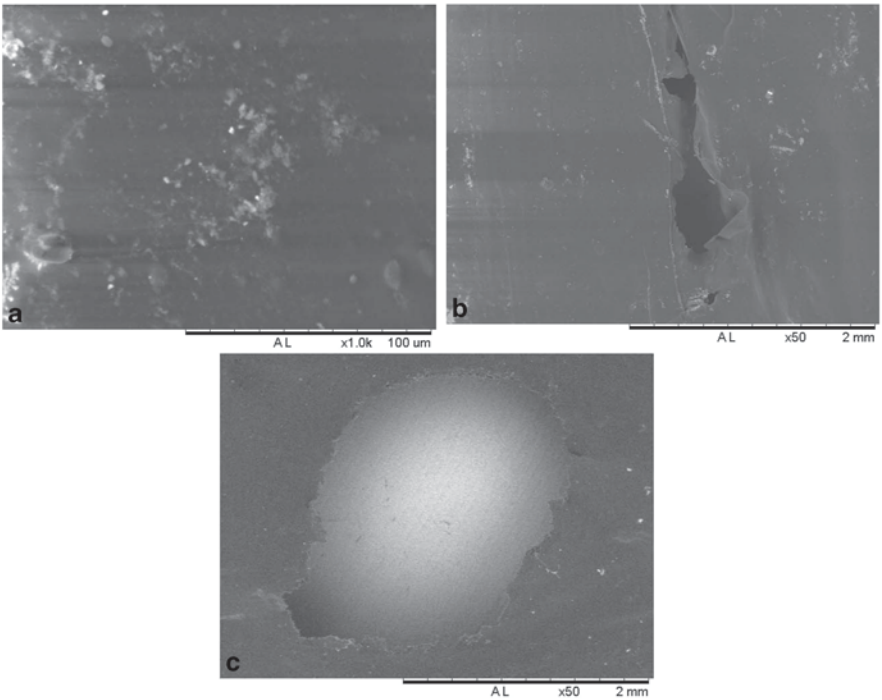

Fig. 4 Scanning electron microscope (SEM) micrographs of LDPE/RH (95:5 wt%) composite films showing the progression of biodegradation with time **a** 2, **b** 4, and **c** 6 months. *LDPE* low-density polyethylene, *RH* rice husk

Conclusions

LDPE/RH extrusion blown films with the overall aim of making ecofriendly packaging material were manufactured successfully. Morphological studies revealed that there are micro-voids between RH and LDPE matrix, and composite films with RH content beyond 5 % showed fibre agglomeration in the matrix. The presence of micro-voids and RH agglomerates decreased homogeneity of the film and, in consequence, its performance properties. Tensile modulus was found to be significantly higher with increasing the RH loading. As the filler loading increased, the tensile strength of the composites decreased, which is a logical consequence of poor interfacial adhesion between RH and LDPE. In contrast to dry samples, water-aged samples followed an opposite trend. Decrease in modulus may be because of degradation of fibre matrix interfacial from differential swelling of RH. These mechanical measurements are in agreement with morphological observations. Oxygen permeability was found to be higher for higher fibre loading. Biodegradation effect was more obvious with increased filler loading and enhanced time of burial under the soil environment. From these findings, we can conclude that these biocomposites films can fulfil the requirements of biodegradable packaging, where long-lasting and highly barrier polymers are not entirely adequate. In order to improve their compatibility and interfacial adhesion, the incorporation of a compatibilizing agent into the lignocellulosic material–thermoplastic polymer biocomposites is recommended.

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Extraction of Lignin from Biomass for Biodiesel Production

A.H. Bhat, Y.K. Dasan and Imran Khan

Abstract The renewable biorefinery concept involves transforming a pulp mill into a multipurpose biofuels, biomaterials, and biopower production facility in which these products are produced in an ecofriendly and sustainable manner. A key challenge in this process is the recovery of lignin from process streams such that it can be utilized in a variety of innovative green chemistry processes. This chapter focuses on the various methods used for the recovery of lignin and application of lignin. The study also discusses about the production of biofuel, specifically biodiesel via Lignoboost lignin pyrolysis as biofuel, steam gasification/pyrolysis of kraft lignin for biofuel, lignin hydrocracking for biofuel and hydrogenation of black liquor. Besides this, the study also throws some light on the availability of biomass, its sources, and global production of biodiesel.

Keywords Biomass · Lignin · Biodiesel

Introduction

The increasing industrialization and motorization of the world have led to a steep rise for the demand of petroleum-based fuels. Today, the fossil fuels take up 80 % of the primary energy consumed in the world, of which 58 % is consumed by transport sector (Savaliya et al. 2013). The major energy demand is still supplied from conventional fossil fuels such oil, coal, and natural gas. Utilization of fossil fuels over the past century and following years has drastically increased the level of greenhouse gases (GHGs) in the earth atmosphere (Talebnia 2010).

The rising concern over depleting fossil fuel and GHG limits has resulted in a high level of interest in nonconventional fuel originating from biorenewable sources in-

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cluding sugars, starches, and lignocellulosic materials (Limayem and Ricke 2012). Currently, biodiesel is the most attractive alternative to traditional fossil-based fuel, but its development and application have been hindered by the high cost of the required feedstock. However, the use of biorenewable sources considered to be the most promising candidates to replace the traditional feedstock, such as vegetable oil, could result in shortage of edible oil, and increase in food prices (Yousuf 2012).

Lignin, as a third most abundant natural polymer, has been sought for decades for productive uses. One especially attractive possibility is that of developing value-added products including biodiesel production from lignin (Saito et al. 2012). Lignin as a renewable raw material currently has technical limitations, although certain remarkable applications can be highlighted (Gosselink 2011).

The most common technique for producing biodiesel is transesterifications, which refers to a catalyzed chemical reaction of vegetable oil with an alcohol to produce fatty acid alkyl esters (biodiesel) and glycerol. The production of biodiesel from residual, agricultural biomass would have environmental benefits that far exceed its economical benefits (Yousuf 2012). Significantly, there are advantages in the use of biomass. Biomass is a renewable resource that has a steady and abundant supply, especially those biomass resources that are by-products of agricultural activity. Its use is carbon neutral, can displace fossil fuels, and helps reduce GHG emissions while closing the carbon cycle loop. As the debate on food versus fuel intensifies, biomass can provide added income to farmers without compromising the production of main food and even nonfood crops. According to International Energy Agency, biomass provides approximately 14 % of the total worldwide energy needs and represents an important contributor to the world economy (Koçar and Civaş 2013).

The chapter intends to review the published investigation on lignin conversion to biodiesel and aims to present a brief overview of the available and accessible technologies for biodiesel production using renewable sources. This study also examines different feedstocks used and global markets demand for biodiesel production.

Biomass

Biomass is the name given to all the earth's living matter. It is the general term for material derived from growing plants or from animal manure. It is a rather simple term for all organic materials that stem from plants, trees, crops, and algae. The components of biomass include cellulose, hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, starches, water, hydrocarbon components (HC), ash, and other compounds (Demirbas 2005). The chemical composition of biomass varies among plant species, but it generally consists of approximately 50 % carbon, 44 % oxygen, and 6 % of hydrogen (plus water), in the form of 25 % lignin, and 75 % of cellulose and hemicellulose (carbohydrates). Most species also contain about 5 % of smaller molecular fragments such as resins, collectively known as extractives (Sims 2002).

There are five basic categories of biomass (Jansen 2012):

a. Virgin wood from forestory or waste from forest products: palm kernel shells, woodpellets, woodchips, and sawdust.
b. Energy crops, that is, high-yield crops grown specifically for energy applications: hybrid eucalyptus, jatropha, pongamia, and pennial grasses like Miscanthus and Napier grass growing on marginal land, not fit for agriculture\agricultural residues: bagasse from sugarcane, corn husks, coconut shells, and straw.
c. Food waste, animal fat, residues from food and drink manufacturing, preparation and processing, such as used cooking oil from sunflower oil, tallow, and greases. Great examples of companies processing their waste are McDonald's (oil) and Tyson Foods (slaughter residues, fats).
d. Industrial waste from manufacturing and industrial processes.

Different type of biomass, such as woody plants, herbaceous plants, grasses, aquatic plants, agricultural crops and residues, municipal solid waste and manures contain different amount of cellulose, hemicellulose, lignin and extractives. (Agbor et al. 2011). The value and recalcitrance of particular types of biomass depend on the chemical and physical properties of the large molecules from which it is made (McKendry 2002). The properties such as lignin content, cellulose accessibility to cellulose (CAC), and cellulose crystallinity (CC) determine overall digestibility (Agbor et al. 2011).

The biomass resource can be considered as organic matter, in which the energy of sunlight is stored in chemical bonds. When the bonds between adjacent carbon, hydrogen, and oxygen molecules are broken by digestion, combustion, or decomposition, these substances release their stored chemical energy (McKendry 2002).

Biomass produced in a sustainable way the so-called modern biomass excludes traditional uses of biomass as fuelwood and includes electricity generation and heat production, as well as transportation fuels, from agricultural and forest residues, and solid waste. On the other hand, "traditional biomass" is produced in an unsustainable way and it is used as a noncommercial source usually with very low efficiencies for cooking in many countries (Goldemberg and Teixeira Coelho 2004; Heinimö and Junginger 2009).

Biomass fuel is defined as any solid, liquid, or gaseous product derived from a wide range of organic raw materials, either directly from plants or indirectly from industrial, commercial, domestic, and forest or agricultural wastes, and produced in a variety of ways. Report of the Intergovernmental Panel on Climate Change (IPCC) shows that 400 EJ/year will be feasible from energy cropping by 2050. Together with biomass estimates from forest, cereal, and sugar cane residues (39 EJ/year), animal manures (25 EJ/year), and municipal solid wastes (3 EJ/year), then by 2050 about half the total annual global supply of primary energy could be met by biomass (Sims 2002). Biofuels production is divided into four generations depending on the nature of biomass used to produce it which is shown in Table 1.

Table 1 Classification of transportation-based biofuels

Types of biofuel	Description	Examples
First generation	Edible feedstocks	Sugarcane, sugar beet, and starch crops. oil-based crops like rapeseed, sunflower, soybean, palm oil, and waste edible oils. Starch-derived biogas
Second generation	Non-edible feedstocks	Biogas from waste and residues lignocellulosic materials (agriculture, forestry, and industry residues) biofuels from energy crops such as sorghum
Third generation	Aquatic microorganism like algae	Biodiesel from algae algal hydrogen
Fourth generation	High-solar efficiency cultivation	Carbon-negative technology: technology of the future

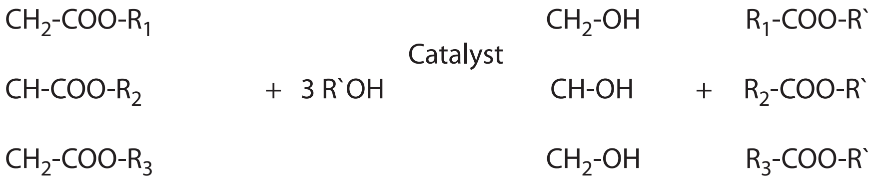
Biodiesel

As per the American Society for Testing and Materials (ASTM), biodiesel is a fuel consisting of monoalkyl esters of long-chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat (Hoque et al. 2011; Knothe et al. 2005; Sarin 2012). There have been a number of names applied to the ester fuels in the past decade. Technically, the esters can be called “transesterified vegetable oils (or animal fats).” In the early 1980s, the term MESO (methyl esters of soybean oil) was coined by the Volkswagen (VW) corporation. Other specific names such as RME have been used for rapeseed methyl esters. In our early work, we used the term “M-diesel” (for methanolated waste vegetable oil diesel). The Novamont Co. uses the term Diesel-BI. Recently the term “biodiesel” (for biomass-based diesel) has been widely used for ester fuels (Pop et al. 2012).

Theoretically, 1 mol triglycerides is reacting with 3 moles alcohol producing 3 moles esters and 1 mol glycerol through transesterification process with low molecular weight alcohols (Mousdale 2010) as shown in Fig. 1. This reaction is most commonly catalyzed by a homogeneous base catalyst that could be sodium hydroxide among others (Mario 2011). Methanol is the major alcohol used for transesterification process because of its most volatile fatty acid esters and also low price. However, other solvents such as ethanol, isopropanol, and butanol also can be used for this purpose (Knothe et al. 2005).

History of Biodiesel

It is believed that the term biodiesel was coined around 1984, as one the article cites the existence of a flyer from Bio-Energy (Australia) pty Ltd that promotes equipment to produce low-cost diesel fuel which is called as “Bio-Diesel” (Sarin



$$\begin{array}{lclcl} CH_2\text{-}COO\text{-}R_1 & & CH_2\text{-}OH & & R_1\text{-}COO\text{-}R\text{`} \\ & \text{Catalyst} & & & \\ CH\text{-}COO\text{-}R_2 \quad + \quad 3\ R\text{`}OH & & CH\text{-}OH & + & R_2\text{-}COO\text{-}R\text{`} \\ CH_2\text{-}COO\text{-}R_3 & & CH_2\text{-}OH & & R_3\text{-}COO\text{-}R\text{`} \end{array}$$

Fig. 1 Transesterification reaction. (Mario 2011)

2012). The first diesel engine was created in 1893 by a German mechanical engineer, Rudolph Diesel. The diesel engine is an internal compression-ignition engine that uses the compression of the fuel to cause ignition, instead of a spark plug for gasoline engines. As a result, a higher compression ratio is required for a diesel engine, which for the same power output (when compared to a gasoline engine), is more efficient and uses less fuel. The higher compression ratio requires the diesel engine to be built stronger so it can handle the higher pressure; consequently, the longevity of a diesel engine is generally higher than its gasoline equivalent. These vehicles therefore require less maintenance and repair overall, thus saving money (Vasudevan and Fu 2010).

The first demonstration of the diesel engine was at the 1900 World's Fair in Paris. Knothe (2001), in a book chapter, describes that the diesel engine built by the French Otto Company was tested at this event using peanut oil. It is not totally clear whether Rudolf Diesel had the idea to use peanut oil because, apparently, Diesel gives credit of this to the French government. Furthermore, he has stated the interest of French government in vegetable oil fuels for diesel engines because of its availability in their colonies in Africa, thereby eliminating the need to import liquid fuel or coal (Songstad et al. 2011).

The use of vegetable oil as an alternative fuel in diesel engine gave a sense of energy self-sufficiency to those countries producing oil crops, especially for those countries in Africa in the 1940s. During World War II, fossil fuels were diverted to the war effort, so they become hard to get and more expensive (*Solar Water Heating: A Comprehensive Guide to Solar Water and Space Heating Systems–Revised & Expanded Edition*). As a consequence of this, even Brazil prohibited the exportation of cottonseed oil so it could be used as a substituent for diesel engine. In China, tung oil and other vegetable oils were used to produce a version of gasoline and kerosene. Furthermore, prompted by fuel shortages during World War II, India conducted research on conversion of a variety vegetable oils to diesel. This interest in biodiesel was also evident in the USA where research was performed to evaluate cottonseed oil as a diesel fuel (Songstad et al. 2011). Another approach proposed at this time was the use of fatty acids' ethyl or methyl esters obtained by transesterification or alcoholysis of vegetable oils or esterification of fatty acids combined with transesterification of triglycerides (Pousa et al. 2007).

Then in 1973, the Arab oil embargo sent crude oil prices through the roof. With gas and diesel suddenly four times more expensive than before, interest in biofuels returned. But there was a dilemma: Pure vegetable oil was too thick for modern diesel engines; it plugged injection systems and did not spray evenly into compression cylinders. Short of going back to older engine designs, two options remained: either heat the oil with an onboard system to make it less viscous (the method used by today's "Greasecars," which run on straight fryer grease) or make the oil's molecules smaller (Schmidt 2007).

The latter option led to biodiesel. In 1979, most producers chose a manufacturing method called transesterification, which the South Africans used to make fuel from vegetable oil before World War II. With that process, refiners mix the oil with alcohol in the presence of a catalyst, usually sodium hydroxide. The alcohol and fatty acids react, creating biodiesel and a by-product of glycerin. The alcohol used is usually methanol, yielding a biodiesel consisting of fatty acid methyl esters (Schmidt 2007). Since the 1980s, biodiesel plants have opened in many European countries, and some cities have run buses on biodiesel or a blend of petrol and biodiesels.

Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany, and Sweden. France launched local production of biodiesel fuel (referred to as diester) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5 %, and into the diesel fuel used by some captive fleets (e.g., public transportation) at a level of 30 %. Renault, Peugeot, and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiments with 50 % biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up: By 1998, the Austrian Biofuels Institute had identified 21 countries with commercial biodiesel projects. Hundred percent biodiesel is now available at many normal service stations across Europe. Today's diesel engines require a clean burning and stable fuel that performs well under the variety of operating conditions. Biodiesel is the only alternative fuel that can be used directly in any existing unmodified diesel engine (Abdulkareem et al. 2012).

In September of 2005, the state of Minnesota became the first US state to mandate that all diesel fuel sold in the state contains a certain part biodiesel, requiring a content of at least 2 % biodiesel (B2 and up). This established that biodiesel blend fuel is no longer a choice, but a standard and mandate. On April 23, 2009, the European Union (EU) adopted the renewable energy directive (RED) which included a 10 % target for the use of renewable energy in road transport fuels by 2020. It also established the environmental sustainability criteria that biofuels consumed in the EU have to comply with, covering a minimum rate of direct GHG emission saving as well as restrictions on the types of land that may be converted to production of biofuel feedstock crops (Knothe et al. 2005).

Biodiesel as an Alternative Fuel for Diesel Engine

The successful introduction and commercialization of biodiesel in many countries around the world have been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are

Table 2 Properties of biodiesel fuel and No. 2 diesel fuels. (Moser 2011)

Property	Biodiesel	No. 2 diesel
Fuel standard	ASTM D6751	ASTM D975
Lower heating value (Btu/gal)	−118,170	−129, 050
Density (Ib/gal)	7.328	7.079
Water and sediment (% volume)	0.05 max	0.05 max
Carbon (wt. %)	77	87
Hydrogen (wt. %)	12	13
Oxygen (wt. %)	11	0
Boiling point (K)	590–625	455–625
Specific gravity (kg/L)	0.87–0.89	0.84–0.86
Cetane number	46–70	47–55
Cloud point (K)	262–289	256–265
Pour point (K)	258–286	237–243
Flash point (K)	408–423	325–350
Sulfur (wt%)	0.0000–0.0024	0.04−0.01
Ash (wt%)	0.002–0.01	0.06−0.01
Iodine number	60–135	–
Kinematic viscosity, 313 K	3.7–5.8	1.9–3.8
Higher heating value, MJ/kg	39.3–39.8	45.3–46.7
Lubricity SLBOCLE (g)	>7000	2000–5000
Lubricity HFRR (microns)	<300	300–600

ASTM D6751 and the European standard EN 14214, which was developed from previously existing standards in individual European countries (Knothe 2005).

While the suitability of any material as fuel, including biodiesel, can be influenced by contaminants arising from production or other sources, the nature of the fuel components ultimately determines the fuel properties. Some of the properties included as specifications in standards can be traced to the structure of the fatty esters comprising biodiesel (Knothe 2005**).** The biodiesel esters were characterized for their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility (Demirbas 2010) which is shown in Table 2.

Biodiesel is often used as a blend B20 (20 vol. % biodiesel and 80 vol. % conventional diesel) rather than using B100 (100 vol. % biodiesel). It is asserted that 90 % of air toxics can be eliminated by using B100 whereas 20–40 % are reduced using B20. A further assertion is that the risk of illness and life-threatening diseases can be reduced using biodiesel blends. Furthermore, using blends of biodiesel in oil-fired boilers can reduce NO_x and SO_2 emissions by 20 % (Joshi and Pegg 2007).

Biodiesel thickens at warmer temperatures than No. 2 diesel fuel, but additives are available that will lower the pour point. Pour point is the point at which flow of the fuel ceases. Mixing biodiesel with No. 1 diesel as is currently done with No. 2 will lower the pour point. Installing an in-tank or fuel line heater may also be needed to keep the fuel flowing in cold weather. A blend of biodiesel/diesel fuel has a lower pour point than 100 % biodiesel, but gelling may still occur unless care as mentioned earlier is taken (Hofman 2003).

Advantages and Disadvantages of Biodiesel

Biodiesel has attracted considerable interest as an alternative fuel or extender for petrodiesel for combustion in compression-ignition (diesel) engines. Biodiesel is miscible with petrodiesel in any proportion and possesses several technical advantages over ultralow sulfur diesel fuel (ULSD, <15 ppm S) (Moser 2011). The most significant advantages of biodiesel given in the literature include domestic origin, reducing the dependency on imported petroleum, liquid nature-portability, readily availability, and renewability (Group and Management 2009). Life-cycle analyses have shown that the source-to-wheel CO_2 emissions from neat biodiesel combustion account for at least 60 % savings with respect to petroleum diesel fuel, whereas for the most popular B20 blend it is of the order of 15–20 % (Giakoumis 2013).

A number of technical advantages of biodiesel fuel: (1) It prolongs engine life and reduces the need for maintenance (biodiesel has better lubricating qualities than fossil diesel); (2) it is safer to handle, being less toxic, more biodegradable; and (3) It reduces some exhaust emissions (although it may, in some circumstances, raise others). Biodiesel is an efficient, clean, 100 % natural energy alternative to petroleum fuels. Among the many advantages of biodiesel fuel, include the following: safe for use in all conventional diesel engines, offers the same performance and engine durability as petroleum diesel fuel, nonflammable and nontoxic, reduces tailpipe emissions, visible smoke, and noxious fumes and odors. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability (Bozbas 2008).

Biodiesel can be pumped, stored, and handled using the same infrastructure, devices, and procedure usually employed for conventional diesel fuel. In fact, as biodiesel does not produce explosive vapors and has a relatively high flash point (close to 150 °C), transportation, handling, and storage are safer than with conventional diesel (Yusuf et al. 2011). Biodiesel is nontoxic and degradable about four times faster than petroleum diesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation and shows better emission parameter as compared to petroleum diesel (Moser 2011).

Despite advantages of biodiesel, the other environmental impact shows the other side. Photochemical oxidation potential (POCP) or summer smog is the result of reactions that take place between nitrogen oxides (NO_x) and volatile organic compounds (VOC) exposed to ultraviolet (UV) radiation. Higher level of POCP was directly caused by VOC (hexane) emission during the vegetable oil extraction The other environmental impact potential, eutrophication (EP) and acidification potential (AP), has showed a significant increase compared with fossil fuels. The higher EP and AP potential in the life-cycle system of biodiesel were primarily caused by the upstream emissions of nitrate and phosphate leaching into the groundwater, and ammonia and nitric oxide (NO_x) into air from N and P fertilizer application (Hafizan and Zainura 2013). The economical drawbacks of biodiesel would be the production cost, depending in part on governmental taxes and subsidies (Black 2001).

The technical disadvantages of biodiesel/fossil diesel blends include problems with fuel freezing in cold weather, reduced energy density, and degradation of fuel under storage for prolonged periods. One additional problem is encountered when blends are first introduced into equipment that has a long history of pure hydrocarbon usage. Hydrocarbon fuels typically form a layer of deposits on the inside of tanks, hoses, etc. Biodiesel blends loosen these deposits, causing them to block fuel filters. However, this is a minor problem, easily remedied by proper filter maintenance during the period following introduction of the biodiesel blend (Bozbas 2008).

The energy efficiency of a vehicle is the percentage of fuel's energy delivered as engine output. The energy content per unit of volume measure (kilocalories per liter) of biodiesel is somewhat lower than that of petroleum diesel, so biodiesel may be less economical to use. Studies in the USA show that biodiesel contains 8 % less energy per gallon than typical No. 2 diesel and 12.5 % less energy per pound. The differences are due to the fact that biodiesel is slightly more dense than diesel fuel, so there are slightly more pounds in a gallon of fuel. Furthermore, all biodiesel regardless of its feedstock provides about the same amount of energy (Bucholtz 2007).

Moreover, it has been proven that the direct use of vegetable oils and/or the use of blends of the oils generally does not satisfy for direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are obvious problems. The probable reasons for the problems and the potential solutions are shown in Table 3 (Demirbas 2008).

Sources of Biodiesel

The large-scale production of a renewable and environmentally sustainable alternative fuel faces several technical challenges that need to be addressed to make biodiesel feasible and economical. The two main concerns with any renewable fuel are raw materials and the technologies used for processing. Advances in genetic modification and other biotechnologies are resulting in new or modified feedstocks that have significantly increased the yields of alternative fuels, such as genetically modified *Clostridium* to improve alcohol production. Technological advancements are also being made to convert the feedstocks into fuels by improving techniques or developing completely new and environmentally friendly approaches to biofuel production (Vasudevan et al. 2010).

Table 3 Problems and potential solution for direct usage of vegetable oil in diesels. (Bozbas 2008)

Problem	Portable cause	Potential solution
Short term		
Cold weather starting	High viscosity, low octane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
Plugging and gunning of filters, lines, and injectors	Natural gums (phosphatides) in vegetable oil	Partially refine the oil to remove gums. Filter to 4 microns
Engine knocking	Very low octane of some oils. Improper injection timing	Adjust injection timing. Use higher-compression engines. Preheat fuel prior injection. Chemically alter fuel to an ester
Long term		
Coking of injection on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils	Heat fuel prior to injection. Switch engine to diesel fuel when operation at part load. Chemically alter the vegetable oil to an ester
Carbon deposits on piston and head of engine		
Excessive engine wear	Possibly free fatty acids in vegetable oils. Dilution of engine lubricating oil due to blow by vegetable oil	Increase motor oil changes. Motor oil additives to inhibit oxidation
Failure of engine lubricating oil due to polymerization	Collecting of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs	

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production. Table 3 shows main feedstocks of biodiesel. The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel. As much as possible the feedstock should fulfill two main requirements: low production costs and large production scale. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions, and agricultural practices of any country. Selecting the cheapest feedstock is crucial to maintain the low production cost of biodiesel. In general, biodiesel feedstock can be divided into four main categories as below (Table 4) (Atabani et al. 2012):

a. Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm, and coconut oil
b. Nonedible vegetable oil: *Jatropha, Karanja,* sea mango, algae, and halophytes
c. Waste or recycled oil
d. Animal fats: tallow, yellow grease, chicken fat, and by-products from fish oil

Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of 1 mol of glycerol and 3 mol of fatty acids

Table 4 Sources of biodiesel feedstock. (Atabani et al. 2012; Singh and Singh 2010)

Edible oils	Nonedible oils	Animal fats	Other sources
Soybeans (Glycine max)	Jatropha curcas	Pork lard	Bacteria
Rapeseed (*Brassica napus L.*)	Mahua (Madhuca indica)	Beef tallow	Algae (Cyanobacteria)
Safflower	Pongamia (Pongamia pinnata)	Poultry fat	Microalgae (Chlorellavulgaris)
Rice bran oil (Oryza sativum)	Camelina (Camelina sativa)	Fish oil	Terpenes
Barley	Cottonseed (Gossypium hirsutum)	Chicken fat	Poplar
Sesame (Sesamum indicum L.)	Karanja or honge (Pongamia pinnata)	–	Switchgrass
Groundnut	Cumaru	–	Miscanthus
Sorghum	Cynara cardunculus	–	Latexes
Wheat	Abutilon muticum	–	Fungi
Corn	Neem (Azadirachta indica)	–	–
Coconut	Jojoba (Simmondsia chinensis)	–	–
Canola	Passion seed (Passiflora edulis)	–	–
Peanut	Moringa (Moringa oleifera)	–	–
Palm and palm kernel (Elaeis guineensis)	Tobacco seed	–	–
Sunflower (Helianthus annuus)	Rubber seed tree (Hevea brasiliensis)	–	–
–	Salmon oil	–	–
–	Tall (Carnegiea gigantean)	–	–
–	Coffee ground (Coffea arabica)	–	–
–	Nagchampa (Calophyllum inophyllum)	–	–
–	Croton megalocarpus	–	–

and are commonly known as triglycerides. Biodiesel contains fatty acids with different levels of unsaturation. The fuel properties of biodiesel are dependent on the amount of each fatty acid present in the feedstock. Important physical and chemical characteristics that influence the biodiesel production and its quality are mentioned below (Karmakar et al. 2010).

The source of biodiesel usually depends on the crops amenable to the regional climate. In the USA, soybean oil is the most commonly biodiesel feedstock, whereas the rapeseed (canola) oil and palm oil are the most common source for biodiesel, in Europe and in tropical countries, respectively. A suitable source to produce biodiesel should not competent with other applications that rise prices, for example, pharmaceutical raw materials. But the demand for pharmaceutical raw material is lower than for fuel sources. As much as possible, the biodiesel source should fulfill two requirements: low production costs and large production scale. Refined oils have high production costs, but low production scale; on the other side, nonedible seeds, algae, and sewerage have low production costs and are more available than refined or recycled oils (Singh and Singh 2010).

Global Production of Biodiesel

Global demand for renewable energy continued to rise during 2011 and 2012, supplying an estimated 19 % of global final energy consumption in 2011 (the latest year for which data are available), with a little less than half from traditional biomass. Useful heat energy from modern renewable sources accounted for an estimated 4.1 % of total final energy use; hydropower made up about 3.7 %; and an estimated 1.9 % was provided by power from wind, solar, geothermal, and biomass, and by biofuels. Total renewable power capacity worldwide exceeded 1470 GW in 2012, up about 8.5 % from 2011. Hydropower rose 3 % to an estimated 990 GW, while other renewables grew 21.5 % to exceed 480 GW. Globally, wind power accounted for about 39 % of renewable power capacity added in 2012, followed by hydropower and solar photovoltaics (PV), each accounting for approximately 26 % (Al Jaber et al. 2012).

Biodiesel has been in use in many countries such as USA, Malaysia, Indonesia, Brazil, Germany, France, Italy, and other European countries. However, the potential for its production and application is much more. Biodiesel has a massive potentiality to be a part of a sustainable energy mix in the future. Globally, annual biodiesel production increased from 15,000 barrels per day in 2000 to 289,000 barrels per day in 2008 as shown in Fig. 2. It is believed that, 85 % of biodiesel production comes from the EU. The demand for biodiesel in European countries is expected to be up to 10.5 billion liters by 2010 (Lim and Teong 2010).

National Biodiesel Board in USA had reported production of 1.9 million liters of biodiesel in 1999 while the following year, in 2000, saw that figure increased more than tenfold to 25.4 million liters. In 2004, the Government of Philippines had made it compulsory for the incorporation of 1 % of coconut biodiesel blend in diesel fuel for use in government vehicles. Elsewhere in USA, Minnesota had become the first state in the nation to mandate the use of diesel fuel with at least 2 % of biodiesel blend in 2005. Biodiesel as a proven fuel was further bolstered when ASTM International published new quality specifications for biodiesel blends in 2008. Now, biodiesel blend fuel is available at many normal service stations across Europe and USA while the world biodiesel production output is estimated to be 11 million t in the year of 2008. By 2010, total biodiesel production can be as high as 20 million t. Boeing, the largest aircraft manufacturer, plans to start using biodiesel in its air car-

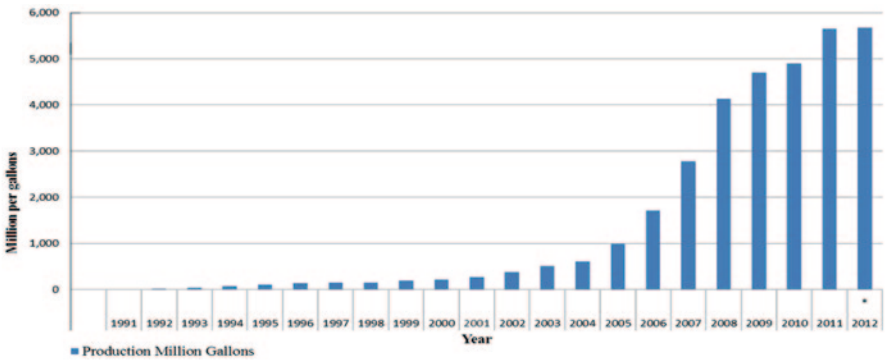


Fig. 2 World biodiesel production for the period 1991–2012

riers in 2014 which will surely increase the biodiesel demand substantially in the future (Lim and Teong 2010) (Fig. 2).

Lignin

Lignin is the most abundant natural aromatic polymer which can be found on earth. It comprises 20–30 % of woody plant cell walls and by forming a matrix surrounding the cellulose and hemicellulose, it provides strength and protection to the plant (Schoemaker and Piontek 1996). The lignin heteropolymer is an integral cell wall constituent that significantly influences the physical properties of plants via its involvement in architectural support, water transport, and defense (Robinson and Mansfield 2009).

Long after Anselme Payen (1839) first described the "encrusting material" in wood, researchers were unclear about the nature of this very abundant material. Although it had a higher carbon content than the carbohydrates, its chemical nature remained obscure for a long time; indeed, it was not until about 20 years later that the term "lignin" became accepted for this material (Schulze 1857). In 1998, about 1 % of all lignin generated in paper production worldwide was isolated and sold. The remaining 99 %was either burned in an energy recovery step for the pulping process or disposed of in waste streams. The global production of lignin products was reported by Lin and Zhong to amount to 138,500 t/year in 1990. Extrapolating these 1 %numbers leads to a worldwide production of more than 10 million t/year of available renewable raw material (Thielemans et al. 2002).

Most industrial lignin is obtained as a waste product during the paper pulping process, but it can be found in all plants like rice and straw. While cellulose is used for paper production and natural oils are mainly used in the food industry, the industrial applications of lignin are rather limited, despite its widespread availability (Thielemans et al. 2002). The recovery and usage of lignin have been studied over years to convert lignin into high value-added products. Initially, lignin has been

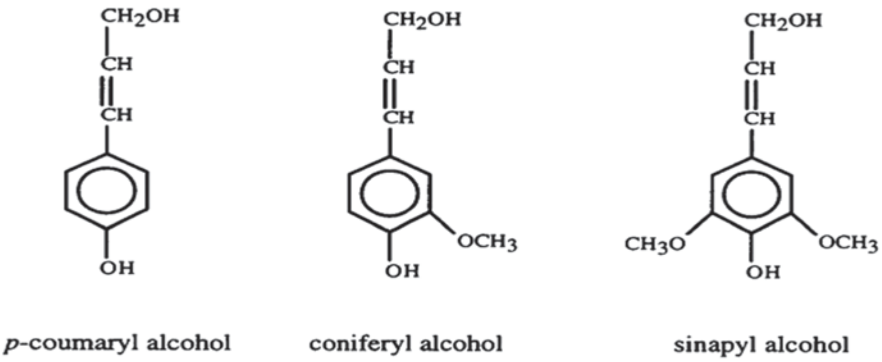


Fig. 3 Phenylpropanoid precursor of lignin. (Castillo de pilar 1997)

used as a boiler fuel in the production of octane boosters, and in biobased products and chemical production. However, the different types of lignin exist depending upon the isolation protocol and biomass sources (Gopalakrishnan et al. 2010).

Chemical and Physical Properties of Lignin

Lignin is a natural phenolic macromolecule present in the vegetal cell wall that is made up of three main phenylpropane units (monolignols), namely coniferyl alcohol (G), sinapyl alcohol (S), and *p*-coumaryl alcohol (H) (Fig. 3). Lignin structure is very complex and consists of a three-dimensional randomized net linked to hemicelluloses (LCC). The main function of lignin in the plant is as a biological barrier and asglue that retains hemicelluloses and celluloses linked shaping the cell wall.

Lignin is a highly branched and heterogeneous three-dimensional structure made up of phenylpropanoid units which are interlinked through a variety of different bonds. Lignin is biosynthesized via a plant-peroxidase-catalyzed oxidation of (methoxy-) substituted para-hydroxycinnamyl alcohols. The benzylic hydroxy groups are introduced via quinone methide intermediates (Bhanu Rekha 2013).

Complicating the molecular picture of lignin further is that native lignin chemistry can vary depending upon its origin. Plant species, plant tissue type, and the external environment all have roles in determining the chemistry of a specific lignin sample. Lignin from different plant families is known to be derived from different monolignols, and lignin is often classified according to its botanical origin. The two major classifications are gymnosperm lignin, derived mostly from coniferyl alcohol monolignols, and angiosperm lignin, derived from both coniferyl and synapyl monolignols. Each type also generally contains a small proportion of *p*-coumaryl units, though nonwoody lignins generally contain a higher amount of *p*-coumaryl units than woody lignins. There are exceptions to the rule, such as cases in which gymnosperm lignin was found to contain high amounts of synapyl alcohol units, or in which angiosperm lignin was found to be largely composed of coniferyl units.

Other phenolic monolignols have been identified, but they generally make up a much smaller portion of the lignin molecule (Fox and McDonald 2010).

Recovery of Lignins

The principal objective of isolating lignin from wood is to be used in paper production. There are two main separation processes involved for the separation of lignin such as degradation of lignin into soluble fragments and is removed by separating the solid residue from spent liquor and selectively hydrolyze polysaccharides and leave lignin along with some condensed carbohydrate deconstruction products as a solid residue (Azadi et al. 2013).

Lai and Sarkanen (1971) have published a critical review of methods for the isolating lignin. The commonly used method to isolate lignin from wood is thorough milling of the plant material, followed by extraction with dioxan ± water; this material is referred to as milled wood lignin (MWL). However, the yields are usually low, and the possibility of chemical changes occurring during the isolation process must always be taken into account (Brunow 2005).

Kraft pulping method of removing lignin produces strong pulps for use in corrugated boards, liner boards, and paper bags. Besides kraft pulping, the second historically important pulping process is the sulfite process. Other wood pulping processes have been developed, though they are not usually used on an industrial scale like kraft or sulfite pulping. “Organosolv” lignin is produced by pulping wood in organic solvents with catalysts in both acidic and alkaline conditions. This process is more environmental friendly as compared to kraft or sulfite pulping due to the absence of sulfur compounds. However, solvent pulping is not currently in place on an industrial scale in North America, although one plant in Canada did use the process briefly in the 1990s (Fox and McDonald 2010).

Even though numerous methods exist to isolate lignin from plant biomass, only limited methods are recognized for lignin recovery and utilization since lignin is generally considered as a waste material and also the chemical structure of lignin changes during recovery process (Gopalakrishnan et al. 2010).

Kraft Lignin Recovery

The kraft pulping process, which uses sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to pulpwood, is the dominant pulping process in the pulp and paper industry. About 130 million t/year of kraft pulp are produced globally, accounting for two thirds of the world’s virgin pulp production and for over 90 % of chemical pulp. The kraft pulping process favored over the other methods due to the ability of the process to handle almost all species of softwood and hardwood, and the favorable economics due to high chemical recovery efficiency (about 97 %) give the kraft

Table 5 Sulfite-pulping conditions for lignin removal

Process	Reactive agent(s)	pH	Temperature (°C)
Acid sulfide	SO_2/HSO_3^-	1–2	125–145
Bisulfite	HSO_3^-	3–5	150–175
Neutral sulfite	HSO_3^-/SO_3^-	6–7	150–175
Alkaline sulfite/anthraquinone	Na_2SO_3	9–13	50–175

process and advantage over other pulping processes (Dickinson et al. 1998; Hough 1985; Singh 1980).

During kraft pulping process, lignin is removed from the wood chips and, following brown stock washing, it ends up in the spent pulping liquor (weak black liquor). This black liquor is typically concentrated from about 15–20 % to 70–80 % solids, with an evaporator train, and then fired into a recovery boiler for the production of steam, electricity, and inorganic chemicals (in the form of a smelt) for internal mill use (kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood). Several processes for the recovery of lignin from the black liquor are available, among them a process developed by FP Innovations and currently commercialized by NORAM, and another one, developed by STFI (now called Innventia) and licensed to Metso.

Two main approaches which are used for lignin separation in the kraft pulp process were acid precipitation and ultrafiltration (UF). Generally, precipitation is used to extract lignin from kraft black liquor, whereas UF has been used mainly to purify the lignin fraction in cooking liquor from sulfite and kraft pulp mills in order to use it as a valuable chemical product. The optimal dry substance for precipitation is reported to be 27–30 %. The kraft black liquor used for precipitation is therefore commonly withdrawn after the third evaporation stage in the recovery system. The concentration of the liquor to be treated by UF is not that critical, even though the flux of the membranes is reduced as the concentration increases. This means that there is considerable freedom in the choice of liquor for treatment with UF (Wallberg et al. 2005).

Sulfite Lignin Recovery Ligninsulfonates are produced from waste liquid from softwood, using several salts of sulfurous acid (sulfites or bisulfites) to extract the lignin from wood by the sulfite-pulping procedure. The process is well known and can be carried out under several conditions as shown in Table 5. Ligninsulfonates present both hydrophobic and hydrophilic properties; they are water-soluble and chemically modified with sulfonate groups, carbohydrates, and small amounts of wood extracts and inorganic compounds. They are prepared mainly as calcium, magnesium, and ammonium salts. The procedure is less aggressive than kraft pulping, and the molecular mass of the final product is higher than kraft lignin, rendering a structure that is more similar to the original lignin.

There are various methods for isolating and purifying lignosulfonates from spent pulping liquors. For instance, the Howard process is one of the most widely used industrial processes, where calcium lignosulfonates are precipitated from spent pulping liquor by addition of excess lime. In addition, other methods used industrially include UF and ion exclusion, which uses ion-exchange resins to separate lignin from sugars. Laboratory methods for isolating lignosulfonates include dialysis, electrodialysis, ion exclusion, precipitation in alcohol, and extraction with amines (Li 2011).

Solvent (Organosolv) Lignin Recovery

Organosolv lignins known as lignins are produced from a number of different organic solvent-based systems. Two of the most common organosolv processes are ethanol/water pulping (alcell) and pulping with acetic acid containing a small amount of mineral acid such as hydrochloric acid or sulfuric acid (acetosolv). Since 1993, carbon fibers originating from organosolv lignins have been studied where it was shown that fibers could be produced by melt spinning of hardwood acetic acid lignin isolated from spent liquor (Brodin 2009). Lignin precipitation in acid organosolv pulping is carried out by diluting the spent liquor with water, which decreases the proportion of organic solvent, reducing significantly the solubility of lignin and producing its precipitation. The precipitated lignin corresponds to the fraction of high molecular weight, the other fraction remaining in the spent liquors. Another method used to precipitate the lignin by recovering the alcohol from spent liquors in a recovery tower by vacuum. However, this procedure is usually ineffective and difficult to control, since lignin tends to precipitate as a sticky tar in the internal surfaces of the recovery tower, fouling it and reducing the effectiveness of alcohol recovery (Fernando et al. 2010). A new approach of organosolv lignin recovery, consisting of simultaneous precipitation and dissolved air flotation (DAF), is proposed. DAF offers a low-energy, low-maintenance alternative to centrifugation and filtration (Macfarlane et al. 2009).

Recovery of Lignin from Pyrolysis of Lignocellulosic Biomass

Fast pyrolysis is a high-temperature process in which biomass is rapidly heated in the absence of oxygen. As a result, it decomposes to generate mostly vapors and aerosols, and some charcoal. The yield of the brown powder, known as pyrolytic lignin, obtained from the abovementioned method can be as high as 28 wt%, indicating that a large fraction of lignin partitions into bio-oil upon fast pyrolysis of biomass. The elemental analysis of the pyrolytic lignins obtained from several different lignocellulosic species revealed that they are composed of approximately 66 % carbon, 6 % hydrogen, and 27 % oxygen, almost independent of the original feedstock. It is also important to note that the carbon content of the pyrolytic lignin is 9–15 % and 3–9 % higher than the corresponding values in the bio-oil and in MWL obtained from the same feedstock, respectively. As a result of higher carbon content, the heating value of the pyrolytic lignin is significantly higher than the original bio-oil and the MWL (Azadi et al. 2013). Pyrolytic lignin can be recovered by precipitation since it is insoluble in water under neutral or acidic conditions (Bridgwater and Peacocke 2000).

Steam Explosion Lignin

Lignin can be recovered from steam explosion of woody materials. When wood is treated with steam at high temperature/pressure (i.e., about 180–2008 °C), followed by a sudden decompression in the presence of some chemicals, a partial hydrolysis of lignin occurs. Under these conditions, a water-insoluble lignin material with a low level of carbohydrate and wood-extractive impurities results. With this procedure, the lignin itself has a somewhat reduced molecular mass because some acid hydrolysis reactions take place. This type of separation process is often combined with enzymatic hydrolysis to produce carbohydrates for fermentation (Calvo-Flores and Dobado 2010).

Applications of Lignin

Lignin from various plant material and pulping processes provides an important source of raw material that may be converted into value-added products by chemical or enzymatic means (Mattinen et al. 2008). Applications of lignin began in the 1880s when lignosulfonates were used in leather tanning and dye baths. Since then, a number of studies have been encountered to explore applications of lignin including dyes, vanilla, plastics, base exchange material for water softening, and the cleavage products of lignin from nitration, chlorinate, and caustic fusion (Gopalakrishnan et al. 2010).

The use of lignin has increased due to the high yield pulping process which includes sulfite and kraft pulping (Kutscha and Gray 1970). Sugar-free lignosulfonates from softwoods (conifers) serve as starting material to make vanillin—a flavoring for food, ice cream, and bakery goods. The anionic charges (negatively charged ions) in lignosulfonates make them good emulsifying agents or auxiliaries for preparing or stabilizing oil-in-water or wax-in-water emulsions (for example, in polishes and furniture creams or sprays) (McMillen 1967). Another major application of lignosulfonates is for mud viscosity control during deep oil well drilling. Lignosulfonates are also included in some adhesives. They act as extenders for the phenolic resins used in manufacturing particleboard, nonwoven fiber padding, and molding powders. (Browning and Perricone 1962).

In binders, about 50 % of kraft lignin or lignosulfonate lignin can be added instead of phenol to phenol-formaldehyde resins without substantially modifying of the final product properties. The substitution of phenols by lignins is not only environmentally friendly but also less expensive than other binders used in the wood composite industry. Some physical and mechanical properties are modified, for example, in novolac-type resins, the addition of lignin leads to polymeric systems with increased rigidity (Calvo-Flores and Dobado 2010).

Kraft lignins are used in some foam fire extinguishers to stabilize the foam and in printing inks for high-speed rotary presses. Kraft lignin products are generally used in high-value applications after the modification process. These include usage as emulsifying agents/emulsion stabilizers, as sequestering agents, as pesticide dispersants, as dye dispersants, as additives in alkaline cleaning formulations, as complexing agents in micronutrient formulations, as flocculants, and as extenders for phenolic adhesives. Furthermore, it can also be used as an extender/modifier, and as a reinforcement pigment in rubber compounding (Li 2011).

Production of Biodiesel from Lignin

The basic structure of all woody biomass consists of three organic polymers: cellulose, hemicelluloses, and lignin in the trunk, foliage, and bark. These three structural components are having rough formulae as $CH_{1.67}O_{0.83}$, $CH_{1.64}O_{0.78}$, and $C_{10}H_{11}O_{3.5}$, respectively. Added to these materials are extractives and minerals or ash. The proportion of these wood constituents varies between species, and there are distinct differences between hardwoods and softwoods. In general, hardwoods contain about 43 % cellulose, 22 % lignin, and 35 % hemicelluloses while softwoods contain about 43 % cellulose, 29 % lignin, and 28 % hemicelluloses (on an extractive-free basis). One of the major differences between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels from 10 to 44 % while petroleum has essentially none, making the chemical properties of biorenewables very different from petroleum. For example, biorenewable products are often more polar and some easily entrain water and can therefore be acidic (Demirbas 2009).

As one of the biorenewable resources, lignin can be converted into useful biofuels via biomass upgrading and biorefinery technologies. Biomass upgrading processes include fractionation, liquefaction, pyrolysis, hydrolysis, fermentation, and gasification. Upgraded bio-oil from biomass pyrolysis can be used in vehicle engines as a fuel (Demirbas 2009). The biorefinery economy is a vision for a future in which biorenewables replace fossil fuels. The transition to a biorefinery economy would require huge investment in new infrastructure to produce, store, and deliver biorefinery products to end users (Balat 2008; Demirbas 2008; Mohan et al. 2006).

LignoBoost Lignin Pyrolysis as Biofuel: One of the separation processes of kraft lignin from black liquor is called LignoBoost. The final product can be used as a fuel in power boilers. For isolation of lignin, acid precipitation was selected as the most potentially promising route. The lignin starts to precipitate at a pH of approximately 11.5, with the yield increasing to approximately 60 % of the original lignin content at pH 10. The precipitation varies according to the acid strength. As the addition of the weak acid carbon dioxide gave slightly lower yield than precipitation with sulfuric acid, for pulp mill process economy carbon dioxide was chosen for future studies. To get purified lignin, the filtration properties of the lignin precipitate were systematically investigated by using a test filtration equipment with well-defined conditions (constant pressure, constant solid concentration of the feed and, minimized influence of sedimentation). The average specific filtration resistance of the filter cake was found to strongly depend on both precipitation pH and precipitation temperature. The large differences in filterability were shown to be caused by smaller lignin particle sizes formed at higher precipitation pH and/or at lower precipitation temperatures. Furthermore, washing the lignin after precipitation is an important step for the removal of residual black liquor and metal ions (especially sodium) (Axegård & STFI-Packforsk 2007). The filter cake, consisting of lignin, is re-dispersed and acidified again, resulting in slurry. This slurry is filtered once more and the filtrate is also brought back to the evaporation plant. However, some part of the filtrate is used for the re-dispersion of the filter cake from the first filtration. The filter cake is finally washed with the use of displacement washing. The posttreatment of the produced filter cake is, e.g., drying and pulverization (Hedlund 2010).

Pyrolysis of LignoBoost lignin extracts directly yields useful and valuable products that are currently extracted from nonrenewable fossil fuel resources (Janković 2011). Pyrolysis of lignin involves heating at 400 °C for 2 min and followed by removal of char on top heating element. The biomass samples were dropped onto the heating plate in 50 mg increments up to 1.2 g. Helium was used as a purge gas and also as a means of maintaining an inert environment. The resulting gases were fed to a condenser immersed in liquid nitrogen. At the end of the experiment, the condenser was allowed to heat back up to room temperature, and the bio-oil samples were collected (Nagy 2009).

Steam Gasification/Pyrolysis of Kraft Lignin for Biofuel

Steam gasification was carried out at atmospheric pressure in a continuous down-flow fixed-bed microreactor which operates at 600, 700 and 800 °C. The reactor was filled with a sample of accurately weighed lignin char (1–2 g) mixed with quam chips (mass ratio 19). The system was tested for leaks prior to the steam gasification run. Heating was started and when the reactor attained a temperature of − 110 °C, water was fed into the reactor at the desired flow rate using a micrometering syringe pump (Eldex model A-604). The reactor had a long preheating section. Thus, there was sufficient time for the water introduced into the reactor to vaporize and to produce steam (at the gasification temperature used) before contacting the lignin char. It took approximately 25–30 min to reach the desired operating temperature. The run was continued for another 30 min until no more gas was produced from the reactor. The product leaving the reactor was condensed and separated into liquid (mainly unreacted water) and gaseous fractions. The liquid product fraction was collected in a glass trap, which was cooled with flowing tap water. The gases were collected over saturated brine. After each run, the spent lignin was removed from the reactor and weighed. The difference in combustible content of lignin before and after the run was taken as an estimate of the lignin or char converted (Bakshi et al. 1999).

The liquid product that obtained from fast pyrolysis of biomass can be converted to value-added products such as aromatic hydrocarbons and cyclic aliphatic hydrocarbon over HZSM-5 zeolite catalyst. The experiments were conducted at atmospheric pressure using a continuous down-flow fixed-bed microreactor operated over a temperature range of 500–650 °C and weight hourly space velocity (WHSV) range of 2.5–7.5 h-1 (for the lignin and acetone solution). The reactor was a 400-mm long, 11.5-mm ID (made of 316 SS) placed coaxially in a furnace. The catalyst particle size range was 500–1410 pm. The catalyst was held by a plug of quartz glass wool which was placed on a supporting mesh inside the microreactor (Bakshi et al. 1999; Bridgwater et al. 1999)

Lignin Hydrocracking for Biofuel

This material can be pyrolyzed to make a pyrolysis oil, but due to the high water content of the pyrolysis oil, often greater than 25 %, high total acid number of approximately 70, and phase incompatibility with petroleum-based materials, pyrolysis oil has found little use. The pyrolytic lignin is separated from pyrolysis oil and contains potentially high-value products in the form of aromatic and naphthenic compounds. Pyrolytic lignin is a complex structure that comprises aromatic rings that are linked by oxygen atoms or carbon atoms, and can be broken into smaller segments when decarboxylated or hydrodeoxygenated and further reduced under mild hydrocracking conditions, while maintaining the aromatic ring structures (Marker and Petri 2009).

The deoxygenated light oil stream is passed to a separation process where the deoxygenated light oil is separated into an aqueous stream and an organic stream. The organic stream is passed to a hydrocracking where mild hydrocracking is performed, thereby generating a product stream. The product stream comprises aromatic and naphthenic compounds for use in gasoline or naphtha boiling range products. A small amount of diesel is produced which can be put into diesel boiling range products. The product stream can be further processed by passing the product stream to a reforming unit. The reforming unit reduces the naphthenic content and generates an aromatic rich product stream for use in gasoline (Marker and Petri 2009).

Hydrogenation of Black Liquor

Creasy and Covey have done some research on hydrogenation of kraft black liquor. The black liquor used in the experiments originated from batch kraft eucalyptus pulping. The liquor was diluted with water to give a concentration of 15.8 % black liquor solids. The experiments were performed in an autoclave with a volume of 1 L. The idea was to use the water gas shift reaction (WGS reaction) as the source of hydrogen for the liquid-phase hydrogenation. Sodium was used as a catalyst for the WGS reaction in all experiments. During the trials, the reactor was heated to 350 °C which took about 45 min. The reaction rate of the pyrolysis is rather slow during the heating period, while the WGS reaction almost reaches equilibrium. There are some ways to make the reaction rates more equal: The CO can be added when 350 °C has been reached or, e.g., borax can be used as a catalyst for the pyrolysis (Hedlund 2010).

An experimental design was constructed where experiments with and without borax was conducted, CO was added at 15, 350 °C or not at all, and the black liquor was kept at 350 °C for 20 min or quenched directly. In total, 14 experiments were carried out. After each test, the product was acidified with HCl and filtrated. Both the retentate and the filtrate were extracted with 1,1,1,tri-chloroethane. The solids from the retentate extraction composed the char fraction, while the extract from the filtrate was evaporated and the residue was added to the retentate extract. The oil fraction was formed by combining the two extract residues. The mean value of the specific energy value was 28.1 kJ/g for the chars produced and about 32.7 kJ/g10 for the oil. The tests without CO gave a low amount of oil, while the best yields were obtained when CO was added at 15 °C. For those tests, the yield increased when the reaction was continued for 20 min at 350 °C. However, for the tests where CO was added at 350 °C, the additional 20 min did not give good yields. Altogether, the hydrogenation gave four products; a gas phase (CO_2 and H_2), an aqueous phase containing most of the original sulfur and sodium, and char and oil which can be used as fuel. Thirty to 50 % of the fuel value was found in the aqueous phase, which can be used if it is brought back to the weak black liquor for evaporation and finally for incineration in the recovery boiler (Hedlund 2010).

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Potential Agrowastes for Biofuels

Visweswara Rao Pasupuleti, Rayees Ahmed Shiekh, Nelli Giribabu, D. K. Venkata Ramana and Naguib Salleh

Abstract Biofuels are fuels which contain energy from biologically modern carbon fixation. These fuels are generally produced from plants, agricultural wastes, and microorganisms. This biomass (plant-derived products, microorganisms) can be converted to suitable energy mainly in three methods. They are chemical conversion, thermal conversion, and biochemical conversion. Conversion of this biomass results in three forms, such as fuel in solid such as charcoal, fuelwood liquid such as bioethanol, and gas such as biogas. The research and the public pay much attention towards the production of biofuels due to the drastic increase in the oil prices which are used in the motor vehicles as energy source. There are numerous biofuels which have been produced to meet the variety of global needs. The various types of biofuels are biobutanol, biodiesel, bioethanol, biogas, biohydrogen, etc. This chapter therefore aims to deliver the existing status and future directions of biofuel production using both agroindustrial-based waste products and conventional substrates.

Keywords Agricultural wastes · Bioethanol · Biofuel · Biodiesel · Biohydrogen

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Introduction

Due to the swift escalation in population and industrialization, there is a tremendous need and demand for ethanol, which has been rising day to day globally. The main fuel used as an alternative for petrol is bioethanol. The major source of sugar required to produce ethanol is fuel or energy crops. These crops are purposely grown for ethanol production and energy use. The plants include sugarcane, corn, wheat crops, maize, willow and popular trees, waste straw, cord grasses, Jerusalem artichoke, myscanthus, reed canary grass, sawdust, and sorghum species. Sugarcane and corn are deliberately used for bioethanol production and now these crops also are not capable to meet the global demand in producing bioethanol due to their crucial value in food. Consequently, materials such as wastes from agricultural feedstock are appropriate for bioethanol production. Agricultural wastes are profuse, renewable, and lucrative. The production of bioethanol from agricultural waste might be a potential tool. But there are several restrictions and confronts in the process such as transportation of biomass, handling the biomass and well-organized pretreatment techniques for delignification of lignocellulosic biomass. Lignocellulosic biomass symbolizes a prospective ample source of renewable energy. These lignocelluloses biomass is not suitable to be used as a food source and might be considered as a superlative substance for the production of bioethanol (Zhang and Lynd 2004). These substances contain lignin, cellulose, and hemicelluloses. Celluloses are linear polymers of glucose and hemicelluloses are the heterogeneous polymers of glucose molecules. Agricultural lignocellulosic biomass contains 35–50% cellulose (Agbogbo et al. 2006). The major substances of these polysaccharides are fermentable sugars such as glucose and xylose. Pretreatment plays an important role in the production of biofuels. Accurate pretreatment techniques can definitely enhance the absorption of fermentable sugars after enzymatic saccharification, thus advancing the effectiveness of the entire progression. This chapter deals with the present status of agricultural wastes used in the production of biofuels.

Types of Biofuels

Biofuels can be classified into three types. They are present in solid, liquid, and gaseous states. The conversion of this biomass results in three forms such as fuel in solid such as charcoal, fuelwood liquid such as bioethanol, and gas such as biogas (Fig. 1).

The modern development and escalation of energy markets redesign the role of agriculture. Most significant is the sector's increasing role as a provider of feedstock for the production of liquid biofuels for transport—ethanol and biodiesel (Fig. 2).

Biofuels

Among the biofuels, biohydrogen is a moderately latest form of biofuel, which is in gaseous state. Production of biohydrogen takes place in anaerobic fermentation of

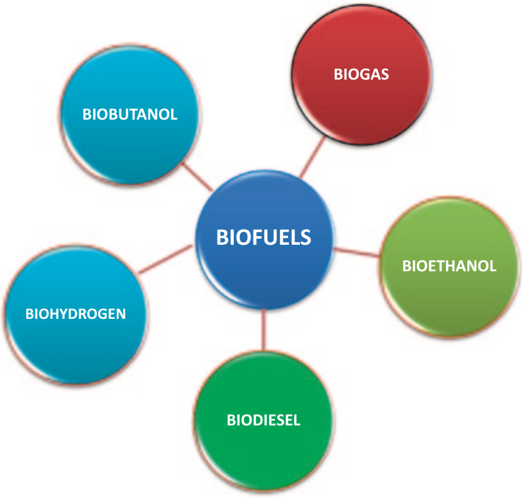

Fig. 1 A schematic representation of various types of biofuels

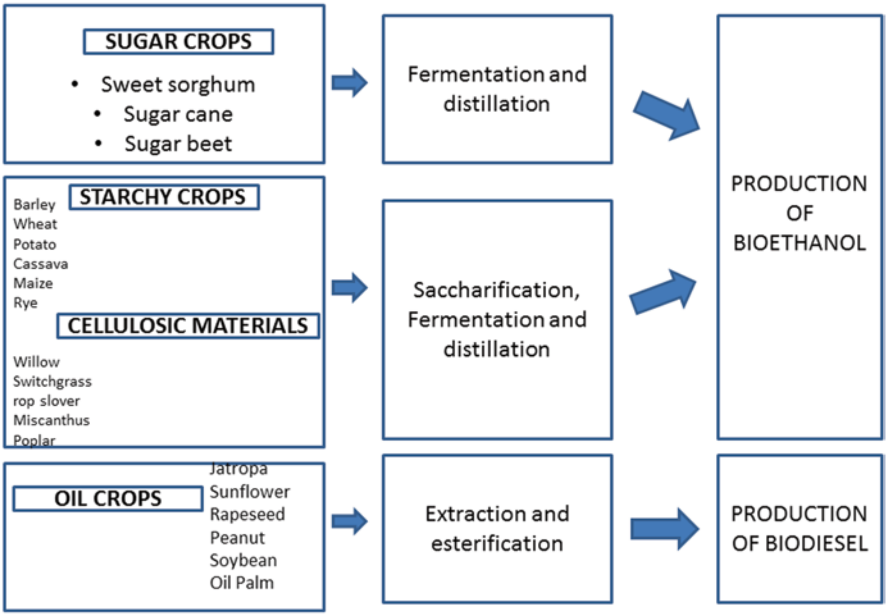

Fig. 2 Conversion of agricultural feedstocks into liquid biofuels

wastes from agroindustries by using groups of bacteria such as acidogenic, methanogenic, and hydrogenic bacteria. In contrast, liquid form of biofuels has been classified into biodiesel and bioethanol. Biodiesel is now being used as a prospective alternative for petrol or diesel. In the recent times, bioethanol has also acquired invigorated significance on the current energy crisis globally. Different kinds of biofuels are conferred here.

Biogas

Biogas is naturally produced by using the organic substances in the anaerobic conditions. Biogas is produced by anaerobic digestion of agricultural wastes such as sewage, green waste, manure, plant-related wastes, municipal-related wastes, and crop remaining wastes with various types of anaerobic bacteria or fermentation(Risberg et al. 2013). It is mainly made up of methane ($CH_{4\text{–}55\text{–}}70\,\%$) and carbon dioxide ($CO_{2\text{–}30}-45\,\%$) and might comprise petite quantities of moisture, hydrogen sulfide (H_2S—50–2000 ppm), siloxanes, saturated water vapors, and different types of hydrocarbons (Amigun et al. 2008; Kashyap et al. 2003; Sreekrishnan et al. 2004).

Biogas from Agricultural Wastes

Biogas production from agricultural wastes has many probabilities for the development of agriculture and energy in the rural regions. Production and consumption of biogas from agricultural wastes is one of the most important elements of power system based on renewable sources (Chodkowska-Miszczuk and Szymańska 2013). The biogas consumption is cost-effectively managed, only if it is done concurrently with the other related renewable energy sources exploitation (Budzianowski 2012). The residues from food crops which are not palatable (e.g., agricultural wastes and vegetable wastes) and keen energy crops (e.g., beets, maize, and wheat) provide a great prospective for anaerobic digestion.

Cellulose is a substance which can be easily degraded anaerobically to an amount of about 80 %. It is making the approach to grow the crops like grasses, which hold high-cellulose content. (Appels et al. 2011). Various types of materials such as wheat straw, sorghum straw, and rice straw are extensively accessible cellulose-containing waste substances for the production of biofuels. Much attention needs to be paid towards the selection of the species and crops in order to gain the high quantity of methane per hectare. The major factors such as time of harvesting, type of preservation, pretreatment of biomass, and digestion are vital in the production and yield of biofuels. Sunflower and maize are the vital energy crops used for digestion (Amon et al. 2007; Fig. 3).

There might be a chance to have a large amount of nondegradable substances in the cellulose-containing crops. The exact methane yield from the cellulose-containing crops can be apprehended only after pretreatment, because the nondegradable contents may be removed in the pretreatment. (Bauer et al. 2009; Petersson et al. 2007). Several types of pretreatment techniques are available such as mechanical, thermal, acid pretreatment, alkaline, oxidative, and combinations of ammonia and

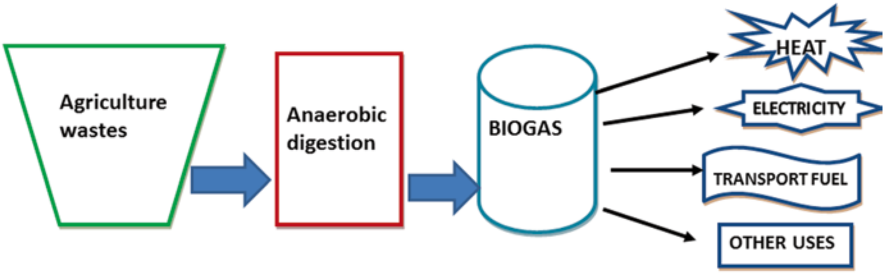

Fig. 3 A schematic illustration of production of biogas from agricultural wastes

carbon dioxide pretreatment for the methane yield (Hendriks and Zeeman 2009). Especially for methane production, acid pretreatment has the most potential when compared to the ethanol production. The reason involved in this is that methanogens can hold the compounds like hydroxymethylfurfural (HMF) and furfural to a specific concentration until they adapt to the conditions (Xiao and Clarkson 1997).

Fruit and vegetable wastes are feasible to degrade and are generally co-digested with other feedstocks. The waste from fruits and vegetables was co-digested with cattle slurry, and a high quantity of volatile fatty acids was found. The combination of cattle slurry and fruits and vegetable waste (FVW) with proportions of FVW of up to 50 % in the supply furnished with a high-quality co-digestation in the methane yield (Callaghan et al. 2002).

Biohydrogen

Hydrogen is one of the vital elements with utmost availability in the nature. But, production of biohydrogen from renewable resources remains a main challenge. Biohydrogen is produced biologically by using bacteria, algae, and archaea. Biohydrogen is one of the prospective biofuels accessible from both agriculture and waste organic materials (Demirbas 2009).

At present, the direct conversion of hydrogen from sunlight may give superior hypothetical possibilities (Akkerman et al. 2002) when compared to the 0.2–2.6 % photosynthetic effectiveness in energy crops (Klass 2004). Though, the technical and practical viability of the development requires more improvement, and the expenses of maintaining the photobioreactor will also be the main challenge. Indirect biohydrogen involves in inhibiting the oxygen and production of hydrogenase from carbohydrates (Demirbas 2009; Fig. 4).

Hydrogen from Agricultural Wastes

Agricultural residues such as green leaves, fruit shells, nutshells, straws, fruit seeds molasses, and plant stalks are prospective renewable energy assets. There are various technologies available to produce biohydrogen. They can be divided into two

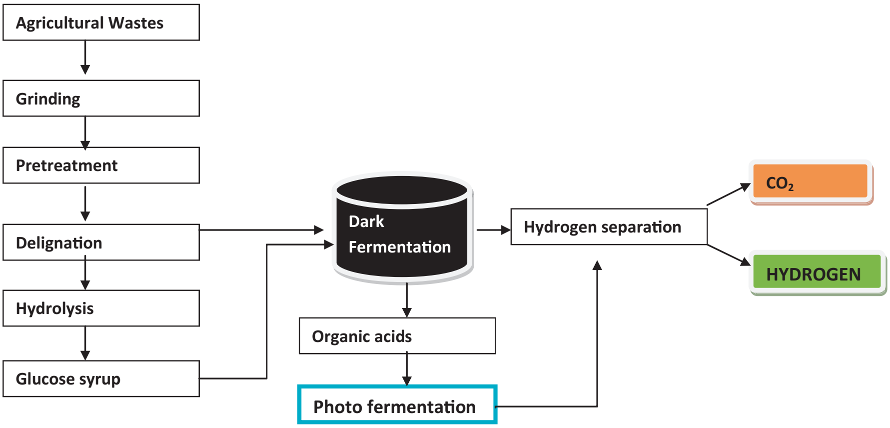

Fig. 4 A schematic diagram of production of biohydrogen from agricultural wastes

technologies such as photosynthesis (indirect biophotolysis, direct biophotolysis, and photo fermentation) and dark fermentation (anaerobic fermentation). Photosynthesis is a light-dependent process, whereas the dark fermentation does not require light and is a light-independent catabolic process (Vardar-Schara et al. 2008). There are three types of microorganisms that generate hydrogen. They are cyanobacteria, photosynthetic bacteria (algae), and fermentative bacteria. Photosynthetic bacteria and cyanobacteria produce hydrogen using light by photosynthetic processes (Srikanth et al. 2009), while fermentative microorganisms produce hydrogen through the acidogenic stage of the anaerobic digestion. The yield of the hydrogen in fermentative processes is always better than the photosynthetic method and it does not depend on the availability of light (Fig. 5).

The fermentative bacteria also exploit multiple carbon sources such as wastes from various fields, agriculture wastes, organic compounds, insoluble cellulosic materials, wastewaters, etc. This process is cost-effective, needs less energy, technically simple, and stable also. The cyanobacteria decompose water directly to hydrogen and oxygen in the presence of light through the process of photosynthesis (Venkata Mohan 2009). Photosynthetic bacteria utilize organic materials such as organic acids and convert them to the desired products. Anaerobic bacteria exploit organic matters as the exclusive resource of energy and convert them into hydrogen. A flourishing conversion of organic biomass to hydrogen relies sturdily on the processing of raw materials to generate feedstock, which could be easily fermented by the microorganisms (Hallenbeck and Benemann 2002; Fig. 6).

Numerous organic wastes such as solid wastes like blackstrap molasses and rice straw have been productively used for the production of hydrogen (Nath and Das 2003). The majority of the experiments revealed significant production of hydrogen using limited number of thermophilic strains. The potato steam peels also have been used for the production of hydrogen (Djomo et al. 2008; Mars et al. 2010)

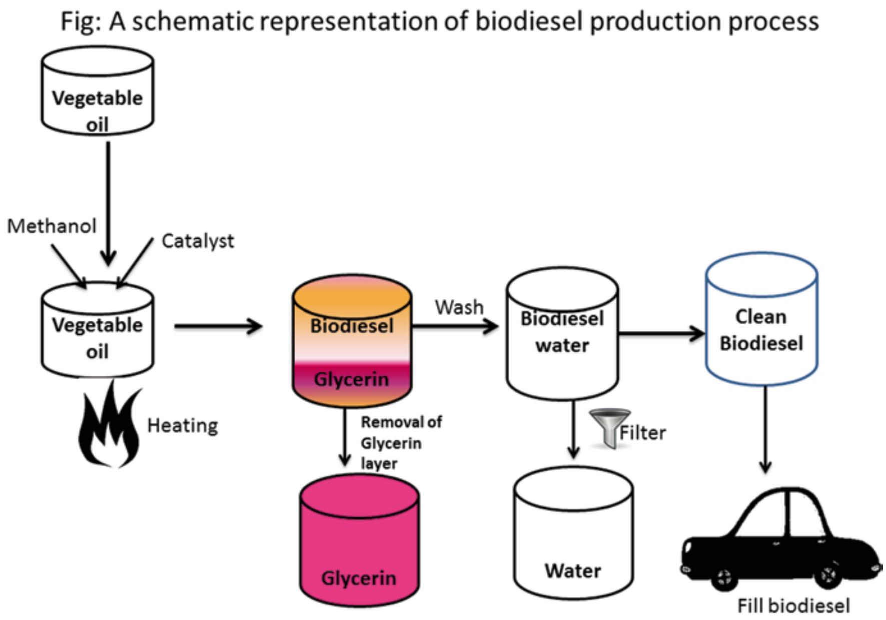

Fig. 5 A schematic diagram of production of biohydrogen from agricultural wastes

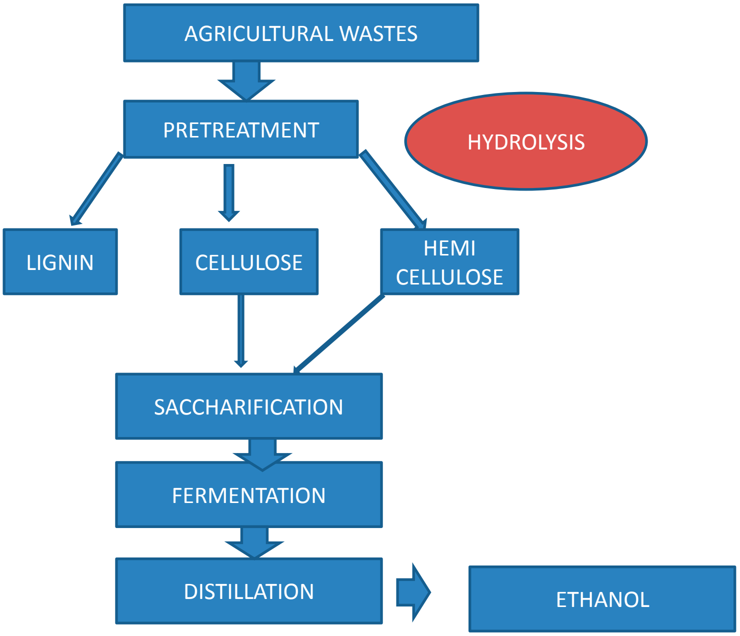

Fig. 6 A schematic diagram of production of biohydrogen from agricultural wastes

Biodiesel

Biodiesel is a nontoxic, renewable, eco-friendly alternative fuel, which can be used as it is or in combination with petroleum or diesel (Peterson and Reece 1994). Biodiesel is made up of completely with agricultural wastes, vegetable oil, or fats from animals. Biodiesel does not contain polycyclic aromatic hydrocarbons and releases diminutive amounts of carbon dioxide, carbon monoxide, sulfur dioxide, and other particulates which significantly lessen the health hazards when compared to the diesel or petroleum. Usually, the diesel engines face problems due to the presence of triglycerides, their viscosity, and fluctuating temperature (Fukuda et al. 2001). By using the vegetable oils and their derivatives, the engines do not encounter the problems due to less or no triglycerides. Generally, transesterification is an extensively used practice in which the triglycerides react with an alcohol in the presence of a chemical catalyst (acid or alkali) or biological catalyst (enzyme) to generate the esters, especially monoalkyl esters which are commonly known as biodiesel. The catalysts are different when the acyl acceptor is not similar. For example, potassium hydroxide is used as a catalyst when ethanol is the acyl acceptor, whereas sodium hydroxide acts as a catalyst when methanol is the acyl acceptor due to solubility concerns (Ranganathan et al. 2008).

Biodiesel from Agricultural Residues

Biodiesel is commonly produced by using animal fats or vegetable oils. A variety of oils such as sunflower oil, soybean oil, palm oil, rapeseed oil, and rice bran oil have been used to produce biodiesel. The preference of vegetable oil to be used in the production of biodiesel totally depends on its ample availability. Not much information exists related to the use of agroindustrial residues for the production of biodiesel. However, there is bioethanol production by using agroindustrial residues and these can be used for the transesterification of oils for the production of monoethyl esters of fatty acids, which can be used as biodiesel**.**

Bioethanol

Bioethanol is a nontoxic and non-petroleum fluid which releases low carbon dioxide and other gases due to free availability of oxygen. Bioethanol is considered as a safe alternative to petrol for use in the vehicles as fuel. The production as well as utilization of bioethanol does not release much carbon dioxide into the environment (Chandel et al. 2007). Bioethanol is a derivative of renewable resource feedstocks, typically plants such as corn, wood, sugar beet, wheat, and straw. Any feedstock contains considerable quantity of sugars or substances that are easily convertible to sugar (cellulose or starch), which can be utilized to generate bioethanol.

Bioethanol from Agricultural Residues

The principal feedstocks for the production of bioethanol are sugarcane and corn. Globally, bioethanol is one of the most extensively used biofuels for transportation. About 60 % of overall bioethanol production is derived from sugarcane and 40 % from all the other crops. At present, the production of bioethanol accounts for more than 94 % of worldwide biofuel manufacture and the greater part of bioethanol production is from sugarcane. The USA and Brazil are the global leaders for the production of bioethanol, which together generate for about 70 % of the worldwide bioethanol.

Currently, cellulosic biomass use is very limited due to the expensive pretreatment required for breaking the crystalline structure of cellulose. Bioethanol is already an established commodity due to its ongoing nonfuel uses in beverages, and in the manufacture of pharmaceuticals and cosmetics. In fact, ethanol is the oldest synthetic organic chemical used by mankind. The main advantage of production of ethanol from renewable and cheap agricultural substances is that it decreases the release of greenhouse gases such as CO_x, HO_x, NO_x, and SO_x and removes smog from the atmosphere.

Future Prospective and Conclusion

There is a huge escalation in crude oil prices. So the need to produce biofuels from the biological wastes has become more popular. The main biofuels available are biomethane, biogas, biohydrogen, biomethanol, and biodiesel. Biodiesel and bioethanol are used as alternative fuels to diesel and petrol, respectively. Bioethanol is produced from cane molasses through fermentation process and could also be generated from a variety of agricultural wastes, whereas biodiesel is usually produced from vegetable oils. Using modern biotechnological methods to produce different types of biofuels from agricultural, industrial, and plant wastes is prospectively efficient. The produced biofuels through these modern techniques will be releasing very low quantity of greenhouse gases and toxic pollutants and thereby protecting the environment from pollution. Several accessible biotechnology methods can be applied to increase the bioenergy production. For instance, expanding better biomass feedstocks and raising the effectiveness of converting the biomass to biofuels. The scientists, researchers, and agriculturists need to focus on the modern techniques which will be cost-effective and more productive to encounter the crisis of biofuels.

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Utilization of Oilseed Cakes for Human Nutrition and Health Benefits

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Abstract Oilseed cakes are the by-products generated from edible oil processing. The oilseed cakes are generally used as animal feed, plant fertilizer or soil compost due to their high protein, carbohydrate, mineral and nitrogen contents. However, there is a strong interest to utilize oilseed cakes as food for humans due to increasing global population and food prices as well as the attractive emerging nutritional information on many of these by-products (e.g. the concentration of secondary metabolites and protein contents). Soy, whey and egg albumin proteins have been widely used for human consumption and food applications for centuries due to their protein qualities and functional properties. The high demand for soybean and its vast cultivation due to global market forces caused a negative environment effect. Production of animal proteins, namely meat, whey and albumin, is not sustainable due to higher carbon and water usage. Therefore, the utilization of agricultural by-products, such as oilseed cakes, provides an opportunity to add value as well as filling a gap in protein demand. The present chapter focuses on oilseed cakes and discusses the opportunities to generate value-added products such as polyphenols, protein isolates and protein hydrolysates. The processing conditions, health benefits demonstrated in *in vivo* and *in vitro* studies of products generated from oilseed cakes are critically reviewed with the aim of determining the best-use options for the various materials. Strategies for the removal of antinutrients found in oilseed cakes are discussed.

Keywords Oilseed cake · Protein isolates · Protein hydrolysates · Polyphenols · Antinutrients

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Introduction

Oilseed cakes are the solid by-products of edible oil industries remaining after the extraction of the oils. The global production of oilseed cakes, on average, increased 2.3 % annually over the past decade to 2010. The world oilseed production was reported to be around 380 million metric t in 2004/2005 (Moure et al. 2006). Among all types of oilseeds, there were about 30,265 metric t of hempseed produced worldwide, while flaxseed production reached 2.3 million metric t in 2009/2010 (Rabetafika et al. 2011). In 2000–2001, the world production of canola was reported to be around 33.86 million t (Karlsson and Martinsson 2011). Sunflower seeds were reported to have an annual world production of 35.6 million t in 2008 (FAO 2010; Pickardt et al. 2011). India, as the world's largest oilseeds producers, produces over 25 million t of oilseed cakes annually (FAO 2010). These by-products of oil production have been underutilized for human usage, and are worthy of investigation for human use. In terms of the oilseed cake quantities produced, soybean seed cake is the world's largest by-product of oilseed cakes, followed by canola seed. Giving the large volumes of the oilseed cakes produced, it is worth to explore the potential of adding value and exploit their nutrients through further processing.

Traditionally, oilseed cakes are used as animal feed and soil compost, which have been seen as an economical way to dispose the by-product and gain some benefit without additional cost. Oilseed cakes are useful animal feed due to their abundant protein, energy, carbohydrates and mineral contents. For example, young calves fed cold-pressed hempseed cake had similar live weight gain to calves fed with a mixture of soybean meal and barley (Hessle et al. 2008). Hempseed cakes have favourable amino acids and the protein resists degradation in the rumen (Mustafa et al. 1998), which can offer some advantages as animal feed. Higher egg weight and total egg yolk linoleic and linolenic acids were obtained from hens fed with hempseed cake-based diet compared to hens fed with wheat-, barley- and corn-based diet (Silversides and LefranÇois 2005). Furthermore, Hempseed cake was used as an aquaculture feed for farmed fish (Lunger et al. 2007). Addition of hempseed cake into fish meal improved the texture of fish fillet (Lunger et al. 2007) and the growth rate of fish (Callaway 2004) compared with soybean meal and soybean isolate.

Another use of oilseed cakes without further processing is to use as compost for plants. The effect of supplementing spent rice straw substrate with oilseed cakes, as a source of extra organic nitrogen, was studied for the production of the mushroom *Pleurotus sajor-caju* (Shashirekha et al. 2002). The supplementation of oilseed cakes (mustard oil cake, sunflower oil cake, cottonseed cake and soybean cake) with rice straw substrate colonized by the mushroom *P. sajor-caju* increased the mushroom yields by 50–100 % compared to the unsupplemented substrate (Shashirekha et al. 2002). Cotton seed cake was shown to produce the highest mushroom yield (up to 12 times higher than to those of unsupplemented spent straw and higher than the other oilseed cakes). Cottonseed cake-supplemented mushrooms also had higher protein and fat contents and lower carbohydrate content compared to other treatments and controls. Seed cotyledon powders from tea (*Camellia sinensis,* L.) and from oak (*Quercusrobur,* L.) were used to control soil nitrification (Kholdebarin and Oertli 1992). The seed powders decreased the amount of NO_3- in soil due to fixation and immobilization of nitrogen by organic substances present in seed powders rather than direct effects on nitrifying organisms.

The seed cakes of *Jatrophacurcas, Madhucaindica, Azadirachtaindica* and *Pongamiapinnata* are used for the production of biofuel and bioenergy in India. It is recommended to use nonedible oilseed cakes for biofuel processing rather than edible oilseed cakes since they possess toxic compounds and are not fit to be used as animal feed or for human consumption.

Recent developments in oilseed cake utilization are focused on human health and nutrition to meet the global increasing needs of protein and bioactive compounds. One of the earliest reviews on the topic was published more than 40 years ago (Meyer 1971) that discussed the processing, functional and nutritional properties of soybean isolate, as well as protein extractions from other oilseed cakes. More recently, the use of oilseed cakes as a source of antioxidative peptides was reviewed by Sarmadi and Ismail (2010). Various techniques for the extraction and fractionation of protein and peptides from plant tissues have also been reviewed by Martínez-Maqueda et al. (2013). However, there is no detailed review of clinical studies examining the health benefits and bioactive properties of products extracted from oilseed cake.

Several bioactive compounds, such as polyphenols, protein and oligosaccharides, can specifically be obtained from the oilseed cakes since many of the seeds, as source of new seedlings, are naturally well designed to alleviate any risks that a new life may face.

Processing of Oilseed Cakes for Health-Benefiting Products

The target bioactive products can be obtained using different processing methods of the oilseed cakes (Table 1). Generally speaking, the bioactive compounds that can be obtained from oilseed cakes can be either protein, carbohydrates or phenolic compounds. The best use of the material will depend on the type(s) and concentration of the compounds as well as how easy the extraction process is.

Carbohydrates

Flaxseed cake is rich in mucilage or dietary fibre, which can be extracted by alkali aqueous solution at pH 12, followed by centrifugation to collect the supernatant (Gutiérrez et al. 2010). The sticky mucilage solution can be freeze-dried, spray-dried or vacuum-dried to generate a shelf stable powder product. The mucilage can be used as a thickening and emulsifying agent in food, pharmaceutical and cosmetic applications due to its desirable physical properties. Apart from its physical properties,

Table 1 Processing conditions of oilseed cakes for health-benefiting products

Oilseed cakes	Processing conditions	Target product	References
Flax	Acidification to the isoelectric point at pH 4.4	Protein	Gutiérrez et al. (2010)
	Purification of supernatant from protein isolation process using trichloroacetic acid for 12 h, centrifugation to remove remained protein, precipitated with ethanol for 12 h at −18 °C, centrifugation at 7000 rpm for 30 min at 4 °C. The pellet was dissolved in hot water and neutralized with 1 M NaOH, dialysis and lyophilisation	Polysaccharides	
	Removable of mucilage at pH 12, followed by extraction of polyphenols with 50 % aqueous ethanol, solid–liquid ratio (1:60), in a shaker for 30 min at 200 rpm at 25 °C	Polyphenols	
	Hydrolysis with hydrochloric acid (1 M) at 100 °C for 1 h followed by an extraction with a mixture of ethyl acetate and hexane (90:10 v/v)	Lignans (secoisolariciresinol and anhydrosecoisolariciresinol)	Lehraiki et al. (2010)
	Flax hulls were extracted with 20 ml of 70 % aqueous methanol for 16 h at 60 °C under continuous stirring. The solid residue was centrifuged 15 min at ca. 2000 g Alkaline hydrolysis was performed on the supernatant of extraction mixture with 0.1 M sodium hydroxide at room temperature for duration ranging from 0 to 48 h. The solid residue was centrifuged 15 min at ca. 2000 *g* and was then neutralised with acetic acid The resulting neutral hydrolysate supernatant was subsequently evaporated to dryness at 40 °C and resuspended in 1 ml of buffer containing enzyme at a concentration of 1 unit ml^{-1}) of cellulase R10	Secoisolariciresinol	Renouard et al. (2010)
Olive	1 g of olive cake in 25 ml methanol for 1 h at 23 °C in a water bath of 60 °C was extracted twice for free phenolics extraction. The remaining residues were hydrolysed with a dilute alkaline solution (25 ml, pH 12.0, 0.1 M NaOH, 12 h/23 °C) in a water bath under a stream of nitrogen, followed by hydrolysis with a dilute acid solution (25 ml, pH 2.0, 0.1 M HCl, 12 h/23 °C) in a water bath under a stream of nitrogen to obtain bound phenolics	Polyphenols	Alu'datt et al. (2010)
Groundnut, mustard, sesame, linseed, coconut, copra, madhuca, and cotton	*Bacillus licheniformis* CUMC305, incubated at 49 °C for 16 h	α-amylase	Krishnan and Chandra (1982)

Table 1 (continued)

Oilseed cakes	Processing conditions	Target product	References
Pumpkin	Defatting process with hexane, extraction in water (pH 10.00) and the slurry was filtered; the pH of filtrate was adjusted to 5.00. After centrifugation the resulting residue was collected and air dried at room temperature (20–23 °C)	Protein	Peričin et al. (2009)
Grape seeds vinification wastes	Supercritical antisolvent extraction (SAE) at 15 MPa and 40 °C	Antioxidants (catechin, epicatechin, gallic acid and resveratrol)	Marqués et al. (2013)
Camelina sativa	Extraction with 80 % (v/v) methanol using a defatted seed/cake-to-solvent ratio of 1:10 w/v. by shaking for 8 h at room temperature, the solid was recovered by filtration and subjected to two additional 45 min long extraction steps under the same solid to liquid ratio conditions, using ultrasound instead of a shaker	Phenolics	Terpinc et al. (2012)
Watermelon	Hydrolysis with 0.12 g/L NaOH solution, 15 min extraction time and 70:1 (v/w) solvent/meal ratio at 50 °C	Protein	Wani et al. (2008)
Sunflower kernel and shell	Sample (1 g) was extracted twice by stirring in 280 mL aqueous methanol (60%, v/v) for 1 h at ambient temperature	Polyphenols	Weisz et al. (2009)
Tamarind seed and palm kernel cakes	Palm kernel cake (5 g) and tamarind seed cake (5 g) were separately added to 250 ml Erlenmeyer flasks, moistened with 5 ml of salt solution (0.5 % w/v NH_4NO_3, 0.1 % w/v $MgSO_4 \cdot 7H_2O$ and 0.1 % w/v NaCl), autoclaved at 121 °C for 20 min, cooled to room temperature and inoculated with 1 ml of the *Aspergillus niger* ATCC 16620 spore inoculum (11×10^9 spores). The contents were mixed thoroughly and incubated at 30 °C for 96 h in an incubator; The fermented substrates were mixed thoroughly by keeping the flasks on a rotary shaker at 150 rpm for 10 min after adding 50 ml of distilled water with 0.01 % Tween 80. Crude enzyme from the fermented medium was filtered. The filtrate was collected in vials and preserved at 4 °C for further analysis	Tannase	Sabu et al. (2005)
Tea seed cake *Camellia oleifera*	Tea seed cake (3.0 kg) was extracted four times with MeOH under reflux (2 h each). After concentrated to a small volume (2.5 L), the extract was partitioned with petroleum ether three times to afford a defatted fraction (420 g). Part of the defatted fraction (86 g) was subjected to a Sephadex LH-20 column, eluting with H_2O–MeOH (1:0, 4:1, 3:2, 2:3, 1:4, 0:1, v/v, each 800 ml) and finally 50 % aqueous acetone (800 ml) to give four fractions. Further silica gel fractions and elution resulted in pure compounds	Kaempferol acetylated glycosides	Gao et al. (2011)

several health benefits have been attributed to flax mucilage. For example, it can be used as a dietary fibre source in human nutrition or serves as a prebiotic for the healthy growth of gut flora. Mucilage can also be used in fermented dairy products to support the growth of lactic acid bacteria and favourably modify the product texture at the same time (Nezhad et al. 2013). In addition, *in vivo* studies showed that flax mucilage has anti-ulcer activity and it significantly reduced the number and length of gastric ulcers induced by ethanol in rats (Dugani et al. 2008). Polysaccharides or oligosaccharides from flaxseed cake were reported to possess antitumour property as a result of their antioxidant properties (Gutiérrez et al. 2010). The authors suggested that the antiradical activity of the saccharides prevents the oxidation of proteins, lipid or DNA, thus preventing the leading causes of cancer. Chitooligosaccharides from flaxseed cake demonstrated antimicrobial properties against pathogenous bacteria and fungi such as *Candida albicans, Penicillium chrysogenum, Fusarium graminearum* and *Aspergillus flavus* (Xu et al. 2008).

Polyphenols

Lignans from flaxseed cakes demonstrated various preventative actions, supported by preclinical and clinical studies, in various cardiovascular complications such as atherosclerosis, hyperlipidaemia, ischemia, hypertension and cardiotoxicity (Zanwar et al. 2014a, b). Earlier attempts to extract lignans used a solvent mix of 1,4-dioxane and ethanol (1:1 v/v) (Bakke and Klosterman 1956). Basically, polar solvents such as aqueous methanol or ethanol solvents were used as the first step in lignan extraction from flaxseed cake. The incorporation of acid treatment step, using diluted hydrochloric or acetic acids, after the initial extraction by aqueous methanol or ethanol, followed by extraction with ethyl acetate:hexane (1:1 v/v) improved the yield of lignans (Meagher et al. 1999; Charlet et al. 2002). More recently, direct aqueous acidic extraction followed by extraction with ethyl acetate:hexane (1:1 v/v) was found to be optimal for the extraction of lignans (Lehraiki et al. 2010). The use of the alkali extraction step after the aqueous polar solvents extraction followed by neutralization was also reported in various reports (Müir and Westcott 2000; Zhang and Xu 2007; Rybarczyk et al. 2008; Renouard et al. 2010).

Polyphenols from oilseed cakes possess high antioxidant properties that are associated with positive health effects such as lowering lipid in plasma, skin photoprotection, vasoprotection, neuroprotection, antiageing, anticancer, antimicrobial, antifungal and antiviral activities (Marrugat et al. 2004; Atten et al. 2005; Su et al. 2011; Bekhit et al. 2011; Jacob et al. 2012; Cheng et al. 2012; Menaa and Menaa 2014). Polyphenols exist naturally in all plant materials and consist of a common structure of flavone. Polyphenols is a large family of compounds that include derivatives such as flavonoids, catechins, flavonones, isoflavones, flavanols, dalbergin, anthocyanins, proanthocyanidins, anthocyanidins, phenolic acids, phenolic alcohols, polyphenolic amides (avenanthramide, capsaicinoid), stilbenes, chalcones, lignans and other non-flavonoids such as resveratrol, rosemaric acid, gingerol, ellagic acid, secoisolariciresinol, metaresinol, valoneic acid dilactone, lignans, curcumin and hydrolysable tannins (gallic acid, ellagic acid, rosmarinic acid) (Sharma 2014). As shown in Table 1, simple polar solvents extraction is used for the extraction of polyphenols from oilseed cakes. In order to maximize the extraction yield and eliminate the use of organic solvents, technologies such as supercritical fluid extraction, ultrasonic, alkali and acid hydrolysis were incorporated in polyphenol extraction from the oilseed cakes (Amza et al. 2011; Tan et al. 2011; Teh et al. 2014). There are several published reviews on health benefits and bioavailability of polyphenols from plant material (El Gharras 2009; Sharma 2014; Acosta-Estrada et al. 2014). The focus of the present chapter is on polyphenols extracted from oilseed cakes with the emphasis on published *in vivo* and *in vitro* studies.

Biological Activities of Phenolics from Seed Cakes

Polyphenols such as gallic acid, tannic acid, quercetin and salicylic acid were found to have high antioxidant activities as well as antimicrobial activities against *Streptococcus mutans* (Sendamangalam et al. 2011). Antimicrobial activities and modes of action of penta-, hexa-, hepta-, octa-, nona- and deca-*O*-galloylglucose (gallotannins) isolated from mango kernels were found to have minimum inhibition concentrations (MICs) of 0.2 gL^{-1} or less against *Bacillus subtilis, Bacillus cereus, Clostridium botulinum, Campylobacter jejuni, Listeria monocytogenes* and *Staphylococcus aureus*. Higher concentrations (0.5–1 gL^{-1}) were required to inhibit enterotoxigenic *Escherichia coli* and *Salmonella enterica,* but lactic acid bacteria were unaffected by the extracts (Engels et al. 2011). Bound phenolic extracts (referring to the insoluble phenolics that are chemically bound to the plant matrix by hydrogen bonds between the hydroxyl groups on phenolics and an oxygen molecule from the polysaccharides glycosidic linkages, hydrophobic interactions and covalent ester bonds between phenolic acids and polysaccharide, cellulose, hemicellulose, lignin, pectin and proteins) from mango seed kernel flour were more effective (MIC of 0.06–0.157 %) than free phenolic (soluble phenolics that are not bound to the plant matrix) extract (MIC of 0.117–0.191 %; Govardhan Singh et al. 2013). Furthermore, mango seed extracts showed high antioxidative and tyrosinase inhibition activities (Maisuthisakul and Gordon 2009).

The antioxidative properties of polyphenols have been associated with their protective effects against several human diseases such as diabetes, cardiovascular diseases, cancer, osteoporosis and neurodegenerative diseases (Graf et al. 2005). Polyphenols accept electrons from oxidants and form relatively stable phenoxyl radicals in order to disrupt oxidation reactions in cellular systems. In addition, polyphenols are potent inhibitors of low-density lipoprotein (LDL) oxidation and this type of oxidation is considered to be a key mechanism in the development of atherosclerosis. Polyphenols exert antithrombotic effects by means of inhibiting platelet aggregation, and thus preventing coronary heart diseases. Several mechanisms such as estrogenic/antiestrogenic activity, antiproliferation, induction of cell cycle arrest or apoptosis, prevention of oxidation, induction of detoxification enzymes and regulation of the host immune system, anti-inflammatory activity and changes in cellular signalling were assigned to polyphenols to explain their chemopreventing activity (García-Lafuente et al. 2009). Polyphenol extracts from oilseed cakes such canola, evening primrose, borage seed cakes (Table 2) exerts high antioxidative activities. In *in vivo* studies using rats, oral doses of polyphenol extracts from evening primrose seed cake demonstrated a hypocholesterolemic effect (Bałasińska 1998). Similarly, oral doses of polyphenol extract of the shells of Japanese horse chestnut seed (*Aesculus turbinata* Blume) inhibited the elevation of blood glucose after oral administration of starch to the rats and showed antiobesity effect (Kimura et al. 2011). Low-molecular procyanidin of grape seed exhibited antihypertensive activity by reducing the systolic and diastolic blood pressure of spontaneously hypertensive rats (SHR) in a dose-dependent manner up to 375 mg/kg with the peak activity found 6 h post administration (Quiñones et al. 2013).

In vitro studies reported that polyphenols from grape seeds increased endothelial progenitor cells (EPC) viability, adhesion and migration, and prevented the negative effects of high *D*-glucose; including the production of reactive oxygen species (ROS; Felice et al. 2012). Furthermore, grape seed extract reduced [^{3}H] cholesterol uptake by up to 66 % in HT29, Caco2, HepG2 or HuTu80 cells at half maximal effective concentration (EC$_{50}$) of 83 µg/mL, which means 83 µg/mL of grape seed extract exhibited 50 % of its maximal effect (Leifert and Abeywardena 2008). The authors also reported the inhibition of the proliferation of HT29 colon adenocarcinoma cell and an increase in apoptosis and 5-lipoxygenase (5-LOX) activity with a half minimal (50 %) inhibitory concentration (IC$_{50}$) value of 13 µg/mL (Leifert and Abeywardena 2008). Ultraviolet (UVA) radiation promotes the production of ROS, which consequently attacks lipids, proteins and other intracellular biomolecules leading to oxidative stress, cellular damage and ultimately cell death (Jaszewska et al. 2013). Aqueous *Oenotheraparadoxa* defatted seed extract decreased UVA-induced release of lactate dehydrogenase (LDH) into the culture medium, the ROS production and lipid oxidation compared to the control cells (incubated without the extract), indicating that the extract of *Oenotheraparadoxa* is useful for the prevention of UVA skin damage (Jaszewska et al. 2013).

In vivo and *in vitro* studies that evaluated the health benefit properties of polyphenols from plants, fruits and herbs have been reported (Peschel et al. 2007; Soto et al. 2008; Felice et al. 2012). The majority of studies conducted on phenolics in oilseed extracts determined the total phenolics, the total flavonoids as well as the antioxidative activities of crude or semi-purified oilseed cakes extracts. While these studies suggested the potential of the material as a source of bioactive compounds, more studies on the composition of these extracts and clinical studies on the therapeutic effects of polyphenols from the oilseed cakes are needed to support any prospective use of the by-products from oil processing.

Table 2 Health benefits of polyphenols from oilseed cakes by *in vitro* and *in vivo* studies

Sources	Compounds	Types of test	Results	References
Canola	Phenolic acids	(i) $ABTS^{\cdot+}$ radicals assay (ii) β-Carotene–linoleic acid (linoleate) assay (iii) $DPPH^{\cdot}$ assay (iv) Reducing power assay	Highest antioxidant capacities of extract were obtained with subcritical water extraction at 160 °C on per gram of meal basis. Ethanolic extracts (95 % v/v) exhibited the highest total phenolics contents and antioxidant capacities on per gram of extract basis	Hassas-Roudsari et al. (2009)
Borage (*Borage officinalis* L)	Phenolic acids	(i) $DPPH^{\cdot}$ scavenging assay	(i) EC_{50} for the $DPPH^{\cdot}$ scavenging activity achieved by 1200 mg/L and 3900 mg/L of enzymatic methanolic extract and methanolic extract, respectively (ii) Rosmarinic acid, syringic acid and sinapic acid are the major phenolic compounds present in the ethanolic extract of borage meal	Soto et al. (2008)
Grape	Polyphenols	(i) Endothelial progenitor cells (EPC) viability, migration. Adhesion and reactive oxygen species (ROS) production assays	(i) Grape components (skin or seed) and red wine increased EPC viability, adhesion and migration, and prevented the high *D*-glucose effect ($P<0.01$). ROS production induced by HG was significantly reduced only by grape seed extract and RW ($P<0.01$). $N^{+}(60)$–Ch acted as an effective enhancer of polyphenol permeability across the excised rat intestine	Felice et al. (2012)
	Polyphenols	(i) *In vitro* cholesterol uptake assay (ii) Cell proliferation assay and apoptosis assay (iii) 5-Lipoxygenase activity	(i) Incubation of HT29, Caco2, HepG2, or HuTu80 cells in a medium containing $[^3H]$cholesterol in the presence of a grape seed extract (EC_{50} 83 µg/mL) or red wine polyphenolic compounds (EC_{50} 60 µg/mL) inhibited $[^3H]$cholesterol uptake by up to 66% (ii) Red wine polyphenolic compound and grape seed extract dose inhibited HT29 colon adenocarcinoma cell proliferation, which was accompanied by an increase in apoptosis (iii) Red wine polyphenol and grape seed extracts inhibited 5-LOX activity with the IC_{50} values being 35 and 13 µg/mL, respectively	Leifert and Abeywardena (2008)
	Low-molecular procyanidin	(i) Antihypertensive activity by oral feeding to spontaneously hypertensive rats (SHR)	(i) Grape seed procyanidin extract significantly decreased systolic and diastolic blood pressure of SHR dose-dependently up to 375 mg/kg (maximum decrease 6 h post administration) and it caused hypotensive effect in Wistar–Kyoto rats.	Quiñones et al. (2013)

Table 2 (continued)

Sources	Compounds	Types of test	Results	References
Evening primrose (*Oenothera-biennis*)	Polyphenols	(i) Activity of released lactate dehydrogenase (LDH) from human skin fibroblast cells (NHDFs) (ii) Quantification of intracellular reactive oxygen species (ROS) (iii) Lipid peroxidation assay	(i) Extract of defatted seeds of *O. paradoxa* causes in irradiated NHDFs a concentration-dependent decrease in release of lactate dehydrogenase (LDH) into the culture medium as compared to the control cells (incubated without the extract) (ii) After 24 h treatment, all the tested concentrations caused a statistically significant (*P* 0.05) decrease in ROS production, which amounted to about 1.8-, 2.7- and 2.9-fold, (in relation to the control) for 0.1, 1 and 10 µg/ml, respectively (iv) There was also about a 1.6-fold decrease in UVA-induced lipid peroxides production for the highest concentration (10 µg/mL) of extract	Jaszewska et al. (2013)
Evening primrose (*Oenothera-biennis*), sesame, woad (*Isatistinctoria*) and burdock (*Arctium-lappa*)	Phenolic acids	(i) Total phenolics (ii) DPPH$^{\cdot}$ assay (iii) Superoxide anion scavenging activity (iv) Inhibition of linoleic acid oxidation	(i) Evening primrose had the highest total phenolics (696.4±29.0 mg GAE g^{-1} dry extract), followed by burdock (268.67±21.07 mg GAE g^{-1} dry extract), woad (106.10±2.10 mg GAE g^{-1} dry extract) and sesame (65.02±14.44 mg GAE g^{-1} dry extract) (ii) At the concentration of 10 µg mL^{-1}, evening primrose had the highest DPPH$^{\cdot}$ scavenging activity, 91.31±0.94 % compared to other extracts (iii) At the concentration of 20 µg mL^{-1}, evening primrose had the highest superoxide anion scavenging activity, 40.13±2.57 % iv) At the concentration of 0.4 mg g^{-1}, evening primrose exhibited 191.92±12.93 % inhibition of linoleic acid oxidation	Peschel et al. (2007)
Evening primrose (*Oenother-aparadoxa*)	Polyphenols	(i) Hypocholesterolemic effect by oral feeding to male Wistar rats	(i) Dietary evening primrose seed cake extract significantly decreased plasma total cholesterol (TC) and low-density lipoprotein cholesterol (LDL-C) but did not change the high-density lipoprotein cholesterol (HDL-C) either in rats fed cholesterol-free or enriched-in-cholesterol diets	Bałasińska (1998)

Table 2 (continued)

Sources	Compounds	Types of test	Results	References
Seed shells of Japanese horse chestnut (*Aesculus turbinata* Blume)	Highly polymeric proanthocyanidins	(i) Inhibitory activity on the elevation of blood glucose levels after oral administration of starch to rats (ii) Antiobesity effect by oral feeding to rats	(i) The extracts suppressed effectively the elevation of blood glucose from oral starch, but not from oral glucose, suggesting the preferential inhibition of the digestive enzymes of carbohydrates (ii) Antiobesity effects became more evident after 9 weeks as determined by the attenuation of the elevation in body weight, the mass of peritoneal adipose tissues, and the plasma levels of total cholesterol and leptin The extracts normalized the increased size of hepatocytes and the generation of steatosis with micro- and macrovesicles in liver	Kimura et al. (2011)
Mango seed kernel (*Mangiferaindica* L.)	Phenolic acids	(i) Fe^{2+} chelating activity (ii)$DPPH^{\cdot}$ radical scavenging activity (iii) ABTS radical cation-scavenging activity (iv)Tyrosinase inhibition activity (v) Acute skin irritation	(i) 50–80 µg/mL of extract to achieve 50 % of Fe^{2+} chelating activity (ii) 0.56–14.0 µg/mL of extract to achieve 50 % of Fe^{2+} chelating activity (iii) 0.44–1.03 mmol of trolox/g ABTS radical cation-scavenging activity (iv) The highest i tyrosine inhibition activity found in extract with refluxing in acidified ethanol (v) No acute skin irritation effect	Maisuthisakul and Gordon (2009)

ABTS 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), *DPPH* 2,2-diphenyl-1-picrylhydrazyl, *UV* ultraviolet

Protein

Many studies reported the isolation of protein from oilseed cakes using an alkaline extraction step followed by protein precipitation at the isoelectric point of a particular protein (Table 1; Wani et al. 2008; Peričin et al. 2009; Gutiérrez et al. 2010). Protein isolates from different oilseed cakes can exhibit differing functional properties such as emulsification, creaming stability, water- and oil-holding capacities; thus, they offer wide range of applications in the food industry. The protein quality of some protein isolates from oilseed cakes such as hemp, canola, sunflower and palm kernel seed protein isolates are comparable to that found in soy protein isolates (Tang et al. 2006; Wang et al. 2008; Tan et al. 2011; Chee and Ayob 2013); therefore, it can be used as an alternative for soy protein. The modification of the functional properties of protein isolates in food products was reviewed by Moure et al. (2006). Oilseed protein isolates have limited bioactive properties apart from the amino acid content and composition (Table 3 and 4). In order to improve the biological functions of protein from seed cakes, hydrolysis (chemical or enzymatic hydrolysis) of protein isolates is required to produce protein hydrolysates (Vaštag et al. 2011; Girgih et al. 2013). The protein hydrolysates exhibit angiotensin-converting enzyme (ACE) inhibitory activity and higher antioxidant activity compared to protein isolates (Marczak et al. 2003; Girgih et al. 2013), which increase their application as functional ingredients in health products.

Utilization of Oilseed Cakes for Protein Sources

The world population is increasing every year and the demand for food supply and protein is equivalently increasing. The cost of food production is increasing due to increased prices of raw material, energy, competition for land use, as well as cost associated with addressing environmental pollutions and soil deterioration. Sustainable methods for producing alternative food sources to feed the world by utilising reusable and renewable sources such as agrowastes and oilseed cakes for food production are very promising to be part of strategies for food security. Oilseed cakes can be used as a good source of protein for human nutrition (Table 4). Edible plant proteins should be non-toxic, easily digested, nutritionally sufficient and functionally useful, and this can be achieved by processing oilseed cakes (Table 3). Protein isolates can be obtained using traditional alkali aqueous extraction, followed by protein precipitation at the isoelectric point using pH adjustment of acidification (Gutiérrez et al. 2010; Tan et al. 2011). However, the use of enzymes to extract protein isolates from palm kernel cake offers the potential of higher protein yield compared to alkali–acid extraction (Chee and Ayob 2013). Isolation of protein from oilseed cakes is not expensive, and hence it can be considered as a sustainable approach for protein production to meet the global food demand.

Removal of polyphenols before protein extraction is recommended for oilseed cakes, such as canola and sunflower, which have high polyphenol content (Mansour et al. 1993; Xu and Diosady 2002; Salgado et al. 2012) because polyphenols will

Table 3 Utilization of oilseed cakes for protein sources

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Akebiatrifoliata var. *australis* seed protein isolate (API)	Alkali extraction at pH 10 followed by isoelectric precipitation at pH 4.5	The solubility of API, albumin and glutelin fraction was the lowest at pH 4.0–5.0. The high surface hydrophobicity indices of these three proteins were observed at pH 7.0, while the excellent emulsifying properties were displayed at pH 9.0. Circular dichroism measurements indicated that API, albumin and glutelin were rich in β-strand and random coil structures	Albumin (51.65 %) and glutelin (46.40 %) were the predominant protein fractions. The major amino acids were glutamic acid and aspartic acid, while the contents of sulphur-containing amino acids and threonine were very low	Du et al. 2012
Gingerbread plum (*Neocarya macrophylla*) protein isolate	Defatted flour (150 g) was mixed with 1.5 L of water (pH 10 with 0.1 N NaOH), solubilized protein was precipitated at pH 4.5	Foaming capacity (160 ml/100 mL), emulsifying capacity (28 %), water-holding capacity (0.94 g/g), oil-binding capacity (1.23 g/g)	Higher sodium, potassium, calcium, iron and phosphorus in protein isolate can be used as natural source of calcium supplementation for pregnant and lactating women, children and the elderly people. Compared to soy protein isolate, gingerbread plum protein isolate had higher levels of arginine, valine, tryptophan, glutamic acid, cysteine-s, serine and proline, similar contents of phenylalanine, leucine, glycine, alanine, and tyrosine, lower contents of histidine, threonine, methionine, isoleucine, lysine and aspartic acid. Gingerbread plum protein isolates can be used can be used as good sources of protein for feeding infants and children	Amza et al. (2011)

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Palm kernel protein isolate	Trypsin (1.36 g/100) reacted on palm kernel cake (PKC) slurry (1.1 g/100 mL) at 50 °C, pH 9.5	Palm kernel protein isolate had better solubility (30.12 ± 97.79 vs. 9.15 ± 69.78 g/100 g) emulsifying activity (143.25 vs. 32.57 m^2/g); but lower emulsifying stability (37.83 vs. 43.08 %), foaming capacity (22.5 vs. 100.0 ml/100 ml) and foam stability (3.70 vs. 19.20 ml) than the soy protein isolate	The essential amino acids of palm kernel protein isolates except lysine met the suggested requirements of FAO/WHO for 2–5 years old infants. The *in vitro* digestibility, essential amino acids/total amino acids (E/T) value, biological value and computed-protein efficiency ratio (C-PER) value for palm kernel protein isolate were significantly ($P < 0.05$) higher than that of soy protein isolate	Chee and Ayob (2013)
Flaxseed protein isolate	Flaxseed cake (0.152 g/mL) in distilled water as solvent, mixed with ultrazyme (6.9 mL/L), alcalase (3.1 mL/L) and viscozyme (10 mL/L), temperature 50 °C, time 1.5 h, agitation speed 200 rpm resulted in 152 g of protein yield from 1 kg of seed cake	N/A	N/A	Ribeiro et al. 2013
Canola protein isolate	Alkali extraction (pH 10–12) followed by acidification at isoelectric point (pH 3.5–4)	Emulsifying activity, foaming and gelling properties were different according to process and cultivar	Canola proteins have better amino acid profile than soybean protein isolates that meet the amino acid requirements by FAO/WHO/UNU for both adults and children	Tan et al. (2011); Tzeng et al. (1990)

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Canola protein isolates	Defatted canola seed cakes (10 g) was mixed with 180 g distilled water (pH 12), followed with acidification at pH 4.5 to 5.5, the precipitated proteins were washed with distilled water and separation of proteins was done by centrifugation (repeated three times). The supernatants from the washing were ultrafiltered followed by diafiltered and dried	N/A	N/A	Ghodsvali et al. (2005)
Canola protein isolate	Alkali extraction at pH 12, followed by expanded bed adsorption technologies to separate Napin and Cruciferin, the two protein isolates were ultrafiltered, diafiltered and freeze-dried.	Cruciferin at pH 7 showed 200 % water-holding capacity. Both protein isolates had more than 500 % oil-holding capacities. Both protein isolates had stable foam capacities at pH 7. Cruciferin at pH 7 had the highest gel strength than pH 4	N/A	Kristjansson et al. (2013)

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Hemp proteins isolate (HPI). 11S- and 7S-rich hemp protein isolates (HPI-11S and HPI-7S).	Defatted hempseed cake (100 g) mixed with 1.5 L deionized water (pH 10), acidification at pH 5.0. The precipitated protein was washed with deionized water, dispersed in deionized water with adjustment pH 7.0, dialysed and freeze-dried. Preparation of HPI-11S and HPI-7S was extracted at pH 10, followed by addition of 0.98 g $NaHSO_3$/L, adjustment pH 6.4 to precipitate HPI-11S, then adjustment pH 4.6 to precipitate HPI-7S		HPI, HPI-11S had more than 90 % protein content on wet basic while HPI-7S had 87 % protein content. All HPI are comparable to soy protein isolates which can be used as protein source and alternative for human nutrition. Higher sulphur-containing amino acid (methionine and cysteine) were found in all HPI compared to soy protein isolate. The proportion of essential amino acids to the total amino acids (E/T) for HPI was significantly higher than that of soy protein isolate, suggesting that the HPI have more nutritional amino acid patterns than that of SPI. *In vitro* digestibility test by pepsin and trypsin showed that HPI is a good source of much more digestible protein as compared to soy protein isolate, which is highly suitable for the human consumption	Wang et al. (2008)
Hemp protein isolate	Alkali extraction at pH 10 and precipitation at pH 5.0	Compared to soy protein isolate, HPI had lower the emulsifying activity index, emulsion stability index, and water-holding capacity but similar oil-holding capacity	The main protein component is edestine. The essential amino acids in HPI (except lysine and sulphur-containing amino acids) are sufficient for the FAO/WHO suggested requirements for 2–5-year-old children	Tang et al. 2006

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Pumpkin seed protein isolate	Alkali extraction at pH 10 and precipitation at pH 5.0	N/A	The administration of pumpkin seed protein isolate after carbon tetrachloride (CCl_4) intoxication of low protein fed rats resulted in significantly reduced activity levels of all four enzymes (lactate dehydrogenase, alanine transaminase, aspartate transaminase and alkaline phosphatase). Pumpkin seed protein isolate administration was effective in alleviating the detrimental effects linked with protein malnutrition	Nkosi et al. (2005)
Low phenolics content sunflower protein isolate	Extraction of phenolics at pH 5 in 1 g/L Na_2SO_3 solution, followed by alkali extraction at pH 9, isoelectric precipitation at pH 4.5	Surface hydrophobicity of sunflower protein isolate was higher than the sunflower seed cakes, indicating that the protein isolate can be used as foaming and emulsifying agents	Phenolics were reduced by 33.33 % from defatted sunflower seed cake. Sunflower protein isolate exhibited high protein digestibility *in vitro*, even in the presence of phenolic compounds, and maintained high protein solubility for at least 6 months of storage	Salgado et al. (2012)

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Canola and flax protein isolates	Isoelectric-precipitated canola protein isolate was extracted in 1 M NaOH and precipitated at pH 4. Salt-precipitated canola protein isolate was prepared 0.05 M Tris–HCl buffer (pH 7.00) containing 0.1 M NaCl at 1:10 ratio (w/v) and stirred at 500 rpm for 2 h at room temperature. The suspension was centrifuged, followed by dialysis (6–8 kDa cut off) against water at 4 °C for 72 h, precipitated salt soluble proteins were collected by centrifugation, freeze-dried. Isoelectric-precipitated flax protein isolate was extracted at pH 8.50 using 1.0 M NaOH, followed by precipitation at pH 3.8 Salt-precipitated flax protein isolate was extracted in 50 mM Na3PO4 buffer (pH 8.00) containing 0.8 M NaCl at 1:10 ratio (w/v), centrifuged, supernatant was collected and dialysed (6–8 kDa cut off) and freeze-dried	Salt-precipitated protein isolates had higher protein solubility than isoelectric precipitated protein isolates. All protein isolates had comparable emulsifying capacity to whey protein isolate, but lower stability index. Both flax protein isolates had higher emulsifying activity index than canola protein isolates. Salt-precipitated canola protein isolate had higher emulsifying activity index than isolectric-precipitated canola protein. Isoelectric-precipitated canola protein isolate and both flax protein isolate had comparable creaming stability to whey protein isolate. However, salt-precipitated canola protein isolate led to rapid separation of an aqueous layer in emulsion	N/A	Karaca et al. (2011)

Table 3 (continued)

Oilseed protein isolates	Processing condition	Functional properties in food	Health and bioactive properties	References
Canola protein isolate fraction, Napins	Extraction by different pH 2, followed by centrifugation and napins precipitation and purification by ammonium sulphate	N/A	Napins possessed significant anti-*Fusarium* activity ($IC_{50} = 70$ μM) and a compact secondary structure rich in α-helix, which may explain this bioactivity	Nioi et al. (2012)

FAO Food and Agricultural Organization, *WHO* World Health Organization, *UNU* United Nations University

Table 4 Amino acid composition (g/100 g protein) of oilseed protein isolates

Amino acids	HPI			TRPI	RPI	CPI		FPI		SFPI	SAFFPI	PKPI	FAO/WHO suggested daily requirements		
	[a]	[c]	[f]	[b]	[b]	[c]	[d, e]	[a]	[d]	[a]	[a]	[g]	2–5 years	10–12 years	Adult
Isoleucine	3.99	3.12	4.2	0.23	0.26	1.44	5.18	0.27	2.41	0.25	0.26	2.16	2.8	2.8	1.3
Leucine	6.63	4.9	6.9	0.46	0.47	2.07	9.26	0.38	4.26	0.39	0.43	4.11	6.6	4.4	1.9
Lysine	4.16	1.97	4.33	0.33	0.31	1.16	5.62	0.19	2.53	0.15	0.15	2.16	5.8	4.4	1.6
Methionine	1.39	1.63	1.5	0.15	0.13	0.43	2.6	0.13	0.75	0.13	0.11	1.31	2.5	2.2	1.7
Cysteine	0.17	0.99	0.17	0.21	0.26	0.41	3.56	0.16	0.89	0.1	0.12	0.57			
Tyrosine	3.67	2.71	3.8	0.17	0.17	0.85	3.07	0.18	1.81	0.17	0.19	2.38	6.3	2.2	1.9
Phenylalanine	4.57	3.86	4.96	0.18	0.25	1.69	5.13	0.29	2.61	0.31	0.31	2.53			
Threonine	4.57	3.36	4.8	0.22	0.23	1.49	5.3	0.21	3.65	0.19	0.19	2.08	3.4	2.8	0.9
Valine	4.98	3.9	5.2	0.3	0.33	1.85	5.85	0.34	3.08	0.33	0.33	3.19	3.5	2.5	0.3
Histidine	2.81	2.23	2.9	0.18	0.15	0.48	3.17	0.12	1.52	0.14	0.13	0.82	1.9	1.9	1.6
Tryptophan	–	–	–	0.09	0.09	–	–	0.09	–	0.08	0.08	0.04	1.1	0.9	0.5
Asparagine	9.41	6.55	9.8	–	–	3.13	7.24	–	3.8	–	–	5.29	–	–	–
Glutamine	16.14	11.46	16.8	–	–	6.26	23.21	–	7.12	–	–	13.86	–	–	–
Serine	5.18	3.9	5.4	–	–	1.65	4.4	–	2.43	–	–	2.68	–	–	–
Glycine	3.99	3.19	4.2	–	–	1.95	4.32	–	2.76	–	–	3.32	–	–	–
Arginine	9.91	10.64	10.3	0.41	0.43	3.29	7.66	0.64	3.11	0.6	0.66	8.65	–	–	–

Table 4 (continued)

Amino acids	HPI			TRPI	RPI	CPI		FPI		SFPI	SAFFPI	PKPI	FAO/WHO suggested daily requirements		
	a	c	f	b	b	c	d, e	a	d	a	a	g	2–5 years	10–12 years	Adult
Alanine	4.50	2.73	4.7	–	–	1.49	4.15	–	2.31	–	–	2.93	–	–	–
Proline	4.53	2.66	4.7	–	–	1.29	6.06	–	2.89	–	–	2.04	–	–	–

HPI Hemp, *TRPI* turnip rape, *RPI* rape, *CPI* canola, *FPI* flax, *SFPI* sunflower, *SAFFPI* safflower, *PKPI* palm kernel protein isolates *FAO* Food and Agricultural Organization, *WHO* World Health Organization. Essential amino acids are in italic fonts.

[a] Wang et al. (2008)

[b] Sosulski and Sarwar (1973)

[c] Teh et al. (2014)

[d] Tan et al. (2011)

[e] Tzeng et al. (1990))

[f] Tang et al. (2006)

[g] Chee and Ayob (2013)

exert a dark colour on the protein isolates and affect the functional properties, e.g. emulsifying, foaming, surface hydrophobicity and water-holding activities, of protein isolates. Several interventions can be employed to remove the polyphenols. Salgado et al. (2012) extracted polyphenols from sunflower seed cake using Na_2SO_3 solution at pH 5.0 before extracting the protein at pH 9.0 and isoelectric precipitation at pH 4.5. The resultant protein isolate had better functional characteristics such as lighter colour, higher surface hydrophobicity, protein digestibility and solubility compared to the protein isolate produced using a similar method but without the removal of polyphenols (Table 3). An alternative way to remove low polyphenols from sunflower protein isolates is to use resin (styrenedivinylbenzene copolymer Amberlite™ XAD 16HP), which reduced polyphenols by 85.7 % and increased the colour lightness by 26 % (Pickardt et al. 2011). In addition, the use of NaCl in a range of 1.3–2.0 mol/L suppressed protein–polyphenol interactions and enhanced protein extractability. The resulted sunflower protein isolate had moderate emulsifying activity, 209 mL/g compared to sodium caseinate (1100 mL/g), excellent foaming properties (1070 mL/g) as compared to egg white (~1600 mL/g) and better foam stability, 94 % compared to egg white (~80 %; Pickardt et al. 2011). The use of membrane filtration technology to separate polyphenols from protein has been reported (Xu and Diosady 2002, Karayannidou et al. 2007). Ultrafiltration resulted in high protein content (> 85 %), low phenolic acids (~ 200 mg/100 g) and produced canola protein isolates free of condensed tannins (Xu and Diosady 2002). In addition, lighter colour and higher overall sensory acceptability of canola protein isolates resulted from the use of ultrafiltration.

Another protein extraction process utilizes the use of salts. Karaca et al. (2011) isolated canola and flax protein isolates by salt precipitation (Table 3). Salt-precipitated protein isolates had higher protein solubility than isoelectric-precipitated protein isolates. This supports earlier publications that reported high solubility of calcium-precipitated (1 M $CaCl_2$, ~78.8 %) and ultrafiltration-obtained (~90 %) canola protein isolates compared to the acid-precipitated canola protein isolate at pH 7.00 (< 6 %) (Aluko and McIntosh 2001, Yoshie-Stark et al. 2008). The lower solubility of isoelectric-precipitated protein isolates is due to protein denaturation during the acid precipitation step, interactions between protein and nonprotein components and the formation of insoluble phytic acid–protein complexes. In fact, the micellization (extraction with 0.5 M NaCl solution followed by ultrafiltration and isoelectric precipitation) reduced phytic acid and pentosans that interfere with the solubility of flax protein isolate (Krause et al. 2002). The emulsifying capacity for salt-precipitated (528.9 g oil/g protein) and ultrafiltration-obtained canola protein isolates (693 mL oil/g protein) was greater than the isoelectric-precipitated canola protein isolate (502.2 g oil/g protein) (Yoshie-Stark et al. 2008; Karaca et al. 2011). The emulsion activity index (EAI) of the calcium-precipitated canola protein isolate (81.9 m^2/g) was significantly higher than that found with the isoelectric-precipitated canola protein isolate (25.1 m^2/g) (Aluko and McIntosh 2001), and higher EAI values for flax protein isolate were produced by micellization compared to isoelectric-precipitated protein isolate (Krause et al. 2002).

Oilseed protein isolates have several functional properties of great importance to the food industry, e.g. emulsifying, foaming, surface hydrophobicity and water-holding activities that can modify the texture of a food system. Several studies had evaluated the functional properties of the protein isolate isolated from oilseed cakes (Table 3) and this is an important step in determining the optimal use of the protein extract. Hemp protein isolates have lower EAI, emulsion stability index and water-holding capacity but have similar oil-holding capacity compared to soy protein isolate (Wang et al. 2008). However, hemp protein isolates have better protein film-forming capacity compared to soy protein because the hemp protein isolate interacts with glycerol leading to a protein film with high surface hydrophobicity and tensile strength and low solubility (Tang et al. 2009c). The gingerbread plum seed protein isolate exhibited high emulsifying capacity and water-holding capacity, oil-binding capacity and bulk density than the commercial soy protein isolate (Amza et al. 2011). Canola and flax protein isolates have higher emulsifying activity as they have slightly more effective interfacial tension reduction (~43.1 mN/m) than whey protein isolate (~44.5 mN/m) (Karaca et al. 2011) but these (canola, flax and whey proteins) have comparable creaming stability.

In terms of the nutrition of protein isolates from oilseed cakes, the amino acid profiles are better or comparable to soy protein isolate (Tables 3 and 4) and can have several advantages in the nutrition of infants and elderly diets. Gingerbread plum seed protein isolate had higher levels of arginine, valine, tryptophan, glutamic acid, cysteine, serine and proline than the soy protein isolate, thus offering a better replacement in infant formula (Amza et al. 2011). The high calcium content of gingerbread plum seed protein isolate enables its application as a natural source of calcium supplementation for pregnant and lactating women, children and elderly people. Palm kernel protein isolate have all essential amino acids, with the exception of lysine, at concentrations that met the suggested requirements of Food and Agricultural Organization/World Health Organization (FAO/WHO) for 2–5 years old infants. In fact, canola, hemp, flax protein isolates offer a favourable amino acid profile to meet the amino acid requirements by FAO/WHO/United Nations University (UNU) for both adults and children (Tang et al. 2006; Tan et al. 2011; Teh et al. 2014) once fortified with lysine. Alkali extraction of hemp protein isolate, acid extraction of hemp, flax and canola protein isolates were found to have higher concentration of methionine than soy protein isolate (Teh et al. 2014). Similarly, higher sulphur-containing amino acid (methionine and cysteine) were found in hemp protein isolates compared to soy protein isolate (Wang et al. 2008), which can be advantageous for use in infant formula. Canola seed protein isolate is rich in glutamic acid, aspartic acid, leucine and proline as well as contains considerable amounts of the essential amino acids phenylalanine, isoleucine and tryptophan (Shahidi 1990). The pumpkin seed protein isolate was shown to be nutritionally sound *in vivo*. Feeding pumpkin seed protein isolate to rats treated with carbon tetrachloride (CCl_4) and low protein reduced levels of LDH, alanine transaminase, aspartate transaminase and alkaline phosphatase that are associated with protein malnutrition (Nkosi et al. 2005).

Bioactive Protein Hydrolysates from Bioconversion of Oilseed Protein Isolates

The enzymatic hydrolysis is a more desirable method in modifying functional properties of plant protein compared to physical and chemical treatments due to required milder process conditions, handy controlling reaction and minimal formation of by-products (Mannheim and Cheryan 1992). Proteases such as pepsin, trypsin, alcalase, flavourzyme as well as other proteases from bacteria, fungus, vegetables and fruits can be used to hydrolyse oilseed protein isolates to produce bioactive peptides. Enzymatic hydrolysis increases the protein solubility due to liberation of smaller peptide from the breakage of peptide bonds. To date, enzymatic hydrolysis has been used in modifying functional properties from oilseed protein isolates such as hempseed (Tang et al. 2009b; Girgih et al. 2013), rapeseed (Marczak et al. 2006) and pumpkin seed (Vaštag et al. 2011) protein isolates.

ACE Inhibitory Activity of Protein Hydrolysates

There are several *in vivo* studies that used a rat model system in evaluating the bioactive properties of oilseed protein hydrolysates (Table 4). Subtilisin-digested canola seed protein hydrolysate was injected into the octadecylsilica (ODS) column to obtain four bioactive peptides (IY, RIY, VW and VWIS) that possessed ACE inhibitory activity (Marczak et al. 2003). All the peptides lowered the blood pressure of spontaneously hypertensive rats (SHR). Oral administration of fractions VW and VWIS at the dosage of 25 µM/kg (7.5 mg/kg for VW and 12.5 mg/kg for VWIS) to SHR exerted a significant hypotensive effect after 2 and 4 h of administration, respectively (Marczak et al. 2003). Recent *in vivo* studies confirmed the blood-pressure-lowering activity of canola protein hydrolysates (He et al. 2013; Alashi et al. 2014b). Alcalase- and pepsin + pancreatin (PP)-digested canola protein hydrolysates decreased the systolic blood pressure by about 24 and 21 mmHg, respectively, after 8 and 24 h of oral feeding to SHR (He et al. 2013). Pancreatin-digested canola protein hydrolysate decreased the systolic blood pressure by 7.4, 7.7 and 15.1 mmHg after 2, 4 and 6 h of oral feeding, respectively (Alashi et al. 2014b). Pepsin hydrolysates decreased the systolic blood pressure by 11.3 and 23.7 mmHg after 2 and 4 h of oral feeding, respectively (Alashi et al. 2014b). Marczak et al (2006) showed that the canola seed hydrolysate peptide arginine–isoleucine–tyrosine (RIY) decreased food intake and gastric emptying after oral administration to rats at a dose of 150 mg/kg by stimulating cholecystokinin (CCK) release. The authors proposed the application of this peptide in weight loss products.

Cationic fraction of flax protein isolate generated by alcalase hydrolysis (Udenigwe and Aluko 2012) was found to decrease the systolic blood pressure in SHR at a dose of 200 mg/kg body weight. The most recent studies showed that the potassium chloride (KCl) recovery 50-kDa peptides (KCI-F1) and the cationic peptide fraction of flax decreased the systolic blood pressure of SHR after 2-h oral feeding with a maximum systolic blood pressure drop was after 4 h (27 mmHg) of administration (Doyen et al. 2014). The flaxseed bioactive peptide fraction was obtained using enzymatic hydrolysis of flax protein isolate by trypsin followed by pronase, and fractionated by electrodialysis with two ultrafiltration membranes (20 and 50 kDa) stacked in the system for the recovery of two specific cationic peptide fractions (KCI-F1 and KCI-F2) by KCl solution (2 g/L), where KCI-F2 had lower molecular weight peptides (20 kDa) than KCI-F1, 50 kDa (Doyen et al. 2014). Both KCI fractions had high concentration of histidine, lysine and arginine. In addition, the KCI-F2 flax peptide fraction possessed *in vitro* antidiabetic activity where it increased glucose uptake in myoblasts that were derived from neonatal rat thigh skeletal muscle (Doyen et al. 2014).

An ACE inhibitory assay was used to determine the *in vitro* blood-pressure-lowering activity of peptides. Basically, natural ACE inhibitor such as bioactive peptides from plant proteins inhibits the ACE (EC 3.4.15.1) to the potent vasoconstrictor angiotensin II that inactivates the potent vasodilator bradykinin (Skeggs et al. 1956). Inhibitors compete with angiotensin I to bind the ACE active site, leading to the function failure of ACE in converting angiotensin I to angiotensin II (Skeggs et al. 1956). Direct inhibition of renin activity offers a better control of hypertension than ACE inhibition since it prevents the production of angiotensin I, which could also be converted to a substantial amount of angiotensin II in some organs via an ACE-independent pathway catalysed by chymase (Udenigwe and Aluko. 2012). However, renin inhibition does not prevent ACE-catalysed bradykinin degradation (Segall et al. 2007; Staessen et al. 2006). Hence, effective blood-pressure-lowering bioactive peptides should exert pleiotropic effects in the inhibition of ACE and renin activities in order to achieve a therapeutic effect.

Alcalase-hydrolysed pumpkin seed protein was found to have 71.05 ± 7.5 % ACE inhibitory activity ($IC_{50} = 0.422$ mg/ml; Vaštag et al. 2011). Another study found that a < 1-kDa fraction of proteinase-K-hydrolysed canola protein hydrolysate had the highest ACE inhibitory activity (86.94 ± 1.14 %) while alcalase-hydrolysed canola protein hydrolysate (1 mg/mL) had the highest (82 %) renin inhibitory activity (He et al. 2013). The latest study reported that alcalase- and chymotrypsin-hydrolysed canola protein hydrolysates had 90 and 88.8 % of ACE inhibitory activity, respectively (Alashi et al. 2014b). The authors found that the < 1-kDa fraction of membrane fractionation of trypsin-hydrolysed canola protein hydrolysate improved the ACE inhibitory activity from the unfractionated trypsin hydrolysate. Furthermore, pancreatin-hydrolysed canola protein hydrolysate had the highest renin inhibition activity (63.2 %), in which the larger fraction (5–10 kDa) of pancreatin hydrolysate exhibited higher renin inhibitory activity than the unfractionated pancreatin hydrolysate (Alashi et al. 2014b).

Antioxidant Activity of Protein Hydrolysates

Several *in vitro* studies were carried out to determine the antioxidative properties of protein hydrolysates. As shown in Table 5, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) $(ABTS)^{+\bullet}$ radical scavenging activity (RSA), 2,2-diphenyl-1-picrylhydrazyl $(DPPH)^{\bullet}$ scavenging assay, chelation of metal ions, ferric reducing antioxidant power (FRAP), hydroxyl radical scavenging, inhibition of linoleic acid oxidation and Fe^{2+}chelating ability were frequently used to determine the antioxidant activity of extracts. These various assays have different modes of actions and provide different information (Thaipong et al. 2006; Nenadis and Tsimidou 2010; Martysiak-Żurowska and Wenta 2012). The antioxidant activity of canola protein hydrolysates has been reported in several studies (He et al. 2013; Alashi et al. 2014a). According to the previous study (He et al. 2013), the alcalase-hydrolysed fraction (< 1 kDa) had a higher oxygen radical absorbance capacity (ORAC) value (2493.71 ± 134.95 μM TE/g protein) compared to other high molecular weight peptide fractions. Alashi et al. (2014a) reported that pancreatin < 1 kDa permeate fraction (EC_{50} 10.1 μg/mL) had the highest $ABTS^{+\bullet}$radical scavenging activity while alcalase and its derived fractions had the highest DPPH radical scavenging activity (EC_{50} 0.5–0.9 μg/mL). In addition, pepsin hydrolysate had 82 % inhibition of linoleic acid oxidation, while the specific pepsin-digested (< 1 kDa) fraction had the highest superoxide radical scavenging activity (SRSA) value of 51.3 % at a concentration of 1 mg/mL (Alashi et al. 2014a). The authors found that alcalase-digested (< 1 kDa, and 1–3 kDa), chymotrypsin-digested (< 1 kDa) and pepsin-digested (3–5 kDa) fractions possessed the highest ORAC values in the range of 2000–2200 μM TE/g.

It was reported that alcalase- and flavourzyme-hydrolysed pumpkin seed protein possessed high antioxidant activity (Vaštag et al. 2011). Higher $ABTS^{+\bullet}$radical scavenging activity and reducing power were found in alcalase-hydrolysed pumpkin seed protein hydrolysate compared to flavourzyme hydrolysates. Alcalase-hydrolysed buckwheat protein had 75 % of $DPPH^{\cdot}$ inhibition (IC_{50} 0.56–0.94 mg/mL), 0.77–1.24 units of the reducing power and inhibition of linoleic acid oxidation activity at concentrations of 1.0, 5.0 and 1.2 mg/mL, respectively (Tang et al. 2009a). Protamex-digested hemp protein hydrolysate had the highest DPPH radical scavenging activity (IC_{50} 2.8 mg/mL) after 2 h of hydrolysis time, while neutrase-digested hemp protein hydrolysate had the highest DPPH radical scavenging activity (IC_{50} 2.3 mg/mL) after 4-h hydrolysis time (Tang et al. 2009b). Trypsin- and alcalase-digested hemp protein hydrolysates had the highest reducing power after 2-h hydrolysis time (Tang et al. 2009b). Neutrase-, protomex- and trypsin-hydrolysed hemp protein hydrolysates were found to have high Fe^{2+} chelating ability (IC_{50} 1.6–1.7 mg/mL) (Tang et al. 2009b). As shown above, different proteases resulted in various degrees of antioxidant activities in different assays. Therefore, the selection of protease and hydrolysis conditions can have detrimental effects on the activity of the generated peptides.

Inhibition of Endothelial Isoform of Nitric Oxide Synthases

Nitric oxide (NO) is synthesized endogenously by the endothelial isoform of nitric oxide synthases (eNOS). The compound is responsible for vascular smooth muscle cell relaxation and vasodilation, regulation of blood pressure and inhibition of platelet aggregation (Bryk and Wolff 1999; Omoni and Aluko 2006). Underproduction of endothelial NO, or an impairment of eNOS activity, is implicated in the pathophysiology of vascular diseases (Albrecht et al. 2003; Omoni and Aluko 2006).The activity of eNOS is an important factor in the production of tumour necrosis factor-α (TNFα) by human monocytes/macrophages; therefore, eNOS may be regarded as a pro-inflammatory parameter (Mühl and Pfeilschifter 2003). Thus, inhibition of eNOS activity could provide beneficial therapeutic effects in such disease conditions. Cationic fractions of flax protein hydrolysate (fractions I and II) have been reported to reduce the activity of calmodulin-dependent eNOS, in which fraction II had ten times the efficiency of eNOS-inhibiting activity compared to fraction I (Omoni and Aluko 2006).

Antinutritive Compounds of Oilseed Cakes

Oilseed cakes contain antinutrients that hinder their application in animal feeds and human nutrition. Examples of antinutrients that can be present in oilseed cakes are summarized in table 6. Canola seed cakes contain glucosinolates, phytic acid, tannic acid and protease inhibitors that can interfere with mineral absorption and lead to failure of internal organs (Mansour et al. 1993). In addition, some antinutrients, such as tannins and other phenolics, are able to bind with protein, which inhibits protein adsorption and causes amino acid imbalance, thus leading to growth impairment (Francis et al. 2001). The major antinutrient in flaxseed cake is cyanogenic glycosides which form hydrogen cyanide during digestion in the gastrointestinal tract. About 50–60 mg of inorganic cyanide is documented to cause acute toxicity in an adult (Roseling 1994). However, one to two tablespoons of flaxseed that contain approximately 5–10 mg of hydrogen is not a lethal dosage to humans. Nevertheless, the human body can detoxify hydrogen cyanide of 30–100 mg/day (Roseling 1994). Flaxseed cakes also contain linatine, a compound that causes pyridoxine deficiency (vitamin B6 deficiency) in fowls. However, linatine in flaxseed does not affect pyridoxide utilization in the human body up to a dosage of 45 g/day (Dieken 1992). Other antinutrients found in flaxseed cake and in almost every oilseed and legume are phytic acid and trypsin inhibitors that cause interference of mineral and protein utilization (Table 6).

Saponins are a heterogeneous group of natural foam-producing trierpene or steroidal glycosides that present in oilseed cakes such as sunflower, mucuna and *Sesbania aculeate* seed cakes (Akande et al. 2010; Siddhuraju and Becker 2001; Hossain et al. 2001). Saponins cause erythrocyte haemolysis and interference of dietary lipids, cholesterol, bile acids and lipid-soluble vitamins (Akande et al. 2010; Jenkins and Atwal 1994). Lectins (also known as phytohaemagglutinins) are glycoproteins that occur in certain oilseed cakes such as *S. aculeate* and x'pelon (*Vigna unguiculata* L) seed cakes. Lectins bind to sugars, carbohydrates, carbohydrate membrane receptors and intestinal mucosa, which lead to indigestion and epithelial lesions within the intestine (Akande et al. 2010; Almeida et al. 1991; Santiago et al. 1993; Oliveira et al. 1989).

Table 5 Bioactive protein hydrolysates from bioconversion of oilseed protein isolates

Compounds	Types of test	Methods	Results	References
Alcalase- and flavourzyme-hydrolysed pumpkin seed protein hydrolysates	*In vitro*	(i) ABTS$^{+\cdot}$radical scavenging activity (RSA) (ii) Reducing power (iii) ACE-inhibitory activity	(i) Highest RSA shown by the alcalase hydrolysate at 60 min, 7.59 ± 0.081 mM TEAC/mg (ii) In alcalase hydrolysates, reducing power increased with increase of DH up to 40 % (iii) 71.05 ± 7.5 % (IC_{50} = 0.422 mg/ml) for alcalase hydrolysate	Vaštag et al. (2011)
Hempseed protein hydrolysate fraction	*In vitro*	(i) DPPH$^{\cdot}$ assay (ii) Chelation of metal ions (iii) Ferric reducing power (FRAP) (iv) Hydroxyl radical scavenging (v) Inhibition of linoleic acid oxidation	(i) Smaller fraction of pepsin- followed by pancreatin hydrolysate had higher DPPH$^{\cdot}$ than the bigger peptide fraction (ii) Hemp protein isolate had the highest percentage of metal ion chelating. Reduced glutathione, fractions 1 kDa and 1–3 kDa had the lowest percentage of metal ion chelating. Fractions 3–5 kDa and 5–10 kDa exhibited moderate percentage of metal ion chelating, 29 and 38.5 %, respectively (iii)Reduced glutathione had higher FRAP value compared to hemp protein hydrolysate and its' membrane fractions (iv) Hemp protein hydrolysate had no hydroxyl radical scavenging activity. However, its membrane fractions exhibited lower hydroxyl radical scavenging activity compared to reduced glutathione (v) Hemp protein hydrolysate had the highest inhibition of linoleic acid oxidation	Girgih et al. (2013)
Rapeseed hydrolysate peptides	(i) *In vitro* (ii) *In vivo*	(i) ACE inhibitory assay (ii) Oral injection to spontaneously hypertensive rats (SHR)	(i) Pepsin and subtilisin protein hydrolysates had the highest ACE inhibitory activity (IC_{50} 0.16 mg/mL). The isolated hydrolysate peptides that processed ACE were VW, VWIS, IY and RIY (ii) All the hydrolysate peptides lowered blood pressure of SHR	Marczak et al. (2003)
Buckwheat protein hydrolysate	*In vitro*	(i) DPPH$^{\cdot}$ assay (ii) reducing power (iii) Inhibition of linoleic acid oxidation	(i) Alcalase protein hydrolysate (1.0 mg/mL) had 75 % of DPPH$^{\cdot}$ inhibition (IC_{50} 0.56–0.94 mg/mL) (ii) Buckwheat protein hydrolysate (5 mg/mL) had 0.77–1.24 of the reducing power (iii) Buckwheat protein hydrolysate (1.2 mg/mL) exhibited inhibition of linoleic acid oxidation	Tang et al. (2009a)

Table 5 (continued)

Compounds	Types of test	Methods	Results	References
Hemp protein hydrolysate	*In vitro*	(i) DPPH˙ assay (ii) reducing power (iii) Fe^{2+} chelating ability	(i) At 2 h hydrolysis time, protamex protein hydrolysate had the highest DPPH radical scavenging activity (IC_{50} 2.8 mg/mL). At 4 h hydrolysis time, neutrase protein hydrolysate had the highest DPPH radical scavenging activity (IC_{50} 2.3 mg/mL) (ii) Trypsin and alcalase protein hydrolysates had the highest reducing power at 2 h hydrolysis time (iii) Neutrase, protomex and trypsin protein hydrolysates had high Fe^{2+} chelating ability (IC_{50} 1.6–1.7 mg/mL)	Tang et al. (2009b)
Cationic fraction of flax protein hydrolysate	*In vivo*	(i) Oral feeding to spontaneously hypertensive rats (SHR)	(i) Cationic peptides (200 mg/kg body weight) resulted in rapid decrease in systolic blood pressure when compared to similar amount of flax protein isolate or the arginine amino acid	Udenigwe and Aluko (2012)
Cationic fractions of flax protein hydrolysate	*In vitro*	(i) Enzyme endothelial nitric oxide (eNOS) inhibition kinetics	(i) Fraction I and II reduced the activity of calmodulin-dependent eNOS. Fraction II had ten times efficiency of eNOS inhibiting activity compared to fraction I	Omoni and Aluko (2006)
Rapeseed hydrolysate peptide derivative, Arg-Ile-Tyr (RIY)	*In vivo*	(i) Oral feeding to rats	(i) RIY decreased food intake and gastric emptying at a dose of 150 mg/kg after oral administration to rats by stimulating cholecystokinin (CCK) release.	Marczak et al. (2006)
Rapeseed protein hydrolysates	(i) *In vitro* (ii) *In vivo*	(i) ORAC (ii) ACE inhibition assay (iii) Renin inhibition assay (iv) Antihypertensive activity by oral feeding to spontaneously hypertensive rats (SHR)	(i) Alcalse 1 kDa fraction had higher ORAC value (2493.71 ± 134.95 µM TE/g protein) when compared to other peptide fractions. (ii) The < 1 kDa fraction of proteinase K hydrolysate had the highest ACE inhibitory activity (86.94 ± 1.14 %) (iii) Alcalase hydrolysate had the highest renin-inhibitory activity (82 % at a concentration of 1 mg/mL) (iv) Alcalase and pepsin + pancreatin (PP) hydrolysates resulted higher decreases in systolic blood pressure by about -24 and -21 mm Hg, respectively after 8 and 24 h of oral feeding	He et al. (2013)

Table 5 (continued)

Compounds	Types of test	Methods	Results	References
Canola protein hydrolysates	*In vitro*	(i) $ABTS^+$ $^\bullet$radical scavenging activity(RSA) (ii) DPPH radical scavenging activity (iii) Superoxide radical scavenging activity (SRSA) (iv) Inhibition of linoleic acid oxidation (v) ORAC	(i) The pancreatin 1 kDa permeate fraction (EC_{50} 10.1 µg/mL) had the highest $ABTS^+$ $^\bullet$radical scavenging activity (ii) The alcalase and its' derived fractions had the highest DPPH radical scavenging activity (EC_{50} 0.5–0.9 µg/mL). iii) Pepsin <1 kDa fraction had the highest SRSA value of 51.3 % at a concentration of 1 mg/mL (iv) Pepsin hydrolysate had 82 % inhibition of linoleic acid oxidation (v) The highest ORAC values in the range of 2000–2200 µM TE/g were possessed by alcalase <1 kDa and 1–3 kDa, chymotrypsin <1 kDa and pepsin 3–5 kDa fractions	Alashi et al. (2014a)
Canola protein hydrolysates	(i) *In vitro* (ii) *In vivo*	(i) ACE inhibition assay (ii) Renin inhibition assay (iii) Antihypertensive activity by oral feeding to spontaneously hypertensive rats (SHR)	(i) Alcalase and chymotrypsin hydrolysates had 90 % and 88.8 % of ACE-inhibitory activity. Membrane fractionation of trypsin <1 kDa improved ACE-inhibitory activity from the unfractionated trypsin hydrolysate (ii) Pancreatin hydrolysate had the highest renin inhibition activity (63.2 %). Larger fraction (5–10 kDa) of pancreatin hydrolysate exhibited higher renin-inhibitory activity than the unfractionated pancreatin hydrolysate (iii) Pancreatin hydrolysate resulted in systolic blood pressure changes of -7.4, –7.7 and –15.1 mmHg respectively after 2, 4 and 6 h oral feeding. Pepsin hydrolysates caused systolic blood pressure changes of –11.3 and –23.7 mmHg respectively after 2 and 4 h oral feeding	Alashi et al. (2014b)
Flaxseed protein hydrolysate fractions	(i) *In vitro* (ii) *In vivo*	(i) Glucose transport assay (ii) Antihypertensive activity by oral feeding to spontaneously hypertensive rats (SHR)	(i) The KCl-F2 fraction increased glucose in both the basal (without insulin) and insulin stimulated conditions in L6 cells, suggesting that KCl-F2 fraction as a specific antidiabetic fraction (ii) The KCl-F1 and the cationic fractions decreased systolic blood pressure of SHR after 2 h oral feeding with a maximum dropping of systolic blood pressure at 4 h (-27 mm Hg)	Doyen et al. (2014)

ABTS 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), *DPPH* 2,2-diphenyl-1-picrylhydrazyl, *ACE* angiotensin-converting enzyme, *ORAC* oxygen radical absorbance capacity

Table 6 Antinutrients of oilseed cakes

Oilseed cakes	Antinutrients	References
Canola seed cake	Protease inhibitors, glucosinolates, phytic acid, tannic acid	Francis et al. (2001)
Sunflower seed cake	Protein inhibitors, saponins, arginase inhibitor, chlorogenic acid	Akande et al. (2010); Francis et al. (2001)
Flaxseed seed cake	Cyanogenic glycosides, linatine, trypsin inhibitor and phytic acid	Ganorka and Jain (2013)
Mucuna seed cake (*Mucunapruriens* var. *utilis*)	Tannins, phytates, saponins, 3,4-dihydroxyphenylalanine ($_{\text{L}}$-DOPA), chymotrypsin inhibitor, trypsin inhibitor,	Siddhuraju and Becker (2001)
Sesbania aculeata seed cake	Tannins, phytates, saponins, trypsin inhibitors, lectins	Hossain et al. (2001)
X'pelon (*Vigna unguiculata*) seed cake	Phytic acid, trypsin inhibitors, lectins	Lara-Flores et al. (2007)
Hempseed cake	Phytic acid, trypsin inhibitors, cyanogenic glycosides, tannins, saponins	Russo and Reggiani (2013)

Removal of Antinutrients from Oilseed Cakes

Several antinutritive compounds such as protease and trypsin inhibitors, cyanogenic glycosides, glucosinolates, phytates and lectin can be effectively removed by heat treatments (Francis et al. 2001). A heat treatment was carried out for 1.5 h in an autoclave-reduced glucosinolates, phytic acid and tannic acid in raw canola seed cake by 93.56, 42.51 and 66.66 % (Mansour et al. 1993). However, heat-stable antinutritive compounds such as saponins, tannins, non-starch polysaccharides, protein antigens and phytoestrogen can only be removed by solvent extraction and fermentation by lactic acid bacteria. Mechanical dehulling prior to oil extraction may be useful to decrease the majority of saponins and tannins since they are mostly located in the outer layer of oilseeds (Drew et al. 2007). It is recommended to wash or soak the oilseeds in water to solubilize several antinutrients such as saponins and tannins from the outer layer of the oilseeds before the extraction of oil. Washing oilseed can lead to significant reduction in antinutrients in oilseeds cakes as shown in quinoa (*Chenopodium quinoa* Willd.) cake fed to broiler chickens (Improta and Kellems 2001). Extraction of protein isolates from oilseed cakes have proved to be useful in eliminating antinutrients (Mansour et al. 1993). Generally, fractionations of protein isolate from oilseed cakes are extracted by NaOH treatment (pH 9–12) and the solubilized protein is precipitated according to the isoelectric point of a particular protein by adjusting the pH using an acid. High pH is able to remove antinutrients from oilseed cakes. As shown by many researchers, isolation of canola protein isolates from canola seed cake by alkali extraction reduced glucosinolates and phytates by 95 and 92 % respectively, while tannins and trypsin inhibitor were totally eliminated in canola protein isolates (Bin et al. 1990; Mansour et al. 1993). The suggested a process flow chart of eliminating antinutrients while processing value-added products is shown in Fig. 1.

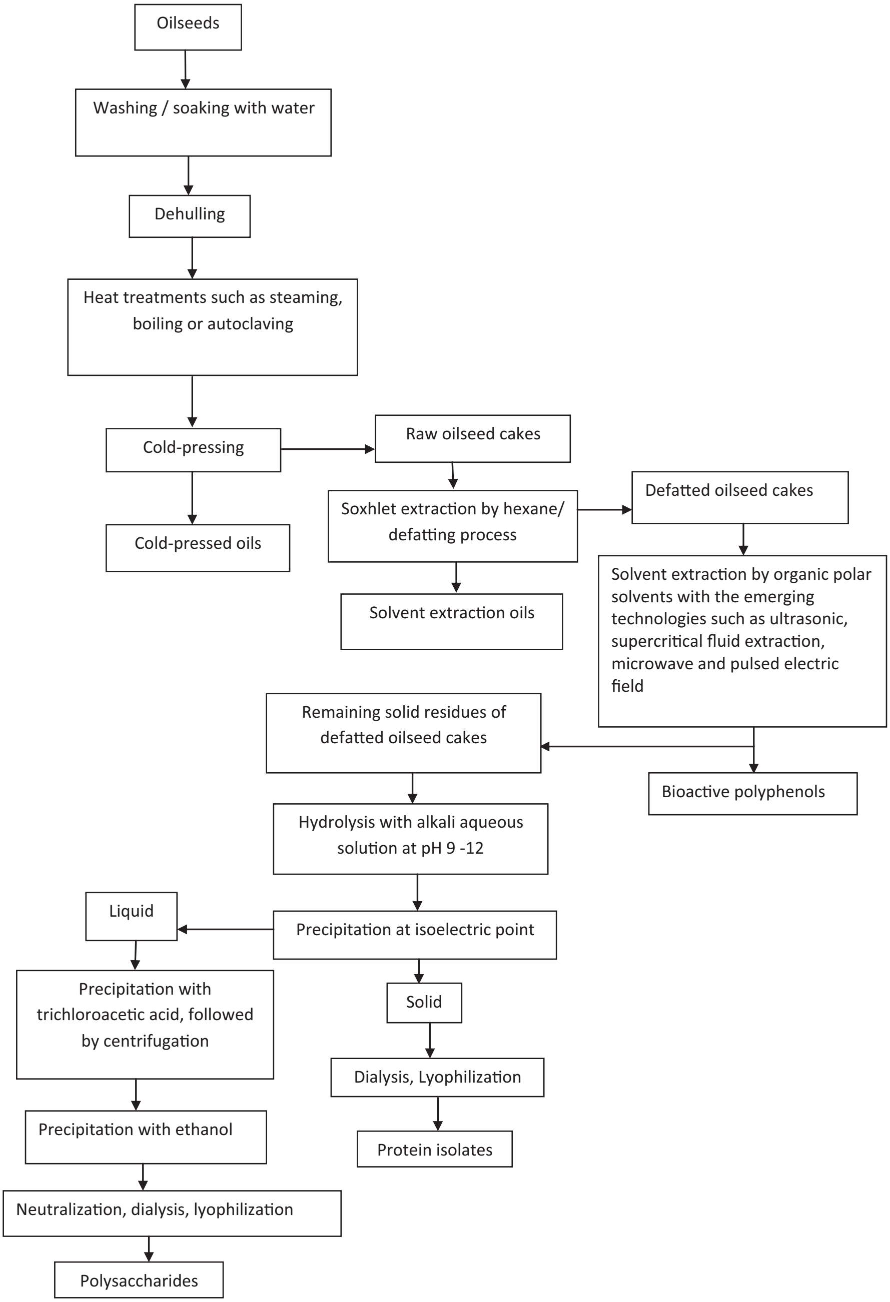

Fig. 1 Processing of value-added products from oilseed cakes

Conclusion and Future Perspective

In conclusion, oilseed cakes are by-products of the oil extraction that have little commercial value. The value of oilseed cakes can be increased by their application in human nutrition and health purpose. Polyphenols can be extracted from the oilseed cakes as functional food products. Further studies need to be carried out to identify the major bioactive compounds from the oilseed cakes. Technologies of polyphenol extraction from the seed cakes and also the optimum processing conditions need to be studied. Oilseed protein isolate need to be introduced in the human diet in order to expand new market for the protein isolate, since the oilseed protein isolates reviewed here have good comparable amino acid content and functional characteristics to soy protein isolates. For bioactive peptides that are generated by the enzymatic hydrolysis of protein isolate, they could be added in food products such as milk powder, cheese and fruit juice for bioactive value addition. In addition, these bioactive protein isolates could be purified and isolated in order to produce functional peptides in pharmaceutical industry. Further studies such as *in vivo* and animal studies need to be carried out to ensure the efficiency of bioactive peptides in human health.

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Bamboo Biomass: Various Studies and Potential Applications for Value-Added Products

Khalid Rehman Hakeem, Shamsudin Ibrahim, Faridah Hanum Ibrahim and Huseyin Tombuloglu

Abstract Bamboo being an industrial crop belongs to the family Gramineae, subfamily Bambusiodeae, and grows naturally in many countries including Malaysia. The cultivation of bamboo for commercial purposes in Malaysia is rather limited due to problems in acquiring suitable land for planting, although it has been widely recognized for excellent production of fiber biomass globally. It produces long fibers derived from outer fibrous bark, and has great potential in the biocomposite industries. In other countries like China and Japan, the plantation of bamboo is common and utilized for many purposes including the production of fiber. Usually, the extraction of fiber from bamboo is done in 3–4-year-old bamboo plantations. Fiber is produced through alkaline hydrolysis and multiphase bleaching processes of bamboo stems and leaves followed by chemical treatments of starchy pulp generated during the process. Bamboo fiber has micro-gaps, which makes it softer than cotton and increases its capability to absorb moisture. Other interesting properties of bamboo fiber are highly elastic, bacteriostatic, antifungal, antibacterial, hypoallergenic, hydroscopic, natural deodorizer, resistant to ultraviolet light, and biodegradable which render the bamboo fiber products environmentally friendly. Furthermore, it is highly durable, stable, and tough and has substantial tensile strength. Due to its versatile properties, bamboo fibers are used mainly in textile industry for making garments, bathrobes, and towels. The plants possess a wider range of adaptation to diverse climatic and soil conditions, and due to its rich cellulose content compared to other plants it has been widely utilized for the production of many products. Thus, it is important to gather and document useful information of its properties and a wide range of products it produces.

Keywords Bamboo · Fiber · Biomass · Biocomposite · Mechanical properties

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Introduction

Bamboo is a fast-growing fibrous plant on the earth, particularly abundant in tropical and subtropical regions. More than 75 genera and 1200 species of bamboo are known globally (Yuming et al. 2004). Bamboo has associated a very long history with the humankind. It has been traditionally used for multitude of household products and recently extended to many industrial applications due to advances in processing technology and increased acceptance of the product quality in the market. In Malaysia, bamboo has been recognized as the second important non-timber forest product (Azmy and Norini 1990) and has the potential to offer itself as an alternative raw material for timber in producing high-value-added products. In realizing the importance of bamboo, there was an attempt to plant bamboo species on a commercial scale by the industry but the initial attempt was shelved due to diversion in the interest of the company to invest in oil palm plantation that gives better internal rate of return. In order to outcompete with oil palm plantations in Malaysia, bamboo needs to capture unique higher-value-added products accepted by the market that will justify the involvement of the private sectors in bamboo plantation. A recent study also indicated that bamboo mat is suitable as a foundation for rubble-mound breakwater on muddy areas along coastal areas (Kamali and Hashim 2010).

Bamboo, being one of the fastest growing plants, needs only 3–4 years to mature before it is ready for harvesting and utilization. This makes bamboo the best possible alternative to replace timber in the future. As a result, bamboo has been the focus of research in recent years. Research covers all aspects of ecology, silviculture, propagation, processing, properties, and utilization of both planted and naturally grown bamboo. In recent years the study on these aspects, particularly on properties and utilization of bamboo for composite products, intensified (Wang et al. 2008; Li et al. 2014; Lo et al. 2008; Montti et al. 2011). However, the study on cultivated bamboo stands in Malaysia has so far been confined mostly to silviculture and fertilizer application to enhance growth (Azmy et al. 2007, 2004), information on the morphology, characteristics, and physical, mechanical, and chemical properties of different age groups of cultivated bamboo in Malaysia is rather limited. Similarly, the molecular biology of growth characteristics as well as the formation of thick lumen in rapidly growing culms is altogether missing.

The anatomy and physical properties of bamboo culms have been known to have significant effects on their durability and strength (Abd. Latif and Mohd Tamizi 1992; Liese 1985; Razak 1998). Studies on the morphological and anatomical characteristics of managed natural bamboo stands *Gigantochloa scortechinii* conducted by Razak et al. (2007) support this statement. Information generated on these properties can be used to determine the possible products that can be derived from naturally grown bamboo stands ranging from traditional household products to high-value-added products such as panels, parquets, furniture, and construction materials. The economy of scale of high-value-added products demands a greater volume to be introduced into the market, and this in turn will put a lot of pressure on greater consumption of raw material. A continuous supply of high quantity of raw material from the natural bamboo stand is highly questionable to meet the demand from the industry due to the nature of the distribution of natural bamboo clumps which are highly dispersed and difficult to manage. The solution to the problem is through bamboo cultivation but there are issues associated with bamboo cultivation that need to be seriously considered before embarking on a large-scale bamboo plantation within the country. The possible choice of local bamboo species to be introduced as a plantation for fiber biomass is unlimited but is controlled by site suitability.

Taxonomy and Distribution

Bamboo belongs to the tribe Bambuseae, subfamily Bambusoideae of the family Gramineae (Dransfield 1992; Mohamad 2000; Wong 1995), reaching up to ~1000 species (Dass et al. 2008; Gui et al. 2007; Ohrnberger 1999).

Bamboos are well distributed worldwide except in Europe and Antarctica. Bamboo is found to be most abundant in tropical and subtropical regions (Gui et al. 2007) which fall within eastern and southern Asia and south and central America (Ohrnberger 1999). In terms of altitude, the range varies between species; Bambuseae was reported to reach up to 4500 m above sea level (Ohrnberger 1999).

Out of 75 genera of bamboo worldwide, 12 can be found in Malaysia such as *Bambusa, Chusquea, Dendrocalamus, Dinochloa, Gigantochloa, Melocanna, Phyllostachys, Racemobambos, Schizostachyum, Sphaerobambos, Thyrsostachys*, and *Yushania* where all genera except *Sphaerobambos* are distributed in Peninsular Malaysia while *Bambusa, Dendrocalamus, Dinochloa, Gigantochloa, Racemobambos, Schizostachyum, Sphaerobambos*, and *Thyrsostachys* can be found in Sabah (Abd.-Razak and Abd.-Latif 1995; Dransfield 1992).

Ecological Studies

Irrespective of the size of the gaps created, bamboo plants are an opportunist to successfully establish in forest gaps that will outcompete the growth of other successional species. Studies have shown that the diversity and species richness of other light-demanding pioneer species were reduced in forest areas where bamboo is dominant (Larpkern et al. 2011; Tabarelli and Mantovani 2000). In bamboo-dominant areas, soil moisture was significantly reduced and this probably represents the most critical factor compared to other growth conditions that eliminate other woody plants to compete with (Grimson and Ashton 2003). Therefore, controlling the distribution of bamboo in disturbed areas posed great challenges to forest restoration. Martins et al. (2004) reported a successful establishment of shrub and tree species of different successional groups in areas where bamboo died. However, in agroforestry projects conducted in Thailand, the biogeochemical role of bamboo was highlighted where soil productivity was proven to be higher in areas intercropped with bamboo plants (Christanty et al.1996,1997). The study observed that dead bamboo fine roots contributed to greater biomass of litter near to the soil surface. Similar results could be interpreted in natural forest where greater biomass of bamboo fine roots helped to improve productivity of degraded soils where Chandrashekara (1996) demonstrated that in certain type of bamboo-rich soils the accumulation of potassium increased. In national carbon accounting, bamboo stands proved to be excellent in providing greater carbon stock resulting in a change of government strategy to have more areas to be covered with bamboo (Chen et al. 2009). Flowering and fruiting of bamboo are rare, and mast flowering and fruiting was never reported. Mast flowering and fruiting of bamboo is mostly restricted to semelparous species that will die once they produce flowers (Keeley and Bond 1999). Efforts have been made to investigate on an experimental basis the ecological requirements of planted bamboo and the best growth was found on sandy clay loam with the application of organic fertilizer (Othman 2001).

Molecular Studies

Bamboo has a basic chromosome number, which is $x=12$. It consists of two polyploids, which are tetraploid ($4x=48$) and hexaploid ($=6x=72$). Usually, tetraploid can be found in monopodial bamboo, whereas hexaploid can be found in caespitose bamboo (Gui et al. 2007). Moso bamboo has a genome size bigger than the rice genome, yet it is similar to maize. Nevertheless, rice and maize contains a very rich repeat elements than moso bamboo. Mostly repeat elements in moso bamboo are Gypsy/DIRS1 and Ty1/Copia LTR retrotransposons while only a few DNA transposons are reported. The bamboo genome size is considered to be 2.45–5.30 pg (Gui et al. 2007).

The largest genomic sequences of tetraploid moso bamboo (*Phyllostachys pubescens*) for subfamily Bambusoideae is sequenced from 13 bacterial artificial chromosome (BAC) clones and are recorded for 1.2 Mb. Repetitive elements between bamboo and rice are quite different, where the bamboo genome contains lower DNA transposons than rice. The results also showed that, during evolution, the rice lineage had seemed to increase in the contents of the CACTA superfamily and miniature inverted-repeat transposable elements (MITEs) of DNA transposons compared to bamboo. Though high genomic synteny has been recorded between bamboo and rice/sorghum, the comparison of the two bamboo-rice-sorghum syntenic regions demonstrated that some Moso bamboo genes seemed to have been lost or moved to other genomic regions after the divergence of bamboo from other members. (Gui et al. 2010). As we know, many crops such as maize, wheat, Chinese sorghum, sugarcane, and rice have nitrogen fixation characteristics which help in enhancing the production of these crops (Xiaoli and Xiaoping 2001). The application of chemical fertilizers in order to maintain fertility and productivity of the soil may lead to environmental problems if the amount applied is excessive and leaching is certainly unavoidable under high intensity of rainfall. Therefore, biological nitrogen fixation is the best option to improve crop production, and Xiaoli and Xiaoping (2001) had determined root nitrogenase activity in several bamboo species in China.

They identified azotobacteria involved in nitrogen fixation activity from rhizophere and four strains of bacteria which had a very high nitrogenase activity were selected and applied to *Ph. pubescens*. This study showed that by innoculating aztobacteria the growth of lateral root and root hairs increased. The finding confirmed an earlier observation made by Ravikumar et al. (1997) that bamboo seedlings infected with vesicular-arbuscular mycorrhizae (VAM) have a significant increase in growth rate and biomass productivity.

Different expressed proteins in different development stages were studied to understand the molecular processes at the genome level underlying the rapid internode elongation of moso bamboo, and the molecular data basis underlying the phenomenon of sequentially elongated internodes for the base to the top was identified (*Phyllostachys heterocycla* cv. *pubescens*). Due to this, several key pathways which are involved in rapid growth of bamboo culms like environmental adaptation, signal transduction, translation, transport, and many other metabolic activities, and gene ontology (GO) terms such as hormone-mediated signaling, cell growth, division and differentiation, primary shoot apical meristem specification, xylem and phloem pattern formation, protein modification, response to stimuli, metabolic process, and biological regulation were also recognized (He et al. 2013)

He et al. (2013) also stated that the different portions of the same plant may be at different stages resulting from the sequential basal–apical elongation of the culm internodes. For example, G1M, G2M, and G3T involved in the initial or ascending stages, and G3M, G4M, and G3B involved in the boosting or descendent stages. Temporal or static omics data, including transcriptome, post-transcriptome and translatome/proteome, played an even bigger part in molecular mechanism study of dynamic bamboo' culm development. By integrating such data with their positive/negative correlation analysis data sets, He et al., (2013) obtained the complete set of gene/protein or miRNA that are activated, their dynamics and interactions, the role that different gene/protein or miRNA have in the process and the differences in processes within and between different growth stages. At last the core genes focused on 64 genes and their correlative 55 miRNAs and 15 proteins were obtained, the GO and pathway analysis revealed that genes involved in response to stimulus, cell cycle, cellular component, regulation of plant hormone levels, many metabolism and signal transduction played major roles in persistently elongating culms of *P. heterocycla*.

The study also mentioned dynamic changes of unimodal-type endogenous hormone concentration while cell nuclei gradually declined and parenchyma and fiber cells gradually elongated during bamboo culm development. Detection of 17 unigenes during the fast-growing stage of bamboo promotes response to stimulus indicating the important role of environmental cues in its rapid growth like carbohydrate, cytokinin, auxin or ABA stimulus, cold, blue light, cadmium ion, and gravitropism (He et al. 2013).

Four major endogenous hormones such as indole-3-acetic acid (IAA), gibberellic acid (GA_3), zeatin riboside (ZR), and abscisic acid (ABA) were identified in the cell elongation phase in moso bamboo. The genes involved in the auxin efflux and ABA-mediated signaling pathway, ethylene biosynthetic process, and response to cytokinin stimulus that indicates environment cues might stimulate cell division, growth or death through controlling hormone transport of influencing the expression of hormone response factors. Moreover, glycan biosynthesis and metabolism, the metabolisms of carbohydrates, lipids, amino acids, nucleotides, energy, and biosynthesis of secondary metabolites are the major metabolic processes in the developing moso bamboo culm which provide supply energy and components especially for the rapid culm elongation under conditions of light deficiency for DNA replication, signal transduction, cellular growth, hormone biosynthesis, cellulose, and lignin biosynthesis (He et al. 2013).

At the late stage of culm development, there is a reduction of nuclei in the cell while the length of parenchyma and fiber cells increased continuously which gave a sign of cell elongation and division. Occurrence of lignification of fiber cells has also been recorded after seventh development. Simultaneous activity of cell division and cell elongation affects the internode elongation and the result in the former was predominant in initial stages whereas the latter was predominant in late stages. Therefore, development from basal internode to top internode showed sequential development throughout the growth period (Cui et al. 2012). Internode elongation in moso bamboo occur when cell division starts to perform and initiate cell length to elongate and decrease the numbers of cell nuclei. Thus, cell division and elongation are correlated with internode elongation (He et al. 2013).

Endogenous growth-promoting hormones such as IAA, GA_3, ZR, and ABA show strong influence in cell elongation of basal, middle, and top internode of moso bamboo (*P. heterocycla*), in which ABA act as an inhibitory factor while the rest act as growth-promoting factors for plant development. The protein concentration was increased from basal to top internode and in the early stage. Data show relatively less dependence of protein expression on the location of the internode on the culm and varied more in response to the developmental stage (Cui et al. 2012).

Gel-based two-dimensional (2D) electrophoretic studies are also known in moso bamboo in order to understand its fast growth. Based on 213 proteins were analyzed using matrix-assisted laser desorption/ionization-time of flight-mass spectrometry (MALDI-TOF-MS) and subsequent bioinformatic softwares, almost half of these belonged to the metabolism category and energy category. Energy was generated from the regulation of anaerobic and aerobic modes of respiration, and in poor photosynthesis activity conditions energy was generated from sucrose degradation. Of the 213 proteins, nine were internode-specific differential proteins that can be found in different developing internodes in the same development stages while 175 proteins were stage-specific proteins which can be found among the different developmental stages in the same internode and the rest were internode- and stage-dependent proteins which can be found at both among different developmental internodes and among different developmental stages. All of these proteins help in the developmental variations but a majority of variations came from the stage-specific differences in proteins. A higher proportion of internode and stage-dependent proteins has been identified to be involved in metabolism, energy, and transcription when compared to stage-specific proteins (Cui et al. 2012).

Proteins that function as internode- and stage-dependent proteins were abundant in the basal internode. The protein involved in lipid biosynthesis was abundant in the basal internode. Therefore, Cui et al. (2012) suggested that it is related to the formation of epidermis cutin. In addition, these 29 proteins that acted as internode- and stage-dependent proteins were found to be related to polysaccharide biosynthesis, fiber biosynthesis, sucrose degradation, tricarboxylic acid (TCA) cycle, glycolysis, and antioxidant enzyme. Five type of proteins were distinguished based on dynamic changes in protein expressed at each internode in different stages, namely gradual increase (U-type), gradual decrease (D-type), transitional increase (A-type), transitional decrease (B-type), and bimodal structure (C-type).

Based on the study by Peng et al. (2013) from different heights of moso bamboo (*Phyllostachys edulis*) by transcriptome sequencing analysis of mixed RNA, a large number of candidate genes involved in transcript factors, plant hormones, cell cycle regulation, and cell wall metabolism were identified. More than 81% of genes which consist of unique and nonunique positions were distinguished from 10,689 differentially expressed genes. The genes of zinc finger protein family, the WD-repeat-containing protein family, and the MADSbox family also can be found in moso bamboo. In addition, when the plant faces environmental stress, the MYB family, the WRKY family, the TGA family, and NAC family will respond to plant hormones especially ABA. Nevertheless, Peng et al. (2013) also stated that the ARF family may also play a different role during the fast growth of shoots due to expression changes of this gene.

The large quantity of gene numbers and high expression levels promoted the common ground between cell wall expansion factors and enzyme involved like expansin (EXP) and xyloglucan endotransglucosylase/hyrolase (XTH). The same traits were possessed by genes that allied with plant hormones, which indicated that most of these genes may have reactions with each other resulting in the fast growth of shoots. Also, an aquaporin *PIP* gene may play an important role in the fast growth of shoot via that regulated by auxin and gibberellin. Candidate genes identified were potentially involved in the growth and development of moso bamboo, thus offering functional gene resources for improving bamboo growth (Peng et al. 2013).

Application of Bamboo Biomass

Traditionally, bamboo has many uses and is mostly confined to household items, but with the advance in processing technologies and better understanding of anatomical properties of bamboo fiber, the prospect of utilizing bamboo fiber as higher-value-added products is greater.

Food and Feedstock

In some species, fresh bamboo shoots are commonly used as foods due to the high concentration of fiber and proteins. Bamboo shoots and fibers are very popular as Asian stir-fry delicacies and as pickled condiment. The most important genus for production of edible shoots is *Phyllostachys*. Bamboo-fiber-derived food products include bamboo tea, bamboo wine, bamboo vinegar, and charcoal-coated dry fruits (Diver 2001). Bamboo fibers are also used for food packaging material like cellophane. The nutritive value of bamboo such as the total carbohydrate content of bamboo leaves decreases throughout the growing season, and remains stable for some time but decreases during winter. Unlike carbohydrates, crude protein content is high in growing season and decreases in winter season. The bamboo has potential as winter forage for goats and some other livestock. Halvorson et al. (2011) reported that bamboo also reduces the exposure of livestock animals to gastrointestinal parasites.

Production of Biofuel

The use of bamboo feedstock for biofuel production is of huge potential because a high level of biomass can be harvested from bamboo plants. Bamboo either as a natural stand or as a plantation can easily be managed, and the issue of sustainable supply of raw material is not a major issue for bamboo. However, the process of converting a bamboo biomass to a liquid energy source can be fairly difficult since the plant is hardy and processing requires necessary pretreatments (Littlewood et al.2013). A standard procedure has been established to produce liquid energy from bamboo but refinement is necessary to improve efficiency. China and Japan are the two leading countries that developed cutting-edge technologies in producing ethanol from bamboo. It is suggested that Malaysia should join the bandwagon to be actively involved in bamboo biofuel research since Malaysia has abundant bamboo resource that can be tapped and processed for biofuel production.

Bamboo is observed to be more productive compared to many other biofuel plants. Bamboo is suitable for fuel production because it has a low alkali index and ash content. Moreover, it has a lower heating value than many of the woody biomass feedstocks. Further research is required on bamboo fibers for commercialization of biofuel (Scurlock et al. 2000).

Building Material

Bamboo is one of the oldest and most flexible constructing materials used. Bamboo has certain qualities which make it suitable for construction purposes. These qualities include its hardness and lightweight. It does not require processing or finishing but remain strong and even resistant to withstand earthquakes (Jayanetti and Follet 1998). Bamboo fibers are used in concrete reinforcement, (Diver 2001) and regarded as an excellent alternative to steel in concrete due to its high tensile strength, tensile modulus, hardness, and other mechanical properties (Youngsi 2007). Ghavami (2005) performed some studies on microstructure of bamboo and revealed that bamboo is a functionally gradient material that makes it suitable for the formation of reinforced concrete composites, used in the construction of strong buildings.

Musical Instruments

Grass bamboo can be used in the preparation of musical instruments like wind, string, and percussion instruments. Bamboo is ideally suited for the manufacture of xylophone bars and chimes, flutes and organs, violins and zithers, and violin bows. Bamboo plates can be used for forming the body and neck of acoustic guitar as it is easily available and is economically viable to produce (Wegst 2008). Bamboo used for musical instruments should be harvested at 3–5 years of age for high strength and durability (Diver 2001). Bamboo is immutable, and this structure is best suited for the production of musical instruments like flute (Grame 1962). Bamboo culms are also used for the production of wind chimes (Perdue 1958).

Paper and Pharmaceutical Industries

The shape, chemical composition, and structure of bamboo are very suitable for pulping. Pulping performance and pulp strength makes bamboo fibers one of the most suitable materials for paper production. In the paper industry, bamboo fiber pulp can be used in the production of newsprint, bond paper, toilet tissue, cardboard, cement sacks, and coffee filters (Vena et al. 2010). The paper produced from bamboo has certain advantages, which include less pressure for wood, less pollution, and being environmentally friendly (Kefu 2002).

Bamboo fibers have an excellent characteristic of inhibiting bacterial growth, absorbing peculiar smells, and high hygroscopicity. Due to these characteristics, bamboo fibers are used as nonwoven medical and hygienic materials (Yi 2004). Flavones can be extracted from bamboo leaf fibers by leaching method. These flavones are used in the preparation of many drugs (Gang et al. 2000). Consuming bamboo fiber reduces the rate of intestinal infections by pathogens, and a bamboo drug for gastrointestinal infections has been produced (Anping 2005). Moreover, bamboo fibers can also be used for the production of sanitary towels, gauze, bandages, absorbent pads, surgical wear, doctors' coats, and medical masks. Bamboo fibers have a gentle makeup, and due to this reason only a few people are allergic to bamboo fibers; this property plays a role in the production of masks which are light, durable, and inexpensive.

Textile Engineering

Bamboo has a great potential to be used in the textile industry. Natural fibers from bamboo have some of the excellent properties, which make it a very potent material to be used in the textile industry (Yueping et al.2010). Refined bamboo fibers with low noncellulosic content can be used in textiles (Liu et al. 2011). Bamboo fiber luster is closer to that of silk. It can be used for knitting and weaving purposes (Yi 2004). A study on bamboo fibers revealed that its chemical composition represents the fiber which has high cellulose content but low lignin content. The structural properties of bamboo are different from those of other plants used in textile production. They are used for the production of socks, underwear, T-shirts, bathing suits, bathing suit cover-ups, towels, sleepwear, face masks, sanitary napkins, bedsheets, pillows, baby diapers, bulletproof vests, table cloth, blinds, and mattresses. Bamboo fibers have excellent characteristics for spinning and weaving (Hengshu 2004). Dyeability of bamboo can be enhanced by plasma treatment. The longer the treatment time, the higher will be its roughness and dyeability, which leads to greater potential for textile and other related products.

Cosmetic Industry

The bamboo has the potential to be used in cosmetic industry (Liese 1992). Bamboo fibers are widely used in cosmetic industry where cosmetic products for acne treatment are produced. Recently bamboo has become an ingredient of choice for many cosmetic companies including L'Oreal and Sally Hansen.

Sports Industry

In the sports industry, bamboo fibers can be used as reinforced composite materials in the production of sports goods like polo balls, baseballs, etc. In terms of durability and high strength, sport items made from bamboo fiber composites are strongly considered suitable materials (Subic et al. 2009).

Conclusion and Future Prospects

Research and investigation on the use of bamboo fiber for the production of many products are constrained by the availability of the fiber. The present techniques of extracting bamboo fiber often resulted in low fiber yield and quality. Improvements in extraction techniques of bamboo fiber need further study. Bamboo fiber is potent for many applications including the production of high-value-added products from inexpensive source of raw materials. The flexibility of bamboo properties to meet the requirement of many products is an added advantage, and an integrated research program on bamboo properties and utilization of local bamboo species in Malaysia has to be properly developed to meet the demand and challenges from other countries, especially China and Japan. These are the two countries where the research on bamboo utilization has very much advanced. It is important that research and development of bamboo utilization in Malaysia focus on niche products like the use of bamboo fiber as a composite material in manufacturing certain automobile and aircraft components. Since the use of bamboo fiber in these high-end industries are still lacking, Malaysia through a strong research and development program and funding should take the lead in pioneering the production of bamboo composite fiber in these two high-end industries where the market is less competitive.

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Mesoporous Silica Powder for Dental Restoration Composites from Rice Husk: A Green Sol–Gel Synthesis

Rayees Ahmad Shiekh and Visweswara Rao Pasupuleti

Abstract Morphologically organized non-crystalline silica powder was synthesized from rice husk by a green sol–gel route. Amorphous sphere-shaped silica powder with a surface area of ~370 $m^2\ g^{-1}$, particle size in the range of 70–250 nm and pore size of ~8 nm was synthesized using sodium silicate extracted from rice husk at most favourable conditions and adding up of phosphoric acid. The degree of accumulation of the mesoporous particles was extremely reliant on sodium silicate predecessor concentration, solvent and pH. For the characterization of silica powder, various techniques were used such as X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR) and N_2 adsorption/desorption, and the morphology of the mesoporous powder was characterized via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The synthesis method adopted was kept green and ecofriendly. The end product silica is a favourable choice in dental composite production.

Keywords Sol–gel technique · Mesoporous silica · Characterization · Rice husk

Introduction

Development in nanotechnology leads to synthesis of nanosilica through sol–gel technique which has been broadly useful in the current development research world (Sun et al. 2005). Stober synthesis (Stober et al. 1968) uses ammonia-catalyzed reactions oftetraethylorthosilicate (TEOS) with water; to produce silica nanoparticles with various characteristics, alcohol has been used. Making possible the reaction conditions (Park et al. 2002), adding up of ionic additives (Kim et al. 2004) and micro-emulsion ways (Kust et al. 2000) are the current challenges used by the

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researchers to condense the size of silica using the Stober synthesis as a platform. Distribution and accumulation of silica nanopowder are two significant issues that govern functional viewpoint in the synthesis of improved nanocomposites (Sun et al. 2005; Boyle et al. 2005). Manufacturing of highly diffused nanoparticles (particles below 10 nm) with small accumulation level in precipitate form is still a challenge as the powder is extremely responsive to the processing environments (Kwon and Messing 1997). The synthesis of silica nanopowder and the amount of accumulation will effectively increase the thickness of the medium matrix, which hints to complexation in providing the medium matrix (Sun et al. 2005). Apart from this, accumulations also condense the silica filling, subsequently in condensed thermo mechanical assets (Shenoy 1999).

Current research on the preparation of mesoporous silica by sol–gel method has expressively improved the progress of silica nanopowder. Dissimilar particle size and structures of silica particles are formed through the sol–gel method by controlled conditions like amount of water, pH, concentration of alkoxide, aging time and solvent (Bailey and Mecartney 1992; Park et al. 2002; Green et al. 2003; Kim et al. 2005). Nevertheless, the synthetic way is time utilizing, expensive and has highly poisonous contact from silicon alkoxide predecessors.

To decrease handing out price and period in systematic experiments, a lot of experimental work has been made available to synthesize silica nanopowder using rice husk as raw material (Huang et al. 2001; Tang and Wang 2005; An et al. 2011; Liu et al. 2011; Dawei and Xifeng 2011; Schlomach and Kind 2004; Kalapathy et al. 2000a, b). This raw material rice husk containing ~18–25 % silica is lavishly accessible in rice-manufacturing nations and delivers a low-price silica foundation. Presently, rice husk is mainly branded to get costly silica, which pollutes air, as there is emission of greenhouse gases, and this ash present in the environment results in silicosis disorder, fatigue, loss of appetite and respiratory malfunction (Foo and Hameed 2009). Hence, the drawing out of silica via rice husk in a more compassionate method becomes more essential, because humanity emphasizes on the excellence and ecological maintenance via justifiable improvement and implementation of green technological skills (Yusoff 2006). A range of approaches has been implemented for synthesizing silica particles from rice husk. In recent times, well-absorbent silica particles have been synthesized from rice husk in not more than 10 h by means of polyethylene glycol (PEG) as a prototype (Dawei et al. 2011) and mesoporous nanosilica with a usual diameter of ~51 nm by using simple sol–gel technique (Adam et al. 2011). Extracted carbons through rice husk have been implemented for the synthesis of mesoporous silica particles with diameters of 28–200 nm (Zhang et al. 2010; Li et al. 2011). Bimodal mesoporous silica particles extracted through rice husk ash and chitosan as an outline had been testified as well (Witoon et al. 2008). Since no researches have yet testified for the synthesis of mesoporous silica powder with fine, distinct morphological structures through rice husk without any costly templates or devour of the energy, mesoporous silica particles are suitable for dental filler applications. It is favourable to flourish a simple, inexpensive procedure that uses a low-energy technique for the synthesis of silica powder having guarded morphological structures through rice husk by utilizing a throwaway product for a cost-effectively value-added product.

Hence, in the present work, the preparation of mesoporous silica nanoparticles with spherical morphology via sol–gel technique from rice husk and sodium silicate (SS) as a predecessor is reported. A precipitating agent (phosphoric acid) used because of its polyprotic assets can manage the hydrolysis reaction and particle formation. Additionally, food industries, medicine and dentistry generally use this acid as an additive. Organized parameters which have an effect on the synthesis of mesoporous silica powder have been conceded out. To find out its possibility as an inexpensive packing biomaterial (filler) for dental restoration applications, physicochemical assets of silica were characterized.

Materials and Experimental Methods

Chemicals used in this research work were hydrochloric acid (37 %), phosphoric acid (85 %) and ethanol (99 %) from Merck; sodium hydroxide (99 %) from Sigma-Aldrich and rice husk collected from a rice mill in Terengganu, Malaysia.

Preparation of SS

To eradicate metallic impurities from rice husk, we treated diluted HCl with rise husk in a water bath at 70 °C for 6 h. After the filtration, distilled water was added for the washing process until pH of filtrate was ~7. At 130 °C for 14 h, the residue was dried in an oven. To a Teflon flask containing 10 wt. % NaOH, dried rice husk was added and boiled at 95 °C for 1 h with continuous stirring. Finally, SS with a specific gravity of 1.14 was obtained by cooling the mixture at room temperature and then filtering.

Chemical Synthesis of Silica Particles

Figure 1 gives a schematic illustration of silica particle synthesis. Ethanol was added in different concentrations to SS along with water followed by constant stirring for 20 min. A chemical titration process was followed for mixture with 3 M H_3PO_4 at different pH values (7, 8 and 9) with the formation of a gel-like product. Finally, this yellowish gel was cleaned up systematically by hot distilled water and was centrifuged to eliminate excess SS and phosphate groups. A freeze dryer was used to dry the sample followed by calcinations in muffle furnace to get the final product—silica particles.

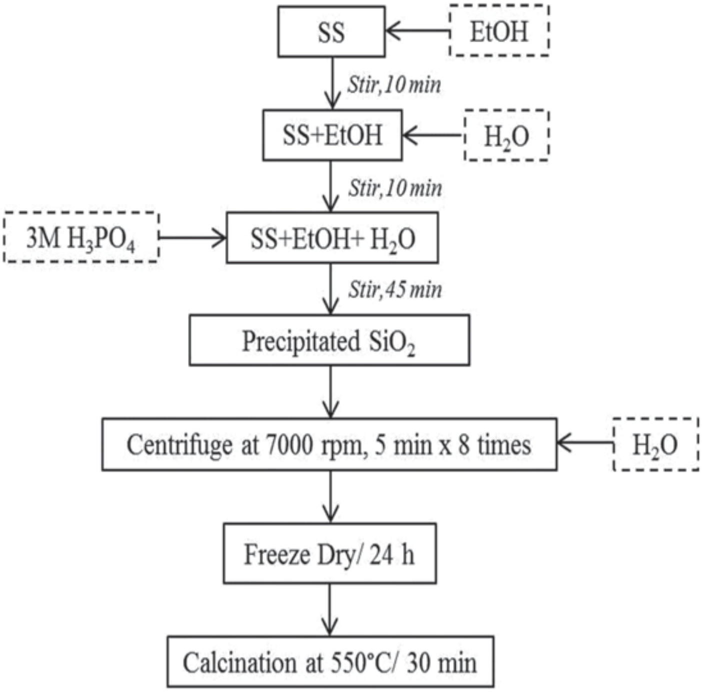

Fig. 1 Synthesis of silica using sodium silicate precursor derived from rice husk: Flow chart (*SS* Sodium silicate, *EtOH* Ethanol)

Chemical Characterization of Nanopowder

Transmission electron microscopy (TEM, Philips FEI CM12) system was used to obtain TEM micrographs, and particle size was measured using analySIS Docu Version 3.2 image processing software. Field-emission scanning electron microscopes (FE-SEM, Quanta FEG450) equipped with energy-dispersive X-ray (EDX) were used to investigate silica particles. The N_2 adsorption/desorption isotherms were calculated by an automatic surface area and pore size analyser (Quantacerome AUTOSORB-1) at 77 K. Brunauer, Emmett and Teller (BET) equation was used for specific surface area. A single-point total pore volume was assessed as the liquid volume of N_2 was adsorbed at a relative pressure of 0.1 and 0.97. Fourier transform infrared (FTIR) was carried out on silica samples by using spectrum (Perkin-Elmer 2000), with wave number range of 4000–400 cm^{-1}. X-ray diffractometer (Philip Electronic Instruments) was used for the X-ray diffraction (XRD) characterization with the diffraction angle scanned from 10 to 80° 2θ at 8° min^{-1}.

Results and Discussion

Preparation of Silica Particles

As discussed above (introduction) the researchers' synthetic way of synthesizing silica particle from rice husk was earlier described. Nevertheless, the formed silica particles are nanostructured and poise numerous arrangements (permeable and accumulate), lacking definite uses.

In the present research work, we have produced silica particles through rice husk via sol–gel procedure by means of phosphoric acid as the triggering mediator. The final product retains required physicochemical assets, having a great prospective for practice in dental composite research, which will be reconnoitred in our forthcoming work.

SS as an originator was acquired by countering rice husk with sodium hydroxide. The procedure for producing silica particles matches the precipitation procedure consuming inorganic acids like HNO_3 (Adam et al. 2011), HCl (Liou and Yang 2011; Rozainee et al. 2008) and H_2SO_4 (Pijarn et al. 2010). Via phosphoric acid as a triggering mediator, the general reaction is as follows:

$$3Na_2SiO_3+2H_3PO_4 \rightarrow 3SiO_2+2Na_3PO_4+3H_2O \tag{1}$$

Throughout the accumulation of phosphoric acid, the ≡Si–OH units are designed and organized to form a siloxane [Si–O–Si] bond as follows:

$$\equiv \text{Si-OH}+\text{HO-Si} \equiv \rightarrow \equiv \text{Si-O-Si} \equiv +H_2O \tag{2}$$

In the beginning, the ≡Si–OH units formed dimmers or trimers or developed into principal units. The accumulation of principal units gives extra stable and firm particles. The formation of various entity morphologies was vastly reliant on conditions of reaction which are studied in the current work.

Optimisation of Reaction Parameters

Ethanol Effect

Figure 2 shows TEM micrographs of silica powder synthesized by various concentrations of ethanol. Shorn of ethanol, the powder was extremely accumulated and asymmetrical in nature (Fig. 2a). Sphere-shaped and extra discrete powder was perceived by growing concentration of ethanol (Fig. 2b, c); this might be because of the great solubility of ethanol that speeds up dispersion into the silicate predecessor. Current activity improves the synthesis of ≡Si–OH and ≡Si–O–Si≡ that yields additional sphere-shaped and bigger particles throughout the aging method (Jung et al. 2010; Godoi et al. 1999).

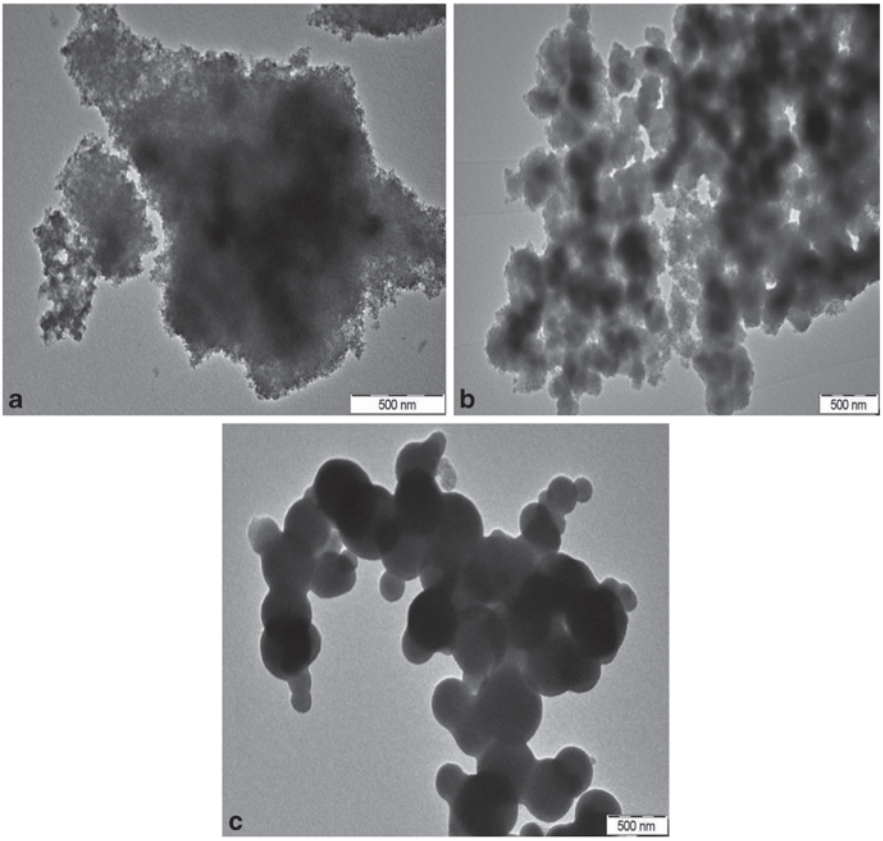

Fig. 2 TEM images of the silica prepared at different concentrations of ethanol based on ratio of SS: H_2O: EtOH at pH 9: **a** 1:0:0 **b** 1:0:0.20 **c** 1:0:0.30. *EtOH* ethanol, *SS* sodium silicate, *TEM* transmission electron microscopy

Table 1 indicates the BET superficial areas were condensed from ~306 to ~75 m^2g^{-1} by increases in the concentration of ethanol. An advanced precise superficial area of silica powder lacking ethanol (sample 1:0:0) might ascribe to permeable properties of three-dimensional cross-networking silica bonds. Nevertheless, with above circumstances, the nature of the powder is asymmetrical, which is challenging to calculate the size of powder particles (Fig. 2a).

pH Effect

pH is a perilous factor that defines the particle dimensions and morphology of silica powder (Kalapathy et al. 2000). Diluted phosphoric acid was added slowly to control the pH of the reaction. At constant solvent ratio and amount of silicate, the particle dimension improved along with the rise in pH (Fig. 3). Results revealed that

Table 1 The BET surface area, single-point total pore volume, average pore diameter and particle size of the silica samples prepared at different parameters

Samples	BET surface area (m^2g^{-1})	Single-point total pore volume (cm^3g^{-1})	Average pore diameter (nm)	Average particle size (nm)	Particle size range (nm)
Effect of ethanol	–	–	–	–	–
1:0:0[a]	304.82	1.17	15.56	NA	NA
1:0:0.20[a]	197.66	0.48	9.72	180.67	98–272
1:0:0.30[a]	74.26	0.14	7.70	288.49	94–631
Effect of pH	–	–	–	–	–
pH 7[b]	197.66	0.24	4.95	230.37	78–435
pH 8[b]	199.49	0.32	6.60	294.79	51–607
Effect of addition of water	–	–	–	–	–
1:1:0.30[c]	370.35	0.72	8.02	150.49	75–252
1:1:0.30[d]	357.86	0.67	7.68	164.49	37–267
1:1:0.30[e]	212.45	1.21	7.7	192.00	28–317

BET Brunauer, Emmett and Teller

[a] Samples were prepared using 3 M H_3PO_4 at pH 9 based on ratio of SS: H_2O: EtOH

[b] Samples were prepared using 3 M H_3PO_4 based on ratio of SS: H_2O: EtOH = 1:0:0.30

[c] Samples were prepared using 3 M H_3PO_4 at pH 7 based on ratio of SS: H_2O: EtOH

[d] Samples were prepared using 3 M H_3PO_4 at pH 8 based on ratio of SS: H_2O: EtOH

[e] Samples were prepared using 3 M H_3PO_4 at pH 9 based on ratio of SS: H_2O: EtOH

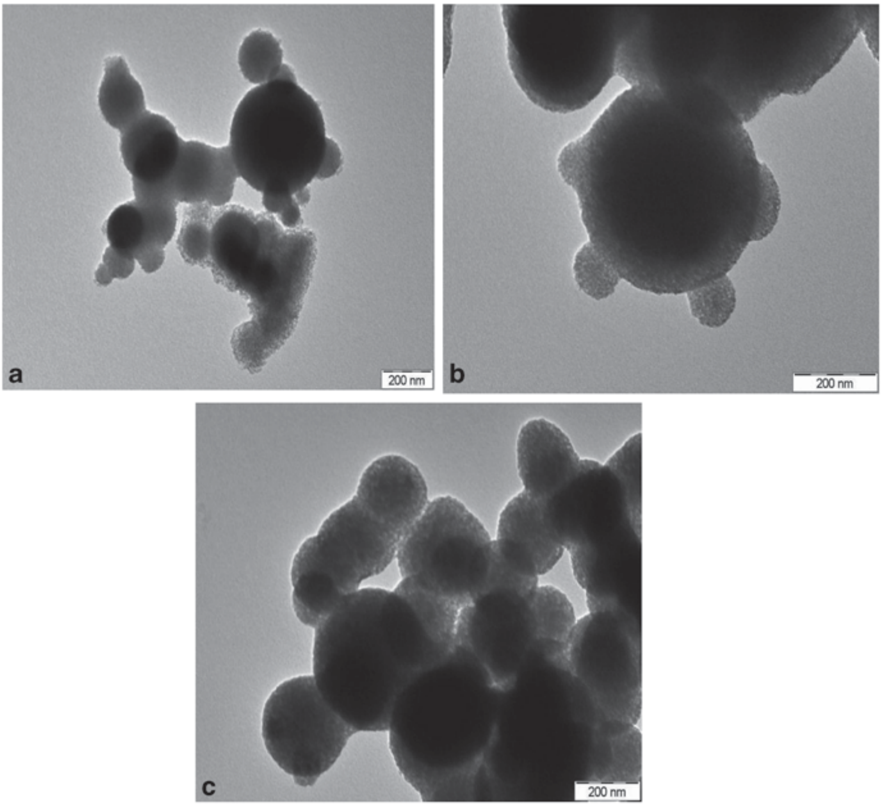

Fig. 3 TEM images of the silica prepared at different pH based on the ratio of SS: H_2O: EtOH = 1:0:0.30 at pH: **a** 7 **b** 8 **c** 9 *EtOH* ethanol, *SS* sodium silicate, *TEM* transmission electron microscopy

as the pH increased, the morphologies of silica powder were further sphere-shaped and the particle dimension grew with extra broad dispersion. High pH concentration stimulates the development and the synthesis of sphere-shaped powder by advanced hydrolysis and compression degrees (reactions (3) & (4); Sing et al. 2008). A solid cream is formed instantly on adding up of phosphoric acid (pH > 9), prominent to solid-accumulated powder; at pH < 7, product turns out to be very watery and ageing takes up to 5 days, unfavourable for the synthesis of silica. Therefore, pH scale in the current work is 7–9.

$$\equiv \text{Si-OH+OH} \rightarrow \equiv \text{Si-O}^{-} + \text{H}_2\text{O} \tag{3}$$

$$\equiv \text{Si-OH+} \equiv \text{Si-O}^{-} \rightarrow \equiv \text{Si-O-Si} + \text{OH} \tag{4}$$

Evaluating N_2 adsorption/desorption isotherms, the BET superficial areas of silica were calculated as ~198, ~199 and ~75 m^2g^{-1} with equivalent pore diameters of 4.95, 6.60 and 7.70 nm, respectively, attained at pH 7, 8 and 9, correspondingly (Table 1). Decline in superficial area tallies with a proliferation in powder dimensions conferred previously. Bestowing to International Union of Pure and Applied Chemistry (IUPAC) arrangement, synthesized silica cream will be categorized as mesoporous materials, for the reason that the pore sizes were in range of 2–52 nm (Liou and Yang 2011; Kalapathy et al. 2000).

Water Concentration Effect

Silicate of sodium is the foundation of ≡Si–OH units. Therefore, its percentage content would disturb reactions (2), (3) and (4), and decide the amount of accumulation of silica powder. Figure 4 shows adding of water molecules on morphologies and dimension of silica powder. SS units were greatly agglomerated because of the huge quantity of hydrolysed units at greater concentration. Hence, they bring out the result in widespread growth of principal particles. The dimension of the silica powder was reduced, the powder was further diffuse and there were rarer aggregates due to the addition of water (Fig. 4b). In the current situation, the absorption of silicate is decreased. Condensation reaction outcomes with relaxed powder progress and condense the powder dimension. The average particle size of silica powder reduced from 230.37 to 150.49 nm at pH 7 (sample, SS:EtOH = 1:0.30). Accordingly, the precise superficial area and pore diameter were improved from 197.66 to 370.35 m^2g^{-1} and from 4.95 to 8.02 nm, correspondingly, under SS:H_2O:EtOH = 1:0:0.30 and 1:1:0.30 (Table 1).

FTIR and XRD Analysis

Distinct XRD with wide-ranging and tall-strength humps at 22° (2θ) is characteristic for the amorphous silica (Fig. 5; Rozainee et al. 2008) and is attributed to the non-appearance of well-organized crystalline structure.

The most important chemical groups of silica were recognised by infrared spectra (IR) of silica powder, and were studied by FTIR spectroscopy ranging from 4000 to 400 cm^{-1} (Fig. 6). The principal absorbance points (peaks) at 1107 cm^{-1} resemble those of distorted atmospheres of the siloxane bond, Si–O–Si. Groups found at 802 and 477 cm^{-1} were consigned to the Si–O proportion stretching vibration and bending vibration, respectively. The groups at nearly 3450 and 965 cm^{-1} are attributed to the SiO–H asymmetry stretching atmospheres and bending atmospheres, correspondingly. The peak at 1634 cm^{-1} has its place at the –OH stretching atmospheres of the silanol or water molecules present in silica surface (Jal et al. 2004).

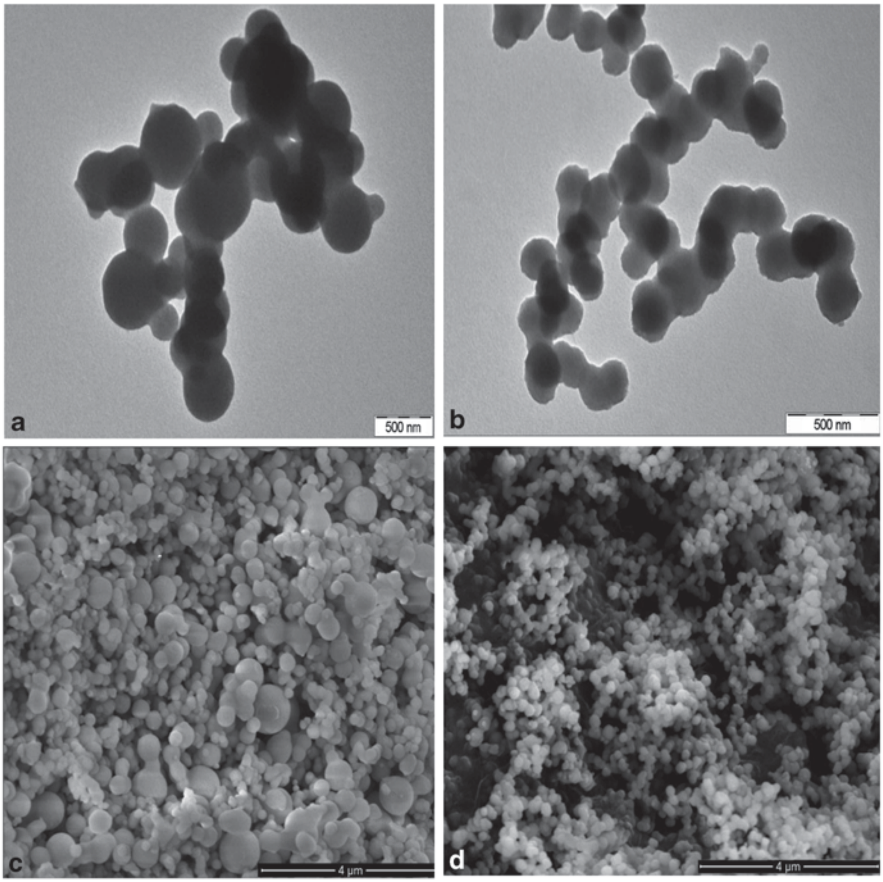

Fig. 4 TEM versus SEM images of the silica prepared at different amounts of water based on the ratio of SS: H_2O: EtOH at pH 8: **a** 1:0:0.30 **b** 1:1:0.30. *EtOH* ethanol, *SEM* scanning electron microscopy, *SS* sodium silicate, *TEM* transmission electron microscopy

Energy-Dispersive X-ray Spectroscopy

The existence of silicon (Si), sodium (Na) and oxygen (O) was distinguished in silica particles (Table 2). The occurrence of oxygen and silicon was because of the creation of silanol groups (Si–OH) and siloxane bonds (Si–O–Si). Sodium was spotted in low quantity, for the reason that the phosphoric acid possibly will remain non-dissolved whole Na^+ ions from SS solution. Phosphates were totally absent from the sample, because all phosphates were either utilized during precipitation or swept away throughout the washing technique.

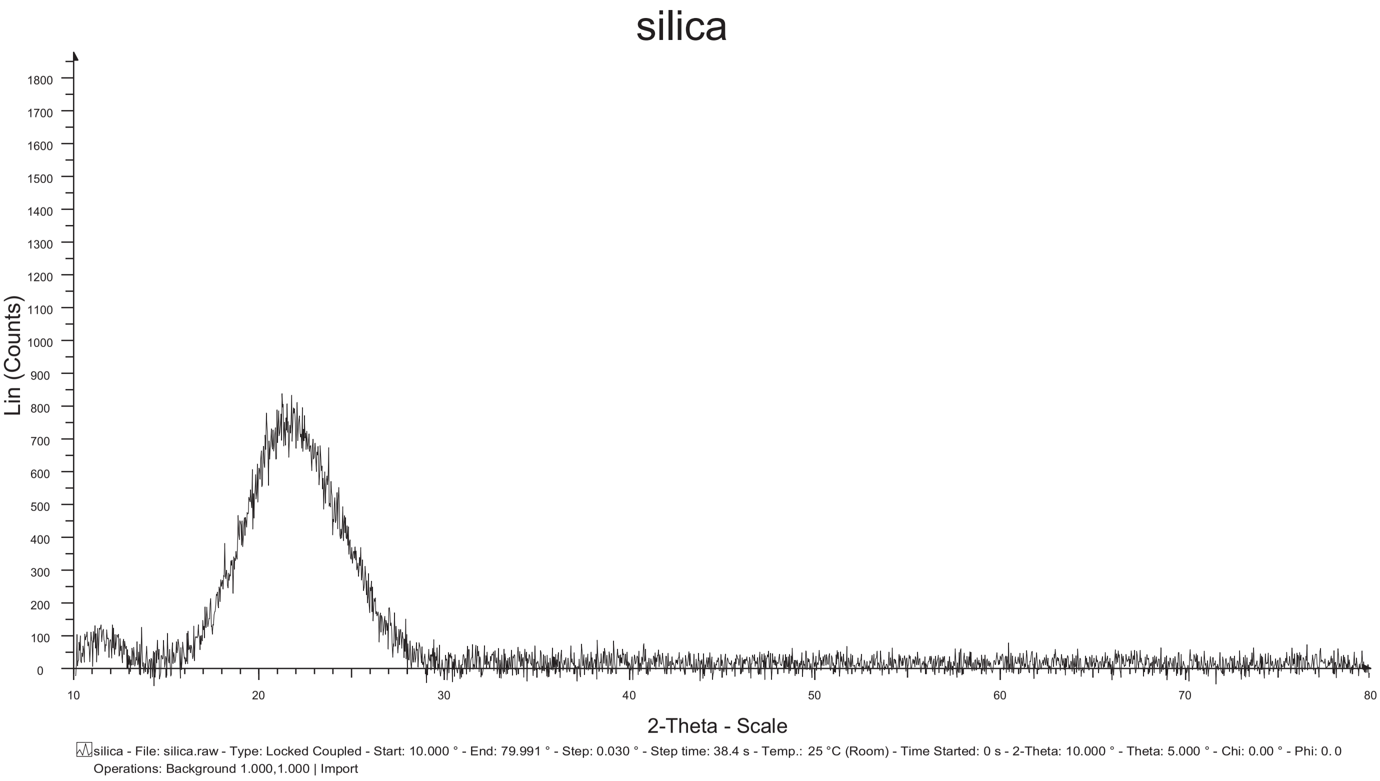

Fig. 5 XRD pattern of the silica sample produced from rice husk. *XRD* X-ray diffraction

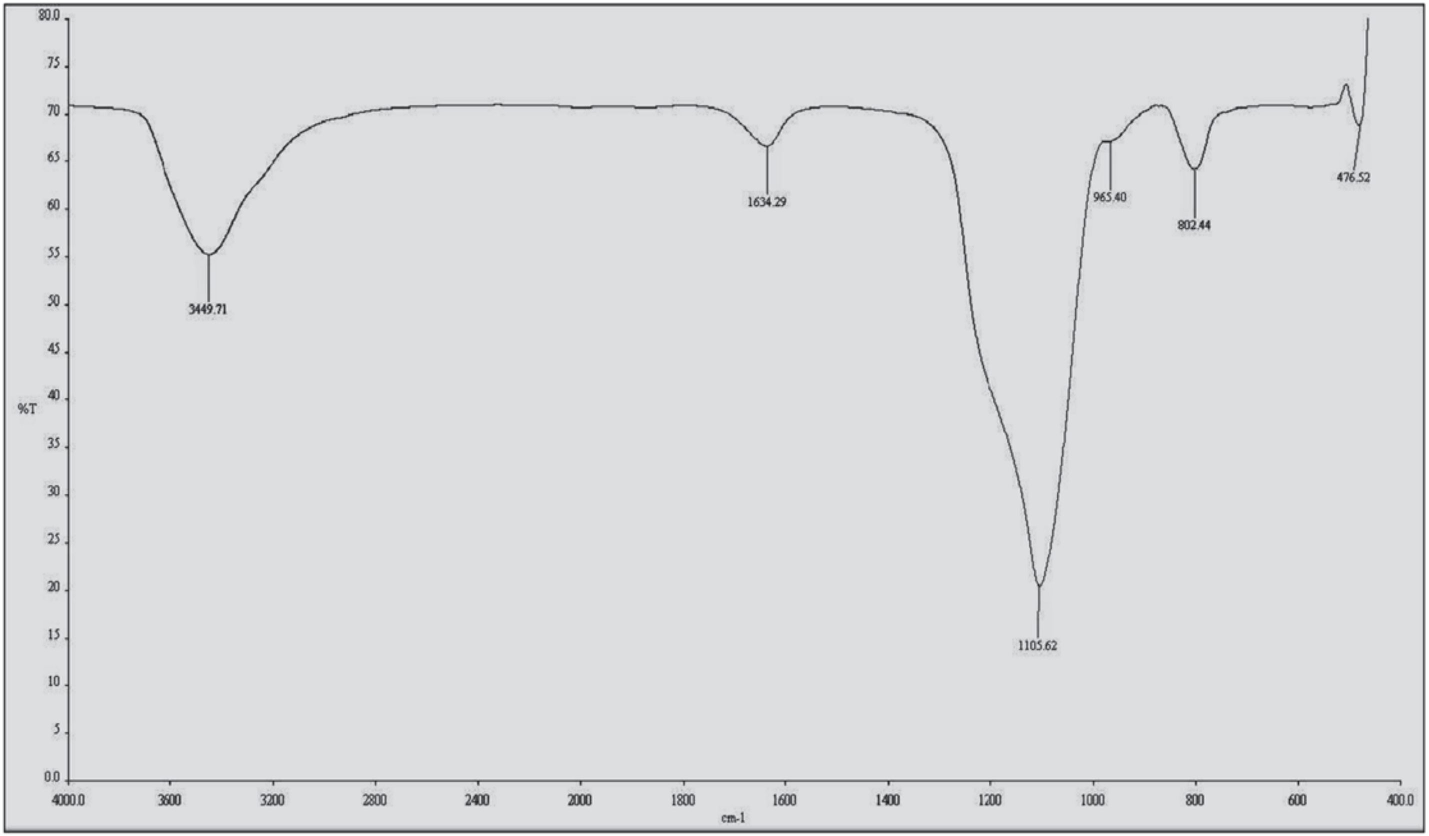

Fig. 6 FTIR spectrum of the silica sample produced from rice husk

Table 2 EDX analysis of the silica powder prepared under conditions: SS:H_2O:EtOH = 1:1:0.30, pH 7

Element	Average weight %
O	59.56
Na	0.64
Si	39.80
Total	100.00

EDX energy-dispersive X-ray spectroscopy, *EtOH* ethanol, *SS* sodium silicate

Conclusions

Rice husks, the main source of SS precursor and sphere-shaped silica powder, were formed productively. By adjusting reaction environments like concentration of ethanol, varying pH (phosphoric acid) and concentration of water, precise superficial area of ~370 m^2g^{-1} and sphere-shaped morphological dimensions were obtained. This economical and ecofriendly method formed silica powders with appropriate properties with high prospective to be used in dental nanocomposites.

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Rheological Properties and Processing of Polymer Blends with Micro- and Nanofibrillated Cellulose

Hesam Taheri and Pieter Samyn

Abstract Recently, scientists have a high interest in using micro- and nanofibrillated cellulose (MFC/NFC) fibers as reinforcing components in nanocomposites together with a biopolymer matrix. This interest is abstracted from the abundant availability of cellulose in nature and the need for renewable resources. Besides chemical aspects, however, the successful formulation of polymer blends with nanocellulose additives requires a good understanding of the physical compounding and mixing properties. Therefore, the rheological features of aqueous MFC and NFC suspensions play an important role for the further development of industrial applications. Generally, the MFC/NFC suspensions show nonlinear behavior in the form of a pseudoplastic or dilatant fluid at higher shear rates. There are different parameters affecting their rheological behavior including processing parameters, such as degree of fibrillation and concentration, and rheometrical parameters, such as shear rate, temperature, rheometer geometry (gap), wall slip, and flocculation. Controlling these parameters is very important before and after the processing of MFC or NFC due to the direct or indirect effects on the viscosity of the suspension. The aggregation of fibrillated cellulose is a conventional barrier to obtain suitable dispersive mixing and an important reason for the loss of mechanical properties of nanocomposites. As outlined in this chapter, better physical understanding of the rheological behavior of MFC or NFC is helpful for further processing of polymer blends by melt extrusion, injection molding, or electrospinning. A better rheological insight helps to control the processing of nanocomposites and avoid the named issues.

Keywords Nanofibrillated cellulose · Suspension · Processing · Rheology

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Introduction

The fabrication of composite materials from renewable materials has become of increasing interest in view of shortage of fossil-oil-based polymer resources. A wide variety of natural, bio-based materials from different resources and their availability under different forms provide a broad pallet of “building” elements that can be combined into composites. Wood is an impressive example of a natural composite with cellulose fibrils embedded in a matrix of lignin and hemicellulose. Understanding its complex hierarchical structure has engaged scientists over decades, yet its organization still remains largely unexplained (O’Sullivan 1997; Klemm et al. 2005; Diotallevi and Mulder 2007). It is uncommon for cellulose to be in a chemically pure form, e.g., without hemicellulose or lignin and other polysaccharides that are contained in the cell wall of wood. However, pure cellulose can be found, for example, in the seed hairs of the cotton plant. Overall, there are many sources from which the cellulose can be obtained, including agricultural residues, water plants, grasses, or marine organisms. In recent years, various chemical pathways have been established to liberate the cellulose from its matrix and use it as natural fiber reinforcement.

By further application of nanotechnological routes, the cellulose can be converted into fibrous structures with several nanoscale dimensions. From a plant physiological point of view, the S1, S2, and S3 layers in the outer cell wall contain a combination of different arrangements of fibrils with different dimensions (Chinga-Carrasco 2011), which can be artificially disintegrated. Different descriptors of these nanofibers are often referred to in literature: (i) cellulose nanowhiskers (CNW), nanocrystals, or even monocrystals are used to designate short crystalline rod-like nanoparticles, while (ii) microfibrillated cellulose (MFC), nanofibrillated cellulose (NFC), or cellulose nanofibers (CNF) should be used to designate long flexible nanoparticles with either micro- or nanoscale fiber diameters, consisting of alternating crystalline and amorphous domains. In this chapter, we specifically focus on the use of fibrillated cellulose because of its beneficial properties: It exhibits excellent mechanical performance at low weight, biocompatible, transparent, and reactive due to the hydroxyl groups on its large fiber surfaces (Klemm et al. 2011). The highly anisotropic shape of fibrillated cellulose with diameters of about 10–20 nm and aspect ratio typically between 100 and 1000 provide them with unique reinforcing ability, in contrast with the CNW that have more homogeneous sizes and shapes. It is known that the aspect ratio will influence the viscosity and steady-state shear properties of the cellulose fiber suspension, as higher aspect ratios result in larger intrinsic viscosity (Iwamoto et al. 2014). The MFC/NFC forms a densely entangled fibrous network with interesting properties for coating applications and/or further processing as a continuous reinforcing phase in combination with bio-based polymer matrixes. In general, such nanoscale fibers can be used to design and create new biopolymer composites with high flexibility and better mechanical properties than their constituent components (Ajayan et al. 2003; Dufresne 2012). The high specific surface area of MFC/NFC fibers not only provides good reactivity towards suitable polymer materials but also implies specific hindrance for homogeneous processing. In order to further improve the performance of cellulose fiber nanocomposites in combination with biodegradable polymer matrix materials (Lee and Wang 2006), many researchers have sought to chemically tailor the fiber/matrix interfacial properties (Rajulu et al. 2001; Saxena and Gowri 2003; Kumar and Siddaramaiah 2005; Kumar et al. 2005; Das et al. 2006; Das and Chakraborty 2006, 2007; Okubo et al. 2004; Mi et al. 1997; Chen et al. 1998) and/or modify the fiber morphology (Takagi and Ichihara 2004; Murali et al. 2007). Recently, other approaches for surface modification and interface compatibilization of MFC are also investigated, relying on the in situ deposition of hydrophobic nanoparticles on the fiber surface (Rastogi and Samyn 2014). While the chemical isolation of cellulose structures under the form of MFC/NFC fibrils or CNW has been the focus of intense research in the past decade (Hubbe et al. 2008; Siró and Plackett 2010), the processing of the nanoscale components and bio-based matrix materials has been more challenging due to their molecular weight and rheological behavior. The latter remains a most critical issue that limits the further application and final breakthrough of bio-based nanocomposites.

The processing ability of nanoscale cellulose additives in combination with polymer matrixes requires the homogeneous dispersion of both phases in order to fully exploit the strength properties of the reinforcing fiber phase. However, the strong tendency of aggregation of cellulose nanofillers due to their hydrophilic character and consequently poor dispersion behavior has largely impeded the widespread use of various processing technologies. In particular, intermediate drying of cellulose nanofibrils from suspensions is critical in re-dispersing the materials (Peng et al. 2011). Different drying processes such as air, oven, and freeze-drying, or atomization and spray drying have been investigated, resulting in the formation of different morphologies and sizes of the dried product (Zepic et al. 2014). It has been indicated that freeze-drying preserved the favorable aspect ratio of MFC/NFC with nanoscale dimensions. The spray-drying process was mostly influenced by the gas-flow rate and resulted in agglomerates of NFC depending on the original fibril properties in the formed droplets (Peng et al. 2012). Depending on the number of drying and re-moisturing cycles, irreversible changes in the cellulose structure are observed due to co-crystallization and hornification (Newman 2004), which alters the fiber quality and dispersibility. The initial rheological properties of the suspension are not recovered after rewetting, which is generally attributed to the formation of additional hydrogen bonding and cross-linking during drying. Therefore, several techniques for (re-)dispersing MFC were developed, adding water-soluble polymeric additives before drying. The dispersibility of MFC can be improved by controlling drying conditions and chemical surface modifications (Nechita and Panaitescu 2013).

Various recent overviews of different processing methods for cellulose nanocomposites have been made (Dufresne 2010). Here, few processing issues are mentioned, as an illustration of the importance of further rheological research. Mostly, bionanocomposites are prepared from aqueous environments, e.g., from hydroxypropyl cellulose (HPC) with dried and re-dispersed carbomethylated MFC powders

(Tingaut and Zimmermann 2011). The solvent casting of acetylated MFC in combination with polylactic acid (PLA) from chloroform solution resulted in films with a maximum loading of 10 wt.% MFC with superior mechanical properties (Bulota et al. 2012). Similarly, MFC–polyvinyl alcohol (PVA) composite films with sufficient homogeneous dispersion of MFC in the polymer matrix are reached up to 10 wt.% MFC by solvent casting (Lu and Drzal 2008).

The melt processing of cellulose nanocomponents in combination with bio-based polymers remains more challenging. First, the processing of biopolymers is often more difficult than synthetic polymers because of their high molecular weight and high viscosity. Otherwise, the most critical point in compounding of MFC/NFC with molten polymers is to feed the nanoscale fibers into the extrusion line and approach a dispersive and distributive state of mixing. The high surface area of fibrillated fibers and their propensity to aggregate are the first obstacles of mixing of NFC in dried form into molten polymer material (Jonoobi et al. 2010; Lee and Wang 2006; Bulian and Graystone 2009). In general, the rheological properties and blending of cellulose nanowhiskers in combination with biopolymers have been more frequently studied than MFC/NFC blends. It has been shown that the chemical modification of nanowhiskers by grafting aliphatic chains or polymer moieties could be an alternative approach to ensure homogenous dispersion of the nanofiller within the hydrophobic matrix using a melt-extrusion technique (Goffin et al. 2011). Recently, the mixing and melt compounding could be favored after (2,2,6,6-tetramethylpiperidine-1-oxyl) oxidanyl (TEMPO) oxidation of CNF, as demonstrated in combination with thermoplastic starch (Cobut et al. 2014). The in situ surface modification of MFC after treatment with potassium hydroxide (KOH) during high shear dispersion combined with ultrasound resulted in good dispersion of the never-dried cellulose with native starch in a single-screw extruder (Ferreira and Carvalho 2014). In another approach, mixing problems can be overcome by using a two-step process, including the production of a master batch with controlled composition followed by extrusion or injection molding. Different techniques have been exploited for the premixing of fibrillated cellulose with bio-based polymers, e.g., nanocomposites of PLA/NFC were prepared by premixing a master batch with high concentration of NFC and subsequent dilution to final concentrations of 1–5 wt.% during extrusion, with the occurrence of aggregates only at highest concentrations (Jonoobi et al. 2012). The premixing of MFC and PLA in an organic solvent and subsequent roller mixing shows uniform dispersion and better mechanical properties (Lee and Wang 2006; Murali et al. 2007). Other techniques such as compression molding of PLA/MFC may result in the formation of a cellular MFC network rather than creating a uniform dispersion, while subsequent twin-screw extrusion may disrupt the MFC network due to limited deformability, resulting in substantial losses in stiffness (Boissard et al. 2012; Plummer et al. 2013). Finally, the appropriate dispersion of MFC in PLA indeed results in an improved fracture behavior of the composite, as obtained by adding 1% MFC using a calendering technique or roller mixing (Okubo et al. 2004, 2009), where the lower MFC concentrations have a positive effect on the mechanical properties of their nanocomposites. The compression-molding technique was also used to form bulk composites from dried premixes of MFC/starch, by curing the blends at 150 °C (Duanmu et al. 2012). A new manufacturing process similar to papermaking could be successfully applied for the production of thin sheets with uniformly distributed PLA/MFC (Nakagaito et al. 2009). In most novel approaches, the extrusion of nanocellulose-reinforced nanocomposites is improved by using MFC nanoparticles encapsulated by physically cross-linked alginate (Lemahieu et al. 2011). The resulting capsules can be fed to an extruder in combination with a thermoplastic polymer. Most traditionally, however, the MFC remains compounded under aqueous conditions. The compounding of poly(vinyl alcohol) or PVOH with MFC in water is favorable to decrease the melting temperature of PVOH and provides well-dispersed samples that could be further extruded in combination with CO_2 and water as foaming agents (Zhao et al. 2014). It was only recently that continuous microfibrillation of pulp and its melt compounding could be effectively obtained by kneading with polypropylene in a twin-screw extruder (Suzuki et al. 2014). In conclusion, the quality of the extruded nanocomposite is affected by various parameters such as, temperature, diameter of die, design of screw, and the amount of MFC or NFC filler. Moreover, the processing of polymers within an extrusion line should be done above the melting temperature of the polymer, which could lead to the degradation of the cellulose polymer chain. Therefore, more fundamental studies on the rheological properties of molten composite blends can reflect the internal structure and processability of those materials within an optimized parametrical window. At the same time, only few studies have investigated the rheological behavior in the molten state to obtain insights on the change in microstructure and degree of dispersion in the melt as well as on the effect of shear stress on the integrity of the MFC network (Mabrouk et al. 2011).

For solvent-based processing techniques such as casting and electrospinning, the precise viscosity control of aqueous MFC/NFC suspensions is required. In papermaking, the rheology of fibrillated cellulose suspensions becomes important in the viewpoint of formation of nanofiber papers on traditional paper machinery, or for the application of fibrillated cellulose suspensions with moderate-to-high solid contents to a paper surface with a blade coater. For incorporating nanocellulose additives in coating applications, a higher viscosity is required for roller coating than for spray-coating applications, and an abnormal high increase in viscosity would cause insufficient leveling of the coating on the substrate (Bulian and Graystone 2009). In another example, good control of the nanocellulose viscosity is required in electrospinning applications (Härdelin et al. 2011). The rheological data can be used to understand the feasible viscosity of cellulose solutions and indicate their potential use as suitable medium for electrospinning at different temperatures. At present, most of the related work on electrospinning of cellulose deals with fundamental studies on the behavior of various potential electrospinning solutions, including *N*-methylmorpholine *N*-oxide/water (NMMO/water; Han et al. 2008), NaOH/urea (Qi et al. 2010), lithium chloride/dimethylacetamide (LiCl/DMAc) (Frenot et al. 2007), and ionic liquids (ILs; Miyauchi et al. 2010). Especially, electrospinning of CNF was reported with different cosolvents (Härdelin et al. 2011), such as dimethylacetamide (DMAc), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). The latter are specifically added to modify the rheological characteristics, the electrical conductivity, and the surface tension of the cellulose-based solutions. From studies on the steady-state shear viscosity of cellulose in different cosolvents with ionic liquids (ILs) as a function of shear rate and in constant stress, it has been demonstrated that certain degree of viscosity and surface tension is needed to form suitable cellulose solutions for electrospinning, e.g., the DMSO-IL has higher viscosity values compared to the DMAc-IL and DMF-IL (Qi et al. 2010). In another study on electrospinning of poly(ethylene oxide) and microfibrillated cellulose (PEO/MFC), rheological data show remarkable changes in viscosity of PEO/MFC dispersions at higher MFC concentrations up to 21 wt.%, while there are almost no influences of surface morphology or fiber diameter (Fortunato et al. 2012). After optimization of the rheological characteristics, MFC is able to form a finely well-dispersed continuous network structure within the electrospun fibers.

The above overview illustrates that huge advances in the processing of NFC/MFC suspensions have been made over the previous decade. From an engineering point of view, the understanding of the viscoelastic properties of nanocomposite blends is of great importance in obtaining fundamental knowledge for predicting the processability of these materials (Dealy and Wissbrun 1999). From a scientific research standpoint, the rheological approach is effective in probing the microstructure and assessing the state of the nanocomposite dispersion and determining conditions of homogeneous mixing directly in the melt state. Moreover, rheology seems to be a unique technique for investigating polymer nanocomposites and exploring the microstructure of the network that is likely to be formed by analyzing its linear and nonlinear viscoelastic behavior (Zhu and Sternstein 2003). Therefore, this chapter aims at summarizing some effects and at providing additional insight in the rheological behavior of micro- and nanoscale cellulose suspensions, before processing them into extrusion line or injection molding.

Fibrillation and Processing of Cellulose Fibers

Selection of Resources for MFC/NFC

Lignocellulosic biomass is obviously the main feedstock for producing MFC and NFC. Bleached kraft pulp from wood is most often used as a starting raw material for MFC (Lavoine et al. 2012; Taipele et al. 2010). However, the concurrential use of wood-based fibers for traditional pulp and paper industry can lead to conflict situations with rising resource prices. Therefore, alternative sources of raw materials such as agricultural crops and/or side products have risen into the spotlight. The needs for change towards these resources are implied by environmental benefits and efficient use of resources, where agricultural residues can be revalorized into high-performance composite materials rather than being used for low-value products or purely energetic recovery by incineration. In particular the lower energy content of agricultural waste products (relatively low lignin content) compared to wood (higher lignin content) makes it feasible to consider these sources for material production. Due to different fiber compositions, the production of MFC/NFC from nonwood agricultural products generally requires lower energy and bleaching processes are less demanding (Lavoine et al. 2012; Alemdar and Sain 2008a). In addition to the lower lignin content in agricultural resources, the cellulose microfibrils are less tightly organized and fibrillation can be done more easily (Dinand et al. 1996). Depending on the composition of lignin, hemicelluloses, and cellulose, the selection of raw materials affects the efficiency of the fibrillation and the eventual needs for pretreatment processes, as further detailed. As such, the presence of residual lignin amounts on the MFC/NFC fibers after fibrillation may reduce the need for further hydrophobic surface modification and improve their compatibility.

The extraction of cellulose fibers from agricultural plants, such as wheat straw, has been known for centuries in the papermaking industry. Several thermal, mechanical and chemical methods have been developed to extract cellulose fibers from waste plant biomass without significant degradation of the cellulose, maintaining a degree of polymerization of above 1000 units (Kopania et al. 2012). In recent years, also MFC/NFC fibers have been extracted from annual plants such as wheat straw (Kaushik et al. 2010), carrots (Lavoine et al. 2012; Siqueira et al. 2010), palm trees (Bendahou et al. 2010), and ramie (Bhattacharya et al. 2008). Agricultural residues such as sugar-beet pulp (Habibi and Vignon 2007), soy hulls (Alemdar and Sain 2008a), banana rachis (Zuluaga et al. 2007), banana peel (Phiriyawirut et al. 2010), or soda-bleached bagasse pulp (Hassan et al. 2011) were also used, eventually in combination with specific additives as retention aid (Djafari Petroudy et al. 2014). While extracting MFC from raw fibers of bamboo trees, fibers with high crystallinity of above 70 % were extracted (Nguyen et al. 2013). Other sources, such as bagasse, delivered MFC fibers with a crystallinity up to 40 %, which is higher than that of native cellulose from cassava bagasse (Wicaksono et al. 2013). A comprehensive review of MFC produced from nonwoody plants with different yields and morphologies has been published recently (Alila et al. 2013) including sisal, jute, and hemp. The efficiency of the disintegration of cellulose from the latter annual plants was optimized by a combination of steam explosion and ultrasound pretreatment in combination with extraction in 0.4 wt.% NaOH (Šutka et al. 2013). In a study on MFC from unbleached pulp of annual plants such as kenaf (Rezayati Charani et al. 2013), it has been demonstrated that fiber suspensions can be produced at higher consistency compared to traditional scotch pine pulp, while the rheological properties were consistent. As a result, the possibility for producing MFC suspensions with higher solid fiber contents (<5 % w/w) makes them favorable to be processed into paper sheets and composites, but the rheological behavior of MFC suspensions at high concentrations may be different from traditional suspensions.

Fibrillation of Cellulose Fibers

Pioneering work on the production of MFC was done in 1983 (Herrick et al. 1983), by isolating MFC from several wood pulp types. The MFC could be dried and redispersed while maintaining the viscosity almost unchanged. Since then, several techniques have been developed for the mechanical separation of cellulosic fibers, including homogenization, microfluidization, microgrinding, cryocrushing, and ultrasonication.

By grinding, the cellulose suspension is fed between a fixed and turning grindstone. By cryocrushing, a mortar and pestle are used for crushing the swollen cellulose fiber after submersing it in liquid nitrogen. Recently, MFC or NFC fibers can be isolated by the processing of fiber pulp within a high-pressure (high-shear-rate) homogenizer. With this technique this technique, high internal shear forces are created into the fiber suspension, allowing to disintegrate the cell walls of native cellulose fibers into a microfibrillar suspension. The homogenizer high-shear-fluid processor relies on the forces of shear and impacts against colliding streams and against the walls to de-agglomerate, fibrillate, and disperse the solid fiber phase into the liquid aqueous phase. The fibrillation process typically takes place within an interaction chamber at average pressures of 300–1300 bar and at a given number of cycles ranging from 15 to 30. The interaction chamber within a homogenizer processor can essentially be considered as a fixed continuous microreactor geometry that provides the turbulent mixing to create a uniform pressure profile for accurate and repeatable size distributions. Inside these chambers, the dilute slurries of cut and eventually pretreated cellulose fibers are exposed to flow velocities and shear rate to yield individualized cellulose micro- or nanofibrils. Mechanical pretreatments to decrease the size of the fibers may include milling and homogenization (to increase swelling), as well as refining (to raise the binding potential of cellulose fibers). As shown in Fig. 1, the fiber dispersion is initially poured into the inlet reservoir.

The intensifier pump for homogenization has two motions: (i) suction phase and (ii) compression phase. During the suction, a portion of the fiber dispersion is drawn into the processor through a one-way valve. The compression device will push this portion of the fiber dispersion through the interaction chamber and then to the outlet reservoir. A correct geometry of the interaction chamber can be selected based on the starting particle size, the application, and the amount of required shear

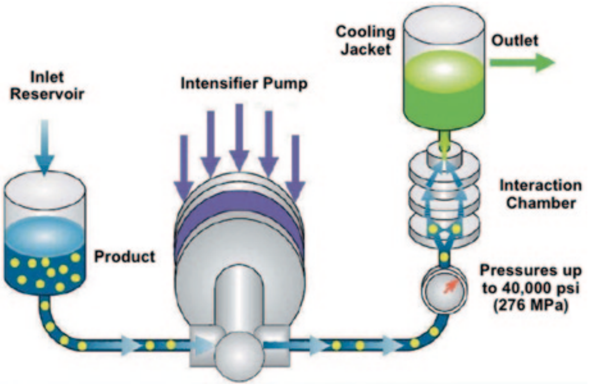

Fig. 1 Schematic of the microfluidizer processor for the production of microfibrillated cellulose (MFC).

and impact. The applied pressure is the mechanism that propels the fiber dispersion through the interaction chamber and achieves the diameter reduction of fiber. Increasing the pressure will increase the rate of shear rate and the degree of fibrillation. Depending on the number of passes and on the chamber sizes, different morphologies and sample sizes can be produced. In this regard, a low number of cycling passes applied through interaction chambers with a large diameter will obviously result in MFC fibers, while a higher number of passes within small interaction will lead to NFC. For instance, at a low number of homogenizing passes the fibrillation typically starts at the fiber surface where small fibrils are pulled out of the fibers. Furthermore, in a typical range between 16 and 30 passes through the homogenizer, a complete fibrillation of the bulk of the fibers progresses, which increases the mechanical properties and the bending strength of the fibers particularly due to the formation of a larger contact surface area (Abdul Khalil et al. 2012). Finally, the fiber dispersions turn to a gel-like suspension with a stepwise increment in viscosity after several passes through the homogenizer.

As one disadvantage, the fibrillation processing hardly provides a uniform MFC/NFC suspension. In this respect, the behavior of the fiber with the highest surface areas is most critical and the use of high-pressure homogenization generally provides fibers with largest surface areas. At the same time, this process consumes more energy than microfluidization or grinding. The nonuniformities in the suspension media are built by the high tendency of aggregation of single cellulose microfibril and/or the flocculation with larger fibers. Figure 2 shows the scanning electron microscope (SEM) images of entangled microfibrils with aggregated fibril. Therefore, additional stabilization mechanisms for MFC suspensions should be implemented.

As another disadvantage, the production of MFC and NFC is a very energy-intensive process as a large input of mechanical energy is required and additional energy-consuming pretreatments are often necessary for its defibrillation. A comparative study on energy and production costs has demonstrated that physical properties of the MFC improve at higher energy consumption (Spence et al. 2011). However, the energy consumption also depends on the rheological flow properties and eventual clogging. The reduction in energy needs for producing MFC on industrial scale is one of the key factors for a further breakthrough of these materials. Therefore,

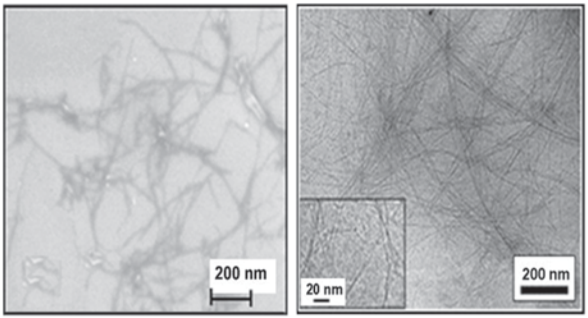

Fig. 2 Scanning electron microscope (SEM) images revealing a network of isolated microfibrils and fibril aggregates. (Abdul Khalil et al. 2012)

fiber pretreatment techniques by means of enzymatic reactions and/or chemical additives help to make the process more energetically and financially efficient (Abdul Khalil et al. 2012; Siró and Plackett 2010), depending on the raw material source. In general, properly chosen pretreatments of cellulosic fibers and/or their combination help to increase access to hydroxyl groups, as they increase the inner surface, alter crystallinity, and break cellulose hydrogen bonds and therefore, boost the reactivity of the fibers. As such, pretreatments can help to decrease the amount of energy consumed for 1 t of cellulosic fiber from 30,000 kWh/t to as little as 1000 kWh/t. Several methods for fiber pretreatment have been developed:

- Enzymatic treatments are generally applied to partly degrade and/or modify the lignin and hemicellulose contents, while leaving the cellulose fibers almost unaffected. The used enzymes can primarily be categorized as (i) cellobiohydrolases (A and B type cellulases) which have most effect on crystalline cellulose and (ii) endoglucanases (C and D type cellulases) that do not attack the cellulose if its structure is not disordered. Mild enzymatic pretreatment can also be applied during refining or homogenization of NFC into the fiber dispersion (Abdul Khalil et al. 2012; Tanpichai et al. 2012).The mild enzyme results in a higher aspect ratio and has a less intensive effect compared to acid hydrolysis. On the one hand, the use of enzymes may have almost no significant effects on the final fibrillar sizes but mostly leads to more fluent processing without clogging (Abdul Khalil et al. 2012; Siddiqui et al. 2011). On the other hand, optimum concentrations of enzyme may have also leads to reduce the fibril size without blockage through homogenizer were reported at around 1 % resulting nanofibers of 38–42 nm (Abdul Khalil et al. 2012; Janardhnan and Sain 2011).
- Alkaline–acid pretreatments need to be used for solubilizing lignin, hemicellulose and pectin, which contain three main phases. At first, the fibers are soaked for about 2 h in 12–17.5 wt. % sodium hydroxides (NaOH) to increase the surface of cellulosic fibers, which are more sensitive to hydrolysis. The second phase includes the hydrolysis of the fibers with hydrochloric acid (HCl) at a temperature of 60–80 °C in order to solubilize the hemicelluloses. The third phase involves processing the fibers with caustic soda (e.g., 2 wt.%) at temperatures and durations that are similar to the previous phases. During the last step, the structure of the lignin is disrupted, and links between carbohydrates and lignin are also broken. Another preparation route includes alkaline peroxide treatment (H_2O_2) that rapidly degrades the lignin and lignin compounds into low molecular weight products (Cristobal et al. 2006). In general, the crystalline morphology of the MFC may be changed from cellulose I to cellulose II with consequent variations in mechanical properties, depending on the intensity of the alkaline treatment. However, the extensive treatment of the MFC fibers by sulfuric acid hydrolysis may result in the presence of sulfated groups onto the cellulose surface, resulting in lower thermal stability and mainly different fiber interactions that influence the suspension properties.
- Organic salts (IL) can alternatively be used as a pretreatment method before mechanical isolation of NFC. These are organic salts with useful characteristics such as nonflammability and thermal and chemical stability. These pretreatments

are used to dissolve cellulose and can be a good pretreatment before high-pressure homogenization. For example, 1-butyl-3-methylimidazolium chloride was used to dissolve bagasse cellulose (Abdul Khalil et al. 2012; Li et al. 2012). After this, it could easily be processed through the homogenizer at high pressure without any clogging until NFC with diameters of 10–20 nm was obtained with final characteristics such as lower thermal stability and crystallinity.

Finally, the rheological features and further processing characteristics of the MFC/NFC suspensions are affected by the pretreatment methods, mainly influencing the degree of fibrillation and eventually introducing surface charges. For example, a suspension of NFC prepared by HCl hydrolysis is more shear thinning than a suspension prepared by H_2SO_4 hydrolysis (Araki et al. 1998). Otherwise, an increase in the ionic strength can result in the strong gel-like behavior and the increasing of viscosity, storage modulus, and loss modulus. In particular, the higher ionic strength at higher salt concentrations leads to reinforcement of the viscoelastic properties with higher moduli (Agoda-Tandjawa et al. 2010): The variations in ionic strength can be related to the electrostatic attractive and repulsive forces between the microfibrils, enhancing the fiber–fiber interactions. As a final step in the processing of MFC/NFC suspensions, alternatives for the conventional freeze-drying have been investigated: After similar preparation protocols of MFC suspensions, it was observed that simple freezing preserved the rheological properties of the suspensions in contrast to freeze drying.

Rheological Characteristics of Fibrillated Cellulose Suspensions

Colloidal Suspension Rheology

Colloidal suspensions refer to the dispersed phase of a two-component system where each component is too small to be easily observed. The stability of colloidal particles are generally attributed to a balance of to gravity, and electrical simply sediment within a suspending liquid medium (Mewis and Wagner 2012). The rotation and orientation of dispersed particles depend strongly on the particle shape and will consequently alter their flow characteristics. Early work on the rheology of nonspherical suspensions can be found in Wierenga and Philipse (1998) and Zirnsak et al. (1994). Indeed, nonspherical particles in a shear flow will change their orientation in a periodic manner but not at constant rate of rotation. This is illustrated by direct observations for rod-like and disk-like particles (Goldsmith and Mason 1967). The rheology of nonspherical particle suspensions can either be affected by regular Brownian motion or can be influenced by non-Brownian motions, where the orientation distribution function results from the particle motion along the so-called Jeffery orbits (Mewis and Wagner 2012). The Brownian motion leads to viscoelasticity even for dilute systems without interparticle interactions.

In general, the Brownian motion may result in deviations of the rotational Péclet number (Pe), with a random orientation at low Pe and more orientation at higher Pe. The alignment of particles into the flow leads to shear thinning that scales with a rotational Péclet number. Such alignment reduces the viscosity, but can also lead to highly nonlinear rheological properties.

The MFC/NFC suspensions can be categorized as nonspherical particle suspensions, where the rheological properties are strongly influenced by fiber morphology, orientation, and aggregation. It is known that the viscosity of suspensions increases for particles with higher aspect ratio and becomes substantially higher than that for spheres. Moreover, the viscosity of MFC/NFC suspensions mainly depends on the distribution of fiber orientation or network orientation. As such, the fibrillated fibers strongly affect the viscosity depending on the type of flow, e.g., for uniaxial extensional flow, even small amounts of fibers resulted into huge increases of viscosity (Mewis and Wagner 2012). In this regard, the viscosity can increase if the aspect ratio is large enough even at fiber concentrations of less than 1 % (Dhont and Briels 2003). These effects are mainly related to the extensive probability of interaction and entanglement between fibers with high-aspect ratio. In dilute NFC suspensions, the interparticle interactions lead to particle flocculation or aggregation, which result in liquid-like behavior but with increment of viscosity. In this regard, the rheological consequence is a high degree of shear thinning for dilute solutions of MFC/NFC with long and slender particles (Mewis and Wagner 2012). Generally, elastic effects can also appear in dilute MFC/NFC suspensions, due to the orientation of fibers or networks. At higher fiber concentrations, flocculation leads to percolation and gel formation with rheological signatures being the onset of a yield stress and elasticity. This gel-like behavior is very weak and has the yield under low strain. A power-law model is often observed for the dependence of the rheological properties of these gels. The yield stress and yield strain of these gels depend on both the strength and the detailed shape of the interparticle interactions.

Rheometer Types

The selection of a suitable rheometer for characterizing MFC/NFC suspensions is essential to get the most precise rheological data. In fact, the rheometer geometry might influence the flow patterns induced in the fiber suspension and hence, promote the occurrence of certain phenomena, e.g., mainly related to the tested volume fractions and fiber interactions, induced flow patterns, interaction of the fiber suspension with the steady wall, and specific issues related to the recipient geometry. The selection of suitable rheometers from an industrial viewpoint is mainly given from the practical availability of the instrument. Nevertheless, more fundamental studies need to compare the suspension behavior under different conditions. More recently, large-scale pipe-flow measurements have been performed on concentrated MFC and cellulose suspensions in combination with ultrasound velocity profiling and pressure difference measurements (Haavisto et al. 2011): As such, the flow properties of complex slurries could be described in function of pressure loss, viscosity, and yield stress. The methods can be used to a large number of model and industrial suspensions containing particles with different sizes and shapes. A comparison of off-line rheometry measurements with the pipe rheometry shows that this method is more versatile and off-line techniques are only valid for suspensions containing particles smaller than the gap width (Wiklund and Stading 2006). Furthermore, by using specific contraction flow geometry, the extensional viscosities of MFC suspensions were measured by forcing them through a hyperbolic nozzle and by measuring the required pressure drop (Moberg et al. 2014). The testing geometry revealed an extensional thinning behavior over the extensional strain rates used. On top of that, the extensional viscosity decreased with the decreasing concentration of the suspensions, similarly to the shear properties of the specimens. Hence, based on the rheological measurements and dispersion conditions, the experimental values can serve as the basis for scaling up the production of nanocellulose fibers at an industrial scale (Loranger et al. 2012).

The general flow behavior of MFC/NFC suspensions is measured by using two main types of rheometers (e.g., cone on plate or cylindrical) according to the availability of rheometers and dilutions of samples. Generally, cone-on-plate rheometers are applied at low shear rate while cylindrical (Couette or Vane) rheometers can be used to apply higher shear rates on the sample. In some studies, parallel plate or cone-on-plate geometries were used for specific rheological studies of MFC water dispersions (Iotti et al. 2011): The time-dependent behavior was monitored in the range of 0–1000 s^{-1} and a hypothesis for the interaction mechanism of fibrils and formation of fibrillar networks was proposed. In the case of very dilute suspensions, however, parallel plate or cone-on-plate geometries cannot provide accurate data due to evaporation, wall slip, or depletion effects. Otherwise, monitoring the quality of process assessment at higher temperature and at different evaporation rates will result from cylindrical or cone-on-plate rheometers, leading to different rheological data: (i) in cylindrical rheometers, the settling of high viscosity samples is difficult but there is less evaporation due to geometry design, while (ii) in cone-on-plate rheometers, the settling of the sample can easily happen but there is more evaporation due to the relatively “open” surface geometry. Therefore, it is recommended to measure the rheological characteristics of dilute NFC suspensions by cylindrical rheometers due to a better control of the evaporation and to the possibility to use samples of higher absolute volume (Larson 1999). This way, the edge problems in cylindrical rheometers are minimized and the sample can be very homogeneous while using a cone rotor in the cup. The critical point when using cylindrical rheometer for suspensions is wall slip or wall depletion problem that induces different states of shear at the boundary and core of medium. This problem is mainly observed in very dilute suspensions such as NFC or MFC. We point out further in this chapter how to minimize this problem in cylindrical rheometers. Moreover, we will point out in the parametrical part how the rheological data vary for different cup types used in a cylindrical rheometer.

Influence of Fibrillation

Most applications of MFC/NFC mixtures are based on their typical rheological features, including shear-thickening and gel characteristics, which make them favorable as additives or rheology modifiers, e.g., MFC can be utilized for increasing the zero-shear viscosity or controlling the shear-thinning behavior of a medium at higher shear rates. The physical understanding of rheological properties for MFC/NFC suspension widely deals with the fiber network properties or entanglement of fibrillated fibers. At the same time, it has been reported that high amounts of fibrillation lead to the higher viscosity of NFC suspensions (Saito et al. 2006).

The gel-like structure of MFC suspensions, even at low concentrations, is determined by the way in which the fibrils are settled within the network or flocculated in the form of flocs, depending on the degree of fibrillation. Some detailed studies on these subjects (Tatsumi et al. 2002; Ono et al. 2004; Hill 2008; Lasseuguette et al. 2008) have indicated that, MFC suspension shows the yield stress and a power-law correlation between storage modulus and concentrations. For instance, the MFC suspensions that are provided by a combination of TEMPO oxidation and mechanical treatment show shear-thinning behavior without an apparent plateau. For this suspension, the viscosity increases at low concentration, whereas the viscosity follows a power-law model at higher concentration with the exponent between 2 and 6, which decreased with shear rate. This system shows a gel-like behavior with a clear yield stress and elastic behavior even at very low concentration around 0.1 %.

The NFC suspensions have both colloidal and noncolloidal features depending on the diameter of fibrils and the degree of fibrillation (Saarikoski et al. 2012). The fiber suspensions and colloidal suspensions were evaluated at macroscopic and microscopic scale, respectively: These studies show the important contribution of flocculation in suspension characteristics (Hubbe 2007; Mewis and Wagner 2009a). At a macroscale, the fiber volume fraction and the fiber rotation in the suspension during mixing cause fibers to collide, entangle, and flocculate. At a microscopic and molecular scale, colloidal interactions between particles with the diameter of nearly 1–100 nm should be considered. The colloidal interactions result from the electrostatic and dispersion effects between fibrils, highly depending on the degree of fibrillation that augments the surface area and introduces more surface charges. According to the processing of MFC/NFC suspensions in a microfluidizer, as already stated before, the less number of passes within large interaction chambers or the more number of passes within small interaction leads to MFC and NFC, respectively. However, it has to be considered that the fiber morphology after several fibrillation steps often contains a heterogeneous composition of micro-/nanofibrils, fiber fragments, and less fibrillated fibers. Finally, the quality and rheological properties of the NFC suspension depends on the internal structure of the suspension and the homogeneity of the fibril size distribution (Saarikoski et al. 2012). Therefore, it can be of interest to consider the average specific surface area per sample as a quantification for the fibrillation process. Theoretically, the viscosity of NFC suspensions is higher than MFC due to higher hydrogen interactions and/or more important entanglements of fibrils within the network (Missoum et al. 2010). It has also been reported that for the same concentration of MFC and NFC, higher shear stresses are observed for NFC due to the higher fibrillation degree. After fibrillation, the formation of a dense MFC network structure in water dispersion is revealed as a hysteresis loop in a shear-rate viscosity measurements and the network formation was further confirmed by slow dynamic studies (Iotti et al. 2011). The interactions at fibrillar level may induce a "memory" or "time-dependent" effects in the fiber suspension with retarded recovery of the deformation state.

The interactions of fibrillated MFC structures can be more thoroughly studied by comparing the rheological behavior of diluted MFC suspensions with that of ideal polymer solutions (Zimmermann et al. 2010). The limiting viscosity (or intrinsic viscosity) is a characteristic parameter of indefinitely diluted polymer solutions considering the interactions between individual polymer chains. Analogously, the intrinsic viscosity of MFC can be interpreted by considering that each molecule of MFC acts independently after infinite dilution in aqueous medium. In the case of 0.5–2 % w/w suspensions, intrinsic viscosities of 100–390 mL/g were reported depending on the source and fibrillation of MFC. The intrinsic viscosity of aqueous cellulose nanofibril suspensions is strongly altered by electro-viscous effects and flocculation (Jowkarderis and Van de Ven 2014).

Parametrical Influence on Rheological Behavior

The MFC/NFC suspensions generally have a quite complex rheological behavior, depending on its composition and operation conditions. In a typical rotational rheological experiment, a shear rate is applied and the change in viscosity and stress of the sample is measured as a function of shear rate, as shown in Fig. 3. The flow curve of NFC suspensions with volume fraction of 1 % shows alternating shear rates in ascending and descending condition in a cylindrical rheometer (Herrick

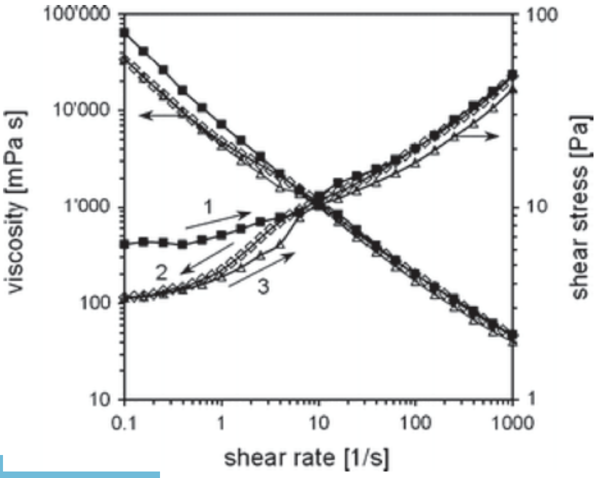

Fig. 3 Flow curves of NFC suspension at 1 % NFC content: (*filled square*) first step from ascending shear rates, (*open diamond*) second step from descending shear rates, (*open triangle*) third step from ascending shear rates (Grüneberger et al. 2014). *NFC* nanofibrillated cellulose

et al. 1983): By comparing the viscosity and in particular the shear stress of the first measurement at ascending shear rates to the second (descending shear rates) and third (ascending shear rates) measurement, it can be concluded that the rheological behavior at shear rates above 10 s^{-1} does not depend on the flow history and on the rotational direction. From the measurement of shear stress during the first run, it can be noticed that the inner network of the NFC suspension slowly breaks down with rising shear rate as long as the yield point is not reached. In parallel, the hysteresis regenerates the transition between the zero- or low shear region and the high shear region.

The first rheological study on NFC described the shear-thinning (i.e., pseudoplastic) behavior for a 2% (w/w) NFC suspension in water (Herrick et al. 1983): This behavior has been likely expressed with the breakup and with the change of the interior structures of NFC suspensions, as the packing aggregation of MFC may limit the formation of a continuous network. Generally, the suspensions behave like a gel with shear-thinning effects as a function of low to medium shear rates, while dilatant behavior may occur in parallel with hysteresis effects at very high shear rates. A transitional regime has been observed in the relationship between viscosity and strain rate at relatively low shear rates. Mainly, the flocculation and internal fiber binding can lead to shear banding and transient behavior. The time-dependent rheology (thixotropy) and transient regimes of NFC suspensions have been modeled in relation to the aggregate sizes (Piusto et al. 2012). It was concluded that wide distributions of fiber sizes were associated with high-to-low shear transitions whereas low-to-high shear transitions occurred through a more narrow size distribution. It is known that the MFC suspensions may have operational conditions with both viscous and elastic response. The viscoelastic behavior is generally quantified by the value of the storage modulus (G′) from dynamic mechanical analysis. The high values of G′ relatively to the loss moduli show that the MFC suspensions form a rather strong network, even at low concentrations. As the applied stress or strain amplitude exceeds a certain limit, the decrease in storage modulus can be interpreted as a breakdown of the entangled fiber network. Otherwise, slight variations in frequency often do not significantly alter the storage modulus, which can be attributed to the properties of the gel-like network structure.

The concentration effects of MFC gels were systematically studied for unbleached kenaf pulp, indicating that the rheological characteristics improved with increasing gel concentration (Charani et al. 2013). A variation in concentration was obtained by subsequent dilution from higher pulp suspension consistencies of about 5%. After dilution of the MFC starting from highly concentrated suspensions, the modulus varied more strongly than under the same strain and frequency compared to immediately prepared poorly concentrated MFC. Additionally, the high value of G′ compared to G″ and almost independence of its value with frequency confirms the formation of a gel-like transient network structure of entangled fibrils at low frequencies. The highly entangled and rigid cellulose network seems to be responsible for an elastic behavior at low frequencies (similar to a homogeneous and organized fibrillar cellulose system), while this network loses its strength and transforms into a viscous behavior at high frequencies (similar to a heterogeneous multi-phase system with cellulose fibrils, hemicellulose, and lignin).

Temperature has slight influences on the rheological behavior of MFC/NFC suspensions in different ranges of applied shear rate (Shafiei-Sabet et al. 2012; Liu et al. 2011). Since rheological behavior is directly affected by dispersion microstructure, the effect of temperature on the steady-shear viscosity is observed. For instance, the viscosity of an isotropic dispersion decreases with the increasing temperature. On the other hand, in lyotropic systems, temperature that changes the viscosity can also be indicative of changes in the microstructure or in the relative fractions of isotropic and liquid crystalline regions (Urena-Benavides et al. 2011). Different results have been reported in literature with regard to the temperature effects on rheological properties of MFC/NFC suspension. In some research, a reduction of the viscosity was reported with the increasing of temperature, but others have reported no change in storage modulus and in modulus by temperature or smooth increment with rising temperature (Iotti et al. 2011; Lowys et al. 2001; Paakko et al. 2007).

Due to the high tendency for flocculation of NFC networks, the internal structure of the suspension highly influences the rheological properties and alters its internal organization between zero-shear and high-shear-rate conditions. It can be estimated that the diameters of the aggregated fibrils are about 10–30 nm, in contrast to the diameters of single cellulose fibrils of 2–5 nm. The sizes of these fiber flocs remain small enough (below the 1 µm) so that colloidal phenomena dominate while gravity and inertia forces can still be neglected (Hubbe 2007). The low intra- and interfibrillar repulsion forces and the high tendency for interactions between the fibrillated fibers facilitate the formation of fiber entanglements (Ono et al. 2004). At the same time, the segmental mobility of the fibers in between the fiber contact points remains as it is and increases under shear rate. These contact points in the fibrous network are strengthened by van der Waals forces, which lead to the compression of flocs and aggregation (Hubbe 2007). At higher concentrations of MFC/NFC suspensions, a rigidity threshold value is reached where fiber flocs are coherent and able to bear mechanical strength (Celzard et al. 2009). The structure of the flocculated fiber network also depends on fibril characteristics, time, and shear-testing conditions. Therefore, flocculation occurs more readily when measuring at low gap sizes relatively to the fibril sizes, and its effects are the highest at low flow rates. For this reason, rheological data of MFC/NFC suspensions should be analyzed with high care as flocculation phenomena may result in false interpretation (Barnes 1995). The defloculation of cellulosic suspensions can be promoted by adding anionic high molecular weight polyelectrolytes, such as polyacrylamides (Korhonen et al. 2014). Indeed, it has been observed from rheological measurements that the MFC network becomes weaker as flocculation is hindered.

Depending on the shear rate, fibrils with different sizes move into the flow direction and between the flocs, while the floc structure adapts to the applied shear conditions (Karppinen et al. 2012). The sheared fibrillar network disintegrates with periodical dynamic reconstruction depending on collisions of fibers by shear and Brownian motion (Barnes 1997; Mewis and Wagner 2009b). According to Fig. 4, the suspension structure approaches a constant floc size for shear rate around 200 s^{-1}. It can be inferred that the structure of fibrils evolve very fast within a short testing time of 0–10 min under high-shear-rate conditions. Hydrodynamic interactions between flocs lead to physical collisions and result in the adaptation of the

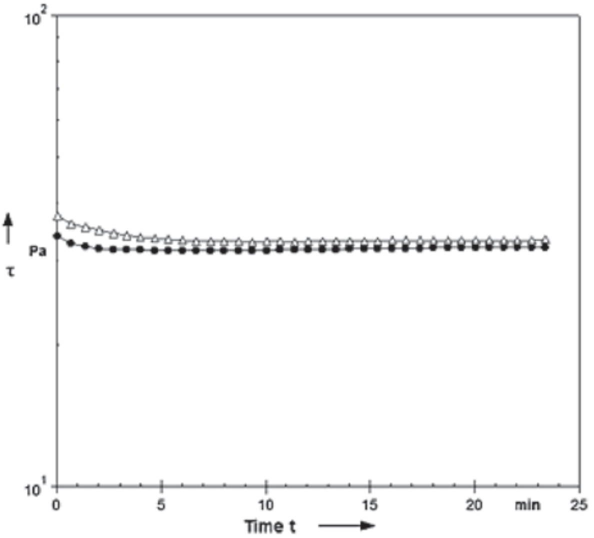

Fig. 4 The leveling of shear stress as a function of time during the pre-shear interval. The geometries in use were stainless steel (gap 1.1 mm, *filled circle*) and glass 2 (gap 1.3 mm, *open triangle*) and the sample was fluidized five times. (Saarikoski et al. 2012)

floc structure to the high-shear-rate condition. In this regard, there is no time for contact point optimization between flocculated fibrils compared to the prevailing shear conditions (Saarikoski et al. 2012). For this reason, with cessation of shear rate, the structure starts to recover immediately. During recovery, the floc structure freezes while the organization of flocs in the suspension is retained without change in macroscopic floc size and floc size distribution that were formed during the previous shear interval. After the recovery period, the flocculated fibril network starts to deform and finally breaks down due to constant shear rate in a series of peak hold experiments. Images of the different steps of this process are portrayed in Fig. 5, for five-times-fluidized NFC suspension. The modulus levels also rise significantly over time even if the apparent floc size is constant during the recovery. The fibrils are limited in local motion at recovery or rest time, and the rises in the moduli levels reflect the optimization of fibril contact points, while the flocs are being precipitated (Saarikoski et al. 2012).

In addition, the effect of wall slip or wall depletion on the rheological feature should be considered. Wall depletion plays an important role in the rheological evaluation of NFC suspensions and recently, this rheological phenomenon has been studied more fundamentally. Wall slip can occur as interfacial slippage in a two-phase system, such as high molecular weight polymer solutions, particles, or flocculated NFC suspensions (Barnes 1995). Wall slip can also be present when a continuous phase enriches at a geometrical boundary and forms a very thin boundary layer depleted of the suspension phase. Due to wall depletion, the real shear rate at the boundary is higher than in the core of the suspension, which results from a higher viscosity than the real magnitude of viscosity within the NFC suspension (Saarikoski et al. 2012). Concurrently, other heterogeneities in the flow pattern of MFC suspensions may be related to shear banding, where the shear becomes

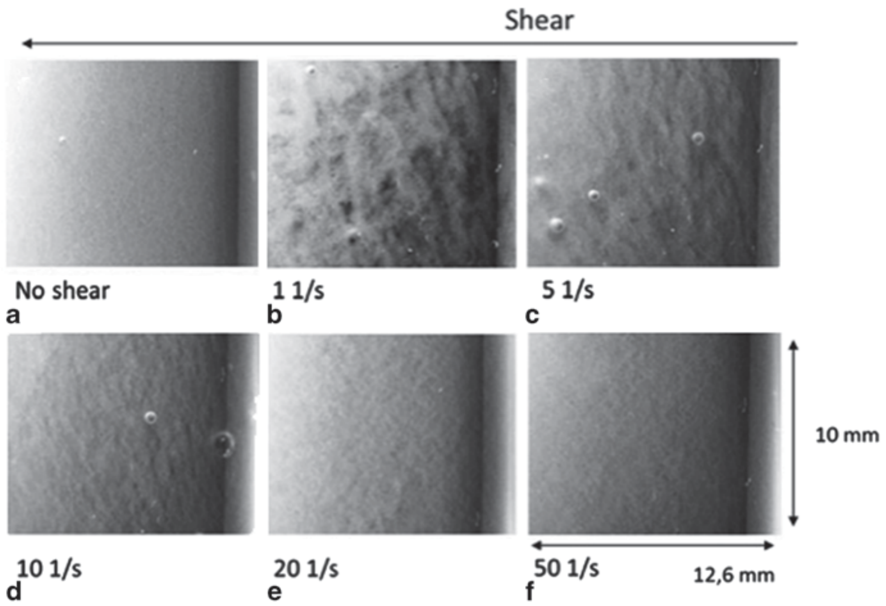

Fig. 5 Different stages in flocculated flow at several shear rates for five-times-fluidized NFC suspension. **a** At rest after the 25-min pre-shear interval at 200 s^{-1}. The floc structure stems from the pre-shear period. **b** 1 s^{-1}, flocs start to move in stress chains. **c** 5 s^{-1}, chain compressing. **d** 10 s^{-1}, chain splitting. **e** 50 s^{-1}, flocculated flow of individual flocs. A picture of each state was taken after shearing 9 min 55 s at the indicated shear rate with the exception of "a" which was taken after 1-h recovery (Saarikoski et al. 2012). *NFC* nanofibrillated cellulose

localized in a distinct fraction of the sample volume. Better insights in the flow properties of complex MFC systems characterized by inconstant behavior with apparent wall slip and shear banding could be obtained by optical coherence tomography (Haavisto et al. 2014). The effects of wall slip and related flow instabilities of some MFC/NFC suspensions have been systematically overcome by roughening the wall of the testing geometry (Nechyporchuk et al. 2014). However, the use of serrated tools did not prevent the wall slip of all pretreated NFC pulp suspensions as it also affects the rate of water release from the suspension.

The gap distance in rheological testing is another important parameter that affects the NFC floc size and wall depletion under high-shear-rate condition. The specific use of a bucket vane rheometer with wide gap was adapted in combination with an algorithm for the conversion of the angular velocity to global shear rates (Mohtaschemi et al. 2014), As a result, quantitative differences in the stress at same shear rates can be up to 40 %. The large gap distances result in the reduction of floc sizes under shear (Saarikoski et al. 2012). In this regard, the wall-depletion effect should be minimized due to floc size reduction at very higher shear rates. Otherwise, the rheological measurements above the yield stress lead to a slipping layer but the bulk of NFC suspension is also under shear throughout the gap (Saarinen et al. 2014). Comparing the average floc size with shear rate shows a relation between floc sizes and shear rate dependency on gap geometry: A gradual increase of the shear rate can lead to growing floc sizes due to the formation of floc chains, or decreasing floc sizes when the fibrillar network breaks down. Figure 6 presents the influences of the gap distances on floc sizes at different shear rates. The starting point reflects the situation after the pre-shear interval, which results in small average floc sizes. Applying shear starting from zero (rest condition) breaks down the fiber bonds between the existing spherical flocs at their weakest points, and the floc movement begins with the formation of single chains. When the shear rate increases, the floc chains break up and the fibrils start to move individually as spherical flocs. The formation of flocs with different sizes and variations in local shear stress at a given nominal shear rate indicates a dependency on geometry boundaries. At higher shear rates, when the flocs become smaller, they are less affected by the gap size.

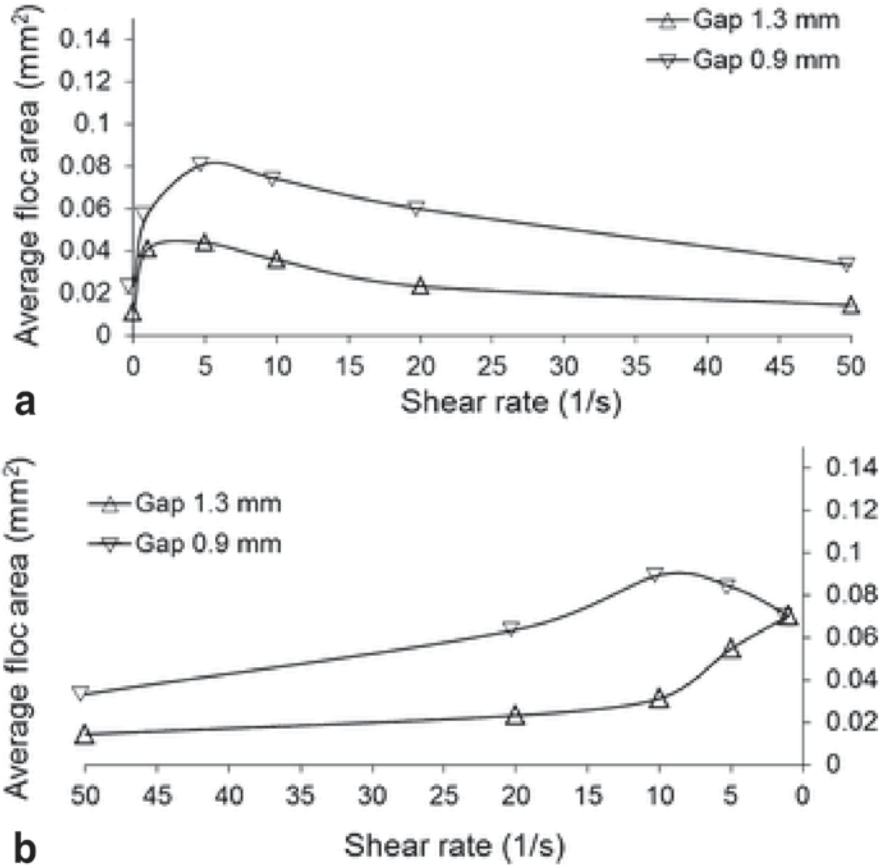

Fig. 6 Influence of changing gap to average floc area for **a** ascending shear rate, **b** descending shear rate. Shear rate 0 represents floc size at rest condition 59 min after a pre-shear period (25 min, 200 s^{-1}). The samples were fluidized four times. (Saarikoski et al. 2012)

From the above discussion, it is clear that different parameters such as wall shear stress and yield stress affect flocculation and wall depletion. Maximum wall shear stress refers to the amount of shear stress that is applied at the moment that the contact between the geometry wall and the bulk of the suspension is lost. There are two different techniques to find a relationship between yield stress: flow curve measurements and the contribution of wall slip, which are determined as (i) initiation of steady-state shear and (ii) constant stress ramp. A test with stepwise increment of the stress as a function of time is an alternative method to analyze the yield stress and to observe at which point the suspension starts to yield (Derakhshandeh et al. 2010). As the yield stress determined by the steady-state shear method highly depends on the speed of rotation, the rotational speed for flow measurements under stepwise incremental stresses should be securely selected (Cheng 1986). It is often difficult to determine precisely the actual specific stress value where the structure starts to yield according to tests with a stepwise incremental torque. Thus, two yield stress values are sometimes reported (Saarinen et al. 2014). According to published data, the provided yield stresses are compared in Tables 1 and 2 for a standard rheometer (TA Instruments) with hard-anodized aluminum geometry (Al_2O_3 surface) and a polymethylmetacrylate (PMMA) cup. The maximum shear stress was calculated at the beginning of steady-state shear conditions and from continuous stress ramp experiments. According to Tables 1 and 2, the rheometer cup type has an important effect on the rheological data. Surprisingly, the flow curves for 0.5 and 1 wt.% NFC overlap somewhat with metal and PMMA outer geometries although the maximum wall shear stresses are different for the different geometry materials. Concerning the limits for precise measurements, the yield stress determined from the start-up method is always above the lower limit of the controlled stress ramp data. The viscosity versus shear rate and shear stress versus shear rate result for 0.5 and 1 wt.% NFC suspension measured with two different cup geometries shows that the shape of

Table 1 Yield stresses and the maximum wall stresses by start-up of steady shear and continuous stress ramp (CR) methods for 0.5 and 1 wt.% NFC suspensions without added ions in solution (Saarinen et al. 2014)

	0.50 wt.%			1 wt.%		
	Start-up stress (Pa)	CR, lower limit stress (Pa)	CR, upper limit stress (Pa)	Start-up stress (Pa)	CR, lower limit stress (Pa)	CR, upper limit stress (Pa)
Yield stress[a]	3.4±0.06	3.1±0.0	3.5±0.0	21.8±0.3	19.2±0.0	21.5±0.0
Maximum wall shear stress[b] (PMMA)	1.1±0.1	0.4±0.0	1±0.0	6.1±1.4	2.4±0.0	6.1±0.0
Maximum wall shear stress[b] (Al_2O_3)	1.7±0.26	1.1±0.0	1.2±0.0	8.5±0.5	4.1±0.0	4.6±0.0

Errors are calculated by standard deviation ($n=4$ in start-up experiments, $n=3$ in continuous stress ramp experiments)

[a] Yield stress assumes yielding at the stress maximum, i.e., at the tip of the vanes

[b] Maximum wall shear stress calculated from stress maximum at the tip of the vanes followed by a stress decay to the outer geometry boundary

Table 2 Yield stresses and the maximum wall stresses by start-up of steady-shear and continuous stress ramp (CR) methods for 1 wt.% MFC suspension with 10^{-3} and 10^{-2} M NaCl. (Saarinen et al. 2014)

	1 wt.% 10^{-3} M			1 wt.% 10^{-2} M		
	Start-up stress (Pa)	CR, lower limit stress (Pa)	CR, upper limit stress (Pa)	Start-up stress (Pa)	CR, lower limit stress (Pa)	CR, upper limit stress (Pa)
Yield stress[a]	22.0±1.2	19.2±0.0	21.5±0.0	18.4±1.3	17.1±0.0	19.2±0.0
Maximum wall shear stress[b] (PMMA)	7.7±1.2	3.8±0.0	7.6±0.0	7.7±0.6	4.3±0.0	17±0.0
Maximum wall shear stress[b] (Al_2O_3)	8.4±0.7	4.6±0.0	5.2±0.0	8.1±0.3	4.6±0.0	5.2±0.0

Errors are calculated by standard deviation ($n=4$ in start-up experiments, $n=3$ in continuous stress ramp experiments). *PMMA* polymethylmetacrylate

[a] Yield stress assumes yielding at the stress maximum, i.e., at the tip of the vanes

[b] Maximum wall shear stress calculated from stress maximum at the tip of the vanes followed by a stress decay to the outer geometry boundary

the graphs for both suspensions is analogous. The differences lie in the shear stress/viscosity levels which are much higher at high volume fraction concentration.

To better understand the apparent shear-thinning behavior of the NFC suspensions in the low-shear-regime conditions, two categories should be considered: (i) if the slip layer is only water, e.g., Newtonian, the slip-layer gap should decrease with decreasing apparent shear rates, which leads to an apparent increment in viscosity. On the other hand, (ii) if the slip-layer thickness remains constant, the slip layer itself must behave like a shear-thinning medium (Ahola et al. 2008). The shear-thinning boundary layers of NFC flows were measured in some research (Salmela et al. 2013), and may exhibit even at very low volume fraction of the NFC suspension. Furthermore, the extent of the slip layer is geometrically limited and the fibers have very little space between the bulk zone and the geometry wall. These attributes lead to an assumption that the slip layer has a shear-thinning behavior. Generally, the apparent shear-thinning behavior above the yield stress reflects the adaptation of the floc structure to the apparent shear rate. Below the yield stress, the flocs stick together and for this reason, the rheological features will vary upon concentration. Increasing of NFC volume fraction leads to lower amounts of water that is held within the NFC network. As such, the formation of an interfacial water layer in contact with the geometry wall may influence the rheological data, depending on the MFC/NFC concentration and applied stress.

Rheological Properties of Modified MFC/NFC

Surface modification of MFC and/or NFC fibers is an important pathway for tuning and improving the network properties in specific applications. For instance, the use of MFC as a strength agent in paper technology requires cationic polyelectrolyte as a fixative (Karppinen et al. 2011; Taipele et al. 2010). Otherwise, the hydrophilic nature of MFC/NFC can be a barrier to use it as reinforcing material in hydrophobic matrices. The hydrophilic properties of MFC/NFC simultaneously influence the rheological properties and flocculation behavior of MFC/NFC suspensions. As a consequence, hydrophobic surface modification agents will affect fiber–fiber interactions and/or surface charges on the fibrils with consequent changes on the flow properties of the suspended fibers. In general, MFC modifications lead to easier handing and better long-term stability during storage of the suspensions.

The rheological effects of surface modification on MFC/NFC fibers were studied in only few cases. After silylation of MFC, a pseudoplastic flow behavior was observed (Goussé et al. 2004), but the modified suspension did not transfer into a gel-like structure even at high concentrations of 3 %. These observations would imply that the flow properties of the MFC suspension become similar to that of polymer solutions. In another example, the behavior of carboxymethylated NFC gels was examined (Naderi et al. 2014): While the surface modification affects the consistency, delamination, and shear during processing, the produced gels showed high elasticity and shear-thinning effects that were almost similar to those of other NFC systems. The shear viscosity and the storage modulus of modified NFC were found to scale with concentration, according to a theoretical power law with exponents 2 and 2.4, respectively. In relation to the work on carboxymethylated pulp suspensions, high ionic solutions such as NaCl were added to homogenize the carboxymethylated pulp suspensions (Naderi and Lindström 2014), which leads to lower magnitudes in the rheological data for NFC compared to electrolyte-free NFC suspensions. However, the carboxymethylated cellulose samples are often less crystalline and consequently have a lower thermal stability for processing. Using electrolytes into NFC suspensions that have been homogenized in deionized water also leads to similar rheological data same as NFC suspensions that have been homogenized in the presence of electrolytes. The decrement of rheological properties in the presence of ionic solution might be caused by the lower delamination of fibers due to the lower swelling of the pulp. Hence, the use of an electrolyte is a method implemented to control the rheology of NFC suspension after production.

In another example, the effect of different polymethacrylates on the MFC suspension has been studied (Karppinen et al. 2011). It was reported that the cationic methacrylate polymer poly([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide) (PDMQ) strengthened the gel structure of the MFC suspension at low volume fractions. This can be justified by the increasing interfibrillar repulsion forces that were introduced by positive surface charges. In addition, other kinds of modifiers could change the rheological nature of the MFC suspension from gel-like into a liquid-like behavior. Similarly, the suspensions of surface modified MFC/NFC are more sensitive to variations in pH, which might influence the surface charges and hence affect the rheological properties. Variations of pH between 7 and 10 have no influence on the dispersion quality but a pH lower than 5 has negative effect on the quality of the dispersion (Loranger et al. 2012). In another example with TEMPO-oxidized cellulose nanofibrils containing sodium carboxyalate groups (Fujisawa et al. 2011), the liquid-like dispersion changed into a gel at pH below 2.0 as the sodium carboxylate groups on the surface change into free carboxyls. The latter process was reversible after washing and sonication with an increase in pH to 4.6.

Rheological Characteristics of Polymer Blend with Fibrillated Cellulose

As nanocellulose composites consist of MFC/NFC fibers as reinforcement within a polymeric matrix, good mixing of the two components should be obtained. The rheological features of both fiber and polymer components have important effects to tune the processing parameters and reach more homogeneous mixing during processing. Thus, good knowledge on the control of the structure and flow properties of both components and their mixtures is required, including viscosity, viscoelasticity, yield stress, and shear-thickening/shear-thinning behavior. For instance, the increase in viscosity of NFC suspensions with high concentrations will entrap more air bubbles in the suspensions, leading to incorrect viscosity measurements and ultimately causing defects in the final composite structure. In general, the addition of MFC can be used for tuning the viscosity of biopolymer blends, e.g., after adding polyethylene glycol (PEG) as plasticizing agent into PLA/PEG blends, a remarkably low viscosity is obtained that limits the further processing, while the addition of 5 wt.% MFC rises melt viscosity of the blend to a desired level. The gelation of carrageenan in the presence of MFC did not show significant rheological differences compared to the pure carrageenan, only an increase in G′ and a more pronounced maximum for the gel with 0.25 % MFC additives was found (Martinez et al. 2012). In order to better understand the interactions between colloidal particles and polymers, different phenomena should be considered in the case of (i) adsorbing polymers (e.g., nonionic polymers) that may stabilize the colloids by steric effects or (ii) nonadsorbing polymers (e.g., polyelectrolytes) where osmotic pressure differences may create an attractive force to the cellulose surface.

In concern to a potential use of NFC in coating compositions, the high viscosity of the MFC/NFC suspensions might be a concern in optimum processing. Based on previous discussions, the shear-thinning and concentration effects may be exploited for lowering and tuning the viscosity values. Notably, the viscosity of acrylate/NFC mixtures was investigated (Grüneberger et al. 2014). The rheological data show that the flow characteristic of the NFC dominates the properties of the acrylate/NFC suspensions, while the type of polymer has a minor importance for the rheological behavior of the mixture. At progressively increasing amounts of NFC, the viscosity will increase exponentially and is predictable in the considered shear rate interval. The rheological behavior of acrylate/NFC is affected by temperature and time, possibly due to the increment of interactions between single fibrils within the network and/or swelling of the NFC. There are also other examples that show the tremendous effect of NFC on rheological behavior of polymer matrix. Similarly, rheological studies of NFC/PLA nanocomposites show that the NFC/PLA nanocomposites have a higher viscosity than the pure PLA and are determined by the NFC additives. This data are essential for using NFC/PLA in foam industry (Cho et al. 2013). The PLA can be processed similarly to low-density polyethylene (LDPE) while cellulose fibers were added into the polymer matrix (Shumigin et al. 2011). They also reported that the increasing of cellulose portion causes the abrupt increment of complex viscosity and elastic moduli for PLA- and polyethylene (PE)-based composites at low shear rate. This can be explained by inhomogeneous dispersion or fiber aggregation/flocculation into the composite, whereas the most significant changes in the rheological properties occur when the filler content is increased up to 10 wt.%.

On the other hand, when biopolymers such as pectin are added into MFC suspensions, the viscoelastic and microstructural properties of the MFC are not significantly altered and determined by the cellulose with or without the additional presence of calcium ions. The flow behavior of MFC/pectin drastically changed upon addition of NaCl with an increase in thixotropic character shear-thinning behavior (Agoda-Tandjawa et al. 2012).

In other research on cellulose/chitosan in ionic liquid, steady-shear rheological results show the pseudoplastic behavior of the mixture and the viscosity of the solution increasing with the increment of cellulose proportions (Duan et al. 2011). Dynamic rheological data also show that the G' and G'' of cellulose/chitosan mixtures in ionic liquid solution shifted to a higher frequency range with an increasing temperature. The temperature effects are likely attributed to the main behavior of the polymer matrix rather than to the nanocellulose fillers. These rheological data can be used to understand the feasible viscosity of cellulose/chitosan in ionic liquid solution, which indicates the potential of NFC/polymer mixtures as an electrospinning medium for processing at different temperature. According to rheological data, similar features have been reported for PVA suspensions. The addition of PVA into NFC suspensions can change the gel structure and will decrease the viscosity of mixture (Hlisnikovská and Järnström 2011). Interestingly, the rate of addition of the same amount of soluble polymer leads to different rheological behavior: In particular, slow addition of the soluble polymer reduced the viscosity more rapidly than a rapid addition. This observation shows that the viscosity of the medium also depends on the strategy of mixing, e.g., geometrical design, energy input, and applied shear rate or strain into the system leading to dispersive and distributive mixing.

The in situ polymerization process is another interesting route for homogeneously blending fibrillated cellulose with polymers; however, the effects on dynamic rheological behavior has only been studied in combination with cellulose nanowhiskers, indicating the progressive effects of gelation and transition kinetics as a function of cross-linker agents (Zhou et al. 2011). In one specific example, the direct grafting of poly-Σ-caprolactone (PCL) on MFC could be controlled with different graft lengths depending on the molecular weight (Lönnberg et al. 2011), resulting in a better dispersion of the MFC in nonpolar solvents and PCL the matrix. Nevertheless, full rheological data on such modified fibers within biopolymer blends are still not fully understood.

Conclusions and Perspectives

The rheological features and processing characteristics of the MFC/NFC suspensions are primarily affected by the origin and fibrillation process of cellulosic fibers, including pretreatment methods, the degree of fibrillation, size distribution, aspect ratio, and surface charges. The measured rheological data should be critically evaluated, taking into account different variables of the rheometer test such as concentration, shear rates, temperatures, and the gap geometry.

Generally, MFC/NFC suspensions behave as gel-like material. The rheological properties and viscosity of MFC/NFC suspensions are strongly influenced by orientation or aggregation of the fibers into the network. Comparing the behavior of MFC/NFC to traditional suspension rheology, it was reported that the viscosity of suspensions increases for particles with higher aspect ratio and becomes substantially higher than that for spherical particles. As a result of the high tendency for flocculation of NFC networks, the internal structure of the suspension highly influences the rheological properties and alters its internal organization between zero-shear and high-shear-rate conditions. Parameters such as wall shear stress and yield stress affect flocculation and wall depletion. As a result of wall depletion, the real shear rate at the boundary is higher than in the core of the suspension, which results from a higher viscosity than the real magnitude of viscosity within the NFC suspension. The rheological data can be used to understand the feasible viscosity, indicating the potential of MFC/NFC mixtures with polymer matrices for processing in melt extrusion or electrospinning. The processing ability of nanoscale cellulose additives in combination with polymer matrixes requires the homogeneous dispersion of both phases in order to fully exploit the strength properties of the reinforcing fiber phase. From a scientific research standpoint, the rheological approach is effective in probing the microstructure, in assessing the state of the nanocomposite dispersion as well as in determining conditions of homogeneous mixing directly in the melt state or processing condition.

While more fundamental understandings on the rheological properties of fibrillated cellulose suspensions have been developed as systematically presented in this chapter, main future challenges lie in the better rheological characterization of surface-modified cellulose additives and their combinations with different hydrophilic/hydrophobic polymer mixtures. Contrarily, the rheological observations of MFC/polymer blends during in situ polymerization reactions remain limited and could provide essential information on the interfacial reactions and compatibility of the polymer blends. As such, the rheological characterization of MFC/NFC blends will be able to support the industrial formulation and further breakthroughs of optimized bio-based nanocomposites.

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Optimization of Admixture and Three-Layer Particleboard Made from Oil Palm Empty Fruit Bunch and Rubberwood Clones

Syeed Osman Al-Edrus Saiful Azry, Paridah Md Tahir and Juliana Abdul Halip

Abstract Empty fruit bunch (EFB) is a biomass that is widely available and has the potential to be used as industrial raw material especially in wood-based industries. This study focuses on producing a particleboard by incorporating EFB with two different rubberwood clones: Prang Besar (PB) 260 and RRIM 2002, respectively. PB 260 is a commercially planted clone and wood from matured (>25 year-old) trees are used by wood-based panel manufacturers. RRIM 2002 is a new clone planted at the Malaysian Rubber Board (MRB) research trial plots and consists of only 4-year-old trees. Two types of particleboards (admixture and three-layer) with different ratios were produced. The Japanese Industrial Standard (JIS-5908 2003 particleboard) was used to evaluate mechanical and dimensional stability properties of the particleboards. From the study, it was found that admixture particleboards showed superior properties compared to three-layer particleboards. Layering EFB and rubberwood significantly decreased board performance for all properties (except internal bonding). The optimum ratios of EFB and both rubberwood clones are found to be 1:1 (50% EFB: 50% rubberwood). Meanwhile, increasing the rubberwood clones ratio to 70% lowered board performance especially for EFB (30%):RRIM 2002 clone (70%) boards which showed the lowest values for all properties for both admixture and three-layer boards.

Keywords Empty fruit bunch · Admixture · Layer · Rubberwood · Particleboard · Mechanical properties · Physical properties

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Introduction

The oil palm (*Elaeis guineensis* Jacq.) is an allogamous arborescent monocot of the Arecaceae family (Hartley, 1988). In Malaysia, oil palms are normally present as single-stemmed, can reach a height of up to 20 m, and can be cultivated easily. Malaysia is the second largest exporter and producer of palm oil in the world, with a total oil palm planted area of 5.230 million hectares as of December 2013 (Table 1; MPOB 2014). The main product from oil palm is palm oil while the rest of the biomass waste is either burned (as the main energy source for power generation in palm oil mills) or dumped as organic fertilizer through natural decomposition (Yusoff 2006; Ng et al. 2012). Biomass of oil palm, namely empty fruit bunch (EFB), mesocarp fibre, palm kernel shell, and palm oil mill effluent are produced daily and are more consistent in terms of supply compared to oil palm trunks (Roslan et al. 2011). Nowadays, palm biomass have gained more attention and are being used as raw material for the production of plywood, laminated lumber, pellets, high-value chemicals, and other products (Sulaiman et al. 2011; Ng et al. 2012).

As reported by KeTTHA (2011), most of the EFB in Malaysia is used in soil mulching as an organic nutrient to reduce the input of inorganic fertilizer. Rahim (2010) mentioned that there are mills that produce particleboards from EFB in Malaysia. However, most particleboard mills in Malaysia use mainly rubberwood as the raw material as rubberwood is regarded as the conventional raw material for the production of particleboard and medium-density fibreboard (MDF) in Malaysia. Presently, Malaysia has 16 particleboard mills which use rubberwood as their major raw material (NATIP (2009). Nevertheless, with an ever-increasing demand for rubberwood, especially from the furniture industry, the rubberwood supply is being strained. Based on Ratnasigam et al. (2011), the total export value of rubberwood products grew by 39.44 % in 2009 compared to 2000. However, issues regarding the shortage of rubberwood supply are a growing concern due to declining rubber plantation areas (Ratnasigam et al. 2011). To date, various efforts have been made to incorporate the usage of rubberwood with other lignocellulose materials including EFB biomass. Oil palm EFB has been seen as an abundant, readily available, and cheap resource for board manufacturing. In terms of fibre strength properties, it has been proven to be comparable with the properties of rubberwood. In addition, high toughness and cellulose content values of EFB make it suitable for composite

Table 1 Malaysia oil palm planted area. (Source: MPOB 2014)

Year	Planted area (million hectares)
2007	4.304
2008	4.487
2009	4.691
2010	4.853
2011	5.000
2012	5.077
2013	5.230

Table 2 Empty fruit bunch and rubberwood fibre properties

Fibre properties (µm)	Empty fruit bunch[a]	Rubberwood[b]
Length	990	1249
Diameter	19.1	29.63
Lumen	–	20.28
Cell wall thickness	3.38	4.88

[a] Law et al. 2007
[b] Naji et al. 2011

applications (Sreekala et al. 2004; John et al. 2008). Fresh EFB from the mill was reported to contain 30.5 % lignocelluloses (45.0 % cellulose, 32.8 % hemicelluloses, and 20.5 % lignin), 2.5 % oil, and 67.0 % water (Ridzuan et al. 2002).

Besides the effort of many researchers to find alternative biomass to partially/fully substitute rubberwood, the Malaysian Rubber Board (MRB) also has come out with a new line of rubberwood clones to address the supply shortage of rubberwood. The series of clones are called latex-timber clones (LTC) and RRIM 2002 is one among them. Clones from the LTC series are expected to produce high latex yield and wood volume. Prang Besar (PB) 260 which has been commercially planted for decades belongs to the latex clones (LC). PB 260 is mainly planted for latex production and is only harvested and used by wood-based industry manufacturers after the trees reach the maximum tapping cycle (>25 years). Paridah et al. (2010) found that 4-year-old clones from the RRIM 2000 series produced comparable wood and particleboard properties to that of matured PB 260.

A comprehensive study on incorporating rubberwood with other biomass such as EFB could reduce the problems faced by the wood-based industry. According to Ratnasingam et al. (2007), the properties of particleboards made from 100 % of EFB are comparable with commercial particleboards and possess certain acceptable properties: mechanical, dimensional stability, and screw withdrawal. In addition, a prior study reported on the properties changes of composite panels made from EFB and rubberwood towards relative humidity, temperature, and storage time (Abdul Khalil et al. 2010). In that study, panels made from a high ratio of rubberwood exhibited superior flexural strength and flexural modulus. Juliana et al. (2012) revealed that mixing rubberwood with kenaf particles significantly improved the mechanical and physical properties of particleboard as compared to particleboard made from 100 % kenaf. Table 2 display physical properties of oil palm EFB fibres and rubberwood. However, problems may arise in the production of particleboard by incorporating EFB and rubberwood especially due to the oil traces in the EFB fibre. Mohd Nor et al. (1994) managed to produce MDF from oil palm frond and rubberwood with a 50:50 ratio. However, its properties were not satisfactory especially the internal bond (IB) and dimensional stability. Liew and Razala (1994) who also produced MDF from oil palm trunk fibres reported a similar board quality. According to Paridah et al. (2000), due to oil traces in the fibres, MDF from EFB has lower wettability, thus is more difficult to be glued or finished.

In this study, the performances of particleboards made from homogeneous and three-layer EFB with rubberwood (PB 260 clones and RRIM 2002 clone) particles were evaluated. The rubberwood clone PB 260 has been widely used as a raw material in particleboard manufacturing. Meanwhile, RRIM 2002 is one of the new clones promoted by Malaysia Rubber Board (MRB) where rubberwood can produce high timber and latex yield to be recommended for rubber plantations. However, the information on properties of this new clone as a raw material for wood-based products such as MDF and particleboard are still lacking. This chapter reports the properties of particleboard manufactured from EFB, PB 260, and RRIM 2002 clone.

Materials and Methods

Raw Material Preparation

EFB was obtained from Sabutek Sdn. Bhd., Teluk Intan, Perak. Two different rubberwood clones was used: PB 260 and RRIM 2002, respectively. PB 260 (age >25 years) wood and chips were supplied by Dongwha Fibreboards Sdn. Bhd., Nilai, Negeri Sembilan. Meanwhile, 4-year-old RRIM 2002 trees were harvested from the MRB research trial plot located at Tok Dor, Besut, Terengganu. The RRIM 2002 logs were then cut into billets and chipped using a Pallmann drum-chipper. All chips from rubberwood (PB 260 and RRIM 2002) and EFB fibre bundles were then flaked using a Pallmann knife-ring flaker to produce particles. The particles were screened using a circulating vibrator screener to classify the particles into various particle sizes retained at 0.5-, 1.0-, and 2.0-mm sieve sizes. Only particles that were retained in mesh 1.0–0.5 mm were used to fabricate the particleboards. The particles were then dried in an oven at 70 ± 2°C until the moisture content reached approximately 6%.

Manufacture of Particleboard

Admixture and three-layer particleboards 340 × 340 × 10 mm in size were manufactured with a target density of 700 kg/m^3. Particleboards manufactured from 100% EFB, 100% PB 260, and 100% RRIM 2002 served as control samples. For admixture particleboard, both particles (EFB and rubberwood) were homogeneously mixed whilst three-layer particleboards were layered with rubberwood particles with EFB as the core layer. The ratio for each rubberwood clone and EFB is shown in Table 3. Urea formaldehyde (65% solid content) at 10% level was used as the resin. One percent (w/w of resin solids) ammonium chloride was used as the hardener and wax was added at 1% (w/w) of oven dry weight particles. Mats were manually formed and cold-pressed for 5 min. The mats were then hot-pressed for 7 min at 170 °C. The boards were conditioned at an ambient temperature and a relative humidity of 65% until it achieved equilibrium moisture content prior to cutting

Table 3 Board types and ratios of EFB and rubberwood

Board type	Composition/ratio
Control	100 % EFB
	100 % PB 260
	100 % RRIM 2002
Admixture	50 % EFB: 50 % PB 260
	30 % EFB: 70 % PB 260
	50 % EFB: 50 % RRIM 2000
	30 % EFB: 70 % RRIM 2000
Three-layer (face : core : face)	25:50:25 (PB 260 %: EFB %: PB 260 %)
	35:30:35 (PB 260 %: EFB %: PB 260 %)
	25:50:25 (RRIM 2002 %: EFB %: RRIM 2002 %)
	35:30:35 (RRIM 2002 %: EFB %: RRIM 2002 %)

EFB empty fruit bunch

into test specimens. A total of 11 particleboard types equivalent to 33 boards were produced for the experiment.

After conditioning for 3 days at 23 °C and 65 % relative humidity, the boards were trimmed and cut into specimen sizes and evaluated for mechanical and physical properties according to the Japanese Industrial Standard, JIS A 5908–2003 (particleboard). The bending and IB strength tests on particleboards were conducted using the Instron Universal Testing Machine.

Results and Discussion

Table 4 summarizes the effects of the board type and ratio of material to the properties of the particleboards. Except for internal bonding, all properties were found to be significantly affected by the board type and ratio of materials.

Table 4 A summary of ANOVA for the effects of board type and ratio of EFB and rubberwood on the properties of particleboard

Source	df	*p*-value				
		Modulus of rupture (MOR)	Modulus of elasticity (MOE)	Internal bonding (IB)	Thickness swelling (TS)	Water absorption (WA)
Type	2	0.0001[c]	0.0001[c]	0.0336[a]	0.0033[b]	0.0001[c]
Ratio	6	0.0001[c]	0.0001[c]	0.0001[c]	0.0001[c]	0.0001[c]
Type*ratio	2	0.0001[c]	0.0001[c]	0.5191[ns]	0.0001[c]	0.0008[c]

ANOVAS analysis of variance, *EFB* empty fruit bunch

[a] Significantly different at $p \le 0.05$

[b] Significantly different at $p \le 0.01$

[c] Highly significant different at $p \le 0.001$

ns Not significant $p > 0.05$

Bending Properties

The bending properties of the particleboards are shown in Table 5. From Table 5, 100 % EFB has a higher modulus of rupture (MOR) but lower modulus of elasticity (MOE) compared to 100 % PB 260 and 100 % RRIM 2002. According to a prior study, EFB fibres cannot withstand the heavy load and this leads to the failure of that fibre which results in composite failure (Sreekala et al. 2002). This might be due to the lower α-cellulose content in EFB fibres compared to rubberwood (Abdul Khalil et al. 2010). Rubberwood is classified as light hardwood, having a specific gravity of 0.57–0.60 (Bosshard 1966; Saiful Azry 2007), while EFB has density of 0.70–1.55 g/cm^3 which is slightly higher than rubberwood. This may contribute to the improvement especially in terms of MOR in EFB boards.

After blending, the EFB with rubberwood particles, both MOR and MOE, have better properties compared to 100 % EFB except admixture board made from 30 % EFB to 70 % RRIM. This shows that the 4-year-old rubberwood RRIM 2000 clone exhibited comparable strength and stiffness when mixed with at least 50 % EFB particles. This finding also implies that, irrespective of the rubberwood age, RRIM is equally advantageous in that less strength variation results from using matured tree. However, the presence of a high ratio of rubberwood (up to 70 %) particles apparently decreased the strength, but comparable to the control boards.

Apparently, a three-layer board has significantly lower strength and stiffness properties compared to admixture boards. The same trend was also observed by Juliana et al. (2012) where they found that three-layer particleboards made from kenaf and rubberwood had slightly lower MOR, MOE, and IB values compared to admixture boards. This is contributed to the presence of more void spaces in the three-layer particleboard. According to Escobar (2008), a number of voids per unit area are sufficient to cause failure under stress. However, this is in contrast with Haygreen and Bowyer (1989) who stated that the layering of multilayer particleboards

Table 5 Bending properties of particleboards

Materials	Modulus of rupture (MPa)		Modulus of elasticity (MPa)	
	Admixture	Layer	Admixture	Layer
100 % EFB	22.48^b		1118^e	
100 % PB 260	20.98^b		2156^b	
100 % RRIM 2002	20.44^c		2145^b	
50 % EFB–50 %PB 260	27.54^a	16.73^d	2138^b	1716^d
30 % EFB–70 %PB 260	23.05^b	18.55^c	2086^b	1982^c
50 % EFB–50 %RRIM	27.83^a	19.88^c	2319^a	2049^b
30 % EFB–70 %RRIM	18.14^d	17.98^d	1645^d	1937^c
LSD	2.15		147	

Means followed by the same letters ^{a,b,c,d,e} in the same column were not significantly different at $p \leq 0.05$

help to increase the bending strength of the boards by altering the properties of the surface and core. Layering is one of the methods to improve the mechanical properties of most composites. It was reported that layering with wood species has significantly enhanced the MOR, MOE, and IB strength of particleboards (Nemli and Ozturk 2006).

In terms of the ratio of materials, surprisingly, the higher ratio (50 %) of EFB for both rubberwood clones for homogeneous boards showed the highest values of MOE and MOR compared to the lower ratio of EFB. This value was higher than those shown by control boards made from 100 % of each material. High stiffness and strength values might be attributed by the high aspect ratio of EFB. From observation, EFB particles are longer and slender compared to rubberwood particles. This property brings EFB to resist higher load to fracture the weakest point area of EFB board during bending. Thus, it resulted in high bending properties on this particular panel. Ong (1981) agreed with this and stated that longer wood particles significantly increased the bending properties of particleboard. As reported by John et al. (2008), EFB also has good toughness and cellulose content. In addition, the presences of a stiff material such as EFB in an admixture board might be able to potentially provide high strength to the board. However, a dramatic decrement was observed when 70 % rubberwood was incorporated. This may be due to excessive rubberwood particles to be filled between EFB particles. This finding contradicted with results obtained by Abdul Khalil et al. (2010). In their study, MDF boards made from 80 % rubberwood showed greater mechanical and physical properties compared to 50 % rubberwood.

Internal Bonding

Good compatibility can be indicated by a high modulus in composite materials (Eichhorn et al. 2001). Compatibility is one of the main problems in composite materials that commonly occur between the adhesion of the matrix and the fibres. Figure 1 illustrates the internal bonding strength of single-layer and three-layer particleboards. Apparently, homogeneous single-layer boards of EFB and rubberwood particles have good compatibility among EFB and rubberwood particles. Comparable IB values of all single-layer boards may indicate that in form of crude particles, the board has good compatibility among EFB and rubberwood particles. This finding concluded that EFB fibre can be used with PB 260 at a ratio of 30–50 %, but only 50 % with RRIM 2000 series to achieve acceptable internal strength properties.

Usually, in many cases, the weak material becomes the core material due to insignificant effect on board strength and stiffness but it may influence the IB properties. A previous study reported that EFB has low performance due to oil traces in the fibres (Paridah et al. 2000). Based on Abu Bakar et al. (2006), EFB fibres have oil residues of 4.5 % and commonly give poor bonding properties in composite manufacture. Therefore, for three-layer particleboards, EFB was placed at the core layers. Meanwhile, rubberwood was placed at the face layers since rubberwood has a higher IB value compared to EFB. Similar to an admixture board, a three-layer

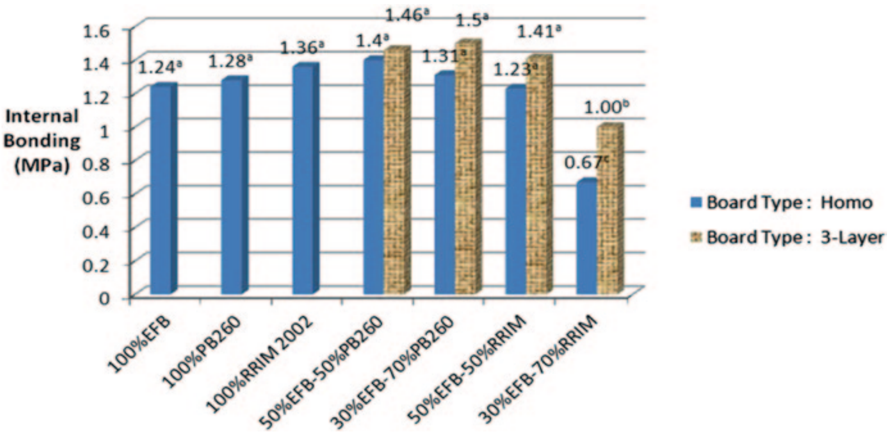

Fig. 1 Internal bonding values of particleboards. Note: Means followed by the same letters ^{a,b,c} in the same column were not significantly different at $p \leq 0.05$

board apparently has good internal bonding with slightly higher improvement, but not significant.

From Fig. 1, all boards were found to be not significantly different in terms of IB value, except for boards made from 70 % RRIM 2002. However, the trend for IB is reversed compared to bending values, where three-layer boards showed better properties compared with admixture and control boards.

Dimensional Stability

Thickness swelling (TS) and water absorption (WA) values are the main indicators to determine the stability of a composite. A board with low dimensional stability is indicated by high TS and WA values. Table 6 shows that the dimensional properties of the particleboards were highly affected by board type and material ratio. Apparently, single-layer and three-layer boards that consist of rubberwood particles show relatively higher TS and WA values. And interestingly, a particleboard made from pure EFB (100 % EFB) has relatively low TS and WA values compared to others. Generally, 100 % EFB has the lowest TS value, followed by boards with 50 % EFB and 30 % EFB with value ranges of 14.59 %, 16.42–18.19 %, and 15.08–26.13 %, respectively. This indicates that most boards made of EFB have low TS values.

It can be observed that boards manufactured from the RRIM 2002 rubber tree clones had higher TS values compared to the other boards. The incorporation of 30 % EFB with RRIM 2002 did not increase the board stability. However, by adding up to 50 % ratios of EFB the stability of three-layer board seem to improve. Table 6 also shows that the WA of three-layer boards was significantly higher than admixture boards. This again might be contributed to the higher percentage of void spaces in the three-layer boards which can be filled with water. Prior studies have stated

Table 6 Dimensional properties of particleboards

Materials	Thickness swelling (%)		Water absorption (%)	
	Admixture	Layer	Admixture	Layer
100 % EFB	14.59^{f}		48.64^{d}	
100 % PB 260	18.10^{d}		57.85^{c}	
100 % RRIM 2002	22.35^{b}		58.03^{c}	
50 % EFB–50 %PB 260	18.19^{d}	17.68^{d}	45.38^{d}	68.17^{b}
30 % EFB–70 %PB 260	15.08^{e}	21.38^{c}	44.73^{d}	67.42^{b}
50 % EFB–50 % RRIM	16.42^{e}	16.47^{e}	48.00^{d}	76.08^{a}
30 % EFB–70 % RRIM	26.13^{a}	23.78^{b}	70.42^{a}	72.23^{a}
LSD	1.58		7.28	

Means followed by the same letters ^{a,b,c,d,e} in the same column were not significantly different at $p \leq 0.05$

that the existence of more voids may also provide spaces which encourage water uptake (Loh et al. 2010; Saad and Izran 2012). In their studies, panels consisting of high amount of voids accommodate some of the swelling of the panel.

A study carried out by Abdul Khalil et al. (2010) showed that MDF made with rubberwood fibres were more stable compared to boards made with EFB fibres. In their study, the lower amount of holocellulose and lignin in rubberwood fibres indicate that rubberwood fibres have a lower amount of free hydroxyl groups. Interestingly, this condition was not observed in this study. Particleboards made from 100 % EFB had significantly lower TS and WA values compared to boards made from rubberwood. This might be due to the waxy surface on EFB (Adlin 2007; Nazir et al. 2013) which may resist water to penetrate into the board and reduce the water uptake. The same trend occurred when EFB fibres were layered with rubberwood particles. Overall, boards with a higher amount of EFB had relatively lower TS and WA values.

Conclusions

From the results obtained, it can be concluded that particleboards made from 100 % EFB has comparable properties with boards made from 100 % rubberwood except for the MOE. EFB particles can be mixed and layered with rubberwood (PB 260 or RRIM 2002 clone) particles up to 50 % (w/w). However, boards (both admixture and three-layer) made from 30 % EFB: 70 % RRIM 2002 gave the lowest values in almost all of the properties.

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Characterization and Use of Coir, Almond, Apricot, Argan, Shells, and Wood as Reinforcement in the Polymeric Matrix in Order to Valorize These Products

Abouelkacem Qaiss, Rachid Bouhfid and Hamid Essabir

Abstract The natural resource materials have an exceptional potential as reinforcement in plastic composites, due to their low cost, good mechanical properties, and biodegradability. This chapter is related to the use of some natural resources (nutshells residues) and their effect on polymer composite with varying filler reinforcement content and type or improving the adhesion between polymer matrix and filler. In this study, the used natural resources as bio-filler were almond shells, coir shells, argan shells, apricot shells, wood powder, and the mixture of these fillers, reinforcing thermoplastic polymer at various filler content (5, 10, and 20 wt.%), through extrusion and injection molding processes. The chemical and physical properties of the bio-filler and bio-filler/polymer composites were defined by using Fourier transform infrared spectroscopy (FT-IR); thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); and tensile, torsional, and rheological tests. Depending on the bio-filler type, there was evidence that some particular difference in the chemical exists and also physical property changes. An increase in the crystallinity of composites is explained by the nucleating agent role of the bio-filler. The thermal, mechanical, and rheological properties of the composites were mostly enhanced with the addition of bio-fillers compared to the neat polymer matrix, and optimal properties were reached. Also, some optimal properties were observed when enhancing the interfacial adhesion by using a coupling agent. As a result, good final properties of the composites were manufactured with low cost. However, a fundamental understanding of the bio-filler structure and chemical composition could be beneficial to reach their full industrial applications.

Keywords Coir · Almond · Apricot · Argan · Shells · Polymer matrix

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Introduction

In the last years, the need of improving living conditions has considerably increased and the utilization of polyolefin polymer material, mainly plastics, as polypropylene (PP), polyethylene, etc., has increased. The use of different plants or their residues as bio-filler in a synthetic polymer matrix has been a successful way to produce and to develop new filler/plastic composite materials with good and various properties (Mirmehdi et al. 2014; Boujmal et al. 2014; Salleh et al. 2014).

The bio-filler (lignocellulosic)-reinforced composites have several advantages in comparison with mineral fillers, including their low cost, low density, biodegradability and availability, ease of implementation, and their specific properties (Malha et al. 2013; Ou et al. 2014). In addition, their high cellulose component makes them biodegradable and recyclable. Lower processing costs, the design flexibility, and the ease of molding the complex parts are also advantages of bio-filler composite materials. These benefits are of interest for applications in various fields such as daily living (furniture, floor, pots, etc.) and automotive industry, which requires high performance, lightweight materials, minimum impact on the environment, and reduced cost of the material. However, the ultimate properties of the polymer composites are influenced by many factors such as the filler composition, filler size and morphology, filler loading, filler dispersion/distribution in a polymer matrix, processing methods, and interfacial interactions (Yao et al. 2013; Elkhaoulani et al. 2013).

Bio-fillers are hydrophilic as they are comprised of cellulose, lignin, pectin, and hemicelluloses, which contain hydroxyl groups with high reactive functionality (Arrakhiz et al. 2012a). These bio-filler are therefore incompatible with the hydrophobic thermoplastic matrix, such as polyolefin, and have a low moisture resistance. It is then necessary to improve the interfacial adhesion between bio-filler and polymer matrix. The importance of the interfacial interactions between the polymer matrix and the fiber was widely renowned in the improved hygrothermal stability and mechanical properties of polymer composites (Sreenivasan et al. 2012; Kuciel et al. 2014; Shinoj et al. 2011). A force applied to the matrix directly on the surface of a composite is transferred to the nearest filler and propagates through the filler matrix and filler interface. If the interface is poor, efficient distribution of strength is not reached and the mechanical properties of composites are impaired (Arrakhiz et al. 2012b, c). Another important factor for obtaining composite with high mechanical properties is the filler dispersion/distribution. Poor dispersion of the fillers in the material leads to the formation of aggregates (Arrakhiz et al. 2013a; Nekhlaoui et al. 2014a). These various problems are the main limitations to the use of these fillers as reinforcing polymers.

Moreover, further search still develops techniques to overcome the main drawbacks of using bio-filler, such as their poor interfacial bonding with polymer matrix, filler distribution/dispersion, and low thermal degradation of bio-filler compared with inorganic fillers. It has been shown that an appropriate treatment applied to the filler or polymer matrix may enhance compatibility between them, which improves the quality of the composite materials. Various methods such as plasma treatment, alkali, heat, graft coupling agent, or other chemical products have improved compatibility of the bio-filler with the matrix (Arrakhiz et al. 2012b, c; Nekhlaoui 2014a). All these studies show that the adhesion between bio-fillers and the matrix plays an important role in the mechanical properties of the composite. It is therefore essential to know the chemical surface interactions between the various components of composites prior to conducting mechanical characterization of the assembly.

In general, bio-filler-reinforced polymer matrix is an interesting area of research. So, many industries have developed their polymeric product by reinforcing them with bio-filler. Wood powder is among the most frequently used natural fillers (Sliwa et al. 2012; Pérez et al. 2012; Zhang 2014; Najafi 2013); however, other natural fillers, such as coir (Mir et al. 2013), doum (Essabir et al. 2013a), sugar palm (Sahari et al. 2013), bagasse (Arrakhiz et al. 2013b), hemp (Etaati et al. 2014), are often employed as new reinforcement agents in polymer-based composite materials. Among these natural fillers, the nutshells could have a promising future as new reinforcement in polymer composites. Generally, when producing fruits, tons of the seeds will be needed and, in turn, tons of shells will become available. Many works reported that the nutshells can be used as an energy source in an open-core gasifier (Wever. 2012; Bahar Tiryaki et al. 2014), a potential alternative fuel for diesel engine and for heating. Therefore, the natural filler derived from nutshell residues could potentially be substituted for inorganic fillers in the composites. In this regard, this chapter attempts to use some local crops such as almond shells, coir shells, argan shells, apricot shells, wood shells, and their mixture to reinforce thermoplastic polymers.

Nutshells' Characterization

Chemical Composition

The cellulose, hemicelluloses, lignin, ash, moisture, and undetermined contents of the natural bio-filler (almond shell, coir shell, apricot shell, and wood powder) are detailed in Table 1. There are other minor products that are extractable by organic solvents, proteins, starch, and other inorganic products. Substances other than lignin, cellulose, and hemicelluloses are known as extraneous components and include

Table 1 Chemical (ligno-cellulosic) composition of selected bio-filler (Bahar Tiryaki et al. 2014; Demiral and Cemrek Kul 2014; Herrera et al. 2014)

Type of bio-filler	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
Coir (jacs 1938, 60, 1506)	53.06	–	36.5	0.61
Almond shells	21.7	27.4	36.1	6.85
Apricot shells	29.57	17.01	47.97	0.95
Wood powder	45.3	23.6	27.6	0.27

extractives and ash. The chemical composition of the bio-filler depends on their origin, but in general it can be said that the major portion corresponds to the cellulose, with about 20–50 %, lignin concentrations range from 20 to 50 % by weight, and those of hemicelluloses from 10 to 30 % by weight. The cellulose fractions were high for the wood powder followed by apricot shells (Table 1; Bahar Tiryaki et al. 2014; Demiral and Cemrek Kul 2014; Herrera et al. 2014). The ash content of the almond shells was 6.85 %, which is higher than other bio-filler materials. These compounds are heteropolymers which have a high variability in chemical composition according to their origin and contribute to the overall properties of the bio-filler.

Structural Properties

Cellulose is the component that provides protection and support in plant organisms. The microstructure composition of cellulose is complex due to the hierarchical organization which varies depending on the origin of shells. The molecular structure of cellulose, which is responsible for its supramolecular structure, determines many of its chemical and physical properties. The individual cellulose chains are associated via hydrogen bonds, and themselves associated with each other to form cell walls. These walls are included in a matrix of amorphous hemicelluloses, pectins, lignin, and some protein. Hemicelluloses comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. Further, lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. The mechanical properties of hemicelluloses and lignin are lower than those of cellulose.

Infrared spectroscopy is considered as a simple, direct, and sensitive characterization technique for the identification of the chemical structure and groups in different materials, which may include bio-filler and their composites. The Fourier transform infrared spectroscopy (FT-IR) spectra of the studied bio-filler (almond shell, coir shell, apricot shell, argan shell, and wood powder) are plotted in Fig. 3. The spectra of bio-filler show a large band at 3329 cm^{-1}which is assigned to the OH stretching vibration of bio-filler's group (Essabir et al. 2013b). In the 2900–1000 cm^{-1} region, the bio-filler spectra were evidenced only by the bands of cellulose, hemicelluloses, and lignin (Essabir et al. 2013b, c, 2014). The band at 2940 cm^{-1} belongs to the C–H stretching vibration from CH and CH_2 in cellulose and hemicellulose components. The band at 1737 cm^{-1} may represent the carbonyl C = O stretching vibration of linkage of carboxylic acid in lignin or ester group in hemicelluloses (Essabir et al. 2013b, c, 2014). The band at 1615 cm^{-1} is assigned to the carbonyl group stretching. The peak at 1465 cm^{-1} corresponds to the CH_2 symmetric bending present in cellulose. The C–O stretching vibration of the acetyl group in lignin and hemicellulose component appears at 1242 cm^{-1}. The strong absorption band at 1040 cm^{-1} is attributed to the C–O and O–H stretching vibration, which belongs to polysaccharide in cellulose (Essabir et al. 2013b, c, 2014; Figs. 1 and 2).

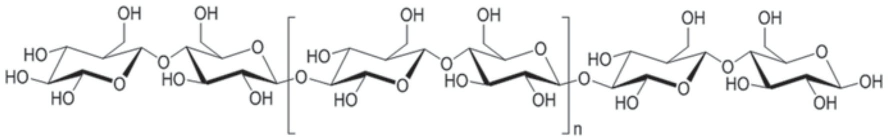


Fig. 1 Structure of cellulose

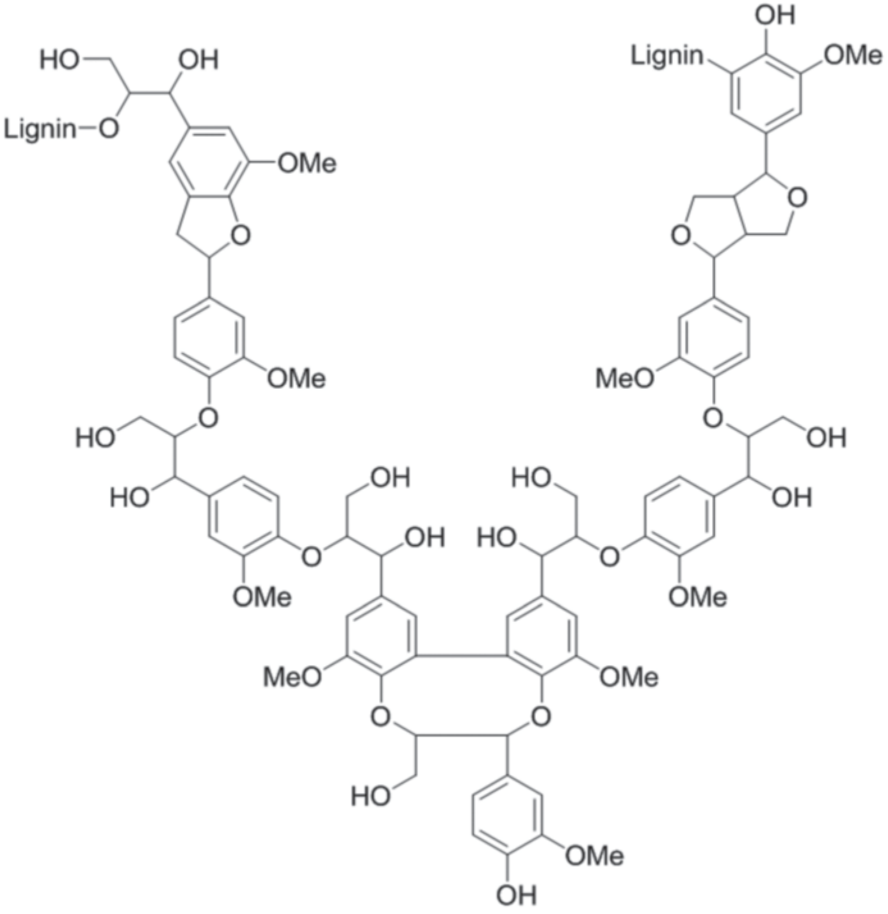


Fig. 2 Structure of lignin

Mechanical Properties

It is well known that the mechanical properties such as Young's modulus of biofillers (nutshells residues) like argan, almond, and apricot shells are lower than those of inorganic fillers commonly used in composites such as clay, talc, and calcium carbonate. Though, in terms of specific strength and specific Young's modulus, the

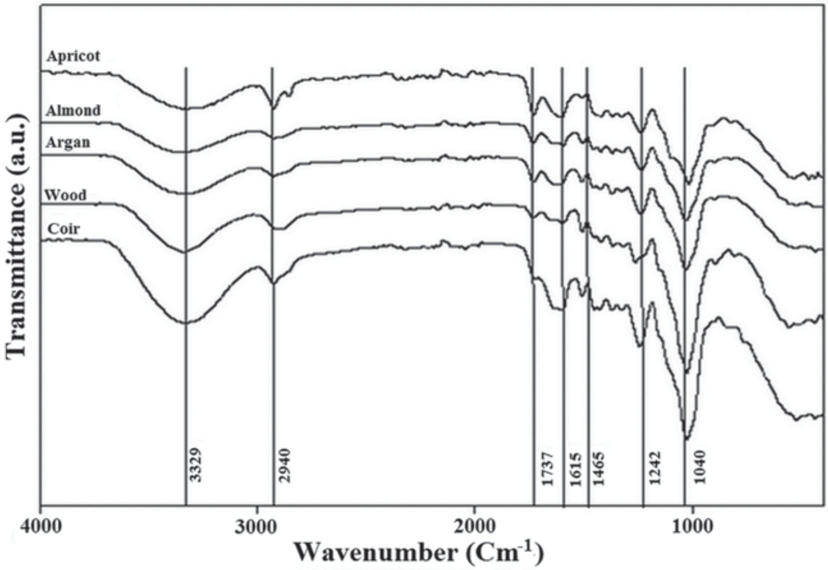


Fig. 3 Fourier transform infrared spectroscopy (FT-IR) spectra of almond, coir, apricot, and argan nutshells

Table 2 Density of selected bio-filler

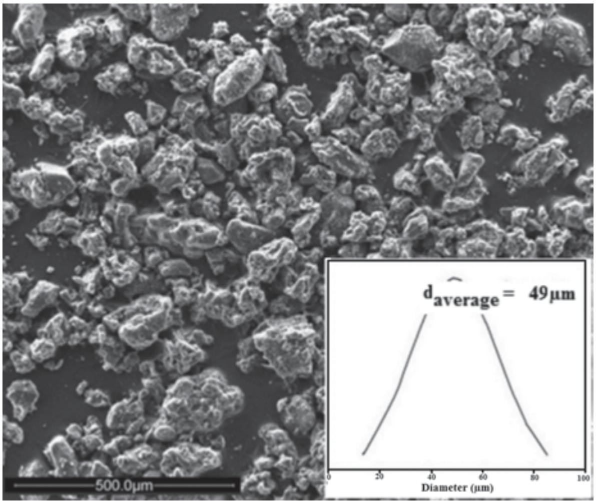
Type of bio-filler	Density (g/cm^3)
Almond shells	1.36
Coir shells	1.21
Argan shells	1.29
Apricot shells	1.28
Wood powder	1.48

bio-fillers derived from nutshells residues are quite comparable to inorganic fillers such as talc and calcium carbonate, because the density of inorganic fillers is higher (clay ≈ 2.5 g/cm^3, CaCo$_3$=2.7 g/cm^3; Nekhlaoui 2014a), while that of bio-filler is much lower (Table 2). This becomes particularly important in automotive and packaging industry, which requires high performance of lightweight materials. Table 2 compares the chemical and mechanical properties of some bio-filler (nutshells) to inorganic filler commonly used in composite materials.

Morphological Properties

One important parameter in filler composite technology is particle size. Figure 4 depicts the bio-filler size distributions before compounding. The morphology of used bio-filler with different particle sizes is shown in Fig. 4 (argan shells as an

Fig. 4 Morphological and size of argan particle



example). As shown in Fig. 4, bio-filler particles (argan) exhibit irregular shape and porous structure. The porous structure of bio-fillers leads to much lower apparent density (1.3 g/cm^3) than that of mineral filler (approximately 2.8 g/cm^3). Therefore, bio-filler can be dispersed in polymer matrix more homogeneously. The average diameter of the used bio-filler is less than 50 µm.

Thermal Properties

Thermoplastic polymers with a high melting flow are commonly used to process composite material-reinforced bio-fillers. So, during composite processing, the bio-fillers are subjected to a high temperature (Salleh et al. 2014). Temperature above polymer processing (above 240 °C) temperature results in decomposition of bio-filler. The thermal decomposition of selected bio-filler was determined by thermogravimetric analysis (TGA) under air and is illustrated in Fig. 5.

It was found from Fig. 5 that the thermal decomposition of all bio-filler occurs in four steps. The first mass loss, in the range 50–100 °C, is due to the evaporation of the water from the particles, while the onset degradation of the three major constituents of the natural fillers—hemicellulose, cellulose, and lignin—occurs at higher temperatures. The first degradation stage was the decomposition of hemicelluloses, followed by that of cellulose, lignin, and lastly their ash (Dehghani et al. 2013; Luo et al. 2014; Hao et al. 2013).

The first phase (280–310 °C) was the thermal depolymerization of hemicelluloses and pectin of hemicelluloses, while the second phase occurs in the range (320–340 °C) and corresponds to the degradation of cellulose present in the bio-filler. Because of the highly crystalline nature of their cellulose chain than the amorphous nature, cellulose is relatively thermally stable. The third phase is assigned to the

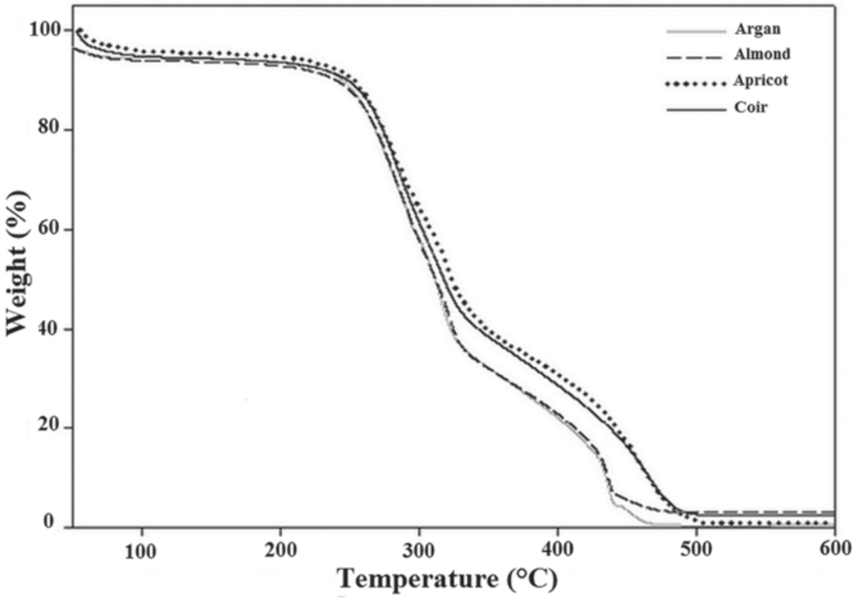


Fig. 5 Thermogravimetric analysis (TGA) curves of nutshells: almond, coir, apricot, and argan

decomposition of lignin between 440 and 480 °C (Essabir et al. 2013b, c, 2014). It was found that because of its complex structure, the decomposition of lignin occurs slowly in the temperature range (from 160 °C) to extend its complete decomposition at a higher temperature (480 °C). This is contributed by lignin, which is a very tough component and known as the compound that gives rigidity to the plant materials.

Use of Shells as Reinforcement in Thermoplastic Matrix

The nutshells were selected to be used as reinforcement in thermoplastics matrix due to the wide amount of research material currently available (energy, adsorption). Many works reported that the nutshells can enhance the thermal and mechanical properties of polymer matrix and can be used as an alternative to mineral fillers such as talc and calcium carbonate. In this regard, the specific nutshells such as almond, coir, apricot, argan, wood powder, and their mixture were used as the reinforcing material since it is abundant in nature and has minimal effect on the environment due to their biodegradable properties (Essabir et al. 2013b, c, 2014).

Almonds are a very important crop throughout the world's temperate regions. Almond shell accounts for about 35–75 % of the total fruit weight consequently; around 0.8–1.7 million tons of almond shells are left annually (Essabir et al. 2013c). Almond shell is the lignocellulosic material forming the thick endocarp or husk of the almond tree fruit which, upon processing, yields edible seeds. Almond shells are separated from the edible seeds and since they have no important industrial usages, they are normally incinerated or dumped. Burning agricultural residues cause environmental problems such as air pollution, soil erosion, and decreased soil biological activity.

Coir is obtained from coconut tree which is found in tropical countries. Because of its hard-wearing quality, durability, and other advantages, it is used for making a wide variety of floor furnishing materials, yarn, rope, etc. However, these traditional coir products consume only a small percentage of the potential total world production of coir nut husk (Arrakhiz et al. 2012b). Hence, apart from the conventional uses of coir as mentioned above, research and development efforts have been under way to find new use areas for coir shells, including use of coir as reinforcement in polymer composites.

The argan tree, called *Argania spinosa,* is a tropical plant, which belongs to the Sapotaceae family. Moroccans traditionally use the fruits of *A. spinosa* to prepare edible oil. It represents the only endemic species of the genus *Argania* (Harhar et al. 2014). As an important traditional alimentary medicine, *A. spinosa* is a valuable potential for the Moroccans. All parts of the argan tree are used by local people: wood and woody shell of the fruit for heating, and the almond fruit for production of argan oil. In cosmetics, argan oil is advocated as moisturizing oil against juvenile acne and flaking of the skin as well as for nourishment of the hair, thanks to its high content of vitamin E, while fruit pulp and seed cake residue from the production of argan oil are used for cattle (Essabir et al. 2013b; Harhar et al. 2014).

Apricot is one of the most popular of the temperate fruits worldwide and is cultivated in all Mediterranean countries (Essabir et al. 2014). Apricot pits are also separated into shells and kernels, which have washing, sorting, cracking, and separating units. The resulting shells are generally used as fuel and the resulting apricot kernels are exported worldwide Fig. 6.

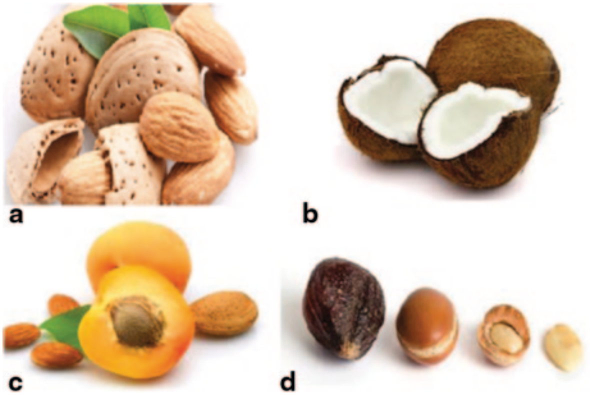


Fig. 6 Photographs of the used nutshells: **a** almond, **b** coir, **c** apricot, and **d** argan

Problematic

Generally, the physical and mechanical properties of final composite materials depend on the type of matrix, filler content, physical and chemical properties of the reinforcing filler, distribution/dispersion of the filler into the polymer matrix, and interfacial adhesion. There are three major challenges to be overcome in using bio-filler as filler: (1) the thermal decomposition of bio-filler at the processing temperature and (2) distribution/dispersion of the filler into the polymer matrix. Better dispersion of the filler can be achieved by effective mixing of the components and an appropriate compounding process (Essabir et al. 2013b, c). (3) The incompatibility between the bio-filler and the polyolefin matrix.

The interfacial adhesion between bio-filler and polymer matrix is the limiting factor of the filler-reinforced composite performance, as it defines the amount of load that can be transferred from one filler to the second by the matrix. The strength of a filler–matrix interface is dependent upon the degree of mechanical, chemical, and electrostatic bonding and the level of interdiffusion between the matrix and fillers. The lack of chemical bonding between filler and polymers is due to the chemical properties of bio-filler that is strongly hydrophilic and to the polymer matrix which is mostly hydrophobic and apolar.

To overcome this incompatibility, the hydrophilic nature of bio-filler can be reduced by chemical modifications. Many researchers have tried chemical treatment of biofiller's surface such as mercerization, benzoylation, acetylation, silanation, grafting copolymerization (Huu Nam et al. 2011; Arrakhiz et al. 2013c), and utilized different chemical treatments to compare the impact of chemical treatment on the mechanical properties of composites. The use of a coupling agent with intermediate properties between those of the fillers and matrix can also be considered, with the coupling agent forming a bridge between them. Arrakhiz et al. (2012a) and Essabir et al. (2013a, c) described studies evaluating the effect of compatibilizer on the mechanical and thermal properties of composites.

It is well known that the use of stiffer filler in the polymer matrix enhances the rigidity of the final material, but in contrast, the ductility of materials decreases. The filler acts as a nucleating agent, reduces the elasticity of the materials, and leads to decreased ductility of the composites. Some industrial application requires materials with a good rigidity/ductility ratio. To overcome these drawbacks during implementation of composites, maleic anhydride (MA) can be used as a coupling agent, which is generally grafted to the same polymer as a matrix. However, to improve the interfacial adhesion and ductility of material, it was found in a previous study that grafting MA with a rubber copolymer as coupling agent enhances the toughness property of the resulted materials (Nekhlaoui et al. 2014b). In this regard, to improve the filler/matrix adhesion and to improve the ductility of composites, the styrene–(ethylene–butene)–styrene (SEBS) triblock copolymer as the rubber support can be grafted with MA, resulting in a coupling agent named styrene–(ethylene–butene)–styrene triblock copolymer-grafted MA (SEBS-g-MA).

Processing Techniques for Polymer Composites

The polymer processing techniques are most frequently used in the implementation of composite materials. The preparation of the mixture of raw materials is performed at a temperature which corresponds to a softened plastic phase. This hot mixing (melt blending) is obtained in several ways and leads to different modes of manufacture. Among these methods of implementation can be distinguished sol–gel process, in situ polymerization, and melt blending. The extrusion, injection, and compression molding are the most usual processes to produce polymer/filler composites with a high homogeneity and a good dispersion/distribution of fillers. It is important to note that the process parameters such as the rotating speed of the mixer, the temperature, time, and moisture influence the properties of the composite product. The extrusion of a blend of cellulosic fillers and a thermoplastic is a technique which allows the achievement of the composite. The fillers are incorporated into the molten thermoplastic using a screw system. The plastic injection is an implementation process of thermoplastics. It is to soften the plastic material to bring it to melt and injecting it into a mold for shaping.

Mixtures of PP and bio-filler will feed an extruder. The extruder was a corotating twin screws which rotate within a cylindrical sleeve with temperature-controlled heating systems and cooling (Arrakhiz et al. 2013b; Qaiss and Bousmina 2011; Fig. 7). The main function of the extruder is to convey, melt, and pressure the material introduced into the hopper so that it can cross the die (Arrakhiz et al. 2013b; Qaiss et al. 2012, 2013). The steps for implementation of the composite during extrusion are described in Fig. 7a. The state of the polymer blend in the machine can distinguish five zones:

1. The feed zone 1, wherein the polymer is entirely solid and preheated.
2. The homogenization zone in which the polymer is soft and the polymer already in the molten state.
3. The feed zone 2, wherein the fillers are blended with the polymer in the molten state. Bio-fillers are added in the third zone to minimize their residence time under high temperature, in order to avoid charge degradation.
4. The homogenization zone dispersion/distribution, wherein the polymer coexists in the molten state with the fillers.
5. The compression zone, wherein the material is fully melted and forced through the die.

In this study, composites were manufactured from PP and PP-grafted coupling agent matrix-reinforced nutshells as bio-fillers. Various concentrations of bio-filler (0, 5, 10, and 20 wt.%) were blended by extrusion and by using a Leistritz ZSE-18 Twin Screw Extruder (Leistritz Extrusions Technik GMBH, Germany). Mixing was performed using a speed of 125 rpm for the main screws and a 40-rpm side-feeder screw speed for particle feeding. The temperature profile of the extruder barrel's seven zones was set, from hopper to die, at 170, 170, 175, 180, 180, 175, 170, and

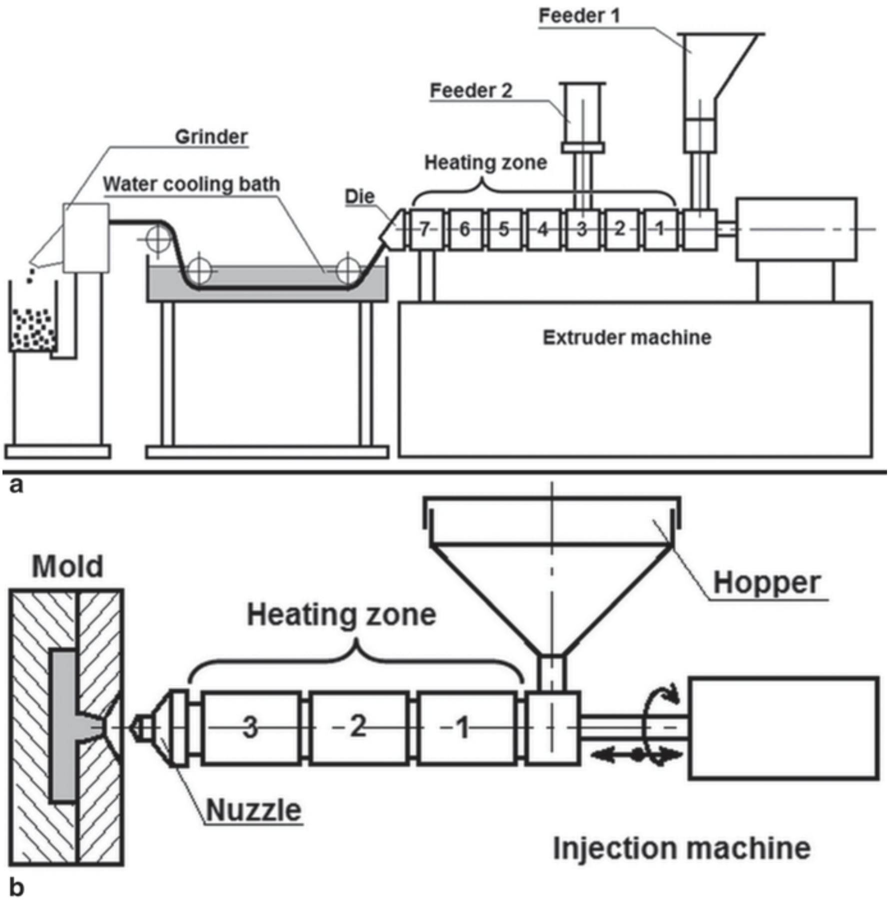


Fig. 7 **a** Extruder machine and **b** injection machine

170 °C (Fig. 7a). The melt-extruded composites were cooled in a water bath and then pelletized into granules of about 2 mm length, from which test samples were molded using an injection-molding machine (Engel e-Victory). The temperature of the injection press barrel was fixed at 180 °C, while the nozzle temperature was set at 170 °C and mold at 45 °C (Fig. 7b).

Composite Characterization

The structural, morphological, thermal, and mechanical properties of final composite materials depend strongly on the filler content, distribution/dispersion of the filler into the matrix, and interfacial adhesion. In this study, the adhesion between bio-filler and the matrix was reached by the addition of SEBS-g-MA as the coupling agent at 8 wt.%.

Structural Properties

The FT-IR analysis proved to be a useful tool for determining the interaction between matrix, compatibilizer, and bio-filler to provide a good interfacial adhesion. It is known that cellulose is the major content of bio-filler; the cellulose has a reactive functionality that can react as strong ester bonds with coupling agent, thus enhancing adhesion between the bio-filler and matrix. The FT-IR spectra of the studied composites (binary and ternary composites) are plotted in Fig. 8. Comparing the spectra of the PP/bio-filler composites with the spectrum of PP, the most major bands of PP are observed in all spectra, but there are also many overlapped bands which contain vibrations from both PP and bio-filler components (Fig. 8b). Table 3 summarizes the assignment of different characteristic bands of PP matrix and bio-filler composites.

Morphological Properties

The physical and mechanical properties of bio-filler composites depend on the type of matrix, the content, properties of the reinforcing filler, dispersion/distribution of bio-fillers into the polymer matrix, and interfacial adhesion. Many studies reporting on the effects of fillers incorporation on the mechanical properties include Arrakhiz et al. (2013a, b). Better dispersion/distribution of the filler can be achieved by

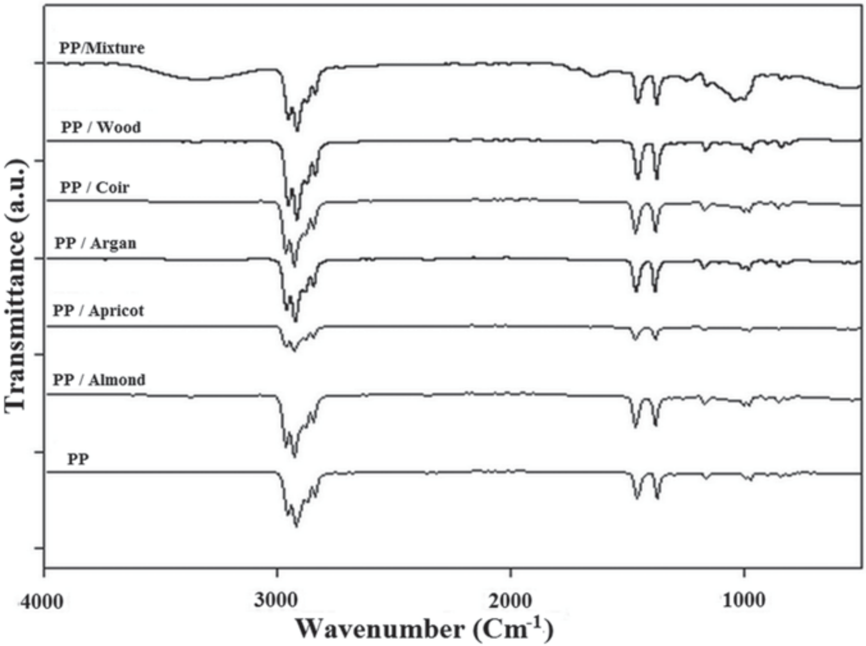


Fig. 8 Fourier transform infrared spectroscopy (FT-IR) spectra of polypropylene (PP) composite with almond, coir, apricot, and argan nutshells

Table 3 Band position and assignment of each composite

Bands position (cm^{-1})						Band assignment
PP	PP/Al	PP/Coir	PP/Argan	PP/Ap	PP/Wood	
–	3370	3460	3341	3356	3500	OH stretching vibration in bio-filler
2956	2963	2956	2959	2956	2955	Asymmetric methyl stretching vibration
2910	2926	2918	2926	2911	2911	Asymmetric methylene stretching vibration
–	2867	2867	2866	–	–	Symmetric methylene stretching vibration
–	2822	2830	2825	2844	2822	Symmetric methyl stretching vibration
–	1733	1730	1736	1741	1748	C=O stretching vibration of carboxyl and acetyl groups in bio-filler
–	1637	1682	1625	1556	1637	Carbonyl group stretching
–	1504	1507	1502	1506	1549	C=C stretching vibration of substituted aromatic ring
1462	1467	1452	1460	1467	1445	CH_3 asymmetric bending vibration in PP and C–H deformation vibration in carbohydrates
1364	1378	1371	1370	1371	1370	CH_3 asymmetric bending vibration in PP and CH deformation vibration in carbohydrates
1302	–	–	–	–	–	CH_2 wagging and CH bending vibration in PP
1258	1252	1256	1259	1259	1244	CH bending vibration in PP and C–O stretching vibration in bio-filler
1166	1163	1163	1170	1148	1155	C–C chain stretching vibration in PP and C–O stretching vibration in carbohydrates
1067	1040	1020	1010	1037	1029	CH bending and CH_3 rocking vibration in PP and C–O and C–C stretching vibration in bio-filler
–	992	970	978	958	–	CH_2 wagging and CH bends vibration in PP and CH_3 rocking vibration in bio-filler
–	970	896	889	963	–	CH_3 rocking vibration and C–C chain symmetric stretching vibration
–	903	–	–	903	–	C–O and C–C stretching vibration in carbohydrates
–	844	844	852	844	830	CH_2 deformation vibration in bio-filler

PP polypropylene

effective mixing of the components and a proper compounding process (Essabir et al. 2013a; Nekhlaoui et al. 2014a). Figure 9 shows the scanning electron microscopy (SEM) micrograph of argan shell composites (20 wt.%) as an example. On the one hand, a good distribution and dispersion of particles on the matrix, at high and low magnification, respectively, which indicates a good affinity at the interface particles/polymer, which is confirmed by the absence of decohesion between particles and matrix was observed. On the other hand, there was no evidence of large agglomerates of particles on the studied fracture surfaces; this is a result of the compounding process which ensures the good dispersion of the used particles in the matrix.

The addition of bio-filler reinforcement to the polymer will enhance some properties of the composite and will result in high moisture sorption in the bio-filler-reinforced polymer. The moisture leads to voids in the filler matrix interface causing deterioration in mechanical properties and loss of dimensional stability.

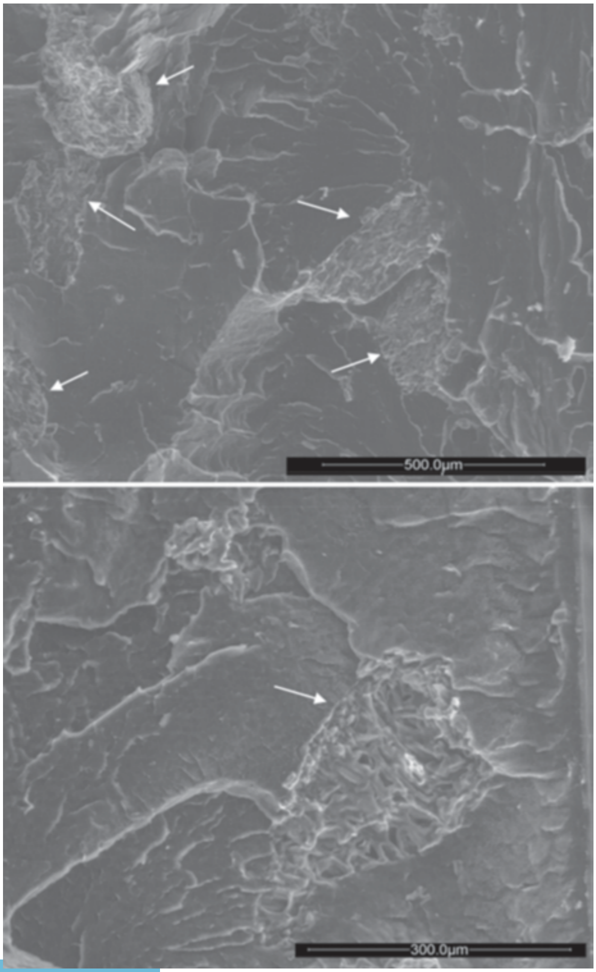


Fig. 9 Scanning electron microscopy (SEM) micrograph of argan shell-reinforced polypropylene (PP) matrix at low and high magnification

The specimens were subsequently immersed in distilled water at 23 °C for 1 month with a daily change of water. The weight of each specimen was determined at stated periods. Water absorption of each specimen was expressed as water weight absorbed, divided by the dry weight of the specimen.

Figure 10 shows the effect of bio-filler content and coupling agent on water absorption of various composites. It can be noted that the water uptake or the absorption of the composite increases with increasing bio-filler content. The hygroscopicity of bio-filler is highly correlated with the free hydroxyl (–OH) groups. Hemicelluloses had the highest capacity to absorb water, followed by cellulose and then lignin.

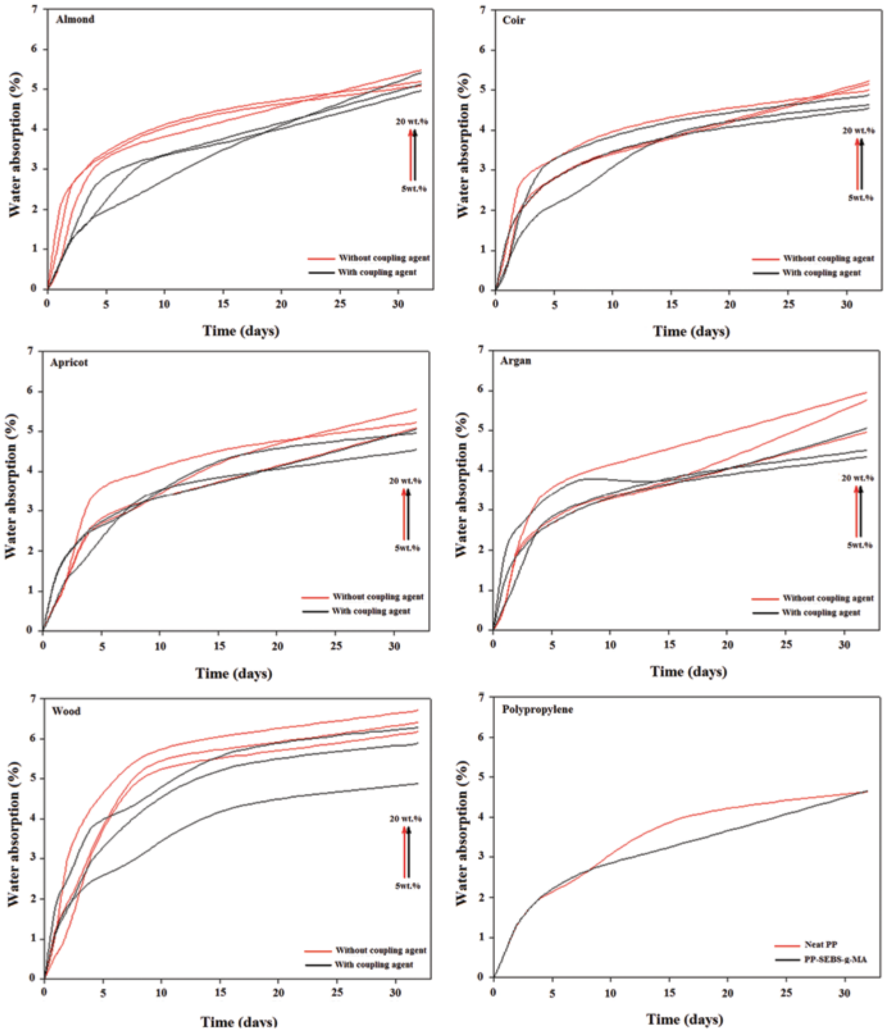


Fig. 10 Water absorption versus time for each composite with and without coupling agent comparing to neat polypropylene (PP)

On the other hand, after the use of coupling agent, the water absorption of the coupled composites was considerably reduced. This reduction is due to the better interfacial adhesion between the matrix and the bio-filler.

The temperature degradation of bio-filler limits the choice of the polymer matrix. During processing of polymer composites, bio-fillers are exposed to high temperature, frequently combined with trapped air, which could lead to degradation (Salleh et al. 2014; Holt et al. 2014). If degradation of bio-fillers occurs at the melt-processing temperature, the mechanical reinforcement effect of the bio-filler can be decreased, with the side effects of discoloration and unpleasant odor of the composites. Therefore, TGA was used to determine the high temperature degradation behavior of the composites.

Thermal Properties

The thermal analysis of binary and ternary composites was conducted to investigate the influence of bio-filler and coupling agent on the thermal properties of composites. Figure 11 shows that the use of bio-filler (e.g., apricot shells) decreases the thermal stability of the final composites material. These decreases are due to reactions and complex interactions between the fillers and the matrix, which cause scission of the polymer chain and thus affect the thermal stability. During the manufacturing process, the mixture is more viscous than the PP, which promotes friction between the polymer and filler.

Figure 11 illustrates the effect of adding a coupling agent on thermal stability when compared to a bio-filler/PP binary system (e.g., binary and ternary composite-reinforced coir and apricot shells). In Fig. 11, the results show a slight increase in thermal degradation temperature with the use of coupling agent; the formed ester bond in the ternary system leads to a good adhesion between bio-filler and the polymeric matrix which explains the thermal behavior of this system compared to the binary one (Arrakhiz et al. 2013a; Essabir 2013c).

A large number of transitions (melting, crystallization, glass transition temperature, etc.) are not accompanied by a change in mass. These transitions which are not detected by the TGA are determined by differential scanning calorimetry (DSC). DSC scanning was employed to evaluate the degree of crystallinity, the melting temperature (T_{m}), specific enthalpy of melting (ΔH_{m}), and temperature of crystallization (T_{c}; Gamon et al. 2013; Table 4).

DSC scanning was employed to evaluate the effect of bio-filler and coupling agent on the melting temperature (T_{m}), specific enthalpy of melting (ΔH_{m}), temperature of crystallization (T_{c}), and degree of crystallinity of the final composites (Table 4). The DSC results of binary and ternary system composites are presented in Table 4. The addition of bio-filler and coupling agent produced no notable change in the melting temperature of composites compared to neat PP (163.8 °C).

From Table 4, a decrease of the melting enthalpy (ΔH_{m}) with the use of filler from 5 to 20 wt.% and coupling agent, in comparison with the neat PP (89.4 J/g) was observed. This reduction indicates an increase in the thermal stability of polymer matrix (PP) with increasing bio-filler content. The fillers absorbed more heat energy

Fig. 11 Thermogravimetric analysis of composites reinforced by coir shell and apricot shell

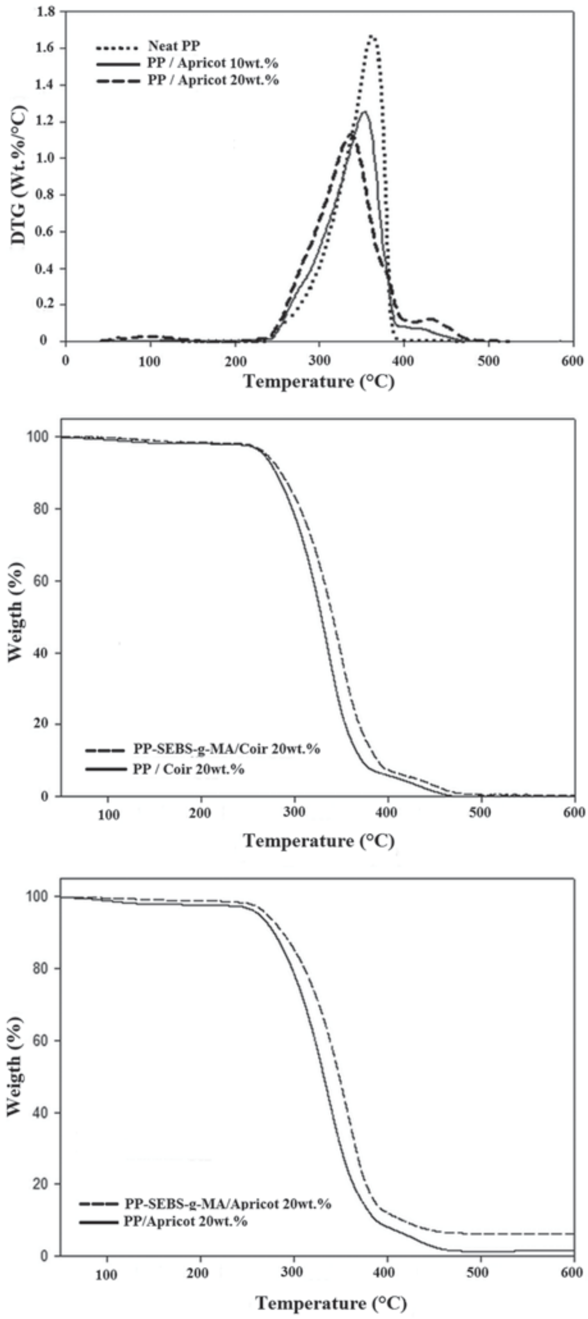


Table 4 Differential scanning calorimetry (DSC) results of composites reinforced by different fillers

Composites			T_m (°C)	ΔH_m (J/g)	T_c (°C)	X (%)
	Matrix	Filler (wt.%)				
Shells	Polypropylene		163.8	90.8	105.57	43.44
Almond	PP	5	162.27	90.43	118.11	45.54
		20	161.32	86.95	119.2	52.00
	PP-SEBS-g-MA	5	162.33	90.68	116.57	45.67
		20	160.53	84.35	117.04	50.44
Coir	PP	5	162.54	90.85	120.23	45.75
		20	162.25	85.98	120.59	51.42
	PP-SEBS-g-MA	5	161	90.73	118.02	45.69
		20	160.54	83.16	119.15	49.73
Argan	PP	5	161.37	90.8	116.95	45.73
		20	162.02	84.06	117.9	50.27
	PP-SEBS-g-MA	5	161.56	88.35	116.82	44.49
		20	161	82.18	117.6	49.15
Apricot	PP	5	161.58	90.63	118.52	45.64
		20	160.55	86.17	118.74	51.53
	PP-SEBS-g-MA	5	161.07	92.85	117.21	46.76
		20	160.19	83.76	117.81	50.09
Wood	PP	5	162.26	90.11	119.23	45.38
		20	161.72	87.87	120.57	52.55
	PP-SEBS-g-MA	5	161.62	85.34	118.22	42.98
		20	161.16	81.78	118.59	48.91

MA maleic anhydride, *PP* polypropylene, *SEBS* styrene–(ethylene–butene)–styrene

in the melting of the composites (Yao et al. 2013; Gamon et al. 2013). In the case of composites with coupling agent, it was observed that the melting enthalpy shows a lower value than those of binary composites that explained the high thermal stability of ternary composites (Ayrilmis and Kaymakci 2013). The formed ester bond in the ternary system leads to a good interfacial adhesion which explains the thermal behavior of this system compared to the binary one.

In general, the polymer molecular chains can crystallize by themselves through a self-nucleation effect or by introducing a nucleating agent (heterogeneous nucleation effect; Arrakhiz et al. 2013c; Parparita et al. 2014). A change of crystallization temperatures T_c of composites with the use of bio-filler and coupling agent can also be noted. The introduction of bio-fillers leads to an increase of crystallization temperature of all composite systems (binary and ternary). The increase in the T_c designates faster crystallization of polymer chains upon cooling; the presence of bio-fillers initiates the germination and spherolites growth. The bio-filler could act as a nucleating agent and thus increase the crystallization temperature of the resulted composites.

The degree of crystallinity (X_c, %) was determined from the melting enthalpy values using the following Eq. 1 (Yao et al. 2013):

$$X_c\% = \frac{\Delta Hm}{(1-\alpha)\Delta H_m^0}, \tag{1}$$

where ΔH_m is the melting enthalpy of the composites (J/g); ΔH_m^0 is the enthalpy value (theoretical enthalpy) of PP while being 100 % crystalline (209 J/g); $(1-\alpha)$ is the weight fraction of polymer in the PP composites.

On the other hand, the degree of crystallinity increased progressively from 0 to 20 wt.% bio-filler content compared to neat PP (43, 44 %), the highest values being registered for all binary composites at 20 wt.% (more than 50 %). This behavior may be due to the fact that the bio-filler introduced in the PP matrix can serve as a nucleation agent, resulting in an enhancement of the overall crystallization rate. On the other hand, all the filled ternary composites show a higher crystallization value compared to PP, but lower than filled binary composites. This may be due to the rubber coupling agent support (SEBS) to amorphous character. As conclusion, from all the DSC measurements, it can be concluded that fillers' addition has an influence on polymer matrix crystallization, which leads to a change in the final properties of material.

Mechanical Properties of Composites

The major advantage of using filler as a reinforcement agent into polymer matrix is the improvement of the physical properties of the manufactured materials in comparison with the neat polymer. However, there are several parameters affecting the mechanical properties of the manufactured material. A better dispersion and interfacial adhesion between the matrix and fillers are both critical factors for the resulting composites to achieve improved mechanical properties. A good dispersion/distribution of the fibers in the matrix can be achieved by effective compounding of the various components and by a suitable compounding process. SEM can be used to evaluate the degree of dispersion/distribution of bio-filler into PP matrix. Better dispersion of the bio-filler can be achieved by effective mixing of the components and a proper compounding process.

It is known that the coupling agent reacts as ester bond with the hydroxyl groups of bio-fillers surface; in this regard, the FT-IR of binary and ternary composites was used to check this bond (Fig. 12). The zoomed area shows the main characteristic peaks of the formed ester bonds (1642, 1599, and 1543 cm^{-1}) between the OH groups on the bio-filler' surface with the MA functions grafted to the PP chains (Arrakhiz et al. 2013a). For a composite without coupling agent, any improvement is achieved by physical anchoring between polymer chains and fibers.

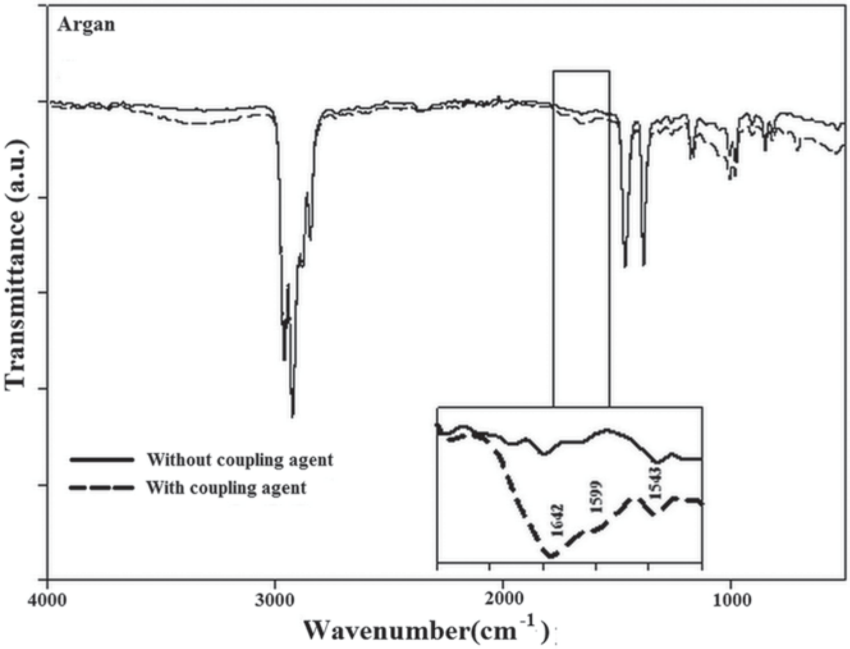


Fig. 12 Fourier transform infrared spectroscopy (FT-IR) spectrum of composites with and without coupling agent

The mechanical tests are essential steps in accessing the characteristic quantities of materials: Young's modulus to the elastic limit, Young's modulus to the toughness or fatigue strength, and that Young's modulus under varying conditions, e.g., temperature or strain rate and elongation at break. In the industry, materials are subjected to mechanical stress and must possess the qualities of resistance to these stresses. The tensile tests consist in subjecting a sample with rectangular section (according to ISO 527-1 (2012)) to a continuous deformation at constant speed and to record the constraint resultant. Figures 13 and 14 show the effect of bio-filler types, bio-filler content, and coupling agent on the tensile properties of the manufactured composites. The trend of tensile properties of the two-studied composites systems as a function of bio-filler content and coupling agent is presented in Figs. 13 and 14. As expected, the addition of bio-fillers enhances the stiffness of the manufactured materials. There is a sharp improvement in Young's modulus values by introducing bio-fillers in the polymer matrix; there are no significant differences between the effects of type of bio-filler. The noted Young's modulus of all filled composites is higher than the neat PP (1034 MPa) and reached a maximum at 20 wt.% of filler content. Thus, the highest Young's modulus was recorded when using argan shells as bio-filler; the obtained gain was 65 % at 20 wt.% argan filler. This value may be due to the higher rigidity of argan shells than other bio-fillers.

For other composites, the Young’s modulus at 20 wt.% is almost equal and gives a gain around 30 %. On the other hand, it was observed that the combination of the five bio-fillers with equal ratio as filler shows the same Young’s modulus trend; the maximum Young’s modulus is reached at 20 % wt.% filler content and the obtained gain is 50 %. According to Fig. 13, it was also observed that Young’s modulus of ternary composites shows a linear increase with the addition of bio-filler and also the argan shell composites shows a maximum value than other composites. Moreover, the binary Young’s modulus is higher than the ternary one; however, the use

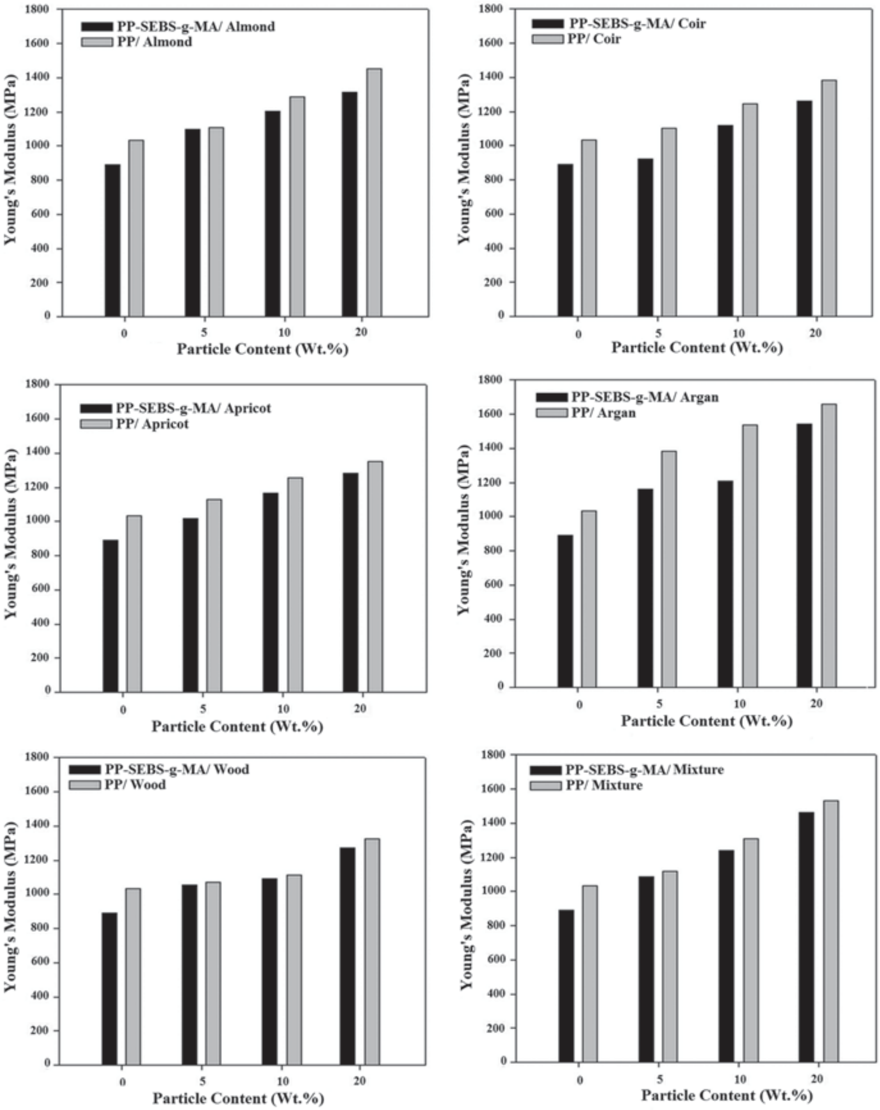


Fig. 13 Young’s modulus versus particle content of different composites

of rubber copolymer, as a support of MA, with lower elastic modulus (7.2 MPa) reduces Young's modulus of the resulted composites (Fig. 13; Essabir et al. 2013a, c).

Figure 14 displays the tensile strength of the two bio-filler composite systems, which show in general a decreasing trend. The increase in the bio-filler content from 0 to 20 wt.% resulted in a decrease in the tensile strength of all composite systems (except PP-SEBS-g-MA/wood composites) compared to neat PP. This reduction in tensile strength is due to the weak interfacial adhesion between bio-filler and matrix under stress, as the filler content increases and the interfacial area increases which generates a decohesion between the matrix and bio-filler. This decohesion and further stress concentration accelerate the sample break (Essabir et al. 2013b, c).

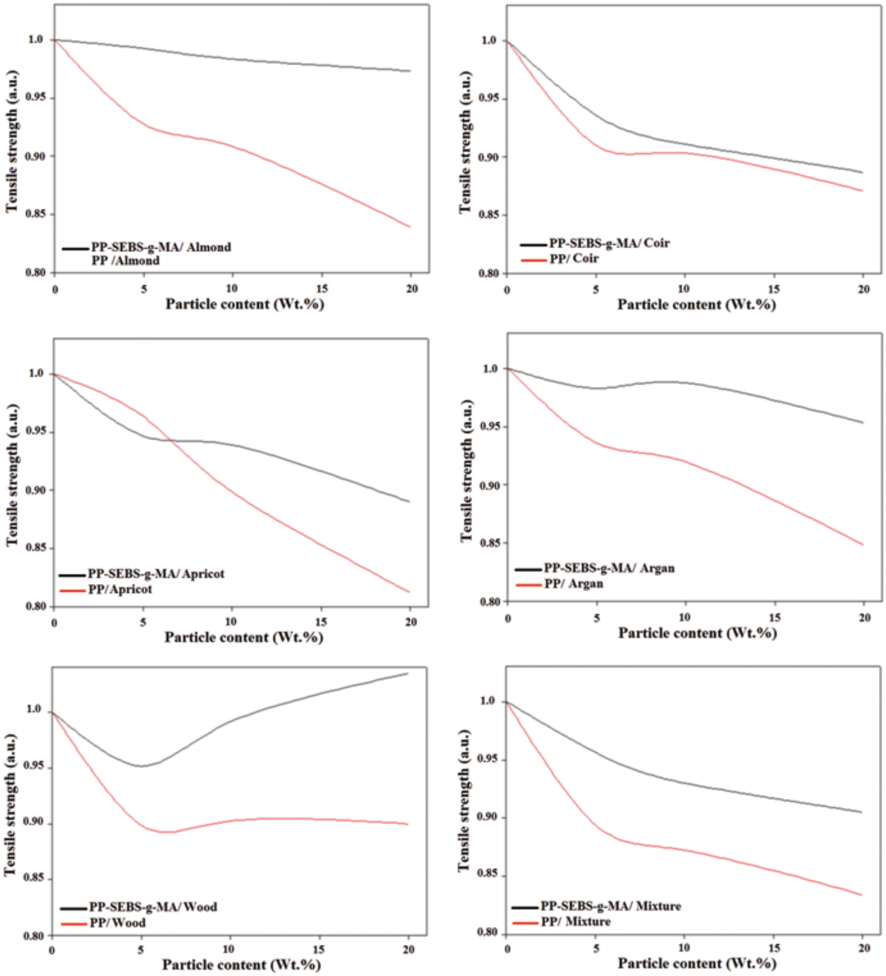


Fig. 14 Tensile strength versus particle content of different composites

Difference in behavior was found for PP/wood composites, which presented beyond 5 wt.% an increase in tensile properties compared to neat PP. An increase in tensile properties may evidence a good interfacial adhesion, which generates greater resistance to stress, and, in consequence, the tensile properties of composites show higher values. A degree of affinity between wood filler and the matrix is higher compared to the other bio-filler used in this work. Addition of coupling agent enhances the interfacial adhesion; the MA molecules grafted to PP make a strong ester bond with the hydroxyl groups present on the filler surface, which leads to a higher tensile strength in ternary composites compared to the binary one. The tensile properties of some composites are higher than those of other composites; this can be associated with the chemical composition and physical properties of each bio-filler system.

As conclusion, the difference in the tensile properties of the composites may be due to the difference in the bio-filler structure/composition. Based on the mechanical properties results, it is possible to mention that, by a combination of the five bio-fillers with equal ratio as filler, the obtained composites (equivalent composite) show a similar tensile strength than the other composites manufactured.

The mechanical characterization of the material, when considered isotropic, requires the identification of at least two independent parameters: Young's modulus and modulus of coulomb. The latter characterizes the shear strength in which the torsion forms a part. The torsion test consists in subjecting a test piece to measure the angular deflection and the torque generated. This test specimen has a rectangular cross section and, for the various measured quantities, a correction factor was used to adjust the fundamental based on samples of circular section. The machine used for this test is the rheometer ARES-LS which ensures the rheology in both the solid state and the molten state. The dynamic mechanical analysis is a characterization technique which consists of subjecting a material to a dynamic stress of low amplitude and measuring its response. The dynamic stress replaces the static stress often used in tests of simple traction.

The elastic and viscoelastic deformation of the components can then be recorded in function of the frequency at a fixed temperature or vice versa. Typically, data are available for the storage modulus (E', G') and loss modulus (E'', G'') and the ratio of these two parameters, namely the loss factor of damping factor (tan δ). This parameter, also called the coefficient of internal friction, is the fraction of energy dissipated in viscous form:

$$\tan\delta = \frac{G''}{G'}. \tag{2}$$

The complex modulus (G^*) of torsion represents the elastic and the viscous parts of the material according to Eq. 3:

$$G^* = \sqrt{G'^2 + G''^2}, \tag{3}$$

where G' and G'' are, respectively, the storage modulus and loss modulus measured by the rheometer.

A strain sweep test was performed on the neat PP compared to the two filled composite systems in order to establish the linear viscoelastic regime and to characterize the strain-dependent viscoelastic properties of the samples. Dynamic frequency tests were then performed using 0.002 strain amplitude.

Figure 15 shows the effects of the bio-filler content and coupling agent on the tensional properties of the various composite systems. It is illustrated that the composites showed an increased torsional modulus (G^*) values, with bio-filler loading,

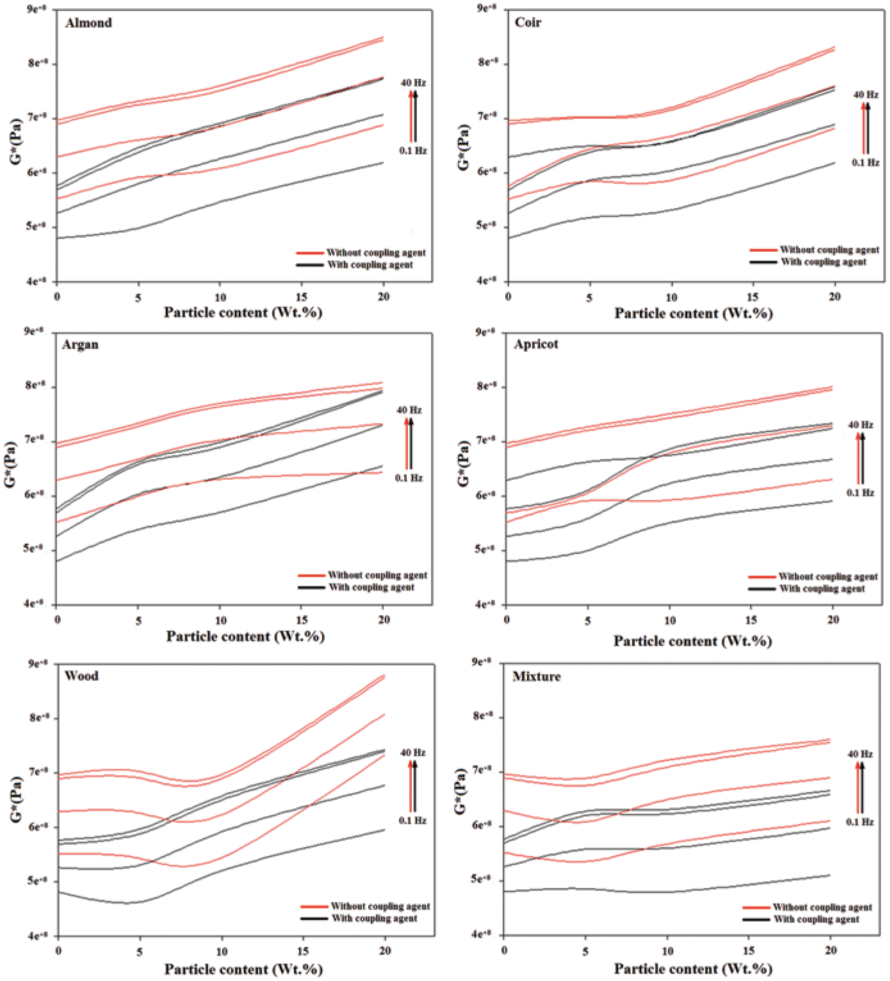


Fig. 15 Complex modulus versus particle content of different composites

related to PP matrix, which may prove the formation of a more rigid material structure. It is evident that all composites show a linear increase excepting the PP/wood composites, which show a modest decrease with increasing filler content until a threshold is reached at 10 wt.% filler content, after which the torsional modulus evolution becomes very significant. At higher bio-filler content, the wettability of the filler into polymer matrix decreases, which promotes filler–filler interaction, leading to increased shear stress modulus.

Moreover, the frequency has also played a role in the composite response, and it is clear from Fig. 15 that the G^* increases with increasing frequency. This can be explained by the normal solid-like behavior of composite materials. The composite material behavior will be more like a solid at higher frequencies at which the molecular polymer chains do not have enough time to attain permanent deformation (Essabir et al. 2013a).

The effect of coupling agent is more marked for the torsional modulus. This property decreases after the use of coupling agent, showing composites with lower torsional modulus compared to binary composites. This reduction may be explained by the rubber character of the used coupling agent. The shear stress from the torsional torque is applied at the filler/matrix interface, which has a rubbery character, leading to lower torsional modulus compared to binary systems.

The loss factor, tan δ, which represents the relationship between the loss modulus and storage modulus, is given by Eq. 2. It is illustrated that the torsional modulus is not affected by the introduction bio-filler. On the other hand, it can be easily observed from Fig. 16 that the ratio of the loss modulus and the storage modulus decreases slightly from 0.1 to 40 Hz when bio-filler is added. This is the common situation in solid state as the elastic character of the material at room temperature prevails over a viscous behavior. In the case of ternary composites, it was illustrated that tan δ is less high compared to the binary composites and the use of SEBS-g-MA with a rubber character increases the viscous behavior of the material composites.

Melt Rheological

Rheology is the science that studies the behavior or response of materials (solid, liquid, and gas) as a result of the stresses and deformations that apply to them. It consists of determining the rheological properties of the material such as viscosity and the elastic and viscous moduli, which are a function of the deformation and the stress applied to the material. However, this science is closely related to the study of plastics. Many studies describe the rheological analysis as a potentially valuable technique for evaluating the microstructure and the dispersion of fillers in the polymer matrix. However, an increase in the complex low-shear viscosity is connected with the good dispersion of fillers in the matrix.

The principle of the rheometer is to subject the sample to a deformation (shear), linear or sinusoidal, at a given frequency and record the normal force and the

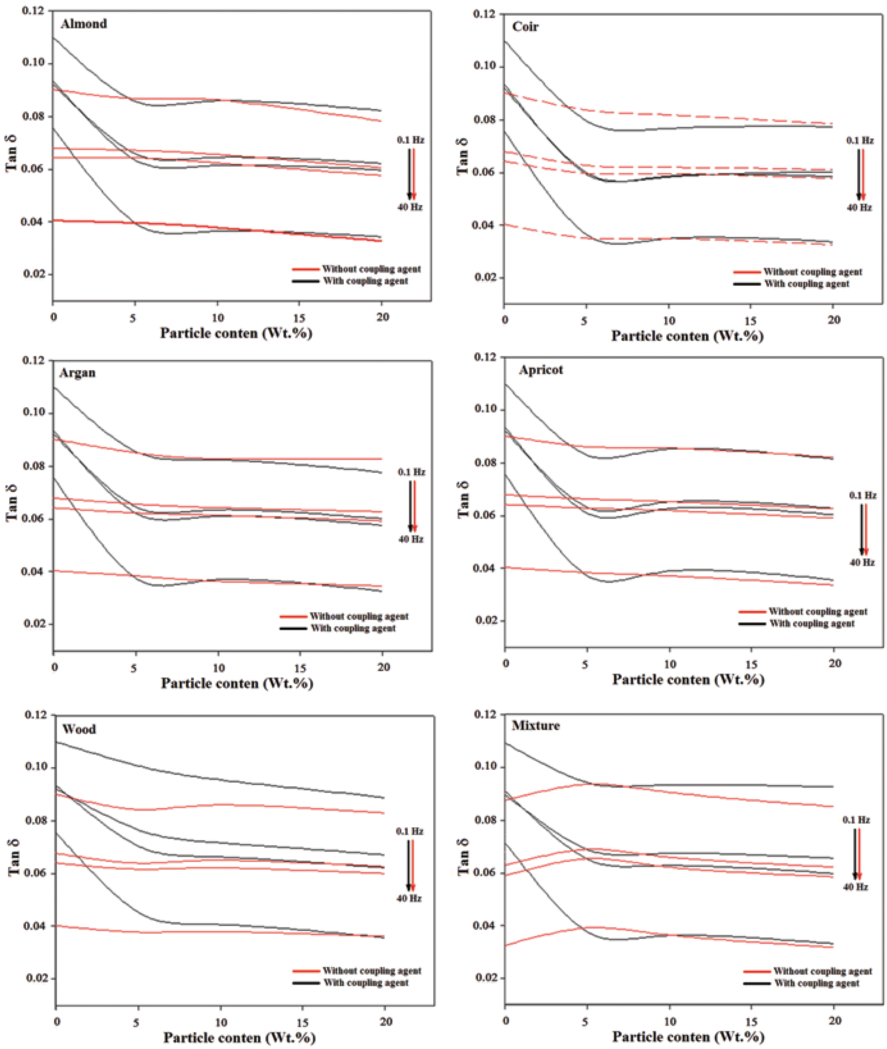


Fig. 16 Loss factor versus particle content of different composites

corresponding torque. Oscillatory melt rheology tests have been realized on an MCR 500 (physica) rheometer equipped with CTD600 device. The measurements were carried out at 200 °C under small amplitude oscillatory shear mode using parallel plate–plate geometry (25 mm diameter). The 2-mm-thick sample disks were used for all tests. Frequency sweeps ranging from 500 to 0.5 Hz were applied at a strain of 5 %, for which the materials exhibit a linear viscoelastic behavior as verified by previous strain sweeps.

In general, rheological properties can reproduce the internal structure and processability of polymeric composites. They present information about the dispersion state of filler into the matrix, percolated network structure, and the interaction between components. Figures 17 and 18 show the effect of bio-filler content, frequency, and coupling agent in the dynamic properties of the manufactured composites. It is evident from Figs. 17 and 18 that both dynamic storage modulus *G*′ and dynamic loss modulus *G*″ increase with an increase in frequency; these results are in accordance with the torsion results. It was also observed (Figs. 17, 18, and 19) for both systems (binary and ternary) that at high-frequency region, *G*′ values are higher than those of *G*″ which indicates a solid-like response in molten state. This behavior is due to insufficient time at higher frequencies to allow polymer chains to relax,

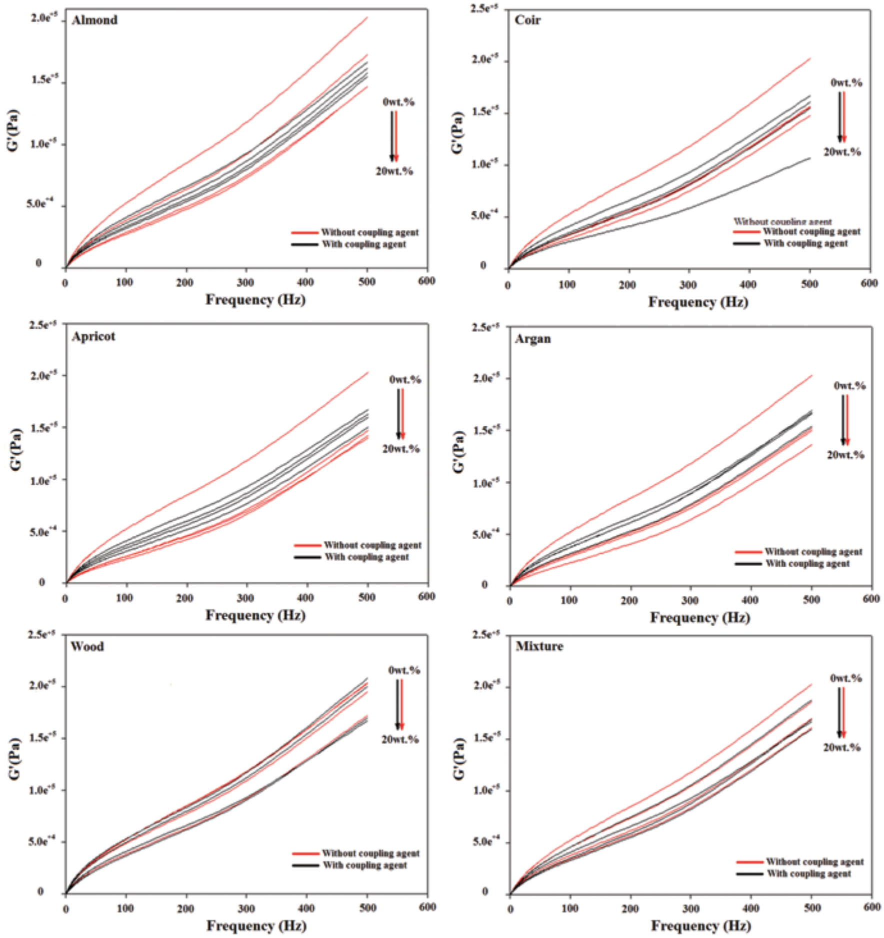


Fig. 17 Storage modulus versus particle content of different composites

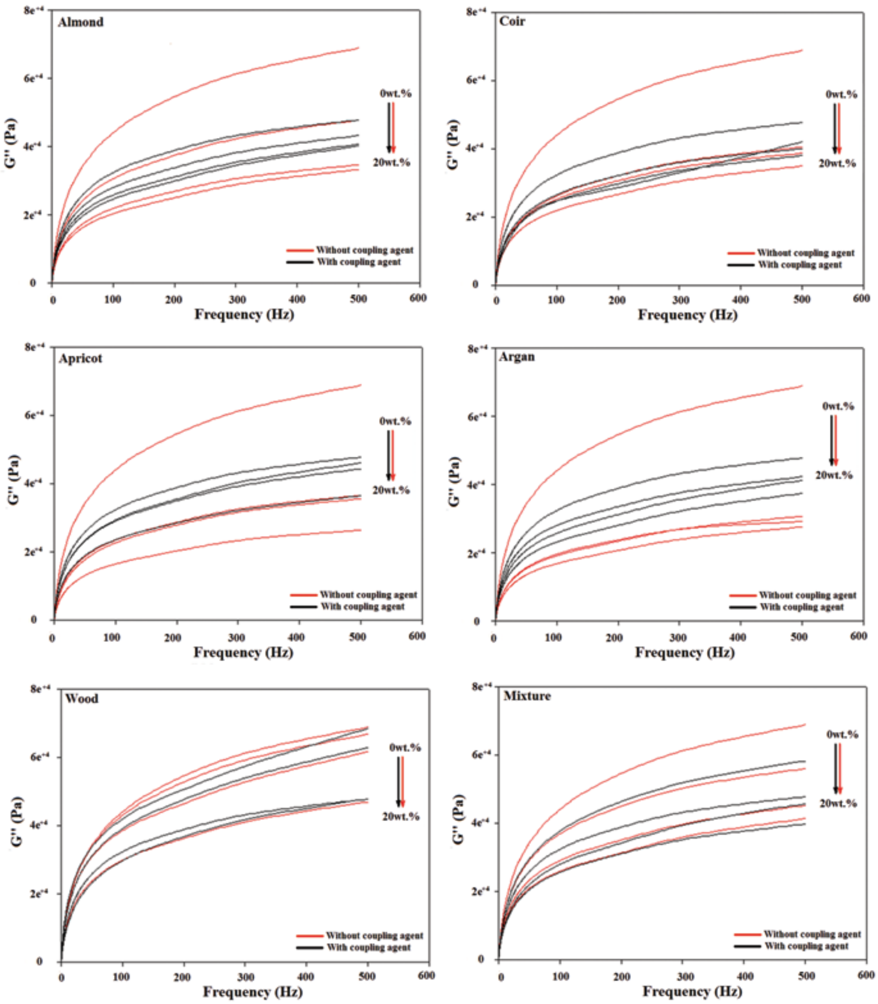


Fig. 18 Loss modulus versus particle content of different composites

which contributed to an increase in the elastic nature of the polymer melt (Spiridon et al. 2012). On the other hand, it can be clearly seen that the incorporation of bio-filler decreases the dynamic properties of composites and the degree of interactions between the components affects the final dynamic properties of composites. The reduction of *G*'' and *G*″ in binary composites is even more than in ternary one, and the use of coupling agent enhances the interfacial adhesion between bio-filler and matrix, which affects the dynamic properties of the resulted material (Essabir et al. 2013c); this result is in accordance with tensile properties which explain a decrease of interfacial adhesion with the use of bio-filler.

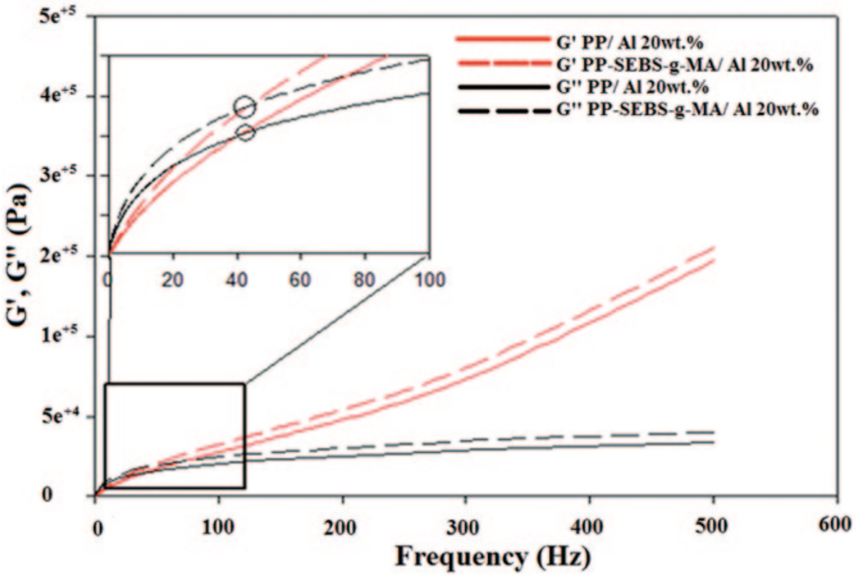


Fig. 19 Illustration of cross point (loss modulus–storage modulus)

Figure 20 illustrates the crossover point of *G′* and *G″*, which indicates a transition from elastic to viscous behavior. The composites at crossing points (crossover frequency) show the same viscous behavior as elastic. It was observed that with the use of bio-filler, the crossover frequency decreases to take place at lower frequency (binary and ternary composites). The reduction of the crossover point designates an increase of the relaxation time of the polymer that can be explained by good interaction with the bio-filler (Tazi et al. 2014). Beyond the crossover point ($G'=G''$), *G″* becomes smaller than *G′* and shows a plateau-like nonterminal behavior which implies elastic characteristic of the melt. On the other hand, for ternary composites, a shift of the crossover frequency to higher frequency compared to binary composites, indicating a decreased rate of transfer from solid-like behavior to liquid-like behavior at high frequency was shown. The use of SEBS-g-MA with a rubber character increases the viscous behavior of the material composites.

The melt rheological response during frequency sweep (complex viscosity) for binary and ternary composites is shown in Fig. 21. It is well established that the addition of bio-filler into the polymer matrix decreases the viscosity of the melt. The incorporation of bio-filler into polymer matrix generates a stress concentration zone, which leads to existence of a yield stress. Yield stress illustrates the degree of interaction of bio-filler with adjacent bio-filler which is in relation with the bio-filler size (Parparita et al. 2014). Generally, the decrease in the viscosity depends on the bio-filler content, concentration, particle distribution, and the size of bio-filler (Parparita et al. 2014). Moreover, it was observed that the melt viscos-

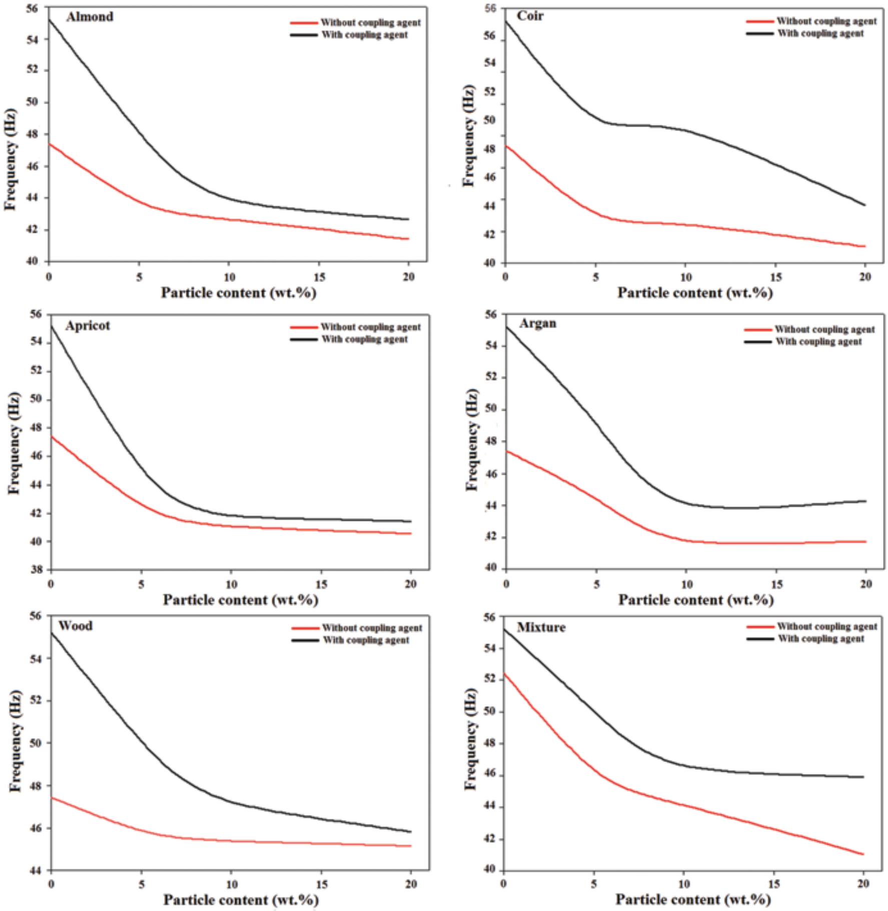


Fig. 20 Cross point (loss modulus–storage modulus) versus particle content of different composites

ity of both composite systems decreases with increasing frequency, indicating the existence of a yield stress. On addition of a coupling agent, the ternary composites' viscosity was still higher than that of binary composites in all bio-filler loading. The observed increase in melt viscosity is presumably due to the combined effect of compatibilizer, with its rubber character and changes in the rheological behavior of the interface. The decrease of viscosity of composites versus bio-filler content and frequency, makes the processing and blending of composites, at higher bio-filler content, easier.

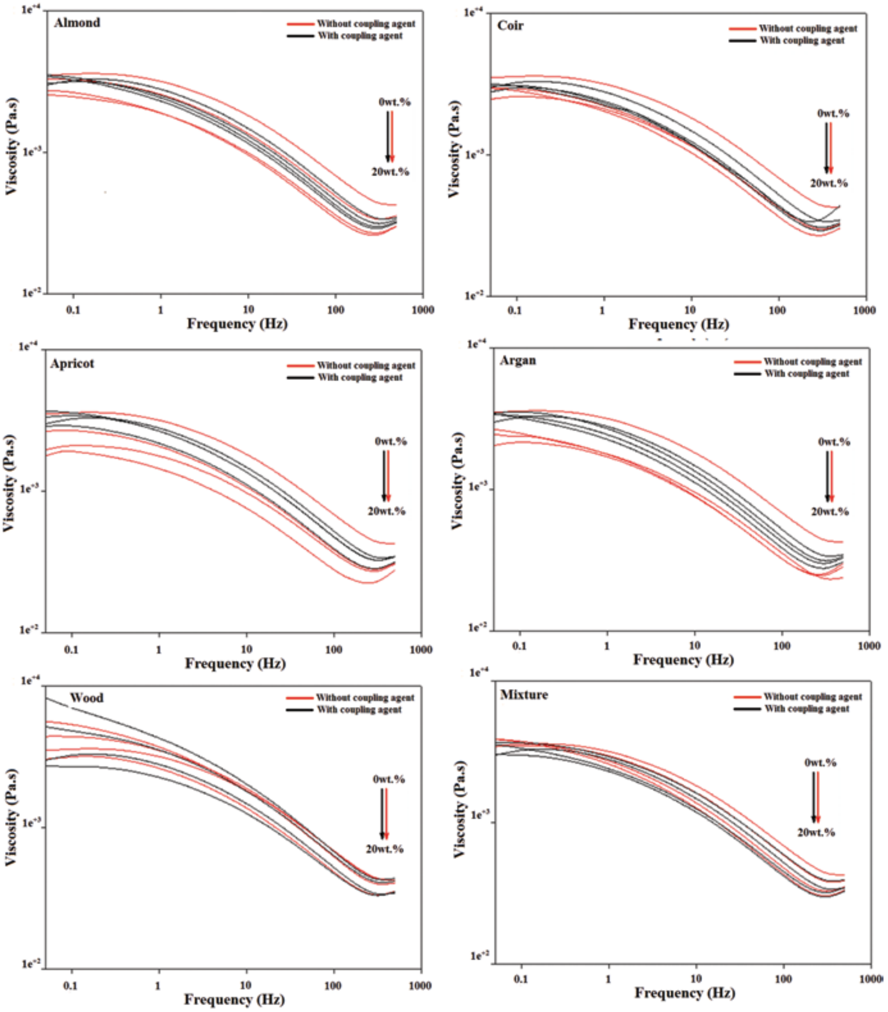


Fig. 21 Viscosity versus frequency of different composites

Conclusion

The incorporation of natural (lignocellulosic) resources as fillers in the polymer matrix represents promising news and ecofriendly products, with high performance and low cost for such industrial application. In order to enhance the use of these materials in more advanced applications, many projects are funded to develop their new uses. The almond shells, coir shells, argan shells, apricot shells, wood powder, and their mixture have been effectively demonstrated to reinforce the polymer composite. The high mechanical properties of the used bio-filler (Young's modulus and tensile strength) provide an increase in the mechanical properties of the final composite. However, many other parameters such as chemical surface modification, filler content, dispersion/distribution of filler into polymer matrix, temperature processing, and the added compatibilizer also influence the mechanical properties and other characteristics of the composites (crystallinity, thermal stability, viscoelastic behavior, etc.). The implementation of a composite material with the greatest properties thus requires the control of all these parameters.

Future Perspective

- Higher bio-filler content, more than 20 wt.%, could perhaps be used in the future.
- Thermoset and rubber matrix could be suggested in future works, with new processing method.
- Overcome the incompatibility between bio-fillers and matrix by the use of other chemical methods such surface treatment or functionalization.
- Prediction of the experimental results by the theoretical models, taking into account the interface as a third phase.
- Supporting the used experiments by a useful application.

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Algae-Derived Biomass for Sustainable and Renewable Biofuel Production

Ibrahim Birma Bwatanglang, Mohammad Faruq, Arvind Kumar Gupta and Nor Azah Yusof

Abstract The rapid increase in demand for energy efficiency and sustainability in recent years, the ecofriendly and renewable sources of energy have taken the center stage by replacing the fossil-based energy resources as they associated with serious environmental and health-related issues. These negative factors ignite to rethink and global shift towards a more carbon-neutral source of energy that is biodegradable, sustainable, and ecofriendly. Agro-based materials from crops and post-harvest residues are currently being explored to meet these challenges as primary feedstock for the production of ethanol, agrochemicals, and biodiesel. However, the cultivation of oilseed crops and other cash crops essentially for biodiesel production will avertedly water down on food supply and security and thus we report in this chapter an ideal alternative source of energy derived from microalgae that hold great promise for the future. Cultivation of microalgae will not compete with food productions and fodder demands, can be cultivated anywhere, will not compete with arable land, has simple growth cycle that can produce lipids all year-round under short period of time requiring less water, and has metabolic pathways that establish atmospheric carbon-neutral effect and balance. With this, the aim of the current chapter is to discuss the potentials of microalgae as third-generation energy source, focusing basically on simple taxonomy, lipid biosynthesis, and various cultivation methods. We also reviewed some simple principles used for the optimization of lipid content in microalgae under various lipid-induction techniques and a brief look into the biosequestration characteristics of microalgae. Furthermore, various methods involved in harvesting and extraction of lipid from microalgae and the chemistry for

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the conversion of lipid extracted from microalgae into biodiesel following simple transesterification process are equally touched at the surface in this chapter. Based on the aforementioned, this chapter comes to conclusion elucidating algae lipid metabolism and production as key fundamentals to consider towards achieving the most desired global energy demand that is sustainable and ecofriendly.

Keywords Biomass · Biofuels · Algae · Oil extraction · Transesterification

Introduction

Ecofriendly and sustainable energy resources have become a global clarion call due to the world's increasing dependency on fossil fuel as the major sources of energy. This clarion call is champion to minimize the environment-related consequences associated with greenhouse gas emissions and other obvious socioeconomic implications (Aguilera et al. 2009). With the increasing attendant consequences observed, the emphasis is currently shifted to explore alternative energy sources that are ecofriendly, renewable, and indeed sustainable to satisfy the raising global energy demands projected to increase oil supply to about 75 mb/day by 2030 (Aleklett et al. 2010). In response to this call, researchers globally are expending resources towards the development of sustainable and renewable sources of energy by expanding the role of agro-based biomass with uncompromising determinations to put an end to the continuous use of fossil-based resources such as coal, gas, and petroleum-derived products; nuclear fusion; etc. (Aguilera et al. 2009; Brown and Brown 2014):

- Undisputed projections postulated that global demand for fossil fuels, especially petroleum and its derivatives, will be skyrocketed in the coming years (Doman 2013; Sieminski 2013; Tariyal et al. 2013). A situation therefore arises in which a choice should be made between renewable and sustainable forms of energy and the undesirable continued burning of fossil fuels at the price of environmental and health consequences.
- Fossils fuels are carbonaceous organic substances obtained from the anaerobic decomposition of plants and animal remains following a series of biotransformations over geological period of years (Agrawal and Gopal 2014; Bolin et al. 1986). These sources of energy are not sustainable and their associated derivatives carry along long-term environmental and health-related consequences, such as greenhouse gas emissions which add to ozone depletion, causes acid rain, and water and air pollutions (Dincer 2000). The associated products obtained from petro-based resources such as plastic and chemicals are not biodegradable and emit toxic fumes when incinerated (Aguilera et al. 2009). These negative factors associated with the use and application of fossil-based products ignite a rethink and global shift towards biodegradable and ecofriendly sources of energy, especially from bio-based resources that are capable of meeting global energy demands and at the same time providing feedstock for other biochemicals and biomaterials.

Biomass

Biomass are classified essentially as the materials derived from forest woods, crops, manures, aquatic plants, microorganism, and other agro-based residues with great potential that can be converted into energy sources either through direct combustion processes to generate heat or could be used to extract biofuels and other agro-based chemicals (Perlack et al. 2005). Biomass can be simply defined as carbon-based materials with stored energy composed of organic molecules and other metals in complex mix such as magnesium in chlorophyll (Perlack et al. 2005). Table 1 summarizes various agro-based resources.

The energy stored in biomass is derived through a simple process of photosynthesis; the plants utilize the light energy from sun to convert the carbon dioxide and water into sugar and oxygen (Alcaine 2010). The biomass from plant and agro-based products are of low-carbon or carbon-neutral forms, the nutrient and energy generated during photosynthesis are released into the atmosphere during combustion/burning processes and subsequently absorbed back during the next crop's growth cycle, producing a reactive cycle of absorption–release–absorption activities, thus establishing a perfect atmospheric carbon-neutral state contrary to what is observed when fossil fuels are burned (Pyörälä et al. 2014; (Schenk et al. 2008; Searchinger et al. 2009; Tilman et al. 2006). Figure 1 summarizes the simple classification of various products derived from agro-based biomass resources.

Biomass are diverse in nature while possessing different compositions in terms of calorific value, moisture content, ash content, etc., and can be converted to end-user products (such as biodiesel, methanol, ethanol, biopolymers, etc.) when

Table 1 Types of agro-based resources. (Perlack et al. 2005)

Forest resources	Agriculture resources
Primary	*Primary*
Residues from logging and conventional harvest	Crops and grains—corn, sugarcane, soybeans, oilseeds, etc.
Residues derived from forest land clearing operations	From stover, small-grain straw, and others
	From sugar beets, sugarcane, etc.
	Perennial grasses
	Perennial woody crops
Secondary	*Secondary*
Residues from primary wood-processing mill	Animal manures
Residues from secondary wood-processing mill	Food/feed processing residues
Pulping liquors (black liquor)	
Tertiary	*Tertiary*
Residues derived from urban wood processing activities and construction	Municipal solid waste and post-consumer residues and landfill gases
Residues from demolition debris, tree trimmings, packaging	
Materials from wastes and consumer durables	

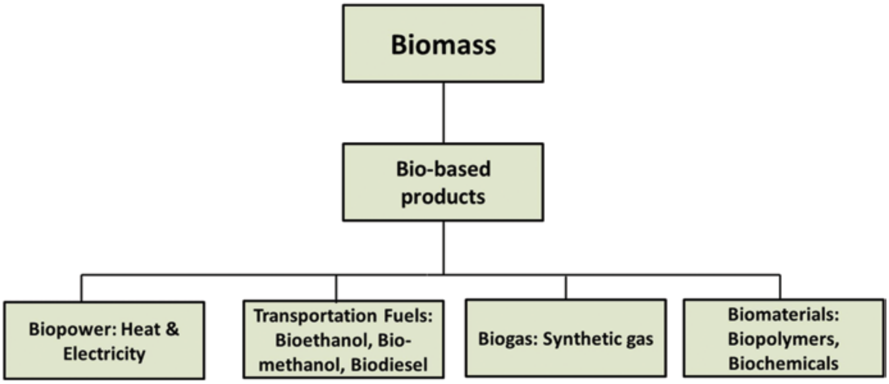


Fig.1 Classification of products that can be generated from biomass resources

subjected to different processing techniques such as combustion, fermentation, hydrolysis, pyrolysis, or gasification (Brown and Brown 2014; Clark and Deswarte 2008; Stephens et al. 2010).

Major Differences Between Biomass and Fossil Fuels

a. Biomass materials derived from forest woods, crops and aquatic plants are renewable through re-cultivation. However, fossils are formed from the decomposition of plants and animal remains buried under the earth's crust following millions of years due to geological transformations and are nonrenewable.
b. When burned, the stored energy in biomass releases CO_2 which is subsequently reabsorbed by the plants in their growing state resulting in atmospheric carbon-neutral effects and maintains the balance level of atmospheric CO_2 at a very short time frame. However, on the contrary, the energy in fossil fuels that was stored over millions of geologic years burns out carbon into the environment and increases the carbon concentration in the atmosphere without being reabsorbed.
c. Biomass is highly dispersed across the world and can be cultivated virtually everywhere, while fossil fuels are largely localized and found deep below the earth's crust or sea level.

Agro-Based Biomass Resources

Driven by the appetite for achieving a sustainable and renewable energy balance, agro-based materials from grains, sugarcane, oilseeds, and post-harvest residues are presently the primary feedstock deployed and are used in the production of ethanol, agrochemicals, and biofuels/biodiesel (Da Costa et al. 2010; Perlack et al. 2005; Pyörälä et al. 2014). Virtually all forms of agro-based biomass can be utilized sustainably and for this purpose, the crops are classified into edible crops, nonedible crops, and shrubs or grasses (Perlack et al. 2005).

The edible crops such as corn, soybeans, sugarcane, sugar beets, and vegetable oilseeds are consumed as food and are competing as feedstock for the production of biofuels, methanol, and other agro-based derivatives. However, the chaffs, straws, nutshells, perennial grass, and shrubs are nonedible feedstock and are best suited for biofuel production (Da Costa et al. 2010; Perlack et al. 2005). This alternative source of energy derived from agricultural resources remains very promising in meeting the world's quest for renewable and sustainable energy requirement, but with a lot of hurdles to be crossed as summarized below:

a. Most of the crops essentially used as biomass-based fuels, especially the wood-based plants, are not perennial in nature and can take years to achieve production age and availability (Perlack et al. 2005).
b. Agro-based residues are very essential in natural replenishing cycle of soil, and the continuous removal of crop residues will affect soil fertility, expose the soil to erosion, and poise a raising risk for food security. This may put pressure on global socioeconomic stability, especially to the less economically endowed regions of the world (Perlack et al. 2005; Teweldemedhin and Mwewa 2014).
c. Extracting biodiesel from oilseeds would create a shortfall for vegetable oil demands essentially needed for human consumption (Tariyal et al. 2013).

With much desired efforts put in place to diversify sources of energy, especially biomass as against fossil-based energy, the agro-based biomass stands out as best option for a lifetime and contextually provides a source of energy that is renewable and ecofriendly. This chapter is designed to carefully explore agro-based biomass potentials; the caviar highlighted above drown on the fact that cultivation of oilseed crops and other cash crops essentially for biodiesel production will avertedly water down on food supply and security. The overall implications, however, are to explore agro-based biomass for biodiesel production that best meets one or all of the following requirements:

a. Will not compete with food production and fodder demands
b. Can be cultivated anywhere with all year-round output and less water demand
c. Establish atmospheric carbon balance

This chapter therefore identifies an aquatic plant called algae that falls and virtually satisfies these conditions essentially for biodiesel production. Before digging into biodiesel production from algae, let us quickly take an overview on the taxonomy of algae briefly.

Algae-Based Biomass

In a milder definition, algae are photosynthetic nonflowering plants or organism that contain chlorophyll but with no definitive roots, stems, leaves, and vascular tissues (Campbell 2008; Dismukes et al. 2008; Munir et al. 2013; Schenk et al. 2008).

Algae can be classified into prokaryotic microalgae (no definitive nucleus) such as chloroxybacteria (cyanobacteria) and eukaryotic microalgae (has both nucleus and organelles) such as the green algae (Chlorophyta), Rhodophyta (red algae), and the diatoms (Bacillariophyta) (Brennan and Owende 2010; Falkowski and Raven 2007). Figure 2 briefly explains the prokaryotic and eukaryotic cells.

Most algae are photosynthetic and exhibit autotrophic energy pathways by converting organic molecules from inorganic raw materials using the basic energy source from sunlight, utilizing the sunlight and absorbed CO_2 with the aid of green pigment (chloroplast) to produce cellular energy. Furthermore, the other forms of algae are nonphotosynthetic and prey on food generated by other organisms such as the fats, carbohydrates, and proteins through heterotrophic energy pathways, while some exhibit both the energy pathways (Bilanovic et al. 2009; Brennan and Owende 2010; Chiu et al. 2009; Falkowski and Raven 2007; Khan et al. 2009).

The most important and widely available forms of algae essential for biodiesel production are the diatoms (Bacillariophyta); green algae (Chlorophyta); blue-green algae (Cyanophyceae); golden-brown algae (Chrysophyceae); and others like the red algae (Rhodophyta), Dionophyceae, Haptophycease, etc. They are categorized largely based on their simple basic characteristics such as pigmentation, life cycle, and biochemical compositions (Lobban and Wynne 1981; Round 1984). We shall discuss only few species in this chapter:

- Red algae (Rhodophyta) are mostly multicellular eukaryotic forms of algae having flagella or centrioles, living in marine habitant, and reproducing sexually. They have the ability to use CO_2 and HCO_3 through photosynthesis and equally use floridean starch (granular carbohydrates) as food source. Their structure consists of an inner wall made of cellulose and pool of jelly-like deposit (agar) housed in the outer layer or wall (Lobban and Wynne 1981; Round 1984). Figure 3 shows different images of some red algae.

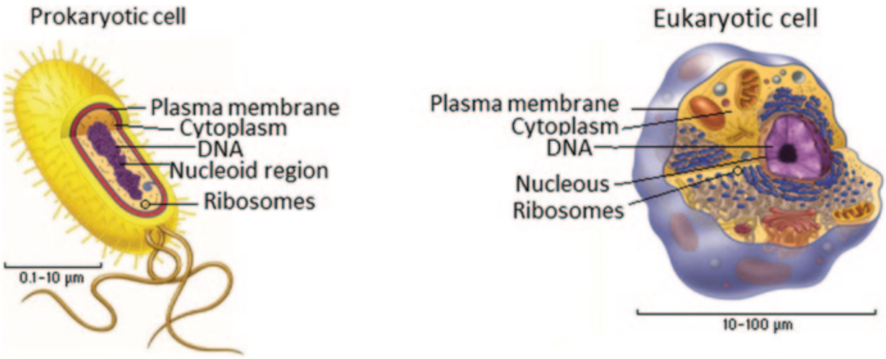
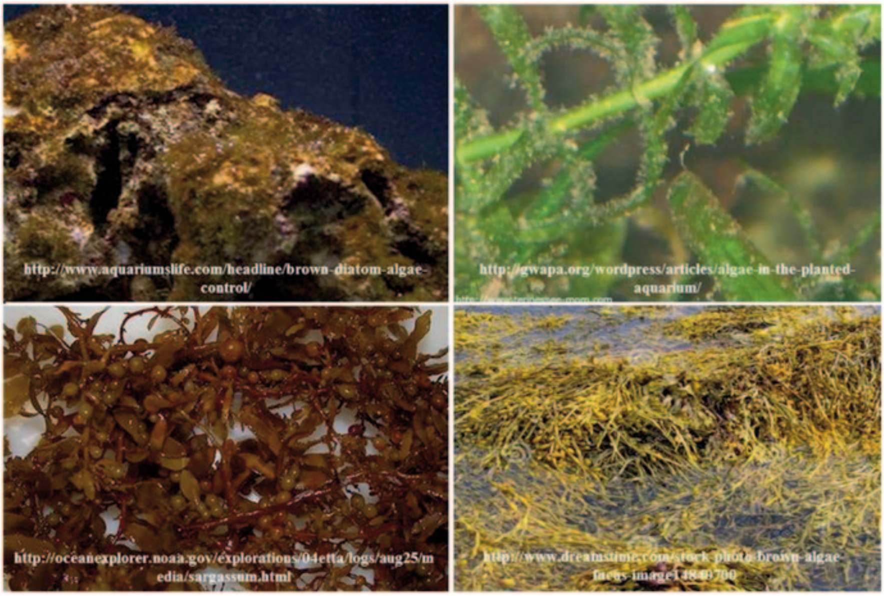


Fig. 2 Prokaryotic and eukaryotic cells

- Brown/diatom algae are eukaryotic organisms containing fucoxanthin pigment which provides the characteristic greenish-brown coloration and also has a developed but uniquely differentiated tissue—a soft organo-shell containing silicon and oxygen elements and water molecules called frustules that give it a unique identification to other 100,000 species of diatoms. They store energy in complex polysaccharides, sugar forms, and as triacylglycerols (TAG) (Lobban and Wynne 1981; Round 1984). Diatom species with its uni-micro size between 2 and 200 µm in diameter are found in large number in the ocean among the phytoplankton and live in brackish and freshwater habitat (Guiry 2012; Round 1984). Other well-known species of diatom are the *Chlorella* sp, *Thalassiosira-baltica, Tabellaria,Amphipleura,* and *Coscinodiscus* among others (Guiry 2012; Round 1984). Figure 4 shows images of some brown/diatom algae.
- Green algae (Chlorophyta) are a classical progeny of plants, highly diverse with about 7000 species in nature and could survive in virtually all habitats. Like normal plants, they trap energy from sunlight to manufacture sugars and leave primarily in aquatic environment. They reproduce through open mitosis without

Fig. 3 Images of red algae in different forms



http://www.aquariumslife.com/headline/brown-diatom-algae-control/

http://gwapa.org/wordpress/articles/algae-in-the-planted-aquarium/

http://oceanexplorer.noaa.gov/explorations/04etta/logs/aug25/media/sargassum.html

http://www.dreamstime.com/stock-photo-brown-algae-fucus-image14840700

Fig. 4 Images of brown/diatom algae in different forms

centrioles and each cell can develop rapidly forming cell colony and are mostly flagellated and motile, others are immobile but do have flagellated stage during their life cycle. Common members of green algae species are the *Chlorella vulgaris* and *Chlorella protothecoides, Scenedesmus obliquus, Haematococcus pluvialis, Dunaliella salina,* and *Tetraselmis* among others (Burrows 1991; Guiry 2012; Palmer et al. 2004). Figure 5 shows images of some green algae.

Potentials of Algae-Based Biomass in Biodiesel Production

Algae-based biomass is one source of energy with a cutting age prospect that answers virtually all aspects of ecofriendly and suitable energy lately; the lipid content or oil stored in large quantity as TAG in algae can be distilled out to produce a number of products, ranging from vegetable oils to carbon-neutral biofuel products when transesterified (Chen and Wu 2011; Schenk et al. 2008; Sharma et al. 2012; Sialve et al. 2009; Stephens et al. 2010). Essentially, what it means is that the carbon emitted during burning of algae-based biomass is reabsorbed as food, producing a net carbon-effect cycle. The energy produced by algae is considerably higher as compared to other agro-based biomass per unit area, easily grown on all habitats and with a great promise as energy source for the future. Table 2 summarizes the oil content yield of algae and some selected crops (Chisti 2007).

Fig. 5 Images of green algae from different sources

Table 2 Oil content yield from algae and some selected crops

Oil content from algae-based biomass		Agro-based biomass oil yields/crop	
Type of algae	*Oil content (% dry weight)*	*Type of crop*	*Oil yield (gallons/acre)*
Botryococcus braunii	25–75	Corn	18
Chlorella sp.	28–32	Soybeans	48
Crypthecodinium cohnii	20	Canola	127
Cylindrotheca sp.	16–37	Jatropha	202
Nitzschia sp.	45–47	Coconut	287
Phaeodactylum tricornutum	20–30	Oil palm	636
Schizochytrium sp.	50–77	Sunflower	102
Tetraselmis suecica	15–23	Algae	6283–14,641

Below are advantages inherent in algae-based biomass production as energy source:

a. The cultivation of algae-based biomass has fewer impacts on food security compared to other conventional biofuel-based crops that are more or less edible by man or are fodders for animals (Chisti 2007; Schenk et al. 2008).
b. Microalgae has a developed survival mechanism to adapt the changes in climatic conditions all climatic conditions; undergo rapid growth cycle; flexibly adapt to a variety of habitats (large number of different species); and could survive in aqueous media, in brackish water, and even on nonarable lands that are considered infertile. This of course will drastically reduce pressure usually associated with land exploitation and utilizations and even lesser pressure on freshwater. Of greater note and interest are no need for herbicide, pesticide, or even fertilizer in algae productions (Brennan and Owende 2010; Rodolfi et al. 2009); thus, providing remarkable opportunity for steady, stable feedstock supply all year-round, doubling the biomass production and oil content percentage (Chisti 2007).
c. As compared to biofuels derived from lignocellulosic-based biomass, the biofuels derived from algae-based biomass have high lipid content with high caloric value and low viscosity and density (Gouveia and Oliveira 2009; Miao and Wu 2004).
d. Algae-based biomass plays a critical role in regulating atmospheric CO_2 through carbon-neutral effects, and helps in improving air purity because of its high CO_2 sequestration or immobilization capacity (Chisti 2007).
e. Algae-based biomass also plays a significant role in contaminated water purification. Since algae makes use of nitrogen and phosphorus available in wastewater, the process serves as a bioremediation platform (Bilanovic et al. 2009; Gouveia and Oliveira 2009).
f. Algae-based biomass produces other associated by-products that are essential feedstocks for other bio-agro-based products such as biopolymers, pigments, animal feeds, fertilizer, etc. (Gouveia and Oliveira 2009).

The above mentioned advantages of algae-based biomass from other agro-based biomass provide a clear and immediate reason to further explore the potentials housed and still untapped in algae and its related species.

Chemistry of Algae-Derived Biofuel Production, Harvesting, and Extraction

Basically, algae has the potential to use its phototropic ability to trap and absorb energy from sunlight, converting the CO_2 from air, from industrial effluents, and from soluble deposits such as carbonate to manufacture energy (Janssen et al. 2003; Wang et al. 2008). Algae, just like biomass, participates in the removal or reduction of atmospheric CO_2 emitted from the greenhouse activity through a process called biosequestration (Jeong et al. 2003; Wang et al. 2008). Among the fuel gases (N_2,

CO_2, SO_x, O_2, NO_x, and water vapor) emitted by burning of fuels, CO_2 contributed more to global warming, causing more environmental consequences such as acid precipitation and rise in earth's temperature and sea level (Brewer 2013; Sahoo et al. 2012). Microalgae biomass consists of about 50% carbon by dry weight, which suggested that algae has higher tolerance for CO_2 and flourishes rapidly in carbon availability. Research documented that it only takes 1.5–2.0 kg of CO_2 to grow about 1.0 kg of algae biomass (Sobczuk et al. 2000), and for efficient algae cultivation, CO_2 availability in addition to the atmospheric percentage is required (Brewer 2013; Jeong et al. 2003; Stepan et al. 2002). Also, algae utilize solar radiation via photosynthetic process to capture CO_2 and reduce it into carbon molecules in the form of energy as shown in Eq. 1

$$6CO_2 + 12H_2O \rightarrow \left(CH_2O\right)_6 + 6O_2 + 6H_2O \tag{1}$$

The above reaction is light triggered and light dependent; however, algae have the potential to utilize the energy synthesis during the light stage (nicotinamide adenine dinucleotide phosphate (NADPH), adenosine triphosphate (ATP)) to convert CO_2 and H_2 ions forming sugar, adenosine diphosphate (ADP), and NADP which are further used to form amino acids and lipids (heterotrophic reaction) according to Eq. 2 (Janssen et al. 2003; Nagaich et al. 2014).

$$\begin{aligned} 3CO_2 + 9ATP + 6NADPH + 6H^+ &\rightarrow C_3H6O_{3+}\text{Phosphate} \\ &+ 9ADP + 8P_i + 6NADP + 3H_2O \end{aligned} \tag{2}$$

Algae species also utilize some essential inorganic nutrients during their growth cycle; silicon accelerates specifically the growth of diatoms species, are capable of fixing atmospheric nitrogen, and can also utilize the soluble form of nitrogen found in urea (Sharma et al. 2012; Welsh et al. 2000).

To fully optimize the production of algae, the following conditions are considered essential:

a. Sunlight availability can be affected by some climatic changes such as diurnal cycles and seasonal variations. This may hamper the effective production of algae, especially when considering the harvesting of biofuels for commercial purposes under natural growth conditions, thereby restricting the expansion of such drive to areas with relatively higher solar radiation all year-round. The mitigation, however, is to use artificial source of light such as fluorescent lamps especially when growing phototrophic species while being mindful of the light absorption characteristic of each species of algae in regard to its pigmentation (Brennan and Owende 2010; Muller-Feuga et al. 1998).
b. Fixing of CO_2 is the path of algae's growth cycle and the availability of CO_2 source either from the atmosphere or from industrial discharge will further accelerate the growth of algae (Janssen et al. 2003; Wang et al. 2008).
c. Availability of nitrogen, phosphorus, and other inorganic nutrients will also hasten the growth of algae; this could be the reason why algae are largely found around wastewater habitat (Sharma et al. 2012; Suh and Lee 2003; Welsh et al. 2000).

The most important and widely used method of algae cultivations that are considered to provide the desired sustainable energy output are the (1) open pond method, (2) closed pond method, and (3) photobioreactor production systems.

Open Pond Method

Open pond production system is the most popular and well-practiced method of cultivation through history lines (Borowitzka 1999). Open pond systems are classified into three types: raceway ponds, central pivot ponds, shallow lagoons, and ponds. Among the basic classification type, the raceway ponds are the most popular and widely used culture systems, especially for large-scale production. For optimum productivity, the raceway system requires a water flow rate of between 20 and 30 cm s–^{1} supported by a paddlewheel (Vandamme 2013). Figures 6 and 7 show open pond systems. In the raceway-based method, the paddlewheel principally aided even circulation of nutrients and water flow across the channels on continued bases, thereby preventing the trapping and settlement of nutrients and sedimentation (Fig. 7; Chisti 2007).

The drawbacks of this system are the possibility of water shortages, and since the pond is open, evaporation will also contribute to water loss (Haag 2007). The possibility of pollutant and contaminants to runoff into the ponds and of greater concern is the reliance on natural source of energy that is susceptible to seasonal variations and diurnal cycle (Muller-Feuga et al. 1998). Selective cultivation of single species of algae could be compromised using the open pond method due to possible competition from other organisms and species (Haag 2007).

Closed Pond and Photobioreactor Method

The technique involved in closed pond method also relies on paddlewheel for water and nutrient circulations, but in this case, the pond is closed and the risk of contaminant running off into the pool is mitigated, eliminating the possibility of competi-

Fig. 6 Photograph of open pond system

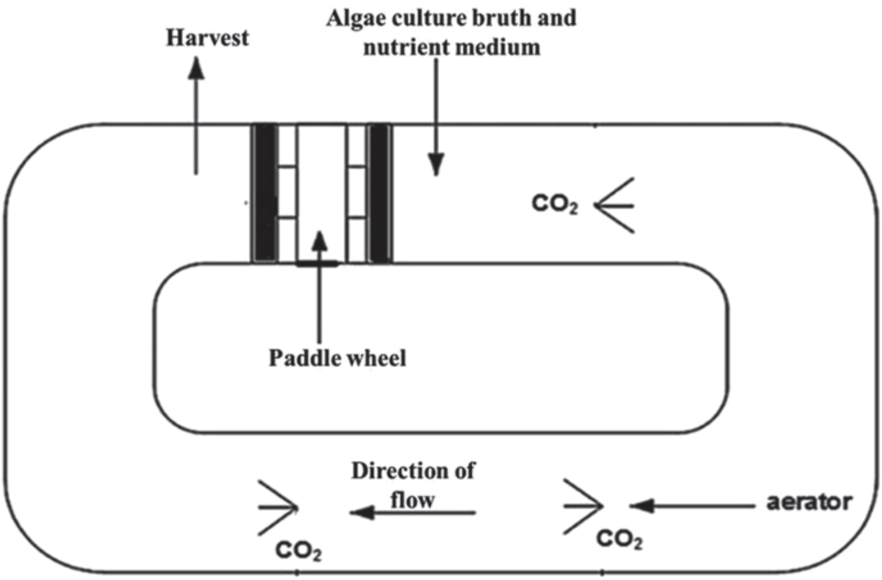


Fig. 7 Schematic of raceway pond system. The algae culture in nutrient medium placed in front of the paddlewheel which aids the circulation across the loop to the harvest extraction point and with the aid of an aerators; CO_2 is made readily available for absorption by algae (Chisti 2007; Brennan and Owende 2010)

tion and interference from other species and unwanted plants/organism (Brennan and Owende 2010; Campbell 2008; Chisti 2007). The photobioreactor method is considered to be the best and is preferred over the closed pond system due to its controlled build in system that completely eradicates the chances of interferences, providing perfect conditions for optimizing the algae production (Becker 1994; Campbell 2008; Chisti 2007). The close pond system and the photobioreactor system are shown in Figs. 8 and 9, respectively. The closed system is made of tubular, flat plate photobioreactors consisting of an array of glass tubes of about 0.1 m diameter that act as solar receivers, as shown in Fig. 9.

Fig. 8 Closed pond system and photobioreactor

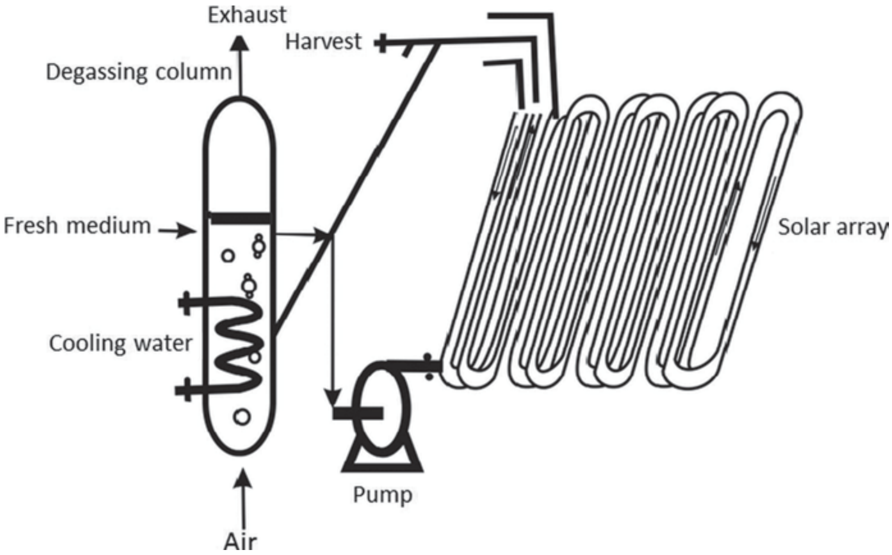


Fig. 9 Schematic of tubular photobioreactor (Chisti 2007)

Optimization of Lipid Production and Synthesis of Microalgae

Microalgae has large reservoir of lipids in the form of TAG consisting essentially of saturated fatty acids (FA) and some unsaturated FA which serves as an energy storage facility in the algae cells (Chisti 2008; Fukuda et al. 2001; Sharma et al. 2012). Lipid availability varies among each species of algae which makes the selection of microalgae for commercial biodiesel production very critical, especially with regard to the total lipid content (Guschina and Harwood 2006; Schuhmann et al. 2012; Thompson Jr 1996). Several research efforts have been conducted to improve the lipid output of microalgae for commercial oil production by enhancing photosynthetic pathways and altering the essential ingredients involved in lipid biosynthesis such as induced osmotic stress, radiation, nutrient starvation, temperature and pH, etc. (Fork et al. 1979; Sato and Murata 1980, Sato et al. 2000; Schuhmann et al. 2012; Thompson Jr 1996). High energy content is produced when CO_2 are converted into inorganic compounds through photosynthetic pathway; the TAG stored in the cytoplasmic lipid matrix of the algae cells are synthesized under light and later used for the synthesis of phospholipids (Lynch and Thompson 1982; Thompson Jr 1996). The study of diversity, habitat adaptation, and survival instinct of microalgae were observed to significantly determine the lipid synthesis and yield content among the species (Guschina and Harwood 2006; Sato et al. 2000; Thompson Jr 1996). This discovery encourages researchers to review the metabolic pathways of algae and maximize oil output by altering some of the intracellular and extracellular environmental conditions of the algae different from what is observed under normal conditions (Guschina and Harwood 2006; Sato et al. 2000; Thompson Jr 1996). Microalgae under altered and induced intracellular or extracellular stress conditions developed a stress-enduring protective mechanism by altering their lipid biosynthetic pathways, diverting and depositing FA into TAG (Sharma et al. 2012). Several techniques such as osmotic stress, radiation, nutrient starvation, temperature and pH, etc., are deployed in inducing lipid induction biosynthesis in microalgae. We shall review briefly the aforementioned induction method and their potential in biodiesel productions.

Nutrient-Induced Stress

Algae cultivation is most favored and accelerated under the availability of three primary nutrients: carbon, nitrogen, and phosphorus and other secondary micronutrients such as silica, manganese, iron, potassium, calcium, and zinc (Dongre et al. 2014; Thompson Jr 1996). While these nutrients are considered very essential in microalgae cell division and growth, they are, however, observed not to slow down the biosynthesis of FA under induced nutrient starvation, as long as the microalgae can access CO_2 and light energy (Thompson Jr 1996). The survival strategy employed by microalgae under nutrient duress is very interesting; since the cell division and growth are grossly impaired by nutrient deficiency, the microalgae in response divert and deposit more FA into TAG by consuming NADPH in the process and replenishing the electron acceptor driver in photosynthetic $NADP^+$ that was depleted as a result of the nutrient starvation (Hu et al. 2008; Thompson Jr 1996). Most species of algae, especially the red, brown, and green microalgae, were observed to accumulate more lipids under nitrogen stress (Alonso et al. 2000; Rodolfi et al. 2009; Xin et al. 2010), while other studies reported a relative rise in neutral lipid level under silicon (Griffiths and Harrison 2009; Xu et al. 2006), potassium (Lv et al. 2010), iron (Liu et al. 2008), and phosphorus (Andersson et al. 2003; Härtel et al. 2000; Reitan et al. 1994). Based on the foregoing, nitrogen starvation significantly slows down microalgae growth in all the species and induces high level of lipid synthesis when denied access to nitrogen (Widjaja et al. 2009). Thus, serving as one of the best nutrients when denied, induces stress and accelerates lipid production in all the algae species (Sharma et al. 2012). Table 3 summarizes the effects of nutrient starvation on algae metabolism and change in lipid profile after induction.

Temperature-Induced Stress

Temperature variation significantly influences the FA profile where decrease in temperature increases unsaturated FA and temperature rise causes increase of saturated FA, especially among species of microalgae and cyanobacteria (Dongre et al. 2014; Lynch and Thompson 1982; Renaud et al. 2002; Sato and Murata 1980). These changes alter the basic properties of the algal cell membranes, allowing normal photosynthesis, ion permeability, and respiratory activities to continue unabated (Somerville 1995). The changes in profile are achieved by altering the skeletal structure of FA, particularly the unsaturated FA that has weak carbon–carbon

Table 3 Effect of nutrient starvation on algae metabolism and change in lipid profile after induction. (Sharma et al. 2012; Dongre et al. 2014)

Change in lipid profile after induction	
Microalgae species	*Nutrient induced stress*
Dunaleiella tertiolecta	Lipid fluorescence increases fivefold under limited nitrogen supply
Chlorella sp.	Under nitrogen starvation, about 53.96 ± 0.63 mg/L d of lipid was obtained
Chlorella vulgaris	Total lipid content increases by 16.41 % under nitrogen limitation
Chlamydomonas reinhardtii	Increase in total lipid observed under short nitrogen supply
Scenedesmus subspicatus	Increase in total lipid observed under short nitrogen supply
Nannochloropsis oculata	Increase in total lipid by 15.31 % observed under short nitrogen supply
Pheodactylum tricornutum	Increase of 69–75 % in TAG level observed under nitrogen-induced stress
Neochloris oleoabundans	Lipid yield of 133 g/L d obtained under limited nitrogen stress
Scenedesmus sp.	Phosphorus and nitrogen limitations increase TAG content
Cyclotella cryptica	Under silicon duress, an increase in total lipid was observed from 27.6 to 54.1 %

TGA triacylglycerol

double bond and a direct link to increase the membrane fluidity (Dongre et al. 2014; Harwood and Jones 1989; Sharma et al. 2012). This observation was supported by an experiment in which haptophyte *Isochrysis galbana* cultured between two different temperatures 15 and 30 °C are harvested and the lipid content evaluated at both exponential and early stationary growth phases. The results showed high accumulation of lipid content in the stationary growth phase and highest at 30 °C than at 15 °C (Zhu et al. 1997). Interestingly, algae species like *Pavlova lutheri* shows a contrary result when cultured at two different temperatures 15 and 25 °C. The results showed a significant increase in acidic lipid and FA content with a slight rise in eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) at 15 °C culture grown compared to the culture grown at 25 °C (Tatsuzawa and Takizawa 1995). A similar observation was reported with S*ynechococus lividus* species cultured at 18 °C as compared to the culture grown at 35 °C (Fork et al. 1979). Table 4 summarizes the effect of temperature variation on algae metabolism and change in lipid profile after induction.

Salinity/pH-Induced Stress

Interestingly, some microalgae, especially *Dunaliella* species, were observed to strive in highly concentrated salty medium (Azachi et al. 2002); the reports show that increase in sodium chloride (NaCl) concentration from 0.5 m (29 g/L) to 2.0 m (58/g/L) increases exponentially the lipid content and TAG percentage of

Table 4 Effect of temperature variation on algae metabolism and change in lipid profile after induction. (Sharma et al. 2012; Dongre et al. 2014)

Change in lipid profile after induction	
Microalgae species	*Temperature-induced stress*
Nannochloropsis oculata	Lipid production increases by 14.92 % within crease of temperature from 20 to 25 °C
Chaetoceros sp.	Total lipid content was increase by 16.8 % cultured at 25 °C temperature
Rhodomonas sp.	Lipid yield increases by 12.7–21.7 % cultured between 27 and 30 °C temperature range
Cryptomonas sp.	Lipid yield increases by 12.7–21.7 % cultured between 27 and 30 °C temperature range
Isochrysis sp.	Lipid yield increase by 12.7–21.7 % cultured between 27 and 30 °C temperature range
Isochrysis galbana	Increase in neutral lipids observed from 15 to 30 °C temperature
Chlorella ellipsoidea	At lower temperature, the quantity of unsaturated FA increased significantly
Nannochloropsis salina	Total lipid content was observed to increase with increase in temperature
Ochromonas danica	Total lipid yield increases with temperature increase from 15 to 30 °C
Selenastrum capricornutum	Oleate FA increases with lowering of temperature from 25 to 10 °C
Dunaliella salina	Increase in unsaturated lipids at a temperature shift from 30 to 12 °C

FA fatty acids

D. tertiolecta species (Dongre et al. 2014). Similarly, diatom *Nitzschia laevis* at 20 g/L concentration of NaCl, total FA, EPA, and polar lipids were observed to be increased significantly (Chen et al. 2008). Other researchers also reported such an increase in pattern with salinity (Jiang and Chen 1999; Zhu et al. 2007). Inducing pH variation in medium containing microalgae was observed to create a change in the lipid profiles; for example, alkaline pH condition induces a decrease in membrane lipids by inhibiting algae growth channeling and energy for the formation of TAG (Guckert and Cooksey 1990) and acidic-mediated condition of pH 1 increased the percentage of total lipids in *Chlamydomonas* species, suggesting an adaptive reaction at low pH to decrease membrane lipid fluidity (Tatsuzawa and Takizawa 1995; Tatsuzawa et al. 1996). Table 5 summarizes the effect of salinity-/pH-induced stress on algae metabolism and change in lipid profile after induction.

Light-Induced Stress

The role played by light in the entire photosynthesis and autotrophic life cycle cannot be over emphasized (Sharma et al. 2012); any alteration or variation in light

Table 5 Effect of salinity/pH-induced stress on algae metabolism and change in lipid profile after induction. (Sharma et al. 2012; Dongre et al. 2014)

Change in lipid profile after induction	
Microalgae species	*pH-induced stress*
Dunaliella salina	Increased concentration of C18 FA on increase of NaCl from 29 to 205 g/L
Dunaliella tertiolecta	Increase in lipid content and TAG on increase of NaCl from 29 to 58 g/L
Dunaliella sp.	Increase in total FA and monosaturated FA on increased salinity from 23 to 234 g/L NaCl
Nitzschia laevis	Increase in unsaturated FA on increased salinity from 10 to 20 g/L NaCl
Crypthecodinium cohnii	Increase in total FA content and DHA on salinity induced at 9 g/L NaCl
Schizochytrium limacinum	Significant increase in total FA C15:0 and C17:0 on salinity increase from 9 to 36 g/L NaCl between temperatures of 16 and 30 °C
Chlamydomonas sp.	Increase in saturated FAs observed at low pH
Chlorella sp.	Increase in TAG under alkaline condition
Euglena gracilis	Increase in total lipids in cadmium, copper, and zinc medium
Chlorella vulgaris	Increase in total lipids to 56.6 % of biomass in Fe^{3+} medium

DHA docosahexaenoic acid, *FA* fatty acid, *TAG* triacylglycerol

availability produces direct effect on the biochemical metabolic activities such as the lipid profile characteristics, pigment, and photosynthetic activities of the microalgae (Siegenthaler and Murata 1998). High light intensity decreases total polar lipid content and neutral TAG, decreases the level of phospholipids content but enhances the level of nonpolar lipid in some species of microalgae, while low intensity facilitates the membrane polar lipid formations (Brown et al. 1996; Orcutt and Patterson 1974). Details of light-induced stress are summarized in Table 6.

Harvesting of Algae-Based Biomass

This is one of the most important stages of algae-based production and somewhat expensive stage that requires recovery of the biomass from the culture medium which depends essentially on the type of algae biomass, processing, and handling methods (Da Costa et al. 2010; Molina Grima et al. 2003). The most commonly used methods of harvesting are the flocculation, centrifugation, flotation, and filtration.

Table 6 Effect of light-induced stress on algae metabolism and change in lipid profile after induction. (Sharma et al. 2012; Dongre et al. 2014)

Change in lipid profile after induction	
Microalgae species	*Light-induced stress*
Tichocarpus crinitus	TG increases at low light exposure
Pavlova lutheri	Exposure to highlight intensity increases total lipid content
Selenastrum capricornutum *Prorocentrum minimum*	An increase in linoleate FA was observed under deprived/dark condition
P. antartica	Slight increase observed under deprived light/dark treatment under low UV-B light; increase in PUFA and structural lipids observed
Tetraselmis sp.	Monounsaturated and saturated FA increase under induced UV-B radiation
Nannochloropsis oculata	PUFA increases under UV-A light
Phaeodactylum tricornutum	Increase in PUFA and EPA observed under UV radiation
Chaetoceros muelleri	Increase in monosaturated FA under UV-A radiation
Nannochloropsis sp.	Increase in saturated FA and PUFA under UV-A radiation
Isochrysis galbana	Exposure to shorter period of light causes slight increase in PUFA

EPA eicosapentaenoic acid, *FA* fatty acid, *PUFA* polyunsaturated fatty acid, *TG* triglyceride, *UV* ultraviolet

Harvesting by Flocculation

To handle the harvested effluent from algae efficiently is to first concentrate the cells from relatively dilute solutions (Munir et al. 2013). Flocculation aggregates the microalgae cells by increasing the effective particle size; alkaline adjustment of the suspension using alum or ferric chloride reduces and neutralizes the negative charges on some microalgae cells to further facilitate the removal of the cell biomass (de-Bashan and Bashan 2010; Vicente et al. 2007). Figure 10 shows flocculation processes, algae cell particle aggregation, and their settling down process.

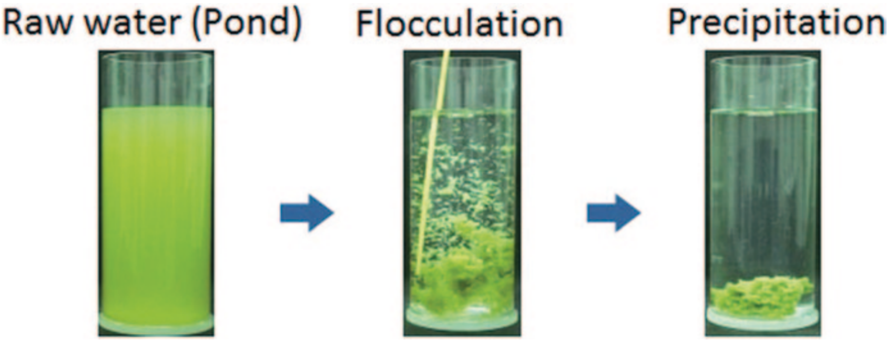


Fig. 10 Harvesting of algae by flocculation. (Source: http://www.et.byu.edu/~wanderto/homealgaeproject/Harvesting%20Algae.html)

Harvesting by Centrifugation

The whole idea is to apply centrifugal force to easily enhance and facilitate algae biomass particle separation based on their relative density differences and cell's radius (Vandamme 2013; Williams and Laurens 2010). The spinning force applied during centrifugation causes relatively dense particles to settle down rapidly, thereby facilitating cell separation time. This method is considered to be more suitable when applied on a commercial scale (Molina Grima et al. 2003). Centrifugation can be operated on continuous basis to separate almost all types of microalgae using either of the centrifuge machines such as "spiral plate centrifuge," "disc stack," or "decanter type of centrifuge" (Molina Grima et al. 2003). Disc stack has a shallow cylindrical bowl spaced between metal discs and is widely used and accepted for commercial purposes due to its suitability for separating minute-sized particles (3–30 μm) with relatively small concentration of about 0.02–0.05 % of microalgae cultures up to 15 % solids (Milledge and Heaven 2013). The decanter centrifuge is the most rugged and durable type of centrifuge and can withstand continuous processing conditions and high production capacity to deliver microalgae biomass concentrates up to 22 % utilizing just 8 kWh m^{-3}(Milledge and Heaven 2013). Spiral plate centrifuge consists of a rotating curved plate within a sliding cylindrical drum design to narrow down the particles' settling distance with the capacity to concentrate microalgae from 0.025 to about 31.5 % under relatively low energy of about 0.95 kWhm^{-3}(Milledge and Heaven 2013). The three different types of centrifugation system are shown in Fig. 11.

Harvesting by Filtration

This process is largely a mechanical separation technique carried out commonly on membrane facilitated by pressure or suction, preferably suitable for harvesting microalgae with larger cell particle size (> 70 μm) (Brennan and Owende 2010; Vandamme 2013). The membrane filtration using hydrostatic pressure is most suitable for smaller microalgae (< 30 μm). For a large-scale production, packed bed filters

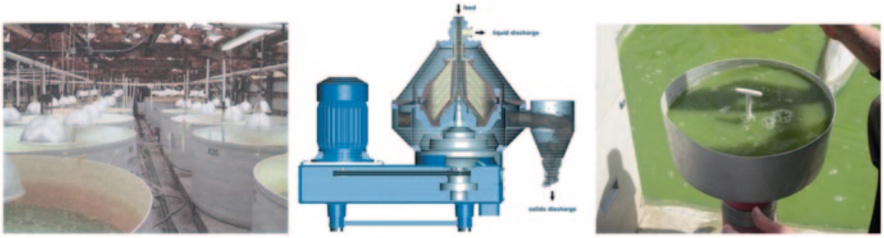
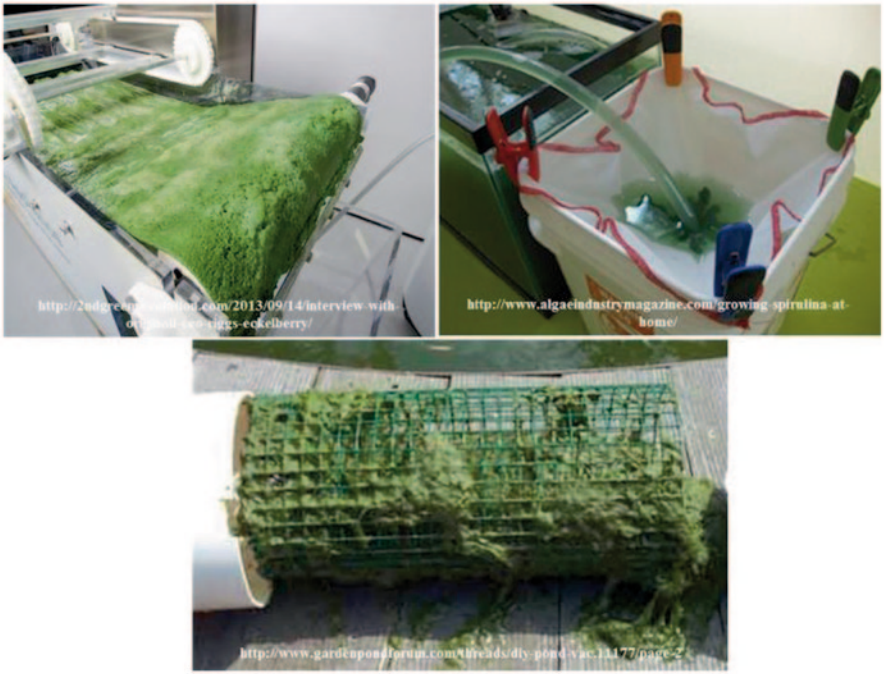


Fig. 11 Harvesting by centrifugation showing different systems in the order of large-scale centrifuge machine, disc stack, and simple rotating centrifuge for small-scale production

made of sand or ceramics are used as filtrating beds. Filtration processes using vacuum drums, simple membrane clothing materials, microstainers, filter presses, and vibrating screens are used for harvesting/filtering microalgae using membranes of different sizes, i.e., from macrofiltration (> 10 µm), microfiltration (0.1–10), ultrafiltration (0.02–2 µm) to reverse osmosis (< 0.001 µm) (Vandamme 2013). Algae species with macrorange size greater the 10 µm are best suited using macrofiltration system such as belt filters which are reported to be capable of filtering up to 20 % with relatively low energy consumption (Vandamme 2013), while the microfiltration as the name implies, satisfies the filtration requirements for most algae species which on a larger extent fall within size range of 0.1–10 µm (Molina Grima et al. 2003). For the recovery of microalgae with fragile cells, ultrafiltration system is one option that satisfies this requirement (Milledge and Heaven 2013). The different types of filtration systems are shown in Fig. 12.

Harvesting by Flotation

In this method, algae cell biomass are made to float under the influence of pressurized gas bubbled into the liquid medium, thereby separating the algae from its



http://2ndgreenrevolution.com/2013/09/14/interview-with-originoil-ceo-riggs-eckelberry/

http://www.algaeindustrymagazine.com/growing-spirulina-at-home/

http://www.gardenpondforum.com/threads/diy-pond-vac.11177/page-2

Fig. 12 Harvesting by filtration methods showing types of filtrating systems starting with belt filter, a simple membrane filter from cloth materials, and vacuum drum filter

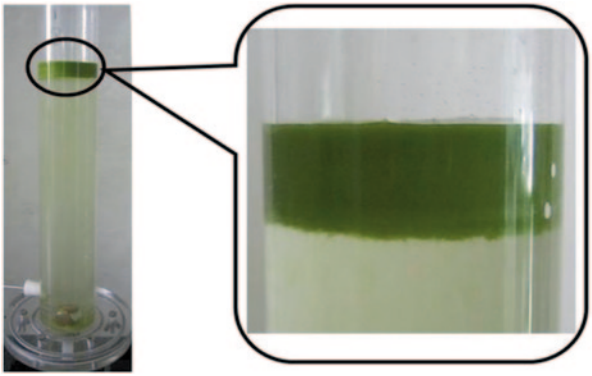


Fig. 13 Harvesting by flotation. (Source: http://english.qibebt.cas.cn/rh/rp/201308/t20130826_108770.html)

culture (Munir et al. 2013). Flotation process of algae separation is efficiently favored under the influence of flocculants; the addition of alum causes flocculation of algae cells' biomass and passing air into the liquid medium causes the bubbled air to adhere to the flucs, thereby increasing the buoyancy and the algae cell biomass floats towards the separation outlets as shown in Fig. 13 (Munir et al. 2013; Srivastava and Prasad 2000). The flotation process is achieved using bubble production method, dispersed air flotation method, dissolved air flotation, and suspended air flotation methods (Vandamme 2013; Wiley et al. 2009). In dispersed air flotation method, air is bubbled into a flotation cell forming foam with the aid of a surface-active chemical in the cells. Dispersed air flotation method is similar to dissolved air flotation, but in the case of the later, air-supersaturated water is pumped under pressure into the floating cells (Hanotu et al. 2012). Suspended air flotation is designed to correct the shortcoming of dispersed and dissolved air flotation methods towards depending on compressor and air–water saturator, but rather employed the use of cationic surfactant to create electrically charged small bubbles with excellent float stability (Vandamme 2013; Wiley et al. 2009).

Algae-Based Biomass Oil Extraction

Post-harvest processing of algae biomass is highly recommended to be carried out immediately because the harvested algae biomass slurry with about 5–15 % dry solid content is perishable and cannot withstand harsh weather conditions (Brennan and Owende 2010; Munir et al. 2013). To extend the relative shelf life of the slurry, dehydration or drying is the fastest, cheap, and commonly used method (Molina Grima et al. 2003; Munir et al. 2013; Williams and Laurens 2010). Dehydration of algae biomass under solar radiation is the cheapest but not entirely efficient, delimited by the factors such as drying time, wide spraying surface area, and handling risk (Mata et al. 2010; Prakash et al. 1997). Spray and freeze drying methods are expensive but efficient in extracting high oil content and value which can be used in the production of biofuels (Desmorieux and Decaen 2005; Dissa et al. 2010).

Oil content in algae is embedded in lipid form within the intracellular mass of the cell; the recovery of the intracellular materials in the algae cell is required and, therefore, the essential component or materials needed most are to be first separated from its complex mixture of the cell organelles such as proteins, nucleic acids, and the cell wall fragments through a process called cell disruption (Krisnangkura 1986; Sialve et al. 2009). There are mechanical and nonmechanical cell disruption methods available for the extraction of oil from biomass.

Mechanical Cell Disruption Method

This method is highly conventional in which the cell wall is physically weakened by pretreatment with acid/alkali or by enzymatic action, breaking the cell wall in the process, freeing and releasing all the intracellular materials in the microalgae cell compartment into the surrounding medium (Chisti and Moo-Young 1986; Greenwell et al. 2009). This method proved efficient, reducing and minimizing external contaminations running in (Chisti and Moo-Young 1986; Greenwell et al. 2009). Tools used in mechanical cell disruption method include:

- *Homogenization.* This method of cell disruption involves the pumping of slurry at a very high velocity through a specially controlled aperture valve which applies unaligned pressure to the liquid causing expansion and a sudden drop in the shear force pressure upon discharge results in cell wall explosion (Brookman and James 1974; Follows et al. 1971). Homogenization method is widely used in a situation where all the value chain products from algae-based biomass are only needed rather than biofuel production (Casey and Lubitz 1963; Doucha and Lívanský 2008).
- *Bead milling.* This method involves inducing a strong kinetic energy by agitating or exciting abrasive particle or beads in suspension, producing a shear force strong enough to cause grinding of the algae biomass between beads, and collision with beads and subsequently weakening the cell wall in the process, causing cell disruption, thereby releasing the biomaterial content of the cell (Doucha and Lívanský 2008; Krisnangkura 1986). This method was reported to be successfully used on a large-scale type of bead mill called dyno-mill using rapidly rotating notched discs (Foglia et al. 1997; Greenwell et al. 2009; Krisnangkura 1986).
- *Ultrasonic-assisted cell disruption.* This method of cell disruption involves the breaking down of cell wall under applied higher frequency sound waves across a metallic tip into a concentrated medium containing algae cell culture and in the process generates cavitation bubbles in the cell suspension. The creation of cell cavities in the suspension and the subsequent collapsing of the bubbles on the cell wall generate propagating wave disturbances (shock waves) and nuzzling out stream of liquid that weakens and breaks the cell wall, releasing the entire biomaterials into the solvent (Cravotto et al. 2008; Munir et al. 2013).

- *Blenders (pressing/expeller) cell disruption.* This tool of cell disruption works by introducing high-pressure force into the algae biomass cell suspension causing the cell wall to rapture and release the oil content (Popoola and Yangomodou 2006; Williams 2007).

Drawbacks of Mechanical Cell Disruption Methods

The entire intracellular content of the cell such as proteins, nucleic acids, and cell fragments is released in its complex mixture when the cell wall is broken. This may cause some interference in separation by increasing the viscosity of the solution, hampering efficient processing. Mechanical cell disruption subjected the algae biomass cell proteins to undergo denaturation under series of pressure and heat, especially when using the homogenizer or pressing mills (Doucha and Lívanský 2008; Foglia et al. 1997; Greenwell et al. 2009; Krisnangkura 1986; Popoola and Yangomodou 2006; Williams 2007).

Nonmechanical Methods

This method of cell disruption is achieved by making algae cell walls permeable and allowing access to the intracellular compartment of the cell to be extracted following the application of solvent and chemical agents. This method of permeabilization is placed into chemical, mechanical, and enzymatic methods among others (Mercer and Armenta 2011):

- *Chemical permeabilization.* Organic solvents such as alcohol, benzene, toluene, ether, chloroform, etc., are utilized to extract intracellular materials embedded in algae biomass cell compartment by making the wall enveloping the cell permeable, creating porous vents through the cell membrane. The oil dissolves in the solvents and the pulp is filtered out and the resulting mixture of oil in solvent is separated by distillation (Cooney et al. 2009; Naglak et al. 1990; Lewis et al. 2000; Zhu et al. 2002).
- *Mechanical permeabilization.* This method is achieved by applying a sudden change in the extracellular osmotic pressure of the algae cell environment. Since the cells are subjected to rapid changes in external osmolarity, it is quite different from its traditional familiar adaptation state and hence the applied pressure triggers and induces stress across the algae cell membrane. Initially, under normal adaption state, the cells are allowed to equilibrate and establish both intracellular and extracellular osmotic pressures by the addition of high concentration of solute such as sucrose, salt, polyethylene glycol, dextran, etc. When the intracellular and extracellular environment is fully equilibrated, the process is then immediately and rapidly altered by diluting away the solute concentrations, causing the osmotic stress. These sudden changes in external osmolarity trigger sudden stress and severe pressure of the cytoplasmic matrix and end up causing the cell

to rapture, releasing the intracellular materials, including the oil in it (Felix 1982; Munir et al. 2013).

- *Enzymatic permeabilization.* Periplasmic or surface enzymes are employed in this method to enhance the hydrolysis of the cell walls to release oil. Complexes such as ethylenediaminetetraacetic acid (EDTA) are used in this process to destabilize the outer membrane of gram-negative cells, thereby opening up the routes for the enzymes to access the cell (Mercer and Armenta 2011).

Transesterification and Biodiesel Production

Biodiesel is an FA ester made from transesterification of organic oils from plant or animal biomass (Campbell 2008; Dongre et al. 2014). The oil in algae is in lipid form called TAG. The process of conversion of these extracted TAGs harvested from algae with alcohol in the presence of a catalyst to produce long-chain monoalkylesters is called transesterification (Alcaine 2010; Campbell 2008). The TAG is primarily serving as energy storehouse and backbone in plant growth and germination and is the essential constituent of the oil found in oilseeds, crops, plants, and animal fats (Alcaine 2010; Campbell 2008; Tariyal et al. 2013). TAG is synthesized in the cytoplasm of prokaryotic cells, and in the case of eukaryotic cells, the synthesis takes place in the endoplasmic reticulum; essentially, the mitochondria and plastid in plants are the organelles doing the job (Brewer 2013; Guschina and Harwood 2006; Sakthivel 2011; Wältermann and Steinbüchel 2005). In the synthesis of TAG, a coenzyme acyl-CoA transfers acyl group through the acylation of glycerol-3-phosphate (G3P) to form lysophosphatidate (LPA) facilitated by G3P acyl-transfererase (GPAT) which catalyzes the first actual step in the phospholipid biosynthesis (Brewer 2013; Guschina and Harwood 2006; Sakthivel 2011; Wältermann and Steinbüchel 2005). The formed LPA undergoes further acylation by acylglycerophosphate acyl-transferase (AGPAT) to generate phosphatidate (PA) which is further dephosphorylated by phosphatidic acid phosphohydrolase (PAP), converting diacylglycerolacyl transferase into TAG catalyzed by acyl-CoA (Brewer 2013; Guschina and Harwood 2006; Sakthivel 2011; Wältermann and Steinbüchel 2005). Figure 14 is a simple representation of the synthesis of TAG by microalgae.

The transesterification reactions in Fig. 14 shows that the fatty acid functional group (–COOH) on the TAG skeleton reacts with the hydroxyl group on alcohol (–OH) to produce ester and glycerin, following intermediate conversion sequence in which the glycerol undergoes periodic removal from the reaction solution in other to drive equilibrium reaction towards completion, from TAG to diglyceride (DG), then to monoglyceride (MG), and finally to glycerol (GL) in the presence of a catalyst (Lang et al. 2011; Munir et al. 2013) (Fig. 15). Acid catalyst such as sulfuric acid is favored when the oil extracted has high acidic value and alkali catalyst in situation where the oil has low acidic value (Munir et al. 2013). The biodiesel obtained from these processes, unlike diesel derived from petroleum product, does not contribute to greenhouse emission (Rakopoulos et al. 2006), with energy heating efficiency

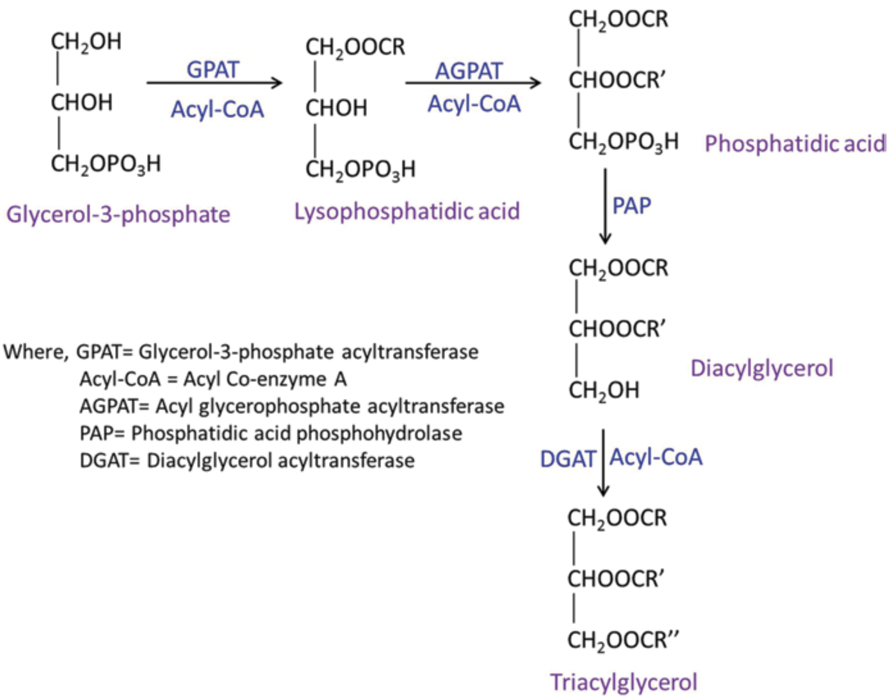


Fig. 14 Schematic representation for the synthesis of triacylglycerol (TAG) in microalgae cells

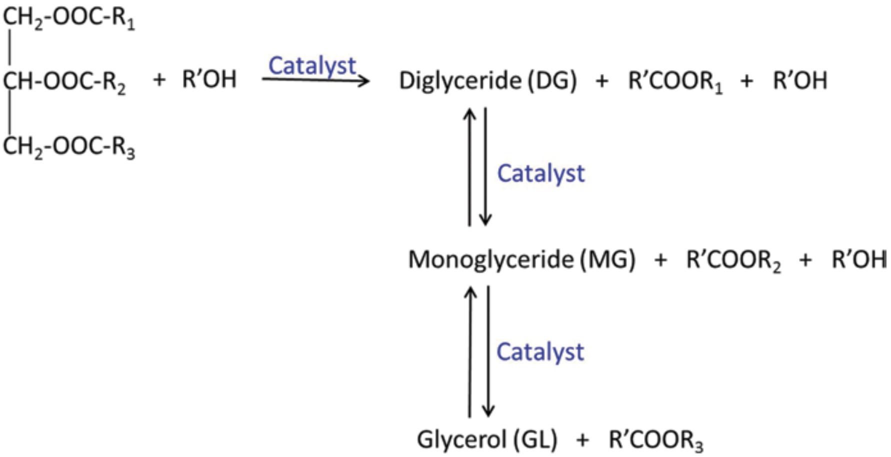


Fig. 15 Schematic of transesterification reaction, where R1, R2, and R3 are fatty acid chains consisting of long chains of carbon and hydrogen atoms

closer to fossil diesels; diesel derived from oilseed crops yields about 37 MJ/kg, algae-based biodiesel yields about 41 MJ/kg as compared to about 42.7 MJ/kg derived from petro-diesel (Brennan and Owende 2010; Campbell 2008; Rakopoulos et al. 2006; Sharma et al. 2012; Xu et al. 2006).

Summary and Conclusion

In this chapter, we have discussed the potentials of biomass as a veritable and ideal replacement for fossil-based resources being appreciative of the environmental time bomb continuous use and burning of fossil fuel and its derivative poised. Fossil fuels such as coal, petroleum, and natural gas are fast depleting and not sustainable, contributing immensely to greenhouse activities such as acid precipitation, water and air pollution, and ozone depletion that bedevil the entire universe. These environmental and health consequences associated with fossil-based products ignite a rethink and global shift towards exploring biodegradable, ecofriendly, and sustainable sources of energy, especially from biomass. Biomass from agro-based resources is reviewed in this chapter as best option for the depleting fossil-based resources based on the following reasons among others:

a. Biomass are biomaterials that are renewable, biodegradable, and sustainable, while fossils are nonbiodegradable, nonrenewable, and not sustainable.
b. The stored energy in biomass when burned releases CO_2 which is subsequently reabsorbed by plants in their growing state, resulting in atmospheric carbon-neutral effects and maintaining balance level of atmospheric CO_2 at a very short time frame, while on the contrary, the energy in fossils fuels that was stored over millions of geologic years only burn out the carbon into the atmosphere and increases the carbon concentration in the atmosphere without being reabsorbed.
c. Biomass are highly dispersed across the world and could be cultivated virtually everywhere, while fossil fuels are largely localized and found deep below the earth's crust or sea level.

With the understanding of biomass potentials discussed in this chapter, the agro-based resources derived from animal and plant sources though promising and environmental friendly also came with some disadvantages. The caviar, however, is on the fact that cultivation of oilseed crops and other edible crops essentially for energy production will avertedly water down on food supply and security. Additionally, continuous removal of the crop residues will affect soil fertility and expose the soil to erosion. The overall implications, however, are to explore agro-based biomass for energy production that will not compete with food productions and fodder demands and can be cultivated anywhere all year-round, with excellent oil content yield, requiring less water for cultivation, and finally establish atmospheric carbon balance. In this chapter, we identified an aquatic plant called algae that falls and virtually satisfies these conditions essentially for biodiesel production.

In this, we have discussed briefly the taxonomy of algae as a nonflowering plant or organism with no definitive roots, stems, leaves, and vascular tissues but constitutes the majority among the photosynthetic organism in the world. Algae can survive in virtually all climatic conditions; undergo rapid growth cycle all year-round; has high lipid content with high caloric value; low viscosity and density; are highly flexible; and could survive in aqueous media, in brackish water, and even on nonarable lands that are considered infertile. They exhibit high CO_2 sequestration or immobilization capacity by ensuring carbon-neutral effect and play a significant role in contaminated water purification and bioremediation. Furthermore, they serve as an essential feedstock for other bio-agro-based products such as biopolymers, pigments, animal feeds, and fertilizer. They strive remarkably under the availability of light radiation, CO_2, and nutrients and are capable of changing their FA and lipid content profile under light and osmotic or nutrient starvation following various induction techniques.

We came to understand that algae has large reservoirs of lipid content compared to other agro-based biomass stored as TAG, synthesized either by phototropic or heterotrophic pathways. The stored TAG can be converted into biodiesel through a process called transesterification. Furthermore, we have discussed various methods of cultivation, harvesting, and extraction of algae for biodiesel production. The open pond method and photobioreactor method are discussed as algae cultivation methods with photobioreactor as the best method of production. The harvesting processes such as flocculation, centrifugation, flotation, and filtration techniques are looked into, followed by various disruption methods adopted in algae oil extraction processes. In conclusion, we came to understand that algae-based resources are promising energy resources and have the potential for revolutionizing the energy sector in the near future. Understanding the fundamentals of algae metabolism is the key to revolutionize the potentials of bio-based biomass.

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Empty Fruit Bunches in the Race for Energy, Biochemical, and Material Industry

Chow May Jinn, H'ng Paik San, Chin Kit Ling, Chai Ee Wen, Paridah Md Tahir, Lee Seng Hua, Lum Wei Chen, Luqman Chuah and Mariusz Maminski

Abstract At present, empty fruit bunch (EFB) is used particularly as a substitute for wood fiber in few industries. Nevertheless, the end products have been reported to be relatively inferior to those made from wood and performed below the par. This chapter provides a platform to delve into the unseen keys and real facts of EFB in renewable energy, derivatives, and material industries. EFB characteristics (cross-sectional observations, chemical compositions, and inorganic element analysis) and qualities (tensile stress test and fiber morphometric measurement) are presented, and a comparison is made with softwood and hardwood. The anatomical features of EFB fiber consist of 75 % fibers and 25 % vascular bundles in terms of volume/volume. In terms of mechanical properties, EFB fibers have relatively lower specific tensile stress value compared to most woods. The presence of round, spiky-shaped silica compounds in EFB may hinder the quality of the panelboard, solid biofuel, and biochemical derivatives industries. Major amounts of alkaline cations in EFB present a problem to the combustion issue for renewal energy. Relating the characteristics and quality of EFB to the respective industries proved that EFB is an encumbrance to them. Conclusively, developing a proper treatment system to manipulate the characteristics and quality of EFB is crucial so that EFB can be pushed toward commercialization.

Keywords Empty fruit bunch · Physicochemical properties · Fiber quality · Industrial application · Specific tensile stress

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Introduction

Forests today are not supplying enough logs for human activities. While thousands search desperately for places to live, construction of urgently needed dwellings is hindered by shortage of timber materials. To make the situation worse, the rapidly growing pulp and paper industry in the world is competing with lumber producers for limited available timber. The raw material shortage looms in timber industry will not be of short duration. This has generated renewed interest in pursuing the development of agricultural biomass that could provide a viable substitute for timbers.

Agricultural biomass can be defined as having composition of cellulose, hemicellulose, and lignin of an organic nature and is generated from agricultural activities. This biomass of a wide variety of category is found in the form of residual stalks, straw, leaves, roots, rice husks, seeds, and perennial grasses. The most common method of disposal of these wastes is landfill, although some products can be made of these wastes. Converting agricultural biomass into commercial products has environmental as well as economic benefits. These include carbon recycling, no harmful substances emissions, and, most importantly, being renewable.

The agricultural biomass is available in abundance, and many of the biomass is virtually free. The presence of type of biomass in the respective country is based on the major economic activities of the countries. In Malaysia, agriculture and agro-based sector make up 7 % of the nation's gross domestic product (GDP; Bernama Media 2014). The plantation crops subsector was the main component in GDP for agriculture, accounting for more than 52 % per annum over the past 10 years with oil palm being the main commodity (contributing 32 % out of the 52 %; Department Statistics of Malaysia 2012).

Oil Palm Biomass

The large-scale oil palm plantations were established by the British as early as 1917. Today, Malaysia oil palm plantations make up 70 % of agricultural land or about 12 % of total land area (Petrus et al. 2013). With such a huge plantation area, Malaysia was placed as the world's second producer of palm kernel and crude palm oil (CPO) after Indonesia. While Malaysia enjoys the economic benefits from the oil palm industry, there are huge amounts of biomass generated from the processing as well as the plantation divisions. It is estimated the biomass can reach 100 million dry t in 2020 (AgensiInovasi Malaysia 2011).

In the plantations, oil palm fronds (OPF) and oil palm trunks (OPT) are the biomass being generated. The former are generated as they are cut together with fresh fruit bunches from the palm trees throughout the year. The latter become available during the replanting of the old oil palm trees. The vast amount of these biomasses is returned to the field for recycling of nutrients and replenishes the soil. In the processing mills, empty fruit bunches (EFB) are left over after the removal of the fruits from the fresh fruit bunches. The other biomass such as palm-kernel shells (PKS) and mesocarp fiber are by-products during the oil extraction process of CPO and palm-kernel oil (PKO), respectively. In addition, the nonsolid biomass, palm oil mill effluent (POME) discharged from washing and sterilization of the palm fruits, is available in huge quantity.

There is a huge economic value to utilize the biomasses for a variety of additional end uses, including but not limited to the production of biomass pellets, conventional wood composite products, bioenergy and biofuels, and biochemical derivatives. Among the biomass produced from palm oil plantation and mills, one third of the oil palm biomass is EFB. The EFB is the biomass investigated most often by researchers for energy, biochemicals, and wood-related products production (Geng 2013). Suffice it to say, EFB will become part of the important portfolio to sustain the development and growth of energy, biochemicals, and materials industry in near future.

Empty Fruit Bunches

In the raw state, EFB has a very fibrous texture and is in wet condition. The EFB remaining after the processing usually contains 30–35 % lignocellulose, 1–3 % residue oil, and roughly 60 % of moisture (Gunawan et al. 2009). The EFB lignocellulose or fiber consists of cellulose, hemicellulose, and lignin in nature. The fiber can be prepared by shredding process of the bunches. Some palm oil mills use the fiber as mulching materials for their own plantation. Other mills mostly landfill the EFB to create organic stock in the plantation soil.

Despite that, oil palm EFB fiber has been identified as the single most important agriculture biomass in Malaysia. It is viewed favorably as a prime candidate to fill up the void of wood shortage due to its locally abundant availability. Malaysia has a long history of being involved in palm oil industry and has emerged as one of the world's leading producers and exporters of CPO. EFB is by-products generated from CPO process and is said to be sustainable and renewable. Due to the huge number of CPO processing mills and large plantation area (covers about 4.85 million ha), about 15 million t of EFB is estimated to be generated annually (Baharuddin et al. 2009; Geng 2013).

Basic Properties of EFB Fibers

Most of the basic properties of EFB tabulated in this chapter were derived from original works and research that stands on its own through extensive sampling and analysis procedures. These properties are represented as the average properties value of the EFB. The basic properties presented here include the fiber characteristics and qualities and were compared with those of hardwood and softwood.

Fiber Bundle Anatomy

The cross section of the fiber bundle presented in Fig. 1 is in the form of round to polygonal in shape. EFB fibers are hard and tough multicellular fibers. They consist of a large vessel element in the core region of vascular bundle as shown in Fig. 1a, b. The vascular bundle is a simple bundle that is surrounded by porous tubular structures-like fibers and embedded in parenchymatous ground tissues. The open spaces around the vessels are probably the areas where the phloem cells had been disrupted by the microtome knife in this study. Figure 1b clearly shows that the vessels had thinner cell wall in comparison to those surrounding tubular structures-like fibers. The volume ratio of vascular bundles to single fiber cell is 1:3. This ratio shows that fibers consist of 75 % volume fraction, while vascular bundles contribute to 25 % of EFB volume. EFB have some special characteristics, including being capable of holding high moisture content (1.5–2 times the weight of the dry material), and this may be due to the volume percentages of vascular bundle presence in EFB (Lani et al. 2012; Ngo et al. 2014). Vascular bundle and parenchyma are naturally spongy and have high capacity in water absorption (Killmann and Lim 1985).

Fiber Morphology

EFB fiber morphology presented in Fig. 2 was observed under Leica image analysis system (LEITZ DMRB) with magnification of 400×. The Average value of EFB fiber dimensions is presented in Table 1. Individual fiber macerated from EFB is in the form of a threadlike sheath with the average fiber cell wall thickness of 3.8 µm and fiber length of 0.90 mm. Similar results of 3.38 µm for cell wall thickness and 0.99 mm for fiber length have been found in the study by Law and Jiang (2001). The average fiber diameter for EFB fiber measured in this chapter is 22.3 µm and lumen diameter is 15.7 µm. This value is close to the result stated by Rushdan (2000) with average fiber diameter of 20.6 µm and lumen diameter of 14.75 µm.

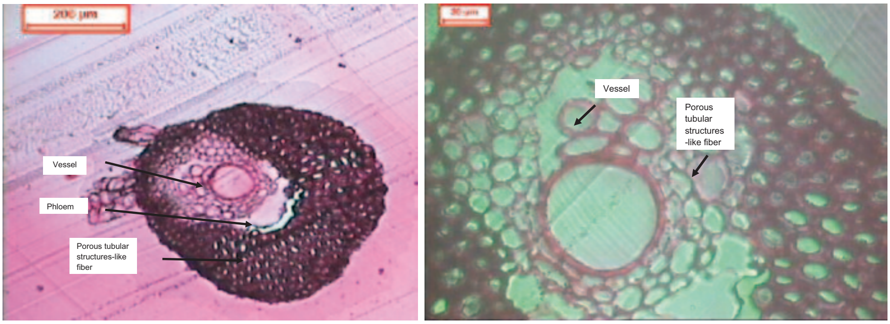

Fig. 1 **a** Cross-sectional view of fiber under magnification of 100×. **b** Cross-sectional view of fiber under magnification of 400×

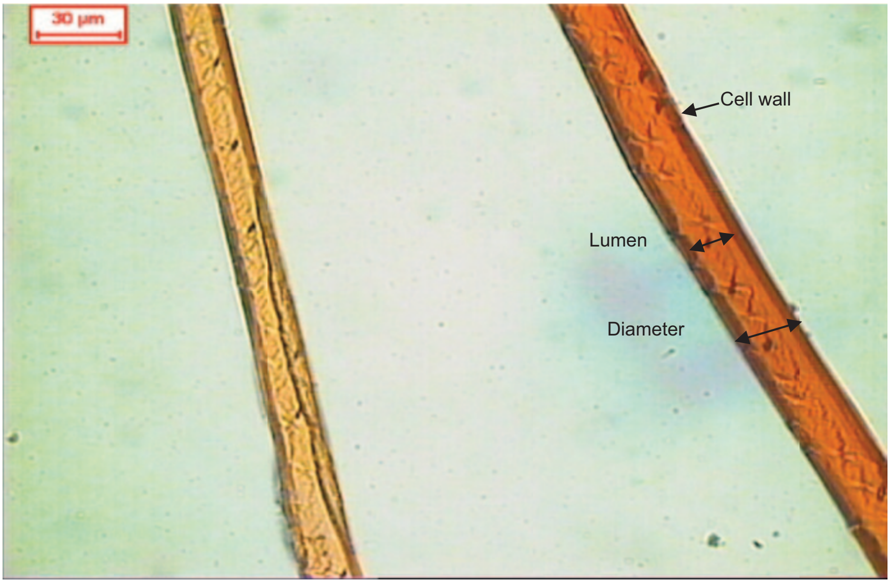

Fig. 2 Fiber under microscopic magnification of 400×

Table 1 Morphological properties of EFB fiber and fiber dimension derived value. (Source: Smook 1997)

Properties	Unit	EFB	Softwood	Hardwood
Cell wall thickness	µm	3.8	1.5–2.5	3.2–6.4
Lumen thickness	µm	15.7	19.8	10.7
Fiber diameter	µm	22.3	26.8	14.7
Fiber length	mm	0.90	2.5	0.8
Runkel ratio	–	0.34	0.35	0.4–0.7
Flexibility ratio	%	70.40	75	55–70
Slenderness ratio	–	40.36	90–120	55–75

EFB empty fruit bunches

In comparison with softwood, EFB generally have thicker cell wall, thinner lumen, smaller diameter, and shorter fibers. EFB fibers have similar cell wall thickness and fiber length, while having thicker lumen and larger diameter when compared with hardwood species. Cell wall thickness is an important feature in imparting fiber stiffness. Fiber morphology influences the physico-mechanical properties such as toughness, tensility, and static bending strength, which in turn might affect the fiber workability (Parameswaran and Liese 1975; Espiloy 1987; Widjaja and Risyad 1987; H'ng et al. 2009; Benazir et al. 2010).

As shown in Table 1, three derived values were evaluated using the fiber dimensions, namely Runkel ratio, flexibility ratio, and slenderness ratio. In general,

Fig. 3 Round spiky shape silica bodies found between fiber under microscopic magnification of 400×

EFB have longer fibers that result in higher flexibility; thinner cell wall gives low Runkel ratio and bigger lumen contributes to low slenderness ratio. Runkel ratio is a microscopic extension of the plant density which indicates the elasticity of the fiber. Runkel ratio is determined using lumen thickness and cell wall thickness of fiber dimensions. Fiber with Runkel ratio below value of one is normally associated with good mechanical strength properties (Istek 2006). On the other hand, the higher the slenderness ratio, the stronger will be the fiber resistance to force of tearing. EFB might have lower slenderness ratio compared to wood but still is in an acceptable range for fiberboard production. The flexibility ratio of elastic efficiency is inversely proportional to tensile strength. Generally, there are four different types of fibers which are classified under flexibility ratio: (1) high elastic fibers having flexibility ratio greater than 75, (2) elastic fibers having flexibility ratio between 50 and 75, (3) rigid fibers having flexibility ratio between 30 and 50, and (4) high rigid fibers having flexibility ratio less than 30 (Istas et al. 1954; Bektas et al. 1999). The EFB fibers were classified under the type 2 similar with hardwood. This kind of fibers easily can be flat and give good paper with high tensile strength properties (Bektas et al. 1999).

As shown in Fig. 3, silica bodies were bounded between the fibers. The silica bodies observed on fiber strands are round spiky shape. The shape, size, and distribution pattern of silica bodies observed on EFB fibers were similar to those in the epidermis of palm leaf (*Syagrus coronata*) as reported by Law et al. (2007) and Lins et al. (2002). Figure 4 shows tensile strength of EFB.

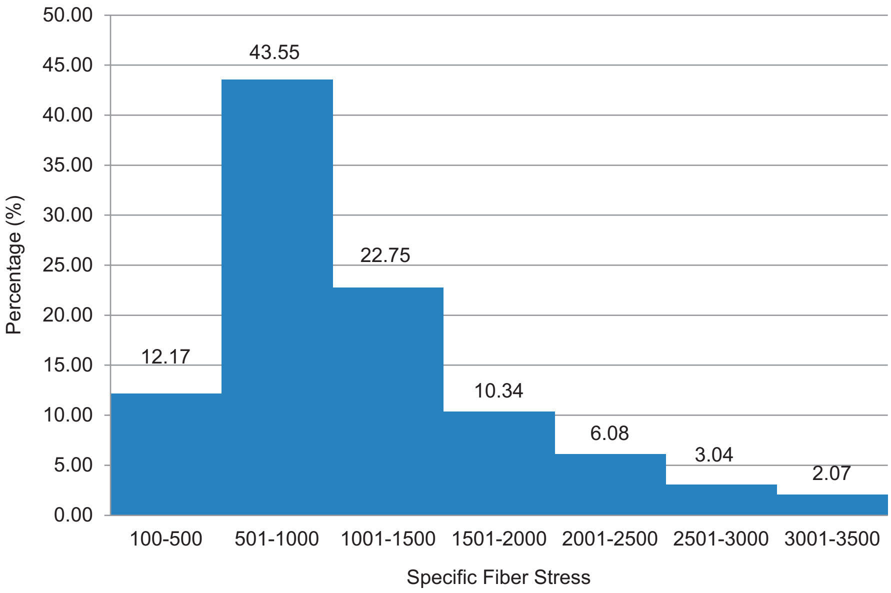

Fig. 4 Tensile-specific fiber stress of EFB. *EFB* empty fruit bunches

Chemical Composition and Inorganic Elements of EFB

The feasibility of the plant material for a certain industry was greatly influenced by the chemical composition of the lignocellulosic material. The chemical compositions of EFB are presented in Table 2. A combination of cellulose and hemicelluloses is referred as holocellulose. Holocellulose accounted for 74.9 %, while the alpha cellulose accounted for 44.2 %. These values are slightly higher in comparison with wood species (Tsoumis 1991; Forest Products Laboratory 2010). The result obtained for the holocellulose and cellulose content of EFB was close to those earlier research findings (Khoo and Lee 1991; Chin et al. 2012). Cellulose shows a strong tendency to form intra- and intermolecular bonds. The fibrous structures and strong hydrogen bonds give cellulose a high tensile strength and make the fibers insoluble in most solvents (Law et al. 2007). The data show that EFB exhibits the highest solubility in alcohol–acetone (%), compared to softwood and hardwood. Oil and grease are also present in the EFB (2.4 %).The lignin content of EFB was found to be lower than that of softwood (21–37 %) and hardwood (14–34 %), whereas the ash content of EFB (4.8 %) was higher than that of softwood (< 1 %) and hardwood (< 1 %). EFB has a lower lignin content but higher cellulose, extractive, and ash content compared to fast-growing hardwood species available in Malaysia (Chin et al. 2012).

As shown in Table 2, EFB is rich in inorganic elements compared to softwood and hardwood. Bondada and Keller (2012) stated that calcium, potassium, magnesium, phosphorus, and other elements are easily accumulated in the fruit stalk

Table 2 Chemical characteristics of efb (%). (Source: Tsoumis 1991; Misra et al. 1993; Mingle and Boubel 1968)

Organic compounds	Unit	EFB	Softwood	Hardwood
Alcohol–acetone solubility	%	6.4	0.2–8.5	0.1–7.7
Acid-insoluble lignin	%	12.7	21–37	14–34
Holocellulose	%	74.9	60–80	71–89
α-cellulose	%	44.2	30–60	31–64
Ash	%	4.8	<1	<1
Oil and grease content	%	2.4	N/A	N/A
Major inorganic elements				
K	mg/kg	13,028.0	22.5–25.3	31.9–112.5
Mg	mg/kg	1147.5	33.2–79.0	25.3–117.0
Ca	mg/kg	803.7	290.5–421.7	211.7–466.0
P	mg/kg	426.3	8.4–12.2	4.8–15.6
Fe	mg/kg	248.7	5.8–35.0	0.9–20.3
Na	mg/kg	123.8	0.6–23.0	0.6–23.0
Si	mg/kg	113.0	46.7–74.8	1.1–46.3
Al	mg/kg	7.3	4.7–11.1	1.4–20.1
Minor inorganic elements				
S	%	0.01	0.01–0.05	0.02–0.05
Cl	%	ND	0.01	0.01

N/A not applicable, *ND* not defined, *EFB* empty fruit bunches

(pedicel) due to fertilization program of such elements made available throughout the plantation period. In general plantation practices, it is common to boost the yield and quality of fruit crops by applying excessive fertilization, especially potassium-rich fertilizer, to the crops. This could be the reason why EFB contained higher inorganic elements than the wood. Potassium content of 13,028.0 mg/kg obtained from the original work of this chapter is the predominant inorganic element for the EFB. Among the eight major inorganic elements presented, aluminum content was found to be the lowest with 7.3 mg/kg.

Specific Tensile Stress of EFB

Currently, no study has been reported on the specific tensile stress of EFB. The specific tensile stress refers to spring constant *k,* which is a measure of the force needed to extend an elastic material by some distances under the proportional limit according to Hooke's law (Degarmo et al. 2003; Smith and Hashemi 2006). The mean value of specific tensile stress of EFB determined to be presented in this chapter is 1100 N/m, which is far below the value of 3600–11,000 N/m reported for wood materials (Bodig and Jayne 1993). In short, the EFB fiber only required one third of force as compared to wood to achieve the same elongated length, thus becoming three to ten times more brittle than wood. Fiber tensile properties are critical to the quality of the fiber and particles composite products. The poor EFB stiffness may be attributed to their nature of low lignin contents and high hemicellulose content. Voelker et al. (2011) stated that reduction in lignin of poplar up to 40 % significantly reduced the wood strength and stiffness although the density is unchanged.

Figure 3 shows the histogram of fiber-specific tensile stress plotted using 800 strands of EFB fiber. The distribution of tensile-specific stress is skewed to the right with skewness value of 1.34 and is considered highly skewed as the value of skewness is greater than 1. The long right tail in the histogram implies that very few EFB fibers have high specific tensile stress. A majority of the EFB fibers exhibit low specific tensile stress as the mass of distribution is concentrated on the left of the histogram.

Issues of EFB Fiber

Keeping the above in view, numerous researches and approaches have progressed in the recent past by channeling EFB into higher-value downstream uses such as composites, pulp and paper, biofuel, and also bio-based chemical (Ramli et al. 2002; Prasertsan and Sajjakulnukit 2006; Law et al. 2007; Nasrin et al. 2008; Sukiran et al. 2009). Moreover, the Malaysian Innovation Agency published a National Biomass Strategy 2020 and 1Malaysia Biomass Alternative Strategy (1MBAS) to align a strategy on capitalization EFB into high-value-end product (AgensiInovasi Malaysia 2011). At a commercial level, the courage and efforts by few companies in Malaysia to divert EFB fiber into biocomposites (Tiang Siang mill and Soon Seng MDF), packaging products (SabutekSdn. Bhd and EcofutureBerhad), composting, and power generation (Kina Biopower, Seguntor Bioenergy and Sahabat biomass power plant) should be praised. Nonetheless, they had halted their projects using EFB after facing many hurdles such as consistency of the materials quality and the consecutive interruption that suppressed the operating system (Mekhilef et al. 2011). The root cause of all these projects being abandoned is due to the inability of EFB to serve as a functional raw material. The current technologies being applied to convert EFB into their products are similar to those of conventional wood processing flow without any modifications. They may overlook the fact that EFB fibers have vast variations in terms of the basic characteristics in comparison to the wood, and this may hinder the quality of products made from EFB. Consequently, this could probably lead to the failure of these projects.

The following sections discuss about the issues of using EFB by the three major industries which include panelboard, bioenergy, and biochemical in Malaysia. Attention has been drawn on relating the EFB characteristics and quality with the impediments faced by those industries during applications and processes of EFB.

Panelboard

Companies in Malaysia had tried to utilize EFB fiber as wood substitute to produce panelboards such as particleboards, fiberboards, and wood–plastic composites for many years. Nevertheless, there are still numerous issues that decelerate the commercialization of EFB composite products. The major contributors to the fruitless application of EFB in wood composite industry are due to the presence of a high amount of ash, oil, and grease in the EFB fibers. The ester components in the oil may affect coupling efficiency between fiber and polymer matrix during panelboard production (Rozman et al. 2001). This may explain why panelboard made from EFB is reported to be inferior when compared with the boards produced from wood (Ratnasingam et al. 2007; Norul-Izani et al. 2012). Besides, huge numbers of silica bodies that attach between EFB fibers cause a high degree of abrasiveness on the cutting tools. Compared to rubberwood particleboard, EFB particleboard is almost two times more abrasive in terms of cutting tool efficiency (Ratnasingam et al. 2008; Norul-Izani et al. 2013) and results in higher tooling cost. Nonetheless, EFB may be suitable for fiberboard production as the silica bodies can be dislodged during the refining process, while low lignin content in EFB will ease the pretreatment process with less chemical usage.

EFB fibers in this study were considered to have low Runkel and slenderness ratio as mentioned in the earlier section. Thin cell wall of EFB is suitable for fiberboard production as they offer more surface contact and better fiber bonding (Dutt et al. 2005). Slenderness ratio of EFB is suitable for producing fiberboard with the acceptable value which is more than 33 (Xu et al. 2006). Besides that, EFB is categorized in the rigid fiber group with elasticity ratio in the range of 30–50. Fibers with high flexibility ratio are said to be supple, crumple readily, capable of creating good surface interaction, and fiber-to-fiber bonding (Benazir et al. 2010).

The majority of the EFB fiber bundles have low specific tensile stress (Fig. 2). This is due to homogeneity and imperfections of the EFB fiber bundles (estimated as about 25 % of vascular bundle and 75 % of fiber volume-to-volume ratio) that give rise to mechanically weak points found in the fiber structure. The inhomogeneity is related to the thin cell wall of vascular bundle and thicker cell wall of fiber. During the tensile test, the vascular bundle is easy to break compared to the fiber with thicker cell wall.

Particleboard made from EFB is hard to achieve the targeted density by using the similar formula to produce board from wood. This is due to the high vascular bundle volume ratio to the fibers (naturally spongy characteristic) with extremely high compaction ratios and volume reduction during the board pressing processes. On the other hand, the large area of vascular bundles may explain why particleboard made from EFB has a high hygroscopic range. As a material with high water absorption properties, dimensional stability was one of the issues in applying EFB to furniture industry. Dimensional stability is defined as the ability to maintain the original intended dimensions when influenced by a foreign substance. The dimensional instability of wood composites not only concerns the dimensional properties of the board but also affects its strength, screw-holding resistance, durability, and edge tightness.

Solid Biofuel (for the Production of Heat and Electricity)

Combustion efficiency of fuels in boilers necessitates considering fuel ash content and calorific values. A tonne of EFB is estimated to generate about 1330 kWh of electricity (Asia Biomass Office 2009). However, several plants using EFB as main biomass fuel have experienced operation losses due to its poor physical properties such as lower electricity production than expected, high wear and tear on moving part in contact with EFB, and also incomplete combustion. All these miserable experiences of using EFB may be due to the inherent property such as undesirable ash-forming elements and special anatomical characteristics as revealed in result.

The EFB has relatively high ash content consisting of alkali metals compounds such as potassium, calcium, magnesium, phosphorus, and silica. These eutectic compounds with low melting points (below 700 °) will create sticky and soft ash which cause reduction in heat rates and accelerated corrosion in the operation system (Lindstrom et al. 2007). From the experience of Kunak Bio Energy Project in Malaysia, the presence of these alkali metals in EFB causes the equipment to undergo significant wear and tear. This results in an increase in maintenance cost. Nonetheless, most of its inadequacy can be prevailed through suitable treatments. Recent studies have shown that additives such as kaolin and dolomite are capable of reducing sintering problems by raising the melting point of the ash (Steenari et al. 2009). This transformation gives a significant increase in the ash melting temperature of 1100 ° and above. Leaching methods have also been proven effective in removing some of the major elements from biomass that caused detrimental effects (Davidson et al. 2002).

High hygroscopic range in EFB is also an undesirable property in solid biofuel industry. The benefits of drying the fuel before combustion have been stressed as moisture will decrease the heating value of fuel (Chin et al. 2012). Torrefaction is a thermal pretreatment process by subjecting wood to temperature levels between 200 and 300 ° in the absence of oxygen. This pretreatment has been recommended as an efficient way to enhance solid biofuel properties by water removal, reduction of the hygroscopic range, and increased grindability (Arias et al. 2008; Yan et al. 2009; Chin et al. 2013). Combining the torrefaction and leaching treatment is considered an interesting option for biomass pretreatment of herbaceous biomass in the solid biofuel industry for heat and electricity (Dai et al. 2008).

Biochemical Derivatives (Using Hydrolysis and Fermentation to Make Fuels and Chemicals)

Biochemical conversion entails breaking down biomass to make the carbohydrates available for processing into sugars, which can then be converted into liquid biofuels and bioproducts through fermentation. Carbohydrates and simple sugars from biomass can be used to produce many biochemicals such as bioethanol and other alcohols, alkanes, single-cell protein, biodiesel, and many more (Haros and

Suarez 1999; Chin et al. 2010, 2011; H’ng et al. 2011). Key challenges for biochemical conversion include the considerable cost and difficulty involved in breaking down the tough, complex structures of the cell walls in cellulosic biomass. Lignin is a protection layer to the carbohydrates from chemical and physical damage (Saheb and Jog 1999). With a low percentage of lignin, EFB would undergo the conversion process more easily and with the utilization of lower amounts of chemicals. The EFB is believed to have the potential for converting carbohydrates into different biochemical with the high content of cellulose and hemicelluloses (about 75 %). Biochemical conversion uses biocatalysts, such as enzymes, in addition to heat and other chemicals, to convert the carbohydrate portion of the biomass (hemicellulose and cellulose) into an intermediate sugar stream (Tay et al. 2013). These sugars are intermediate building blocks that can then be fermented or chemically catalyzed into a range of advanced biofuels and value-added chemicals. The conversion process by microorganism (fermentation) to break down the carbohydrates and reducing sugars can be separated into anaerobic digestion and aerobic digestion. However, conversion of biochemicals from biomass especially EFB has not been perfected yet.

As stated in the results above, EFB contain a high content of inorganic materials, and this may complicate the chemical treatment and bioconversion process of the EFB fibers. The inorganic materials substance might react with the chemicals used for treatment or result in inhibitory effect on the microorganism which will create undesirable results. To provide higher surface area for chemical reactions and microorganism growth, the EFB should undergo shredding or some other particle size reduction process through chemicals or enzymes. Similar to other industries discussed above, high silica content in EFB will create tool wears; therefore, EFB should be pretreated to remove the silica and other inorganic compounds before being further processed in each of the industry.

Conclusion

This chapter has scrutinized deeply the characteristics and qualities of EFB fiber. Various advantages of the EFB fibers have been mentioned, but they also show many weaknesses. Despite a concerted effort made by academia, government, and also the private sector, hitherto the commercialization of EFB fibers is still in its infancy. Understanding the fundamental characteristics of this raw material is the key factor for unlocking the inner potential of EFB for satisfactory use at the industries and making it economically viable. Nevertheless, most of its inadequacy can be prevailed through suitable treatments before diverting them into higher-value downstream products. There is reason to believe that by understanding the limitations and benefits of EFB, the industries should have a thorough consideration in producing a suitable treatment system for EFB. This might be a critical success factor in deploying them. The treated EFB can be expectedly beneficial to the local industries by providing a stepping stone for them to push towards commercialization if proper treatment is carried out.

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Extraction of Lignin from Biomass for Biofuel Production

Sameen Ruqia Imadi and Alvina Gul Kazi

Abstract With the increasing population on planet Earth, the demand for the production of fuel and energy is increasing day by day. Second-generation biofuels are much more efficient as compared to first-generation biofuels as they use agricultural residues and waste products as biomass for the generation of biofuel. These biofuels need huge energy, time, cost, and potential for pretreatment processes. As the biomass is mainly composed of cellulose, lignin, and hemicelluloses, it needs to be treated for removal and extraction of hemicelluloses and lignin, respectively. Biofuel generation is dependent on the quality of biomass used. Different input biomasses for secondary fuel generation include wheat straw, barley straw, sugarcane bagasse, rapeseed residues, switchgrass, and lignocellulosic waste products. This chapter discusses second-generation biofuels, extraction methods of lignin from biomass, and advantages and limitations of lignin extraction from biomass. As soon as the oil refineries are replaced by biorefineries, societies will be benefited by switching from hydrocarbon feedstocks to renewable carbohydrates as a source of energy and biofuels. Finally, the chapter intends to look forward into the future research on biotechnological fuel development.

Keywords Lignocellulose · Hemicelluloses · Second-generation fuel · Switchgrass · Sugarcane bagasse · Bioethanol · Bioprocess technology

Introduction

In recent years, much interest and attention have been diverted to biomass, as it is seen to be a potential agent for the production of biofuel. Biomass can act as a sustainable feedstock that has the ability to diminish the use of fossil fuels for energy

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production (Alonso et al. 2010). Reduction in the use of fossil fuels reduces the emission of carbon dioxide, sulfur dioxide, nitric oxide, and heavy metals. It is now a global effort to develop sustainable energy systems which are based on biomass feedstock (Naik et al. 2010). Biomass from herbaceous plants can be said to be the largest and a renewable source for the production of bioproducts and biofuels (Buranov and Mazza 2008).

Lignin is a material found in the secondary wall of plants. This material is a phenolic polymer and it is the cause of recalcitrance of biomass for industrial processing. Lignin is a necessary agent to be present in second-generation bioenergy crops as it has to protect the plants and perform its functions. However, this lignin has to be degraded or extracted from plants in pretreatments for the generation of bioenergy (Vanholme et al. 2012). Wheat straw can be used for the production of bioethanol, bio-hydrogen, and biogas. Wheat straw is hydrothermally liberated to cellulose-rich fiber fraction and hemicellulose-rich liquid fraction. Enzymatic hydrolysis of cellulose yielded 0.41 g of ethanol per gram of glucose. Bioethanol and bio-hydrogen effluents are further used for the production of methane (Kaparaju et al. 2009).

Biodiesel production is currently performed with the use of biomass from soya beans, rapeseeds, and palm oils. However, restaurant wastes, beef tallow, and yellow grease can also be used for biodiesel production (Demirbas 2011). Hybrid poplars are one of the fastest growing trees in demand in the world as a prominent feedstock for biofuel and some other value-added products (Sannigrahi et al. 2010).

Lignocellulosic biomass constitutes of cellulose polymers, hemicelluloses, and lignin bound in a complex structure (Agbor et al. 2011). As the amount of lignin in biomass decreases, the efficiency of biofuel production increases. This was proved in an experiment conducted in *Sorghum*, in which the lignin component was reduced due to change in genes. This results in the conversion of cellulose to bioethanol in large amounts (Dien et al. 2009). Carbon produced from lignocellulosic biomass can be converted to fuels and chemicals in an easy and sustainable way (Hicks et al. 2011).

Biofuel production from a certain crop or plant needs research on many characters and features of that plant. These features include elemental composition, chemical composition, biopolymer constitution, and biopolymer structure (David and Ragauskas 2010). Multiple biofuel production from a certain plant is also seen to increase the efficiency of plant for the production of biofuel. This was observed in an experiment where wheat straw was used to produce biogas, bio-hydrogen, and biofuel. This resulted in the generation of a large concentration of fuel as compared to monofuel produced from the same wheat straw (Kaparaju et al. 2009).

Lignocellulosic Biomass

Biofuels are obtained from different lignocellulosic materials, which include wood, forest residues, and sometimes agricultural residues. These lignocellulosic materials have a potential to be used as a valuable substitute to gasoline, one of the major fuels used commercially. Biomass can be converted to biofuels and other compounds by the application of many physiochemical structural and compositional factors (Kumar et al. 2009). The biomass residues having lowest lignin content are most suitable for biofuel production. In the above context, potential candidates for bioenergy production include pinewood, wheat, and flax (Naik et al. 2010).

Lignocellulosic biomass has been identified as one of the prime sources of biofuels and value-added products. Lignocelluloses are referred as agricultural, industrial, and forest residuals which account for the majority of the total biomass residues present on the globe. Bioconversion of lignocelluloses to biofuel is dependent on different physical parameters which include pH, temperature, adsorption, and some chemical factors which include nitrogen, phosphorus, phenol compounds, and some other inhibitors (Kumar et al. 2008).

Second-Generation Biofuel

Second-generation biofuels are fuels produced from lignocellulosic biomass. They have been of great importance and much emphasis is paid on their research and production due to the identified limitations of first-generation biofuels (Sims et al. 2010). It is an agreed fact that biofuel technologies must be more efficient in terms of net greenhouse gas emission reduction. Most of the first-generation biofuels do not meet this concern, but second-generation biofuels have been monitored in a way to deal with this concern. Second-generation fuels are being prepared by forest and crop residues, energy crops, municipal wastes, construction wastes, with reduced net carbon emission (Antizar-Ladislao and Turrion-Gomez 2008).

Cost may act as a major barrier in the production of second-generation biofuels. Depending upon the type of biofuels, feedstock price and conversion cost of biomass, the cost of second-generation biofuel production may increase the actual cost of commercial gasoline (Carryquiry et al. 2011). Second-generation biofuels are more energy efficient as compared to first-generation biofuels (Zabaniotou et al. 2008).

Biomass Used

Sugarcane Bagasse

Sugarcane is the principal crop cultivated in tropical regions. Sugarcane generates around 280 million t of biomass which includes bagasse and leaves. Sugarcane bagasse has been explored for its ability for production of second-generation fuels and value-added products such as xylitol, enzymes, organic acids, and single-cell proteins (Chandel et al. 2012). Sugarcane bagasse can be used as an input biomass for biofuel production. It is observed that biomass conversion process for sugarcane bagasse is slightly efficient in energy and is also seen to offer advantages in terms of diversification and variety in products. Biofuel produced from sugarcane biogases is also seen to show a lesser emission of greenhouse gases (Walter and Ensisnas 2010). Sugarcane bagasse produces biofuel which leads to better economic results (Dias et al. 2012).

Sugarcane bagasse can be used as a fuel in bioethanol production for its functions of providing heat and power for the bioprocess plant. Pentoses and lignin are also obtained as by-products of this mechanism. Second-generation bioethanol production from sugarcane bagasse may find competition with electricity production as both processes need lignocellulosic fraction of sugarcane (Dias et al. 2011).

Rapeseed Residues

Rapeseed residues are used for the production of second-generation biodiesel. Fast pyrolysis of rapeseed residues at high temperature, followed by fixed bed air gasification, results in the production of biodiesel with lignin as the by-product (Zabaniotou et al. 2008).

Switchgrass

Switchgrass can also prove as a feedstock for biofuel, as it is perennial grass which has high productivity, adaptability, and potential ease of integration into agricultural operations. These characters when present in any plant make it a promising and strong agent for biofuel (David and Ragauskas 2010). Switchgrass is a perennial cellulosic feedstock for second-generation biofuel. This grass when planted on croplands, which are currently used for first-generation biofuel production, results in an increase in ethanol production up to 82 % and 4 % increase in grain for food, with a reduced nitrogen leaching and greenhouse gas emission (Davis et al. 2012).

The use of switchgrass for biofuel production is highly dependent on biomass yield, elemental concentration, carbohydrate characterization, and total synthetic gas production, which act as indicators for biofuel quality. Biofuel quality is determined by direct combustion, ethanol production, and gasification system for the generation of energy (Adler et al. 2006).

Barley and Wheat Straw

Barley straw is presently considered as a potential lignocellulosic feedstock for the production of second-generation biofuels mainly bioethanol. Barley straw can act as an alternative to starch or sugar containing feedstock. Ethanol yield of nearly 70 % can be obtained as a result of the use of barley straw (Garcia-Aparicio et al. 2011).

Wheat straw is also used as a biomass for second-generation fuel production. The use of wheat straw requires a comprehensive knowledge of plant intake feedstock composition (Lomborg et al. 2010). In an experiment, wheat straw hydrolysate was used for the production of biofuel. Dilute acid pretreatment and enzymatic hydrolysis of wheat straw leads to the generation of hydrolysate with sugar. Wheat straw hydrolysate showed good fermentability with a result of hydrogen production up to 82–97 % (Panagiotopoulos et al. 2013).

Biofuel Produced

Bioethanol

Bioethanol is considered one of the most sustainable and renewable fuels used, due to its environmental and economical benefits. This fuel has been produced by lignocellulosic biomass. Lignocellulosic biomass is available globally; hence, it is the most promising feedstock for bioethanol production (Alzate and Toro 2006). Bioethanol produced from sugarcane bagasse is seen to be economically efficient as compared to first-generation biofuels, especially when it is produced with advanced hydrolysis technologies and pentoses fermentation (Dias 2012). Increasing amounts of bioethanol are being produced for meeting the demands of public. Bioethanol production may counteract the depletion of fossil fuels resources and may escalate oil prices around the globe. Bioethanol, as fuel, can be used in vehicles, transportation, and in the chemical industry. This fuel has been produced by renewable carbon resources and results in less amount of greenhouse gas emission (Rass-Hansen et al. 2007).

Feedstock used for bioethanol production is efficient as it does not threaten food security and cause minimal loss to soil carbon and natural habitats. Waste management systems are also seen to flourish as a result of bioethanol production because these wastes are used as biomass for the bioprocess technology. Environmental pollution can be minimized by bioethanol production; hence, it can be said that this fuel is a sustainable fuel (Sivakumar et al.2010).

Biodiesel

Biodiesel properties can be equated to the world's best existing diesels. Biodiesel is sulfur-, oxygen-, nitrogen-, and aromatic-free and has a very high cetane number (Rantanen et al. 2005). Biodiesel can be produced by an oil seed plant, *Jatropha curcas*. Biodiesel has been accepted as a sustainable alternative to the present commercial diesel used (Findlater and Kandlikar 2011).

Biogas

Biogas produced from biomass comprises of different types of gases, mainly methane. Biogas production can be achieved by crop plants including maize. Biogas potential is strongly dependent on plant species and on the pretreatment technique followed. When drying is used as a pretreatment, 80 % yield of biogas is decreased. Methane contents of biogas are normally 7–13 % higher when obtained from algae as compared to maize (Mussgnug et al. 2010). Biogas production can be increased from digestion of organic residues and energy crops or it can be obtained from by-products of bioethanol and biodiesel production. Biogas possesses several advantages over other biofuels in the environment as well as from the resource efficiency perspective. Biogas may in future prove to be a cost-efficient biofuel with increased economic competitiveness as a vehicle and transport fuel (Borjesson and Mattiasson 2008).

Biogas can be produced from the anaerobic digestion of a wastewater treatment plant. This biogas is further needed to be desulfurized for optimization before its possible use as fuel (Osorio and Torres 2009).

Lignin Extraction from Biomass

Pretreatment refers to a process that converts lignocellulosic biomass from its native form, which shows hindrance to cellulose enzyme systems to a form which does not imply any barrier for cellulose hydrolysis. The converted form shows an effective cellulose hydrolysis. Pretreatment methods involve physical methods, chemical methods, and biological methods (Zheng et al. 2009).

Pretreatment of biomass including wood and residues is performed. Pretreatment aims to change the physical and chemical structures of lingocellulosic biomass which results in an improvement of its hydrolysis rates. When biomass is accessible to hydrolysis, the efficiency of biofuel production increases. Due to these reasons, pretreatment is a necessary step for biomass conversion. Different methods for pretreatment have been used (Kumar et al. 2009). The goal of any pretreatment technology is to alter and remove structural and compositional impediments to increase conversion to fermentable sugars (Mosier et al. 2005). Methods for pretreatment and extraction of lignin are mentioned in Fig. 1.

Chemical Pretreatment Methods for Lignin Extraction

Alkali Treatment

Sorghum biomass treated with dilute ammonium hydroxide results in an increase in ethanol yield. Ethanol conversion yields observed after the ammonium hydroxide

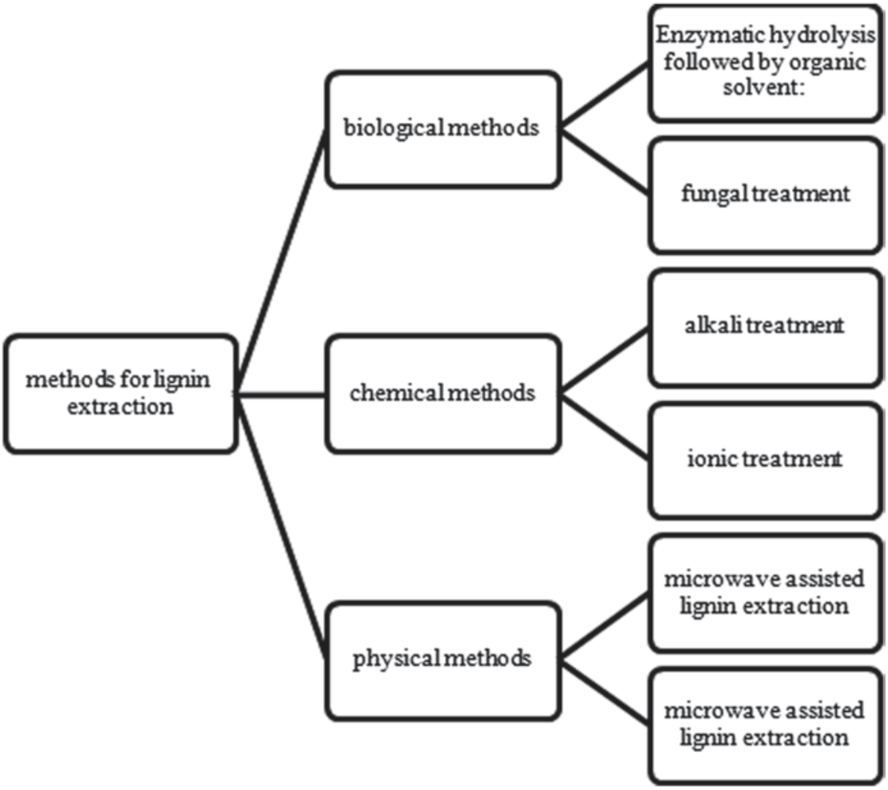

Fig. 1 Methods for lignin extraction

treatment were observed to be 98 mg of ethanol per gram and 113 mg of ethanol per gram dry biomass (Dien et al. 2009). The main effect of alkali pretreatment or alkali swelling is dissolving hemicelluloses and extraction and alteration of lignin structure which provides an improved accessibility of cellulose for hydrolytic enzymes (Hendriks and Zeeman 2009). Two percent of alkaline hydrogen peroxide used to pretreat cane bagasse biomass proved that 50 % lignin content in lignocellulose is solubilized under environmental conditions of 30 °C for 8 h. This results in an increase in the cellulose content by up to 42 % in original cane bagasse and up to 75 % in oxidized pulp of cane bagasse (Azzam 1989).

Sodium hydroxide applied over corn stover showed a disruption in the crystalline structure of corn stover and removal of lignin content within 1 h of treatment (He et al. 2010). The application of sodium hydroxide in high concentration for a long period of time is seen to reduce lignin concentration in biomass by 85.8 % at 121 °C, 77.8 % at 50 °C, and 62.9 % at 21 °C temperature. This results in an increased sugar production and biofuel yield (Xu et al. 2010).

Ionic Treatment

Lignocellulosic biomass is very hard to deal with biotransformation in both the microbial and the enzymatic way. For this purpose, pretreatment is a necessary aspect. It is observed that the pretreatment of wood flour with an ionic liquid, 1-ethyl-3-methylimidazolium acetate, results in easy extraction of lignin as it changes the crystalline nature without solubilization. Extraction of lignin by up to 40 % results in a decrease in crystalline index up to 45. Decrease in crystalline index is associated with more than 90 % cellulose hydrolysis in wood flour (Lee et al. 2009).

1-Ethyl-3-methylimidazolium acetate has been used for the extraction of lignin from triticale, wheat straw, and flax shives. In triticale straw, this ionic chemical treatment showed optimum results of 52.7 % insoluble lignin at 250 °C temperature for 90 min. The extraction of lignin by ionic liquids is a potentially efficient technique for the utilization of lignocellulose (Fu et al. 2010). Pretreatment of corn stover by the same ionic liquid is seen to extract 44 % lignin content of biomass (Wu et al. 2011). A highly efficient method for extraction of lignin from lignocellulosic biomass is the protic ionic liquid (PIL) method. It is an inexpensive method in a way that after the pretreatment step, PIL can be recovered using a distillation mechanism leaving separated lignin (Achinivu et al. 2014).

Room-temperature ionic liquids are emerging as a green solvent for lignocellulosic biomass for pretreatment. Room-temperature ionic liquids are shown to disrupt the three-dimensional network structure of lignin, which is associated with high yields of fermentable sugars that are further used for biofuel production in enzymatic hydrolysis (Mora-Pale et al. 2011). Cholinium amino acid ionic liquids are also a potential candidate for the pretreatment of lignocellulosic biomass. These ionic liquids have been demonstrated to be one of the excellent pretreatment solvents. Cholinium amino acid ionic liquids present an environmental friendly way to pretreat lignocellulose for fermentable sugar production and utilization of biomass (Hou et al. 2012).

Biological Pretreatment Methods for Lignin Extraction

Enzymatic Hydrolysis Followed by Organic Solvent

Enzymatic pretreatment of lignocellulosic biomass is shown to give positive results. Enzymatic hydrolysis is conducted at two cellulose loadings, 15 filter paper units per gram glucan and 3 filter paper units per gram glucan, with and without bovine serum albumin blocking lignin absorption sites. After this, organic solvent-based lignocellulose fractionation is performed. This results in the disruption of cell wall structure resulting in the access of cellulose to cellulose by up to 16-fold (Rollin et al. 2011).

Fungal Treatment

Pretreatment of lignocellulosic feedstocks, *Prosopis juliflora*, and *Lantana camara*, with a white rot fungus showed that delignification takes place under these conditions. *P. juliflora* is seen to be delignified by the use of white rot fungi by up to 11.89 % whereas delignification results for *L. camara* are observed to be 8.36 % after a period of 15 days. As the fungal treatment is combined with an addition of dilute sulfuric acid, sugar release is increased by 21.4–42.4 % and lignin content is further decreased (Gupta et al. 2011).

Advantages of Lignin Extraction

Lignin extracted during the pretreatment process of biomass conversion can be burned as boiler fuel to power the conversion process of biomass and is able to generate extra electricity which can be exported (Wyman 1994). Lignin is obtained as a by-product in the bioethanol production by sugarcane bagasse. It can be used as a fuel increasing the amount of surplus bagasse (Dias et al. 2011).

Limitations of Lignin Extraction from Biomass

High net energy gain is obtained as a result of use of lignocellulosic biomass for the production of biofuel (Yuan et al. 2008). But lignin extraction involves pretreatment processes that are highly expensive (Sticklen 2008). Lignin extraction is necessary because lignin is a hydroxyphenylpropanoid which consists of syringyl, guaiacyl, and p-hydroxyphenyl units which are derived from sinapyl, coniferyl, and p-coumaryl alcohols. Compositional symmetry and ratios of these three moieties in lignin may vary slightly or significantly. This inherent complexity and heterogeneity of lignin in structure and composition makes it difficult to develop a technology that is able to process feedstock with low cost. Hence, lignin extraction needs a procedure to disrupt the whole structure and composition of molecule which is extremely non-economical (Simmons et al. 2010).

Conclusion and Future Prospects

In the recent past, the research on biomass as a sustainable and potent agent for production of biofuel and bioethanol has gained a lot of interest and has managed to retain the attention of scientists. Biofuel has gained interest as its production is coupled with less greenhouse gas emission and sustainability (David and Ragauskas

2010). Biofuels provide a route to avoid global political instability and environmental degradation, which is an effect of petroleum. Currently, biofuel has been produced on large scale but it can only meet limited needs and demands. A promising substitute to lower biomass concentration is the conversion of cellulosic biomass (Sticklen 2008).

The future in bioenergy is ready to pave a way for reaching the goals to replace petroleum-based energy consumption and transportation with an alternative to reduce carbon dioxide emission in the long run. It also leads to environmental and economical sustainability of planet (Yuan et al. 2008). To make a substantial contribution to the energy portfolio, biofuel production needs to grow substantially in the near future by at least tenfold or more (Ragauskas et al. 2006).

Biofuels are seen as a common solution to multiple policy challenges posed by energy insecurity, climate change, and falling farmers' income. Continued research and investment is required in this field within the coming decades so that the biofuel industry can grow on steady rates and may encompass both first- and second-generation technologies that meet agreement on environmental, sustainable, economic, and political goals (Sims et al. 2010).

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Biomass Pellet Technology: A Green Approach for Sustainable Development

Bisma Malik, Tanveer Bilal Pirzadah, Sheikh Tajamul Islam, Inayatullah Tahir, Manoj Kumar and Reiaz ul Rehman

Abstract The supply of sustainable or green energy is the main challenge that mankind will face over the coming decades, especially because of the need to address climatic changes. Biomass being abundantly available in nature can make a substantial contribution to cater future energy demands in a sustainable way. Currently, it is the largest universal contributor of green energy and has significant potential to expand in the production of electricity, heat and fuels. However, handling as well as direct combustion of biomass is restrained due to peculiar properties of this kind of fuel. As raw biomass possesses low density (30–50 kg/m^3) and high moisture content that limits its usage for energy purposes and it needs to be densified prior to its use. The compact and densified biomass possess a high magnitude of density as well as low moisture content which in turn helps to dwindle technical limitations associated with storage, handling and transportation. One immediate solution is the pelletisation of raw biomass that enhances its energy efficiency and enables the competition of biomass with other types of fuels. Besides, biomass pellet technology has gained a rapid momentum in many European countries. The future of the biomass pellet industry is greatly influenced by various environmental, economic, political as well as social aspects that create a multiplex relation among suppliers,

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producers and consumers. Therefore, the main aim of this chapter is to develop a comprehensive review of biomass processing that involves pellet production technology, energy efficiency of biomass pellet, current status, opportunities and challenges for the development of biomass pellet market.

Keywords Biomass · Pellets · Pelleting technology

Introduction

The term biomass refers to all materials derived from plants and animals. It was considered as the cheapest source of energy ever used by humans. Biomass can be used in various ways such as food, timber products, fibre, fertiliser, chemicals or energy. In the context of energy, biomass is often used to mean plant-based material, but biomass can equally apply to both animal- and vegetable-derived material and waste. Biomass is considered as the third largest source of energy followed by petroleum resources in the world (Bapat et al. 1997). These renewable energy resources not only reduce greenhouse gas (GHG) emissions but also help to reduce the dependency on foreign oil. Biomass plays an important role in the production of "green" energy. Tomasz and Zenonin (2012) reported that biomass contributes about 68 % of the total energy generated from renewable resources in the European Union (EU) in 2009. During the nineteenth century, biomass predominated global energy consumption. Even though increased fossil-fuel use has prompted a reduction in biomass consumption for energy purposes over the past 50 years, biomass still provides about 1.25 billion t of oil equivalent or about 14 % of the global annual energy consumption (Zeng et al. 2007). Out of the total global primary energy (230 exajoules), about 56 exajoules (one fourth of the global primary energy) are utilised for agricultural purposes (WEC 1994). It is well accepted that improved consumer energy efficiency is an important and cost-effective option for reducing global GHG emissions (Laitner 2013). Referring to earlier International Energy Agency (IEA) studies, Stern (2007) noted that energy efficiency has "the potential to be the largest single source of emissions savings in the energy sector" by 2050, a view further endorsed by the IEA (2012). However, the diffusion of energy-efficient technologies is relatively slow because energy technologies tend to be long-lived, capital intensive interlocked with other technology networks and have high learning needs. The possibility of accelerating the uptake of energy-efficient technologies is widely seen as a challenge in economics, innovation studies and energy systems (Chai and Yeo 2012). The main biomass energy resources include agricultural residues, municipal solid waste (MSW), forest residues and energy crops. Biomass being attractive and abundantly available in nature needs proper exploitation as it is a renewable and sustainable source of energy. In 2010, biomass accounted for about 12.2 % of global primary energy consumption, which makes up 73.1 % of the world's total renewable energy (Global Status Report 2012) and is the fourth largest source of energy followed by fossil fuels (oil, coal and natural gas; Fig. 1).

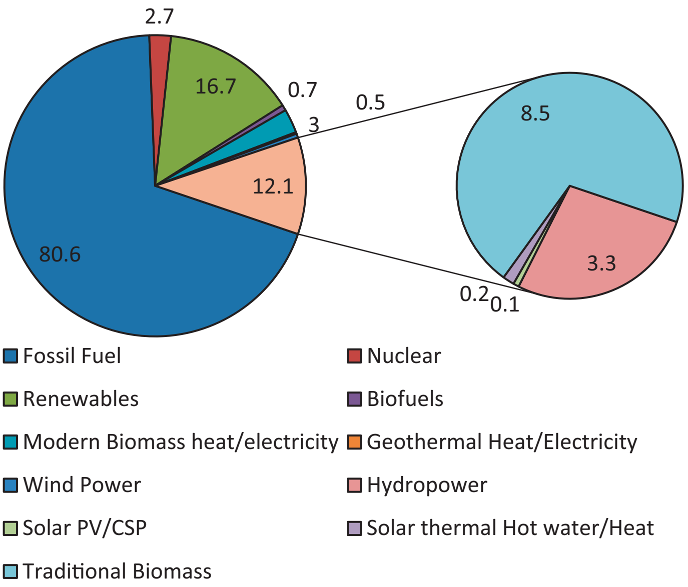

Fig. 1 Global primary energy consumption by source in 2010 (Total consumption = 8823 Mtoe = 369 EJ)

In developing countries, biomass plays an even more significant role in the energy sector, especially as the main source of energy for cooking in the domestic sector and thermal energy for many small and medium industries and commercial establishments (Fig. 2) as it reduces the net GHG emissions when compared

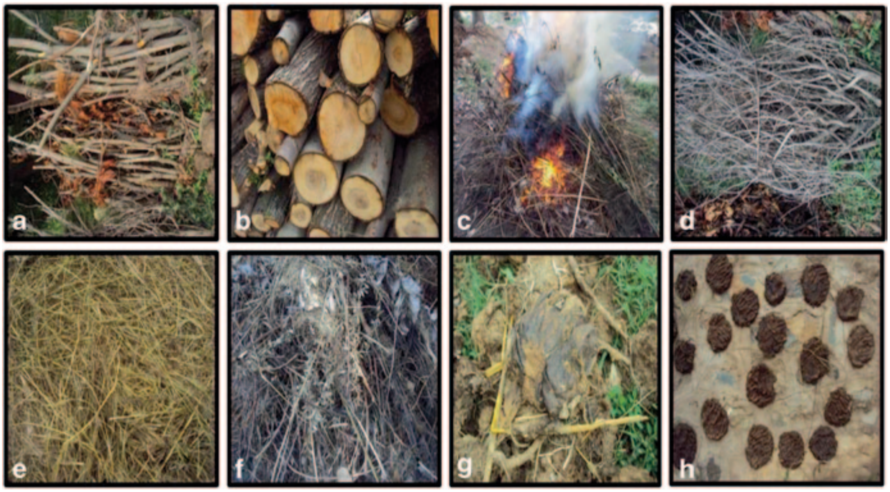

Fig. 2 Wood biomass extracted from pine and Abes forests for cooking purposes(*2B*)-Raw material for preparation of biomass pellets(*2 C*)-Traditional way of using biomass for charcoal preparation(2D-G)-Loose waste agricultural biomass(*2H*)-Classical way of drying cow dung cakes

to fossil fuels and that is why green energy is considered as a clean development mechanism (CDM; Li and Hu 2003). Currently, the cheap sources of biomass are the waste products from wood and agronomic practices; however, the supply of these green energy resources is restricted. To combat these restrictions, countries around the globe have developed various energy programmes in which efficient bioenergy crops can be utilised for the production of pellets and briquettes with consistent quality (high energy density, low moisture content and homogeneous size and shape). Besides short-rotation coppice (SRC) programmes are also run by various governments and other agencies. Previously, biomass resources such as forest and sawmill residues were used for energy purposes but their energy efficiency was low due to high moisture content and low density. Nowadays, with the evolution of the latest technologies, these energy resources can be utilised in a more sustainable manner, viz. densified into pellets. Biomass pellets are cylindrical, 6–8 mm in diameter and 10–12 mm long. Currently, wood pellets are the largest bioenergy resource that have gained worldwide attention in the international market; in terms of traded volume (about 4 million t), they can be compared to biodiesel or bioethanol (Heinimö and Junginger 2009). The consumption of wood pellets has grown rapidly over the past 10 years, leading in Portugal and a little for all over Europe, to the installation of several large-capacity production plants, which exports 90 % of its capacity to northern Europe markets, mainly for the production of electricity and residential district heating. In the USA, most of the pellets are bagged and marketed for domestic purposes such as pellet stoves. Countries like Canada export wood pellets produced from sawdust and wood shavings to European countries (Sweden and Denmark). Although the production of pellets and briquettes requires additional energy input, resulting in increased fuel cost (Mani et al. 2006a), the worldwide pellet market (especially the EU) has a trend of persistent rise. The biomass pellet industry has gained a rapid momentum over the past decade. In order to commercialise the biomass pellets at a large scale, the main focus of various manufacturers is to develop large-scale industries with an annual production capacity more than 100,000 t. There was only one US pellet manufacturer in 2006 who was capable of generating more than 100,000 t of pellets/year and the number of manufacturers with a capacity more than 100,000 t of production increased threefold between 2010 and 2012. The USA and most of European countries are the largest markets for biomass pellets. In the northern USA, the largest pellet production remains for residential and district heating systems. Nevertheless, the industry landscape has changed drastically with the current pellet production expansion in the southern region. Hall et al. (1992) reported that the USA and Sweden procure about 4 and 13 % of their energy, respectively, from biomass and Sweden is implementing initiatives to phase out nuclear plants, reduce fossil-fuel energy utilisation and enhance the use of bioenergy (Björheden 2006).

One of the major drawbacks of biomass for energy purposes is its low bulk density for agricultural straws and grasses (80–100 kg/m^3) and for woody biomass, like wood chips (150–200 kg/m^3; Mitchell et al. 2007). Due to the low bulk density of biomass, it is difficult to handle, store and transport. Besides, it also became a hurdle in coal cofiring technology by reducing burning efficiencies. Therefore, biomass should be densified in order to enhance its energy efficiency by increasing its density about tenfold. Commercially, densification of biomass is performed using pellet mills, other extrusion processes, briquetting presses or roller presses in order to help overcome feeding, storing, handling and transport problems. Densification technologies available today have been developed for other enterprises and are not optimised for a biomass-to-energy industry's supply system logistics or a conversion facility's feedstock specifications requirements. In the recent past, there has been renewed interest in biomass energy resources and technologies, especially as an alternative for fossil fuel systems. Main reasons for this include the following:

- Significant potential, as well as the social, economic and environmental benefits of the utilisation of biomass as a sustainable source of energy, especially in the context of present energy and environment crises arisen from extensive use of fossil fuels
- Progressive increase in fossil fuel prices leads to high cost of energy in many applications and biomass is the main alternative source of energy that could potentially replace almost all categories of fossil-fuel-based technologies/applications
- Technological developments related to energy conversion as well as resource management promise the application of biomass at lower cost and with higher conversion efficiency than was possible previously
- Some biomass resources are presently considered to be waste materials and conversion to energy is one of the effective ways of managing them, while satisfying a variety of local energy needs productively

However, these main issues are not the only stimuli. Biomass is also an indigenous energy source available in most countries in a variety of forms such as fuelwood, wood residues, agricultural residues, animal waste, significant portion in MSW and market waste, and its utilisation may diversify the fuel supply in many situations which in turn will contribute to achieve much-needed energy security. Biomass can generate employment, and its use will contribute to being an additional income for the local people. The development of biomass resources creates wide opportunities for the application of indigenous knowledge, inventions and innovations, thus contributing to the establishment of a knowledge society, a much-needed prerequisite for sustainable development.

Sources of Biomass

Biomass reserves are evenly distributed in a variety of forms. Among numerous biomass resources, wood is still considered as the largest source of bioenergy feedstock today. These include food crops, energy crops, herbaceous plants/grasses and woody plants, and residues from timber processing, agriculture or forestry (Fig. 3).

The supply of these biomass resources mainly comes from traditional plantation, natural forests, forest plantation, home gardens and other agricultural lands. Further, oil-rich algae, animal wastes and the organic component of municipal and in-

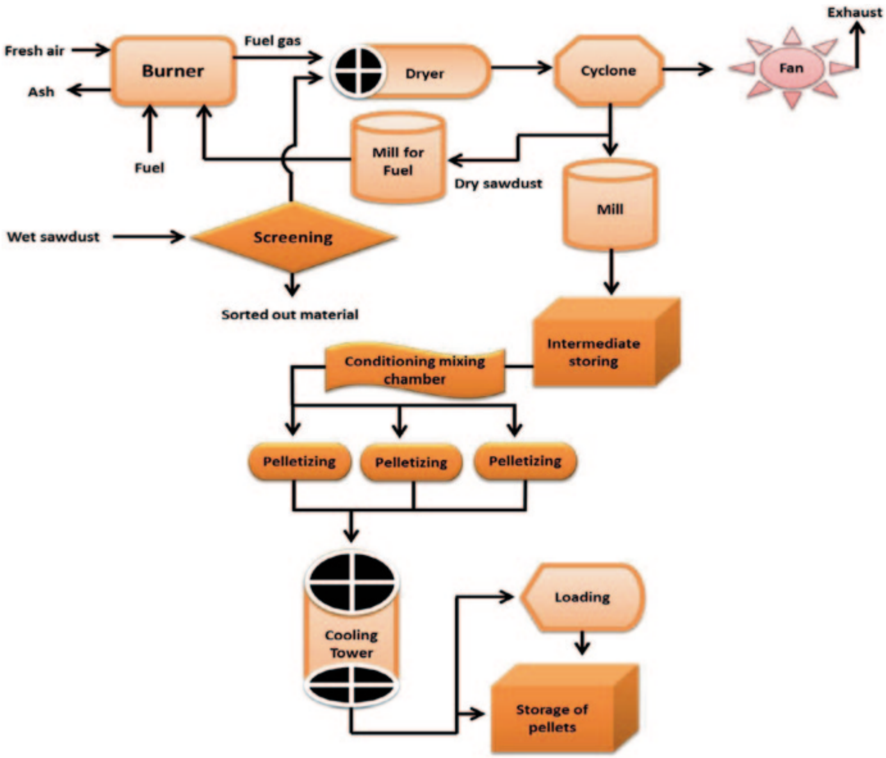

Fig. 3 Overview of biomass pellet production

dustrial wastes are also important forms of biomass resources (Vassilev et al. 2010). A general classification of biomass according to the origin is presented in Table 1.

Woody Residues

Wood remains a major energy source in the developing countries. Wood is often the main household fuel and also contributes significantly to industrial energy consumption. It is estimated that about 55 % of the global wood harvest is burnt as fuel, and the remaining 45 % is used as industrial raw material, a considerable portion of which ends up as primary or secondary process residues, suitable for energy production (Parikka 2004). Wood fuels consist of woody biomass, i.e. stems, branches, twigs, etc. and sawdust (Karkania et al. 2012) and other residues from logging and wood processing activities such as manufacturing of plywood, sawmilling and particle board as well as charcoal from these sources. Both forest as well as non-forest land are considered as the primary sources of wood fuels. Forest and other woodland include natural forests, scrublands, wood and timber plantations, woodlots and

Table 1 General classification of biomass according to the origin

Biomass group	Biomass subgroup, varieties and species
Wood and woody biomass	Coniferous or deciduous; soft or hard; stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species
Herbaceous and agricultural biomass	Annual or perennial and field based or processed based such as: grasses and flowers (alfalfa, *Arundo*, bamboo, bana, *Brassica*, cane, *Miscanthus*, switchgrass, timothy, etc.); straws (barley, rice, wheat, sunflower, oat, rape, rye, bean, etc.); other residues (fruits, shells, husks, hulls, pits, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, etc.)
Aquatic biomass	Marine or freshwater algae; macroalgae or microalgae; blue, green, blue-green, brown, red, seaweed, kelp, lake weed, water hyacinth
Animal and human biomass wastes	Various manures, bones, meat-bone meal, chicken litter, etc.
Contaminated biomass and industrial biomass wastes (semi-biomass)	MSW, demolition wood, refuse-derived fuel (RDF), sewage sludge, hospital waste, paper-pulp sludge and liquors, waste paper, paperboard waste, tannery waste, etc.
Biomass mixtures	Blends from the above varieties

MSW municipal solid waste

dedicated fuelwood plantations. Non-forest land here includes agricultural land, agroforestry systems, wasteland, line trees, home gardens, etc. Biomass productivity of different plants is affected by many interacting factors relating to tree biology, community interactions and environmental constraints. Usually, the yield of biomass in plantations is higher than that from natural communities. For example, in a natural forest, the annual average increment of biomass could be in the range of 500 kg of dry matter/hectare, while even a tenfold increase could be achieved in a dedicated fuelwood plantation. In the case of short-rotation fuelwood plantations, a much higher yield of 30 dry t/ha/year could be expected. Global fuelwood consumption is estimated to be about 2 billion m^3 per year. In Italy, woody residues (mainly pruning off-cuts from vineyards and olive groves) are about 3.5 million t/year in which 85 % unused (Di Blasi et al. 1997). The process of conversion from trees to logs and subsequently to sawn wood is associated with the number of waste streams. These biomass materials can be in various forms of logging as well as other processing wastes. In the timber industry, about 80 % of the original trees go to waste while only the balance 20 % end up in the form of kiln dried sawn wood, generating a significant amount of biomass.

Perennial Plantation Crop Residues

Perennial plantation crops, such as coconut, rubber, tea, cinnamon, cocoa, coffee, oil palm and palmyra palm, generate considerable amounts of wood residues from pruning and replanting activities and a variety of processing residues. For example, coconut trees generate residues in the form of wood, fronds, husks and shells. Some estimates indicate the generation of about 5 t/ha/year of fronds, husks and shells alone from coconut plantations that have a productivity of 7200 nuts/ha/year (Abdul Salaam et al. 2005). In addition, tree trunks are available during replantation, which are used both as fuel and as timber. Rubber plantation is also an important source of fuelwood. In the past few decades, rubber wood has become an important source of timber for the furniture industry. Rubber trees have a productive lifespan of about 25–35 years. During replanting, they yield about 80 t dry wood/hectare. Cocoa trees are planted and used for production for a period of about 25 years, during which they have to be pruned regularly to keep them small, resulting in the generation of a significant amount of biomass. In the case of oil palms, tree trunks and fronds become available during replantation generating about 80 t of dry matter/hectare in a 25-year cycle. Further, approximately 6 t of other by-products such as fibre, shells and empty bunches are generated during processing/hectare. In addition to the above-mentioned crop residues, there are other sources of residues that can be utilised in the bioenergy sector, for instance tea plants where pruning is done every 7–10 years of tea bushes and uprooting after productive life generating sizable amount of biomass and coffee in which pruning of shade trees and uprooting generate biomass (Koopmans and Koppejan 1998).

Agricultural Residues (Annual Crops)

The agricultural sector is considered as the backbone of the nation as it forms an important part of the economy. Besides, crop production large amount of biomass residues are generated every year, constituting about 140 billion tons which can be utilized as a source of bioenergy for domestic as well as commercial purposes. Agricultural residues could be divided into field-based residues and process-based residues. The biomass materials, which are generated in the agricultural farm or field, are defined as field-based residues (e.g. rice straw, sugarcane tops, cocoa pods, tobacco stalks, soybean straw/pods, maize stalks, etc.), whereas those generated during the processing of agricultural products are called process-based residues (e.g. rice husk, bagasse, maize cob/husk, coffee husk, peanuts shell, etc.; Boundy et al. 2011). Such a classification is important, especially under the context of energy application, as the availability of and accessibility to these sources critically depends on this attribute. The availability of field-based residues for energy application is usually limited since collection for utilisation is difficult and there are other alternative uses such as for fertilising and animal feed. However, processed-based residues are usually available in a relatively high concentration and may be used as an energy source for the same industry making no or little transportation and handling cost (Godfrey 2004). During the processing of olive oil, its by-product, i.e. olive pits, can be used as an energy source in domestic boilers or in large industrial plants for cogeneration (Pattara et al. 2010). On the other hand, the olive pit (Robles Fernández et al. 2009) is a competitor to pellets. It is cheaper and needs only conditioning, but not any manufacturing process. Although agricultural residues are used as fuel, a large amount is wasted via open dumping or open burning in the field, and therefore referred to as waste agricultural biomass. As such, the use of these materials for energy applications would be an effective way of managing the waste, while becoming a useful resource than a waste under conventional management practices (Klass 2004).

Energy Crops

Currently, bioenergy crop plantation is the main focus in order to enhance the biomass availability and make the technology cost-effective. In other words, it can be defined in terms of tons of biomass produced/hectare, or it may be the utilisation of vegetable oil for conversion to biodiesel or sugar or starch for fermentation to bioethanol (Pirzadah et al. 2014). Energy crops can be divided into several classes which include short-rotation energy crops, grasses and non-woody energy crops, biofuel plants (agricultural energy crops) and aquatics (hydroponics). The liquid biomass generated for energy application is usually referred to as biofuels, of which ethanol and biodiesel are the most common types that are used as transportation fuels. Sugar-containing materials (or sugar crops) are becoming an important category of energy crops. The basic process of the derivation of fuel involves converting sugar to ethanol which can be used as a valuable liquid fuel for running engines. Sugarcane is the best-known sugar crop. Sweet sorghum is another attractive sugar crop that can give the highest alcohol yield per hectare per year of all sugar crops. Cane molasses, a by-product of sugar production, is also a common raw material for alcohol production. Molasses production is directly related to sugar production and represents a relatively small resource. Another important category of energy crops is represented by starch-containing materials, such as cassava and corn. Cassava is a root crop that can give a high alcohol yield per hectare of land and can be grown on marginal land. Corn is used for alcohol production in the USA. It is mainly used as a food in the developing countries and animal feed. It is grown in rich agricultural land and can be considered for large-scale alcohol production only in countries having large areas of production but unused land. Oil and hydrocarbon (HC) substances produced by certain plants can be used as engine fuel after various degrees of processing. Sunflower and coconut oils for example have been successfully used for running internal combustion engines. The yield of oil-producing ground crops is normally low and ranges from 0.6 to 1.2 t per hectare per growing season of 120–160 days. Coconut palm and oil palm yield about 1.5 and 5 t of oil per hectare per year, respectively, and more promising for energy plantations. Due to the much higher productivity, aquatic plants have attracted substantial interest as a valuable feedstock for second and third-generation biofuels. It is a possible source for a variety of biofuels: biodiesel, bioethanol, biogas, pellets and charcoal briquettes. Sources for aquatic biomass could be categorised as free floating plants, emergent (rooted) fast growing plants (reeds, cattail) and algae. The biomass can be harvested from "nature" or it can be grown in dedicated facilities such as ponds and bioreactors. The growth rate of certain aquatic plants is very high with a yield over 50 t of dry matters per hectare per year. Some plants, such as water hyacinth, water lettuce, *Salvinia* and duckweeds, are available in many places, have no significant use and are often regarded as nuisance. Potentially, these can be used as viable sources for biofuels, in particular for biogas. They are also gathering interest as a source for bioethanol. Dried distillers grains with solubles (DDGS) are the unfermented by-products of the ethanol production process (Kumar et al. 2010). The yield of the ethanol production process is about 370 L of anhydrous ethanol per tonne of grains and 285 kg of DDGS (Tavasoli et al. 2009). As most of the ethanol production plants function using natural gas, it was found that the DDGS with its high yield can be used to supply all or the required heat and electricity in the ethanol plant. DDGS is commonly used as feed for the cattle but it was found that it contains a certain form of fat that some species cannot tolerate (Tiffany et al. 2007). Large amounts of biomass could be grown in the oceans too for use as energy source. The use of aquatic plants to meet energy needs is however, a relatively new concept and may not often be financially viable because of costs involved in harvesting, transporting and conversion. The production and processing of algae currently receives most attention as a source for biofuels, especially biodiesel (Pirzadah et al. 2014). Algae production is the most efficient method to benefit from solar radiation in the production of biomass. Microalgae are considered to become a major source for transport fuels in the future (Mata et al. 2010). A number of grasses, such as napier, switchgrass, *Miscanthus*, are characterised by very high biomass yield (Nixon and Bullard 2001) and in the UK it is common to use *Miscanthus* for cofiring with coal in power plants (Baxter et al. 2011). The average yield of napier grass, for example, has been reported to be more than 100 dry t/ha/year. Research into production and utilisation of grasses for energy is still in its early days.

Animal Waste

The livestock farms, which raise animals such as goats, cattle, pigs, buffalo, poultry (chicken and ducks), horses, sheep, etc., represent an important industry in many countries. Besides, these farms generate tremendous polluting wastes. Previously, these wastes found their application directly as fertilisers or in some instances could be used for landfilling, which resulted in severe environmental problems. An environmentally acceptable disposal route with potential financial benefits lies in biomass-to-energy schemes which generate energy and often produce fertiliser as a by-product (Verma et al. 2012). Animal waste can be decomposed in an anaerobic environment to generate biogas, which contains methane (CH4) up to about 60%. Methane, which is the main constituent in natural gas, is a superior gaseous fuel.

Therefore, biogas is an excellent fuel for use in burners, boilers, engines and gas turbines. There is large potential of producing biogas from animal waste due to the large annual manure production.

Municipal Solid Waste

MSW is the waste produced by sectors such as residential, commercial, industrial and institutional. Economic development and urbanisation have led to an increase in the quantity and complex composition of MSW in cities of developing countries, leading to serious concerns over the proper waste management for local governments. The majority of substances that constitute MSW include putrescible/organic matter, metal, plastic, glass, paper, textiles, rubber, etc. In general, the composition and volumes of MSW differs between high- and low-income countries. In most of the developing countries, it is composed of high organic matter with food and vegetable waste as compared to the developed nations, where more combustible materials such as plastic and paper are contained. The above attributes demand for distinct waste management techniques for MSW in different countries and local regions. Generally, MSW management consists of four main types: landfilling, incineration, composting and anaerobic digestion. Principally, it has been recognised that the challenges and hurdles associated with MSW can be overcome by the adoption of an ecofriendly approach commonly known as integrated waste management that involves reduction, reuse and recycling and effective treatment and ultimately final disposal in an environmentally acceptable strategy. The waste to energy option is thus considered to be one of the most effective ways of final disposal. The feasibility of waste to energy option in a given city in a developing country is highly affected by the collection of waste, treatment and waste disposal practices in that city and by the composition of residential wastes.

Characteristics of Biomass

Biomass Composition

Biomass fuel is the stored solar energy in the form of chemical energy of its constituents, as a result of photosynthetic reaction. The components of biomass include cellulose, hemicelluloses, lignin, proteins, lipids, starches, simple sugars, HCs, water, ash and other compounds. The amount of the compound present in the biomass varies considerably depending on the type of species, plant tissue, stage of growth and the growing conditions. But generally, it is considered that majority of the land biomass is composed of cellulose, hemicelluloses and lignin. It has been found that the composition of the feedstock is the main variable that contributes to the quality of densified materials. The composition of raw biomass includes both low molecular weight and high molecular weight substances. Low molecular weight substances include organic matter, inorganic matter and high molecular weight substances include cellulose, hemi-cellulose and lignin (Mohan et al. 2006). High temperature and pressure, which usually takes place during the densification process, show an increase in softening of the lignin, which in turn improves the binding capability of the biomass. Two important factors, i.e. low thermosetting properties and a low melting point (140 °C), help lignin to take an active part in the binding mechanism (Van Dam et al. 2004). It has been found that protein, starch and lignin present in biomass also take an active part during the pelleting of alfalfa, wheat and barley grinds (Adapa et al. 2002, 2009; Mani et al. 2004). During biomass processing, some compositional changes take place due to the reaction, which in turn helps in understanding the compact behaviour of the process. One of the studies carried out by Thomas et al. (1998) identified some of the important components that affect the quality of pellet, including protein, starch, sugar and non-starch polysaccharides (NSP), fibre, fat, inorganic matter and water. Recently, Kaliyan and Morey (2009) used scanning electron microscope (SEM) studies for understanding the solid-type bridges formed during briquetting and pelleting of switchgrass and corn stover. Additional research is required at the molecular level by employing techniques like SEM and transmission electron microscopy (TEM) which provide knowledge to comprehend the interaction of feedstock and process variables on the ascribed property of densified biomass.

Starch

Starch is composed of branched (amylopectin) as well as unbranched (amylose) D-glucose polymers (Collado and Corke 2003). The property of starch is mainly dependent upon the gelatinisation process it undergoes at elevated processing temperatures. For instance, high temperature and moisture influence the textural properties of many foods and feeds (Shankar and Bandyopadhyay 2006). Although starch undergoes gelatinisation, pasting and retrogradation reactions but the gelatinisation phenomenon exhibits a vital role in the pelletisation process (Collado and Corke 2003). It is an irreversible phenomenon and is mainly influenced by various parameters, such as densification process variables (heat, water, shear and residence time; Thomas et al. 1999). Besides the food sector, starch also plays a lead role in the paper industry where it acts as an adhesive material (Thomas et al. 1999). In pharmaceuticals, it finds great application as a binder or filler in tablet formulations (Alebiowu and Itiola 2002). During the feed formulation, starch acts not only as a binder but also as a lubricating agent, thus helps to ease the flow of materials through a pellet mill or an extruder. During the densification of biomass, starch acts as a binder. However, for efficient densification of starch-rich biomass, the presence of heat and moisture content are very important parameters to produce quality pellets (Wood 1987; Thomas et al. 1998).

Protein

Proteins present in the biomass also aid in the densification process by undergoing a denaturisation phenomenon leading to the formation of new bonds and structures with other protein, lipids and starch present in biomass and enhancing its binding capacity (Thomas et al. 1998; Nyanzi and Maga 1992). Briggs et al. (1999) reported that pellet durability is directly proportional to the protein content of biomass. Moreover, raw proteins are more preferred than denatured proteins to enhance the quality of pellets. In another study carried out by Tabil and Sokhansanj (1996b), sufficient amount of natural protein in the biomass during pelletisation will plasticise under heat and thus enhance its binding properties. Besides, the quality of biomass is also influenced by the interaction between proteins and starch. The feed material with a larger proportion of starch and protein composition produces denser and more stable pellets than biomass with larger proportion of cellulose (Sokhansanj et al. 2005a).

Lipid/Fat
Fat acts as a lubricating agent and reduces the pelleting pressure during the pelletisation process and thus enhances the throughput of the pellet mill (Thomas et al. 1998). However, an increase in fat content decreases its binding capacity and thus requires additional binders to enhance its durability and hardness. Shankar et al. (2008) reported that biomass with high lipid content (8–10 %) requires an additional binder to improve its density and water stability. Briggs et al. (1999) reported that biomass with high oil content produces lower-quality pellets because fats being hydrophobic in nature may interfere with the binding of the feed particles during the pelletisation process.

Lignocellulose
Lignocellulosic biomass being abundantly available in nature is the major raw material for pellet production. It is generally composed of cellulose (40–60 %), hemicelluloses (20–40 %) and lignin (10–25 %; United States Department of Energy 2006). The typical lignocellulosic content of some example plant materials is shown in Table 2.

Cellulose
Cellulose is a polysaccharide composed of D-glucose units linked by β-1, 4-glycosidic linkage (Chen et al. 2004). The hemicelluloses and lignin form an amorphous matrix that reinforces the cellulose microfibrils. The structural integrity of the cellulose is produced by hydrogen bonding that occurs between the glucose monomers (Goldstein 1981). It is tough, water insoluble and is considered as abundant source of carbon (Nelson and Cox 2005). In their article on hot pressing of wood material,

Table 2 Typical lignocellulosic content of some plant materials (Mohan et al. 2006)

	Lignocellulosic content (%)		
Plant material	Hemicelluloses	Cellulose	Lignin
Orchard grass (medium maturity)[a]	40.0	32.0	4.7
Rice straw[b]	27.2	34.0	14.2
Birch wood[b]	25.7	40.0	15.7

[a] Data taken from Van Soest (1964)
[b] Data taken from Solo (1965)

Zandersons et al. (2004) concluded that the binding strength of wood-based products mainly depends on converting the cellulose to an amorphous state.

Hemicelluloses
The hemicelluloses are hetero-polysaccharides composed of xylose, arabinose, etc. or a combination of many other sugars other than glucose units (Shambe and Kennedy 1985). The amorphous structure of hemicelluloses is due to branching and is more easily hydrolyzed or can be dissolved in alkali solution. Some researchers believe that natural bonding may occur due to the adhesive degradation products of hemicelluloses.

Lignin
Lignin is an aromatic biopolymer with a variety of linkages based on phenyl propane units (Zandersons et al. 2004). Lignin is complex in nature and is synthesised from two precursors like phenylalanine and tyrosine (Nelson and Cox 2005), both of which contain aromatic rings. In the pelletisation process, it acts as a glue material to the cellulose fibres. Biomass with high lignin content does not require an additional binder. Van Dam et al. (2004) report that lignin exhibits thermosetting properties at working temperatures of > 140 °C and acts as intrinsic resin in binderless board production. Anglès et al. (2001) reported that lignin permits adhesion in the wood structure and acts as a rigidifying and bulking agent (Anglès et al. 2001). Lehtikangas (1999) states that moisture of about 8–15 % in biomass will reduce the softening temperature of lignin to 100–135 °C by plasticising molecule chains. The adhesive properties of thermally softened lignin are thought to contribute considerably to the strength characteristics of briquettes made of lignocellulosic materials (Granada et al. 2002).

Properties of Biomass/fuel Pellets

The large number of fundamental qualities of biomass has been ruled out for a wide variety of fuel types. These qualities include physical size and shape, elemental composition (ultimate analysis), moisture content, proximate analysis, bulk density, thermal conductivity, and mechanical, heating value, specific gravity, acoustic and electrical properties. One of the key differences between biomass and other fuels is the presence of a considerable amount of moisture in biomass. The moisture content of woody biomass is often considered as an inevitable aggravation. It elevates the density (or weight) of biomass making transportation more difficult and costly, lowers the overall amount of heat utilised from combustion (heating value) and increases the composition of biomass during storage.

Physical Properties

The physical quality properties of wood fuel pellets are moisture content, calorific value, volatile matter content, ash content, ash melting behaviour and content of impurities. Among the quality properties, moisture content (the ratio of water content to total weight) is among the most important, as several authors have stated (Pichler et al. 2006; Jirjis et al. 2006; Lehtikangas 2001; Obernberger and Thek 2004; Fasina 2008; Rhén et al. 2005; Greinöcker et al. 2006). The moisture content of the pellets affects the energy content and causes dry matter loss (microorganisms eat the substance). Hence, it affects the combustion process, i.e. the combustion efficiency and the fuel gas emissions. It also affects storage on account of an increased microbial activity and the self-ignition risks, and it implies health effects. In addition, it affects the mechanical properties, e.g. durability and the bulk density as well as the energy consumption during drying and pelletising. According to the Swedish standard 187170 (1997), measuring the moisture content involves weighing of the sample before and after drying it in an heating oven for 24 h at 105±2 °C. The difference in weight that is obtained is used for determining the moisture content. It is to be noted that dry matter losses occur during drying if the moisture content is only 1 lower than the seller claims it is, it could cost a large biofuel user tens of thousands of euros a year. Moisture present in the biomass expedites fibre solubilisation, starch gelatinisation and protein denaturation processes during extrusion, pelleting or briquetting. Steam-treated biomass is superior, as the further heat alters physiochemical qualities like gelatinisation of starch, denaturation of protein to such an extent that binding between the particles is significantly increased, leading to the modification of densification quality (Thomas et al. 1997). One of the studies carried out by Mani et al. (2006) described that the moisture content in biomass acts as a binder during the densification process and enhances the bonding through van der Waal's forces, which in turn increases the contact area of the particle. Tabil and Sokhansanj (1996), in their study on pelletisation of alfalfa grinds, observed that higher die (7.8 mm) can handle conditioned grind moisture contents above 10 %, but the durability after cooling of the pellets was low. They also found that the smaller die became plugged when the moisture content of the conditioned grinds exceeded 10 %. Tumuluru et al. (2010), in their study on pelleting of DDGS grinds employing a pilot-scale pellet mill, found that steam conditioning before pelletisation and using a smaller die of 6.4 mm size produced more highly durable pellets compared to 7.4 mm. Demirbas (2004) in his study observed that enhancing the moisture content from 7 to 15 % of spruce wood sawdust significantly increased the strength of the pellets. Mani et al. (2006), in their article on densification of corn stover, found that low moisture content (5–10 %) resulted in denser, more stable and more durable briquettes.

The calorific value or heat of combustion is the standard measure of the energy content of a fuel. The calorific value of biomass particularly relies on its constituents. Dry woody biomass consists of cellulose, hemicelluloses, lignin and ash. Therefore, the heating value of dry woody biomass thus can be determined from the heating value and weight fraction of each component. The calorific heating value (CHV) is of great importance to the trade of biofuels. The buyer of the fuel wants to get as much energy out of the fuel as possible. According to the Swedish standard SS-ISO 1928, the determination of the gross CHV must be made using a bomb calorimeter. Subsequently, the net CHV can be calculated. For Scots pine and Norway spruce, the ash contents, containing both inorganic compounds from the wood itself and materials added due to contamination during the processing of the raw material, are low in pure stem wood (about 0.3 % (dw)) but higher in needles and bark (about 3–5 % (dw); Martinsson and Österberg 2004; Savolainen and Berggren 2000; Eid Hohle 2001). Lehtikangas (2001) reports that pellets had a larger ash content and less CHV as compared to the raw material; this might be due to the loss of volatiles during drying. Martinsson and Österberg (2004) show that a lower ash content implies less frequent ash clearing, which is important for the automatic operation of a burner/stove. The ash contains most of the elements and could therefore be spread in the forest to avoid nutrient depletion and increased acidification (Lundborg 1998; Vesterinen 2003; Wikström 2007). The ash, however, often needs pretreatment before it is returned to the forest.

Chemical Properties

The chemical composition of biomass, i.e. wood, is cellulose and hemicelluloses, lignin, extractives and minor and major elements. In fresh wood, the approximate shares of water (total weight), carbon (dry weight), oxygen (dw) and hydrogen (dw) are 50, 50, 42 and 6 %, respectively. The remaining share mostly consists of ash (inorganic material). The extractives, such as waxes, terpenes and phenols, are produced as defence mechanisms against destructive activities. The wax on the needle controls the evaporation of water from the coniferous trees. Apart from this, the extractives have high energy contents, about 35 MJ/kg (dw), which influences the heating value of wooden pellets. In comparison, lignin has an energy content of about 25–27 MJ/kg (dw), cellulose 17 MJ/kg (dw) and wood, on the average, 19.2 MJ/kg (dw). Knowledge of how the extractives affect mechanical properties, such as mechanical strength, is incomplete. However, the extractives might act as plasticisers or inert bulking agents or become part of the matrix. The lignin is probably working as a binding agent within the pellet together with other bonding mechanisms. To get the lignin to work as a binding agent, the glass transition point (melting point) has to be reached. For native lignin (when dry), this temperature is 200 °C. If the lignin absorbs more than 2 % of water, the temperature is reduced to 115 °C (Back 1987). According to Granström (2003), the monoterpenes, such as α- and β-pinene and Δ^3-carene, are the most volatile group of compounds present in wood. They are found in the resin. In Norway spruce, 0.1–0.15 % of the tree's dry substance consists of monoterpenes, for Scots pine the numbers are 0.2–0.6 %. Apart from having several protective functions in trees, monoterpenes have an energy value of about 40 MJ/kg. Neither the major elements (Na, Ca, K, S, Mg, P, Si, etc.) nor the minor elements (Fe, B, Zn, Cu, Mn, Mo, Cl, etc.) are significant energy carriers. The elements also have different effects on combustion—chlorine (Cl), sulphur (S) and potassium (K) contribute to corrosion problems with burner equipment and chimneys (Lehtikangas 1999); magnesium (Mg), calcium (Ca) and phosphorus (P) have effects on pollutant retention in ashes (Hahn 2004).

Overview of Pelletisation Process

Biomass is generally difficult to handle, usually non-uniform and with a low energy density; therefore, pelletisation appears desirable to allow easier and more economic storage, transportation and energy conversion characteristics (Demirbas et al. 2004). Pelletisation is a method of increasing the bulk density of biomass by applying mechanical pressure (Mani et al. 2006). This method can give multiple advantages in biomass: amount of dust is decreased, energy density is increased and fuel becomes uniform and thus allows easier and more efficient control during combustion and gasification (Samson and Duxbury 2000).

Pelletisation Methods: Types of Pelleting Units

The pelletisation process consists of certain subprocesses such as grinding, drying, milling and pelleting (Fig. 3). The properties of these subprocesses are defined in terms of the end use of the pellets. Initially, the pelletisation process was developed for the livestock feed industry but the utilisation of pellets also expanded into the thermal conversion systems such as gasification or combustion. Physical and chemical characteristics of feedstock determine, to some extent, the process of pelletisation. Wood chips, shavings and sawdust, which all can be considered wooden materials, are slightly different in these properties from herbaceous biomass and agricultural residues such as oil seed rape straw or wheat straw. Because of that, the pelleting process properties are also slightly different (Chen et al. 2008). The process of pelletization is affected by the material's moisture content, particle size, density, fibre strength, lubricating characteristics and natural binders (Samson and Duxbury 2000).

Pretreatment

Few of the properties mentioned above can be controlled or can be affected by the feedstock pretreatment. In the pelletisation process, pretreatment mainly consists of two different processes: drying and grinding. Drying is usually required to decrease the moisture content of biomass which in many cases exceeds an appropriate value for pelletisation (between around 6 and 18% moisture content). Milling is also required in order to transform the feedstock into a more uniform material. The material after milling process consists of particles which are of equal size and similar moisture content. This homogeneity makes the pellets more durable (Chen et al. 2008). Furthermore, milling brings size reduction which in turn leads to an increase in particle surface area facilitating interparticle bonding (Sokhansanj et al. 2005). In general, the purpose of pretreatment is to alter the feedstock in a fluidic manner where a low friction coefficient is created between the internal die surface and the fibre (Samson and Duxbury 2000).

Pelleting and Post-pelleting

The pelleting process is typically carried out in a conventional pelletiser. Loose biomass feedstock is fed into the pelletiser where the presence of a die and the pressure of the rollers upon the feedstock force it to pass through the die and form pellets. Pelletisers are usually equipped with knives (or blades) which cut the pellets to the desired length. There are two types of conventional pelletisers: flat die and ring die type. In a flat die pelletiser, the die remains stationary while rollers rotate and compress the feedstock, while in the ring die pelletiser, it is the die itself that rotates (Chen et al. 2008). In any case, when the material passes through the die holes, friction causes the die to heat up and the temperature increases to around 75–85 °C. Then, lignin inside the material starts flowing off the fibre; lignin in this state has the ability to bind the fibres (Samson and Duxbury 2000). The pelleting process results in constructing a uniform fuel with a higher bulk density compared to the loose material and so is attractive to operators of biomass and energy processes. Cooling is considered a very important part in the pelletisation process. The typical pellet temperature after leaving the pelletiser is around 80–90 °C. Cooling of the pellets makes them harden due to lignin stabilisation especially on the surface of the pellets (Chen et al. 2008).

Binding Mechanism

While pressure is not yet applied and particles are in a close distance between them and in a confined space, they start to rearrange and thus form a mass. At that point, the feedstock particle properties are still retained even though that energy has already been dissipated due to interparticle and wall–particle friction. When high pressures are applied, particles are compacted even further subsequently forcing them to undergo elastic and plastic deformation and thus the area of contact between the particles is increased (Sokhansanj et al. 2005). The plasticity of particles can also be affected by the temperature and moisture content. High moisture content leads to an increase of the interparticle space and thus more compression energy is dissipated. On the contrary, low moisture content increases the friction during the process affecting the plasticity (Ryu et al. 2008). Theoretically, the reduction in volume continues until the pellet density approaches the density of the particle. In order to further investigate the binding mechanism, forces between the particles and various binding phenomena should be also mentioned, such as van der Waal forces, solid bridges, capillary pressure or mechanical interlocking. Electrostatic, magnetic and van der Waal forces are the cause of an attraction force between the particles which depends on the particle size and the inter particle distance. In addition, the presence of a liquid such as water enhances the binding of the particles due to the capillary pressure and the interfacial forces (Tabil et al. 1997). Interfacial forces are in general connected with the individual movement of small, in this case, solid particles in the bulk of a phase (Kaptay 2005). During the binding process, interlocking of the fibres also takes place when, due to the pressure, the particles are wrapped and overlap each other, a process which also assists the binding process (Tabil et al. 1997). The binding mechanism is also enhanced by lignin. The addition of heat in biomass forces the lignin to become softer initially and to exhibit thermosetting properties due to irreversible cross-linking and curing. It was observed by van Dam et al. (Van Dam et al. 2004) that at a temperature of around 140 °C, lignin shows an exotherm which basically denotes the irreversible cross-linking of the lignin polymer. That is the reason why pretreatment should always be performed below that temperature.

Effect of Pelleting Properties on the Quality of Pellets

White (1987) showed a linear correlation between the higher heating value (HHV) and lignin content of wood (extractive-free). As the lignin content increases the heating value also increases. It was also observed that pellets had a lower heating value and higher ash content compared to the feedstock because of the loss of volatiles during the drying process (Lehtikangas 2001). There are many other reports that investigate on the effect of fuel characteristics or pelletisation properties to the pellet quality. Kaliyan and Morey (2009) reviewed the pellet durability. Durability is the abrasive resistance of the pellets; adding fats or oils into the feedstock reduces the durability of the pellets. Fats and oils act as lubricants between particles and the die wall. Thus, friction is reduced and pressure is decreased resulting in lower pellet durability. The quality of pellets could be increased by adding starch and protein which could act as a binder. Briggs et al. (1999) managed to increase the pellet quality by increasing the protein content. Alternatively, an increase in oil causes a decrease in pellet quality; the upper oil limit was found to be 5.6 % with a protein content of 20 %. The durability of pellets can decrease if not cooled down; stresses appear between the inner (warm) and the outer (cold) part of the pellet that can cause cracks (Kaliyan and Morey 2009). Experiments and a modelling procedure in reed canary grass showed that moisture content was the most influential factor for bulk density and durability responses (Larsson et al. 2008). Durability also depends on the feedstock particle size. The smaller the particle size is, the greater the durability. Small particles are more susceptible in moisture compared to large particles. Large particles on the other hand are more susceptible in cracks and that causes fracture of pellets (Kaliyan and Morey 2009). Furthermore, a study by Bridgeman et al. (2007) showed that the size reduction process of biomass is not done in a uniform manner and, instead, a partial separation between organic and inorganic matter in different sized particles was observed; larger particles have higher carbon and volatile content that leads essentially to increase heating value. A study by Lehtikangas (2001) confirmed the correlation between durability of pellets and lignin content and furthermore showed that moisture had also a positive effect. Other studies showed that the larger the die length-to-diameter ratio is, the higher the durability is. A decrease of die diameter up to a point can cause an increase in the shear applied to feedstock affecting positively the durability of the pellet (Kaliyan and Morey 2009). In addition, it was found that the pellet length had no influence on bulk density but pellet density had a positive effect on bulk density (Lehtikangas 2001). However, a study by Obernberger and Thekh (2002) did not observe a correlation between abrasion (durability) and particle density as well as a correlation between abrasion and moisture content. An explanation was that pellets were manufactured in different plants, using different pellet equipment, an indication that abrasion may also depend on many different parameters. It can be seen from all the above that the pelleting parameters could play an important role on the pelleting process and the pellet quality. Some of the parameters and their effect in the pelletisation process derived from the literature above can be seen in Table 3.

Table 3 Parameters and their effect in pelletisation process according to literature

Parameter	Effect	References
Lignin	Acts as binder	Lehtikangas 2001
	Linear correlation with heating value	White 1987
Fats/oil—Starch/protein	Oil acts as lubricant	Kaliyan and Morey 2009
	Oil reduces durability	Kaliyan and Morey 2009
	Increased oil reduces quality	Briggs et al. 1999
	Starch/protein act as binder—increased pellet quality	Briggs et al. 1999
Moisture	Acts as lubricant and as binder	Kaliyan and Morey 2009
	Durability—increases pellet durability by adding moisture up to a point	Kaliyan and Morey 2009
	Bulk density—increasing moisture, bulk density increases to a point and then decreases	Sokhansanj et al. 1999
	Density—increasing moisture, decreases particle density	Sokhansanj et al. 1999
Particle size	Durability—the smaller the particle size the greater the durability	Kaliyan and Morey 2009
	Larger particles—higher % of C and volatile increased heating value	Sokhansanj et al. 1999
Die diameter	Durability	Kaliyan and Morey 2009
Pellets density	Bulk density—positive effect	Lehtikangas 2001

The energy required to manufacture pellets plays an important role in the energy balance of the whole process. A review by Chen et al. (2008) for the Supergen Bioenergy project (2008) states that straw as a fibrous material and with low lignin content will require high-energy input (near 50 kWh/t) to be pelletised compared to other non-fibrous materials such as sawdust. Regarding the economics, in general a small-scale pellet plant would be more expensive to operate and that leads to an increase in pellet price due to the scaling economics, cost of personnel, etc. Cheap pellets could be produced from a plant with capabilities of 10 t/h or more. The major cost factors in the pelleting process are the raw material and the personnel while the dryer and pellet mill costs follow (Mani et al. 2006).

Current Global Status of Biomass Pellet Technology

Currently, wood pellets are one of the biggest internationally traded solid biomass commodities utilised particularly for energy applications. It was estimated that in terms of traded volume, about 4 million t produced can be analogised to biodiesel or bioethanol (Heinimo and Junginger 2009). During handling of wood pellets care should be taken; one of the important properties of wood pellets over other varieties of solid biomass (e.g. wood chips or agricultural residues) is their storability and simple handling. One of the interesting qualities of wood pellets for long-distance transport is that they have a less moisture content and comparatively large energy density, about 17.5 GJLHV/t. The transport of wood pellets along a large distance above 9300 km (5000 nautic miles) is economically more viable rather than wood chips. The transportation of wood pellets through a long distance comes across exactly in the year 1998 from Canada to Sweden (Obernberger and Thek 2010). Afterwards, the trade in wood pellets by trucks, boats and to a certain limit by train has been increased rapidly nationally and internationally. The general explanation behind long-distance trade is the substantial availability of low-cost feedstock in some world regions, increased demand in other regions of resource scarcity and the easy availability of energy- and cost-efficient logistics. During the past decade, pellet manufacturing industries have been developed considerably. The least-expensive biomass resources are the waste products produced during wood or agro-processing utilisations but their availability is restricted. To combat this restriction, countries globally are considering biomass crops for energy utilisation and have started generating technologies to utilise biomass crops more effectively. The biomass pellet technology enters the energy market earlier in the USA and majority of the Europe. The USA acquired nearly 4 % energy and Sweden about 13 % of energy from biomass (Hall et al. 1992); besides, Sweden is implementing initiatives to develop nuclear plants, abate fossil-fuel energy utilisation and aggrandise the exploitation of energy from biomass (Björheden 2006). The oil crisis in 1973–1974 made clear that the Western European countries were dependent on energy imports, mainly oil. They are no longer considered self-sufficient in terms of energy. The interest shown in alternative energy sources has therefore increased. For the EU, the White Paper concerning biomass (European Commission 1997) aimed at doubling the share of renewable energies with respect to the total energy demand, going from 6 to 12% by 2010. In addition, the EU published their Green Paper "A European Strategy for a Sustainable, Competitive and Secure Energy Supply" in 2006, in which they stated that all 25 member states have to cooperate to achieve a secure energy supply. Furthermore, it aims at decreasing the energy use and attaining energy-efficient processes. Since the beginning of the early 1980s, with the Swedish governmental energy policy of the 1990s accelerating the process (favouring renewable energy sources in order to phase out fossil fuels), the use of biofuels has increased significantly. The increase is also partly due to the high price of fuel oil and the tax reduction on the installation of biofuel heating systems. The energy policy instruments used were: assize for emission control, financial assistance for combined heat and power (CHP) plants and energy taxation including the introduction of a CO_2 emission tax on fossil fuels (Hillring 1999). There are also taxes on SO_x and NO_x emissions in Sweden. The growth of the Swedish biofuel market, however, is due to several successful strategies. According to Hillring (2002), examples of successful strategies were to increase the information content of products and services and to make size rationalisation, i.e. small biofuel production units have become large biofuel production plants. The reduction of the use of fossil fuels will in all probability imply that the amount of energy coming from biomass will increase. An increase in the use of biofuels is possible; several studies have tried to estimate the possible contribution of biofuels to the global energy supply. However, large uncertainties are involved, such as price development of raw materials, new legislation and policies concerning renewable energy sources, etc. According to Parikka (2004), about 40 EJ year^{-1} comes from woody biomass. However, Berndes et al. (2003) reviewed 17 studies concerning biomass and concluded that in 2050 up to about 115 EJ year^{-1} could come from forest wood biofuels. Today, the world's primary energy supplies amount to approximately 480 EJ year^{-1} (IEA2007). In Sweden, the share of primary energy supplies that originates from bioenergy has increased from 10% in the 1980s to 19% (124 TWh) of the total energy use (625 TWh (114,000 TWh globally)) in 2006 (Swedish Energy Agency 2007). The Swedish Bioenergy Association has stated that the bioenergy use in Sweden could expand by an additional 50 TWh by 2020 (Svebio 2008). Sweden is considered as one of the biggest users of wood pellets globally with a consumption of nearly 2,500,000 t in 2012 (Sikkema et al. 2010). Wood fuel pellets is a biofuel that has increased rapidly in production and use. The wood fuel pellet is a processed renewable energy fuel and transport product that is defined by national and international standards and described in several information sheets (SS 187120, 1998; CEN/TS 14961, 2005; Svebio 2004). Wood fuel pellets are compressed biofuels, cylindrical in shape and with a length of four or five times the diameter (usually 6–12 mm^4) used for heating, both in small-scale combustion units and in large-scale heating plants.

In 2007, the main users in the world were Sweden, the Netherlands, the USA and Denmark, whereas Sweden, Germany, Canada and the USA were the main producers, in this specific order. The energy market of Germany is described by the constant elevation of production and consumption. The majority of pellet consumers are private households. In Germany, electricity produced from pellets by cofiring is not usual and pellets are small raw material for biomass in CHP plants, that operates mainly with coal- and refuse-derived fuels (Carneiro and Ferreira 2012). The common price at mill gate for certified pellets was 175 €/t in 2012 (Smith et al. 2011). In 2012, the bid price for imported pellets from the USA and Canada was 135 €/t CIF Rotterdam, and have the comparable price for pellets from central and Eastern Europe was 145 €/t at mill gate (Goh et al. 2013). In 2006, the amount of produced fuel pellets worldwide equalled 6,733,000 t (Vinterbäck 2008). In 2007, there were 442 pellet plants in the world with a potential generation capacity of 14 million t of fuel pellets a year (Ljungblom 2007). If the market continues to increase, a continued development on a large and small scale is implied, encompassing wood and agricultural fuel pellets and pellets derived from new pellet countries in Africa, South America and Southeast Asia. An increased internationalisation of the biofuel market will also result in increased competition and force down the prices among local producers (Hillring 2002). According to Vinterbäck (2008), it is predicted that the global annual production will amount to 15,000,000 t a year in 2010. In Sweden, the total share of primary energy that originated from wood fuel pellets was more than 1 % or 8 TWh5 in 2007. Altogether, in 2007, 1,715,000 t were delivered to the Swedish pellet market. This includes the domestic production of wood fuel pellets of 1,411,020 t and the importation of 358,435 t of pellets (PiR 2008). The import of wood fuel pellets has doubled in the past 5 years. Recently, the imported pellets came from the Baltic region (Ericsson and Nilsson 2004), but with large pellet plants being established in the USA and Canada more pellets will probably be imported from there. The international biofuel market, however, is still at an early and dynamic stage of development (Ericsson and Nilsson 2004). The Swedish Association of Pellet Producers (PiR) predicts that in 2008 more than 2,000,000 t of pellets will be used in Sweden. The total amount of pellets delivered to the Swedish market has a sales value of more than 2 billion Swedish crowns (about 230 million €). Between 2006 and 2007, the total amount of pellets delivered to the Swedish market increased by 2 %, and it has increased by 90 % over the past 5 years (PiR 2008). In Sweden, about half of the quantity of pellets was used in large-scale heating plants and about 37 % (635,000 t) was used for single-house heating purposes. The latter are more sensitive to changes in pellet quality and require pellets that do not only fulfil the standard but also meet the requirements of the user's heating system. The wood pellets industry in Portugal consists of eight plants of large capacity (> 100,000 t/year) and 16 more small or medium plants (< 40,000 t/year) with a total annual production of 1,200,000 t/year. All the large plants utilised pulpwood or wood chips as the basic raw materials, while the small and medium plants used majorly dry materials. Household production of pellets elevated constantly from 120,000 t in 2006 and attained 1,200,000 t in 2012 (Fernandes and Costa 2010). The utilisation of wood pellets has developed much slower and was evaluated to be 120,000 t in 2012. For these figures, wood pellets describe a minor fraction of the energy market in Portugal yet. In 2012, the common price at mill gate for certified pellets was 160 €/t. When sold in bulk, the price was 135 €/t. About 10 % of the market is for pellet stoves in private households and for industrial boilers, mainly operating in the textile industry, while 90 % is exported in bulk for Northern European countries like Belgium, Sweden or Denmark (Kopetz 2013).

Opportunities and Challenges for the Development of Pellet Market

Biomass pellet technology seems to be an attractive green energy source in near future. However, it will gain its popularity by means of various aspects:

Policy: In order to maintain energy balance, the EU declared the share of renewable energy among the Member States (such as, by 2020 Poland should achieve approximately about 15 % share of green energy sources), besides in the USA biomass pellet technology gains a rapid momentum

- Economic: Bioenergy is regarded as a least capital-intensive process when compared to other renewable energy resources; however, the policy makers should provide subsidies to the farmers in order to commercialise this technology, besides it will uplift the socioeconomic status of the people by providing employment opportunities. For instance, areas where traditional farming ceased to be profitable or in the poor countries of Africa, where the production of good quality goods will not require large investments
- Social: Biomass being abundantly available and evenly distributed in nature does not create any political instability; moreover, the job of policy makers is to create awareness among people regarding bioenergy in order to gain its popularity
- Ecological: Being carbon neutral, green and ecofriendly in nature when compared to fossil energy sources; besides, bioenergy crop does not require any fertile land for its cultivation
- Energy: Bioenergy is considered as a potential energy sources in future. For instance, in Poland, estimated to be 400–800 PJ/a

In pellet production, there is a shortage of woody raw materials in several countries. Also, the price of the wood raw material increases. In Denmark and southern European countries, it is the potential of low forestry. In the near future, agricultural residue has a tremendous potential in biomass pellet industry. It is therefore of great interest to study the characteristics of this new category of raw material, paying special attention to the problems that they may trigger both at production and utilisation level. The information gathered in this report points out both positive and negative subjects affecting agricultural pellets (with a special focuses on straw pellets) in comparison with wood pellets:

- Pellets and agripellets have several positive aspects as fuels compared to firewood, wood chips and briquettes:

  - Pellets have a high energy content per volume unit, 4–5 MWh/t:
    - Increased bulk density (500–700 kg/m^3)
    - Lower transportation costs
    - Less storage is needed
  - Low moisture content:
    - Forest conservation
    - Less loss of product during storage
    - Advance to use of wet wood dust
  - Small variations in fuel quality:
    - Facilitating material handling
    - Rate of flow control
    - Cheaper and simple feeding equipment
  - Dust free:
    - Reducing dust explosion potential
    - Minimizing particle emission
  - Uniform:
    - More efficient control of combustion
  - Homogeneous composition:
    - Fully automatic heating operation
    - Complete combustion
    - Little repairs and high annual time of using
  - An increased energy density in combustion:
    - Better control possibilities
    - Excellent energy efficiency
  - Low emissions during combustion
  - Can be used for trimming of fuels in small and large heat centres
  - Cheap price of raw material

- Naturally agricultural raw materials and pellets have also some drawbacks compared to wood pellets:
  - The supply reliability and quality of the raw material:
    - Soil, climatic conditions and fertilising
    - Growing season, with lower production in abnormally dry years
  - Impurities of raw material:
    - Straw, bark, etc. would present a higher abrasive power
    - An increased wear of the parts of mill

- Moisture:
    - In winter wet and snowy bales
    - The screen of hammer mill jams
    - Quality of pellets will be lower
- The low bulk volume:
    - High transportation cost
    - Demand for large storage capacities
    - Difficulties in pelletising
- The fibre structure is different compared to saw dust:
    - Fibre rotates around the rotating feeding/handling devices
    - Bridging problems
    - Variations in material flow in production
- More difficult handling process at factory than with wood dust:
    - Even the risk of dust explosion
- Mixed pellets:
    - Need for two feeding in lines
- In pressing process:
    - Variation of power consumptions
    - Uneven feed
- Price of raw material can be increased
- Difficulties in combustion, emissions

Cofiring of agricultural pellets with other fuels is also a promising alternative, both technically and economically. For straw pellets, the small-scale markets of devices are still very limited, but some manufacturers already propose multi-fuel grate boilers in the range of 10–60 kW. In all cases, attention must be paid to the flue gas cleaning systems. Pellets made from agro-biomass (and in general other ash-, N-, K- and Cl-rich fuels) should be used primarily in large-scale combustion plants equipped with sophisticated combustion control systems and flue gas cleaning systems, whereas wood pellets should be preferred for residential and district heating system. Assuming that economic aspects concerning the agripellets energy option are favourable, the agripellet market for small-scale use will develop only if equipment manufacturers are encouraged to develop novel, safe and affordable combustion solutions. It is essential to further optimise the alternative pelleting systems in order to be completed on commercial pelleting systems. Various parameters like harvesting time, residence time of high temperature saturated steam, impact of various L/D (L = ratio of length of pelleting channel, D = dimension of the aperture) dies and the impact of pellet diameter on pellet bulk density and durability require further investigation in order to enhance pellet quality.

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Biomass: An Ageless Raw Material for Biofuels

Sk Manirul Haque, Aamir H. Bhat and Imran Khan

Abstract Biomass has always been a reliable source of energy, from the first man-made fire to the utilization of pelletized wood as a feed for thermal plants. Although the use of lignocellulosic feedstock as a solid biofuel is a well-known concept, conversion of biomass into liquid fuel is a considerable challenge, and the more complex the biomass gets (in terms of chemical composition) the more complicated and generally expensive the conversion process becomes. Depletion of the oil stocks combined with the increasing worldwide energy demand has generated an increased interest toward biofuels in the past 10–20 years, although for most of the twentieth century research on biofuel closely followed the price of petroleum. Another growing concern in the past 50 years is the environmental aspects of liquid fuel consumption. With the growing concerns about the greenhouse gas emissions, the use of biofuels, although sometimes criticized, is often a more environmentally friendly option because the carbon balance of biofuel is close to neutral when compared with petroleum-derived fuels such as gasoline, diesel, or kerosene. The "first-generation" biofuels appear unsustainable because of the potential stress that their production places on food commodities. For organic chemicals and materials, these needs to follow a biorefinery model under environmentally sustainable conditions. Where these operate at present, their product range is largely limited to simple materials (i.e., cellulose, ethanol, and biofuels). Second-generation biorefineries need to build on the need for sustainable chemical products through modern and proven green chemical technologies such as bioprocessing including pyrolysis. "Third-generation" algae biofuels and "fourth-generation" biofuels are created

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using petroleum-like hydroprocessing, advanced biochemistry, or revolutionary processes that defy any other category of biofuels.

Keywords Biomass · Ageless raw materials · Lignocellulose · Bioprocessing · Biofuels

Introduction

In the current situation with globalization, the world may face a major energy crisis in future. The alarming increase in climate change and global warming has been attributed to the exploitation of fossil fuels. To cope up with the ever-increasing demand for energy and keeping in view the problems associated with fossil fuel utilization, research has been directed toward the utilization of alternative sources of energy which will help in fulfilling the energy demand and also in mitigating the environmental problems. In comparison to the conventional sources of energy, which are concentrated in a limited number of countries, renewable energy resources exist over wide geographical areas. Deployment of renewable energy technologies is therefore believed to contribute significantly to energy independence of the region along with associated economic and environmental benefits. According to a report (Bridgwater 2003), renewable energy from biomass has the greatest potential to contribute to satisfying the energy needs of modern society in both developed and developing economies worldwide. Methanol (CH_3OH) and hydrogen (H_2) derived from biomass offer the potential for major contributions to transport fuel requirements especially in fuel cell vehicles (FCVs). In the fuel cell, chemical energy of fuel is converted to electricity without first burning the fuel to generate heat to run a heat engine. The fuel cell can increase the energy efficiency and control air pollution emission by using proton exchange membrane (PEM) fuel cell technologies. According to William et al. (1995), the FCV has potential to compete with petroleum-fueled internal combustion engine vehicle (ICEV) in terms of cost and performance including the effectiveness of air quality, energy security, and global warming issues. Fuel cells used in vehicles would probably use as fuel hydrogen and hydrogen carrier that are converted into H_2 in the vehicle. Hydrogen could be stored in the vehicle as liquefied H_2 in a metal hydride that releases H_2 when heated or as compressed H_2 gas. Currently, methanol (CH_3OH) is the preferred liquid carrier that can convert to a mixture of H_2 and CO_2 via steam reforming. Methanol-fueled FCVs would be about two times as energy efficient as compared to ICEVs. The production of electricity and biofuel through the photocatalytic degradation of organic waste in a photoelectrochemical (PEC) cell is an attractive area of research with many environmental advantages; for example, waste material can be consumed as a direct fuel, and solar radiation can be converted into useful energy sources, such as electricity or biofuel.

Today, biofuels have become a significant alternative source of energy. Biofuels are liquid or gaseous fuels and they originate from biogenic material and include fuels derived from conversion of biodegradable materials called biomass. Compared to most other fuels, the main feature of biofuels is that energy produced through these sources can be renewable. This characteristic of biofuels makes them different from other energy sources commonly used today such as nuclear fuels, coal, and petroleum. Since biofuel production leads to the efficient production of energy from organic materials, provides recycling of organic wastes, and prevents environmental pollution, the economic and environmental evaluation of biofuel production has gained importance in recent years. Biofuels are subdivided into two categories, namely first-generation biofuels and second-generation biofuels. Each of the categories contains a number of different fuels generated from different feedstocks. First-generation biofuels are made from sugar, starch, or vegetable oil. They differ from second-generation biofuels in that their feedstock is not sustainable/green or, if used in large quantity, would have a large impact on the food supply. Some examples of first-generation biofuels are bioethanol, biodiesel, vegetable oils like olive oil and sunflower oil, bio-ethers, biogas, and solid biofuels like wood, manure, and seeds. Second-generation biofuels are made from sustainable/green feedstocks such as algae, wood, or grass. Cellulosic ethanol, algae-based biofuels, biohydrogen, and methanol are some examples of second-generation biofuels. Biofuels can be used for generating centralized as well as decentralized heat, electricity, and energy. Globally, biofuels are used for the following purposes: cooking and heating (residential), generating electricity, agricultural uses, and fuel additives.

However, at present, the production of such fuels is not cost-effective because there are a number of technical barriers that need to be overcome before their potential can be realized (Eisberg 2006). Plant biomass represents one of the most abundant and underutilized biological resources on the planet, and is seen as a promising source of material for fuels and raw materials. At its most basic, plant biomass can simply be burned in order to produce heat and electricity. However, there is great potential in the use of plant biomass to produce liquid biofuels. However, biofuel production from agricultural by-products could only satisfy a proportion of the increasing demand for liquid fuels. This has generated great interest in making use of dedicated biomass crops as feedstock for biofuel production (Gomez et al. 2008). The examples of second-generation biofuels are cellulosic ethanol and Fischer–Tropsch fuels. The production of second-generation biofuels is noncommercial at this time, although pilot and demonstration facilities are being developed. Therefore, it is anticipated that these second-generation biofuels could significantly reduce CO_2 production; they do not compete with food crops and some types can offer better engine performance. When commercialized, the cost of second-generation biofuels has the potential to be more comparable with standard petrol, diesel, and would be the most cost-effective route to renewable, low-carbon energy for road transport (www.shell.com). Therefore, due to many advantages and disadvantages of the first-generation biofuels and obvious advantages of second-generation biofuels as shown in Fig. 1 , the approaches to integral utilization of biomass for sustainable development are more reasonable, where all parts of the plant such as leaves, bark, fruits, and seeds can be utilized to useful products.

Fig. 1 Comparison of first-, second-generation biofuel and petroleum fuel (Naik et al. 2010)

Biomass derived from trees, agroforest residues, grasses, plants, aquatic plants, and crops are versatile and important renewable feedstock for chemical industry as shown in Fig. 2. Through the photosynthesis process, plants convert carbon dioxide (CO_2) and water into primary and secondary metabolite biochemicals. Both of these are industrially important chemicals. Primary metabolites are carbohydrate (simple sugar, cellulose, hemicellulose, starch, etc.) and lignin called lignocellulose, present in high volume in biomass. The lignocellulosic biomass can be converted into biofuels. The secondary metabolites are high-value biochemicals such as gums, resins, rubber, waxes terpenes, terpenoids, steroids, triglyceride, tannin, plant acids, alkaloids, etc., and are present in low volume in the plants (Clark 2007). The secondary metabolites can be utilized for the production of high-value chemicals such as food flavors, feeds, pharmaceuticals, cosmeceuticals, nutraceutical, etc. using an integrated processing technique.

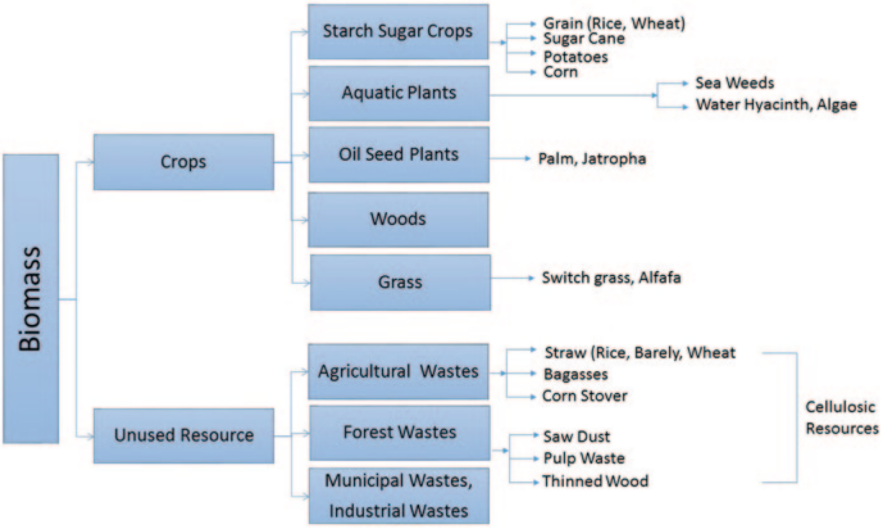

Fig. 2 Biomass as renewable feedstock for biorefineries (Naik et al. 2010)

Chemicals for Biomass

Char from Biomass

Biochar is a name for charcoal when it is used for particular purposes, especially as a soil amendment. Like all charcoal, biochar is created by pyrolysis of biomass. Biochar is under investigation as an approach to carbon sequestration to produce negative CO_2 emissions. Biochar thus has the potential to help mitigate climate change, via carbon sequestration. Independently, biochar can increase soil fertility, increase agricultural productivity, and provide protection against some foliar and soil-borne diseases. Furthermore, biochar reduces pressure on forests. Biochar is a stable solid, rich in carbon, and can endure in soil for thousands of years.

Pyrolysis produces biochar, liquids, and gases from biomass by heating the biomass in a low-/no-oxygen environment. The absence of oxygen prevents combustion. The relative yield of products from pyrolysis varies with temperature. Temperatures of 400–500 °C (752–932 °F) produce more char, while temperatures above 700 °C (1292 °F) favor the yield of liquid and gas fuel components. Pyrolysis occurs more quickly at the higher temperatures, typically requiring seconds instead of hours. High-temperature pyrolysis is also known as gasification, and primarily produces syngas. Typical yields are 60 % bio-oil, 20 % biochar, and 20 % syngas. By comparison, slow pyrolysis can produce substantially more char (~ 50 %). Once initialized, both processes produce net energy. For typical inputs, the energy required to run a "fast" pyrolyzer is approximately 15 % of the energy that it outputs. Modern pyrolysis plants can use the syngas created by the pyrolysis process and output three to nine times the amount of energy required to run. The Amazonian pit/trench method harvests neither bio-oil nor syngas, and releases a large amount of CO_2, black carbon, and other greenhouse gases (GHGs; and potentially, toxins) into the air. Commercial-scale systems process agricultural waste, paper by-products, and even municipal waste and typically eliminate these side effects by capturing and using the liquid and gas products. Switching from slash-and-burn to slash-and-char farming techniques in Brazil can decrease both deforestation of the Amazon basin and CO_2 emission, as well as increase crop yields. Slash and burn leaves only 3 % of the carbon from the organic material in the soil. Slash and char can keep up to 50 % of the carbon in a highly stable form. Returning the biochar into the soil rather than removing it all for energy production reduces the need for nitrogen fertilizers, thereby reducing cost and emissions from fertilizer production and transport. Additionally, by improving the soil's ability to be tilled, fertility, and productivity, biochar-enhanced soils can indefinitely sustain agricultural production, whereas nonenriched soils quickly become depleted of nutrients, forcing farmers to abandon the fields, producing a continuous slash-and-burn cycle and the continued loss of tropical rainforest. Using pyrolysis to produce bioenergy also has the added benefit of not requiring infrastructure changes the way processing biomass for cellulosic ethanol does. Additionally, the biochar produced can be applied by the currently used machinery for tilling the soil or equipment used to apply fertilizer.

Adhesives from Biomass

An adhesive is any substance applied to the surfaces of materials that binds them together and resists separation. The term "adhesive" may be used interchangeably with glue, cement, mucilage, or paste. The use of adhesives offers many advantages over binding techniques such as sewing, mechanical fastening, thermal bonding, etc. These include the ability to bind different materials together, to distribute stress more efficiently across the joint, the cost-effectiveness of an easily mechanized process, an improvement in aesthetic design, and increased design flexibility. Disadvantages of adhesive use include decreased stability at high temperatures, relative weakness in bonding large objects with a small bonding surface area, and greater difficulty in separating objects during testing. Natural adhesives are made from organic sources such as vegetable starch (dextrin), natural resins, or animals (e.g., the milk protein casein and hide-based animal glues). These are often referred to as bioadhesives. One example is a simple paste made by cooking flour in water. Starch-based adhesives are used in corrugated board and paper sack production, paper tube winding, and wallpaper adhesives. Casein glue is mainly used to adhere glass bottle labels. Animal glues have traditionally been used in bookbinding, wood joining, and many other areas but now are largely replaced by synthetic glues except in specialist applications like the production and repair of stringed instruments. Albumen made from the protein component of blood has been used in the plywood industry. Masonite, a wood hardboard, was originally bonded using natural lignin, an organic polymer, though most modern particle boards such as medium-density fiberboard (MDF) use synthetic thermosetting resins.

Valorization of Biomass

In recent years, there is an increasing awareness that this biowaste could serve as a valuable feedstock for the production of valorized products. Valorization has been defined as the conversion of waste and biomass to energy, fuels, and other useful materials, with a particular focus on environmental indicators and sustainability goals. In this chapter, valorization is defined as the process of creating value from biomass waste and residues by making it available for new economic purposes via innovative products or processes. An example of valorization is the processing of vegetable waste into juices, or using milk components in the pharmaceutical industry. Biowaste valorization is embedded in the scientific area of sustainable food production, characterized by complex societal, scientific, and commercial discussions regarding what technology roadmaps to prioritize. The question is raised whether the alternative usage of crops may either substitute or complement for its prime objective, like is the case when bioethanol is produced from corn and energy from bargasse, respectively. This ongoing ethical discussion strengthens the belief that valorizing biowaste would be an opportunity worthwhile to investigate. In order to improve the overall efficiency, effectiveness, competitiveness, and profitability of agriculture and food enterprises, the Food and Agriculture Organization (FAO) introduced the Market Linkages and Value Chains Group. Thus far, most attention regarding biowaste valorization is paid to its technological aspects. However, creating new and connecting existing supply chains to realize optimal biomass valorization in a bio-based economy requires as much attention to its technological as well as to its managerial aspects.

The process of turning food waste into value-added marketable products in mature sectors requires cooperation between biomass suppliers, technology developers, and commercial partners. From an open innovation perspective, inter-organizational relationships bridge resource, technological, and commercial gaps, advancing the dynamic development of product and process innovations. Various reports in the field of sustainable supply chains emphasize the advantage of inter-organizational cooperation. For instance, the Dutch Social and Economic Council (SER) appeals to the stakeholders in the bio-based supply chains to start a dialogue to cooperatively realize a sustainable and profitable development of the bio-based economy. This means that companies must overcome their traditional perspective on competitive advantage and have to establish new inter-organizational relationships that result in new product market combinations, new supply chains, and, eventually, in new industries.

First-Generation Biofuels

First-generation biofuels are produced directly from food crops by abstracting the oils for use in biodiesel or producing bioethanol through fermentation (UN Report2007). First-generation feedstocks are depicted in Fig. 3. Crops such as wheat and sugar are the most widely used feedstock for bioethanol while oil seed rape has proved a very effective crop for use in biodiesel. However, first-generation biofuels have a number of associated problems. There is much debate over their actually benefit in reducing green house gas and CO_2 emissions due to the fact that some biofuels can produce negative net energy gains, releasing more carbon in their production than their feedstock's capture in their growth. However, the most contentious issue with first-generation biofuels is "fuel versus food." As the majority of biofuels are produced directly from food crops, the rise in demand for biofuels has lead to an increase in the volumes of crops being diverted away from the global food market. This has been blamed on the global increase in food prices over the past couple of years. Some of the most popular types of first-generation biofuels are discussed further.

i. *Biodiesel*

This is the most common type of biofuel commonly used in the European countries. This type of biofuel is mainly produced using a process called transesterification. This fuel if very similar to the mineral diesel and is chemically known as fatty acid

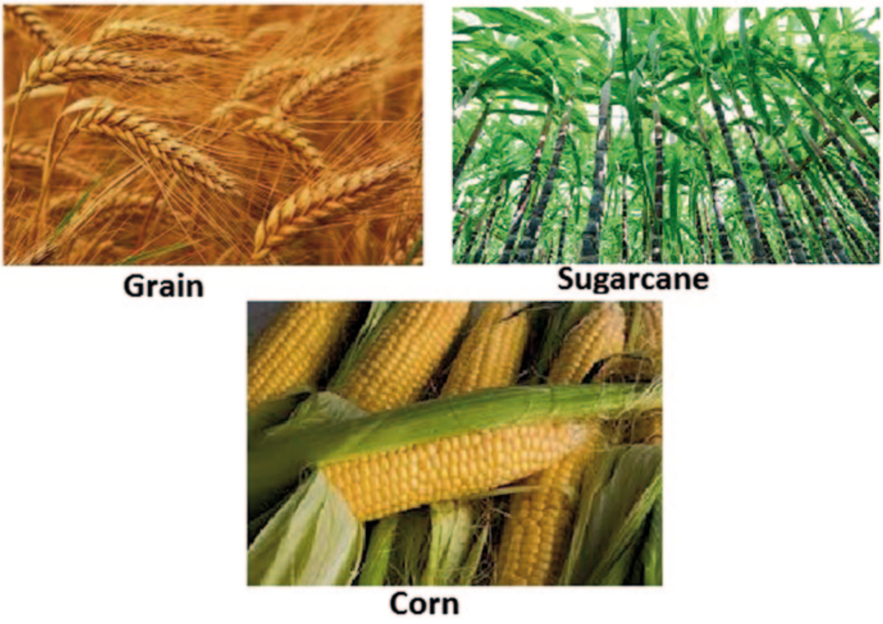

Fig. 3 First-generation biofuels used for production of biodiesel

methyl. This oil is produced after mixing the biomass with methanol and sodium hydroxide. The chemical reaction thereof produces biodiesel. Biodiesel is very commonly used for the various diesel engines after mixing up with mineral diesel. Now, in many countries the manufacturers of the diesel engine ensure that the engine works well even with the biodiesel.

ii. *Vegetable oil*

These kinds of oil can be used either for cooking purpose or even as fuel. The main fact that determines the usage of this oil is the quality. The oil with good quality is generally used for cooking purpose. Vegetable oil can even be used in most of the old diesel engines, but only in warm atmosphere. In most of the countries, vegetable oil is mainly used for the production of biodiesel.

iii. *Biogas*

Biogas is mainly produced after the anaerobic digestion of the organic materials. Biogas can also be produced with the biodegradation of waste materials which are fed into anaerobic digesters which yield biogas. The residue or the by-product can be easily used as manure or fertilizers for agricultural use. The biogas produced is very rich in methane which can be easily recovered through the use of mechanical biological treatment systems. A less clean form of biogas is the landfill gas which is produced by the use of naturally occurring anaerobic digesters, but the main threat is that these gases can be a severe threat if escapes into the atmosphere.

iv. *Bioalcohols*

These are alcohols produced by the use if enzymes and microorganisms through the process of fermentation of starches and sugar. Ethanol is the most common type of bioalcohol whereas butanol and propanol are some of the lesser-known ones. Biobutanol is sometimes also referred to as a direct replacement of gasoline because it can be directly used in the various gasoline engines. Butanol is produced using the process of acetone–butanol–ethanol (ABE) fermentation, and some of the experiments have also proved that butanol is a more energy-efficient fuel and can be directly used in the various gasoline engines.

v. *Syngas*

This is a gas that is produced after the combined process of gasification, combustion, and pyrolysis. Biofuel used in this process is converted into carbon monoxide (CO) and then into energy by pyrolysis. During the process, very little oxygen is supplied to keep combustion under control. In the last step, known as gasification, the organic materials are converted into gases like CO and hydrogen. The resulting gas syngas can be used for various purposes.

Second-Generation Biofuels

Second-generation biofuels have been developed to overcome the limitations of first-generation biofuels. They are produced from nonfood crops such as wood, organic waste, food crop waste, and specific biomass crops, therefore eliminating the main problem with first-generation biofuels (UN Report 2007). The representation of second-generation biofuels is depicted in Fig. 4. Second-generation biofuels are also aimed at being more cost-competitive in relation to existing fossil fuels (Review of EU Biofuels Directive2006). Life cycle assessments of second-generation biofuels have also indicated that they will increase net energy gains overcoming another of the main limitations of first-generation biofuels.

Second-generation biofuels are also known as advanced biofuels. What separates them from first-generation biofuels is the fact that feedstocks used in producing second-generation biofuels are generally not food crops. The only time the food crops can act as second-generation biofuels is if they have already fulfilled their food purpose. For instance, waste vegetable oil is a second-generation biofuel because it has already been used and is no longer fit for human consumption. Virgin vegetable oil, however, would be a first-generation biofuel. Because second-generation biofuels are derived from different feedstocks, different technology is often used to extract energy from them. This does not mean that second-generation biofuels cannot be burned directly as the biomass. In fact, several second-generation biofuels, like switchgrass, are cultivated specifically to act as direct biomass.

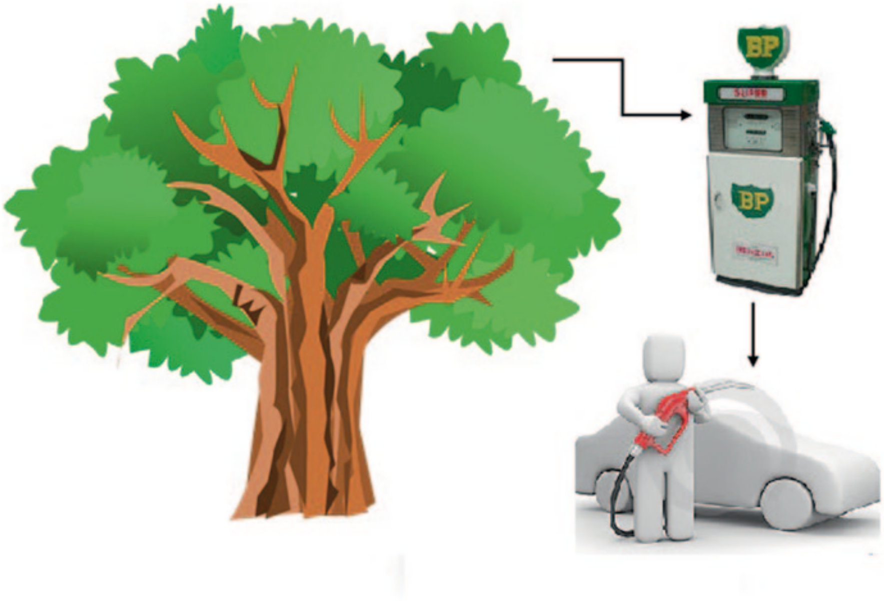

Fig. 4 Second-generation biofuels

For the most part, second-generation feedstocks are processed differently than first-generation biofuels. This is particularly true of lignocellulose feedstock, which tends to require several processing steps prior to being fermented (a first-generation technology) into ethanol. An outline of second-generation processing technologies follows.

i. *Thermochemical Conversion*

The first thermochemical route is known as gasification. Gasification is not a new technology and has been used extensively on conventional fossil fuels for a number of years. Second-generation gasification technologies have been slightly altered to accommodate the differences in biomass stock. Through gasification, carbon-based materials are converted to CO, hydrogen, and CO_2. This process is different from combustion in that oxygen is limited. The resulting gas is referred to as synthesis gas or syngas. Syngas is then used to produce energy or heat. Wood, black liquor, brown liquor, and other feedstocks are used in this process.

The second thermochemical route is known as pyrolysis. Pyrolysis also has a long history of use with fossil fuels. Pyrolysis is carried out in the absence of oxygen and often in the presence of an inert gas like halogen. The fuel is generally converted into two products: tars and char. Wood and a number of other energy crops can be used as feedstock to produce bio-oil through pyrolysis. A third thermochemical reaction, called torrefaction, is very similar to pyrolysis, but is carried out at lower temperatures. The process tends to yield better fuels for further use in gasification or combustion. Torrefaction is often used to convert biomass feedstock into a form that is more easily transported and stored.

ii. *Biochemical Conversion*

A number of biological and chemical processes are being adapted for the production of biofuel from second-generation feedstock. Fermentation with unique or genetically modified bacteria is particularly popular for second-generation feedstock like landfill gas and municipal waste.

Third-Generation Biofuels

The third generation of biofuels is based on improvements in the production of biomass. It takes advantage of specially engineered energy crops such as algae as its energy source (Chisti 2007). The algae are cultured to act as a low-cost, high-energy, and entirely renewable feedstock. It is predicted that algae will have the potential to produce more energy per acre than conventional crops. Algae can also be grown using land and water unsuitable for food production, therefore reducing the strain on already depleted water sources. A further benefit of algae-based biofuels is that the fuel can be manufactured into a wide range of fuels such as diesel, petrol, and jet fuel.

The most accepted definition for third-generation biofuels is fuels that would be produced from algal biomass, which has a very distinctive growth yield as compared with classical lignocellulosic biomass (Brennan and Owende 2010). The production of biofuels from algae usually relies on the lipid content of the microorganisms. Usually, species such as *Chlorella* are targeted because of their high lipid content (around 60–70 %; Liang et al. 2009) and their high productivity (7.4 g/L/d for *Chlorella protothecoides*; Chen et al. 2011). There are many challenges associated with algal biomass, some geographical and some technical. Typically, algae will produce 1–7 g/L/d of biomass in ideal growth conditions (Chen et al. 2011). This implies large volumes of water are required for industrial scale, presenting a major problem for countries like Canada where the temperature is below 0 °C during a significant part of the year. The high water content is also a problem when lipids have to be extracted from the algal biomass, which requires dewatering, via either centrifugation or filtration before extracting lipids. Lipids obtained from algae can be processed via transesterification by the previously described biodiesel process or can be submitted to hydrogenolysis to produce kerosene-grade alkane suitable for use as drop-in aviation fuels (Tran et al. 2010).

Fourth-Generation Biofuels

Fourth-generation biofuels are aimed at not only producing sustainable energy but also a way of capturing and storing CO_2. Biomass materials, which have absorbed CO_2 while growing, are converted into fuel using the same processes as second-generation biofuels. This process differs from second- and third-generation production as at all stages of production the CO_2 is captured using processes such as oxy-fuel combustion (Gray et al. 2007). The CO_2 can then be geosequestered by storing it in old oil and gas fields or saline aquifers. This carbon capture makes fourth-generation biofuel production carbon negative rather than simply carbon neutral, as it is locks away more carbon than it produces. This system not only captures and stores CO_2 from the atmosphere but it also reduces CO_2 emissions by replacing fossil fuels.

Fourth-generation biofuels are simply a step further from the third-generation biofuels. The keywords are carbon capture and storage (CCS), both at the level of the feedstock and/or the processing technology. The feedstock is not only tailored to improve the processing efficiency but also designed to capture more CO_2, as the crop grows in cultivation. The processing methods (mainly thermochemical) are also coupled to "carbon capture and storage" technologies which funnel off the CO_2 generated into geological formations (geological storage, for example, in exhausted oil fields) or through mineral storage (as carbonates). In this way, fourth-generation biofuels are thought to contribute better to reducing GHG emissions, by being more carbon neutral or even carbon negative compared to the other generation biofuels. Fourth-generation biofuels epitomize the concept of bioenergy with carbon storage (BECS). Biofuels are harnessed from genetically engineered microorganisms.

While biofuels appear to be a more sustainable alternative, there are many problems associated with their production and use. For instance, the use of food crops for energy production has brought about food shortages and there is a lot of unrest over diverting land and resources to this anvil. Besides, the costs associated with capital outlay for production, use of special material for transport (as in the case of ethanol), and cost of creating new technology do not necessarily make biofuels an attractive financial option. Further, all biofuels are not totally free of environmental impact and certainly do not have the same fuel efficiency to incite interest for total substitution. The answer lies in advancing more investments in research to make biofuels a clean, sustainable, and economic fuel resource for the future.

Biofuels by Region

The use of biofuels varies by region and with increasing oil prices there is a renewed interest in it as an energy source. Recognizing the importance of implementing bioenergy, there are international organizations such as International Energy Agency (IEA) Bioenergy, established in 1978 by the Organisation for Economic Co-operation and Development (OECD) IEA, with the aim of improving cooperation and information exchange between countries that have national programs in bioenergy research, development, and deployment. The UN International Biofuels Forum is formed by Brazil, China, India, South Africa, the USA, and the European Commission. The world leaders in biofuel development and use are Brazil, the USA, France, Sweden, and Germany. Brazil, Argentina, and Colombia are the only Latin American countries among the world's main producers of bioethanol and biodiesel, according to data from the latest biofuels study published by the Economic Commission for Latin America and the Caribbean (ECLAC).

Biofuels are a subset of bioenergy, which is energy derived from biomass (plant and animal matter) and which can range from manually gathered fuel wood and animal dung to industrially processed forms such as ethanol and biodiesel. Biomass can be used directly for heat, turned into biogas to produce electricity, or processed into liquid forms suitable as alternatives or supplements to fossil fuels for transport. Bioenergy is regionally or locally important in many places around the world; traditional biomass is still used for cooking by 38 % of people worldwide, for example, in parts of Africa and Asia more than 90 % of the populace relies on it. In China and elsewhere in Asia, roughly 48 million biogas plants were built as of 2012 to support rural electrification. The representation of 2012 Global Biofuels Production by Nation from BP statistical Review of World Energy 2013 is depicted in Fig. 5.

The top five ethanol producers in 2012 were the USA, Brazil, China, Canada, and France. But the USA and Brazil accounted for 87 % (61 and 26 %, respectively) of the global total US ethanol production totaled 50.4 billion liters, down about 4 % from 2011; US production depends mainly on corn as a feedstock, and corn prices rose in 2012 due to a severe summer drought in the Midwest. As a result, in the fall the USA briefly became a net importer of ethanol after nearly 3 uninterrupted years

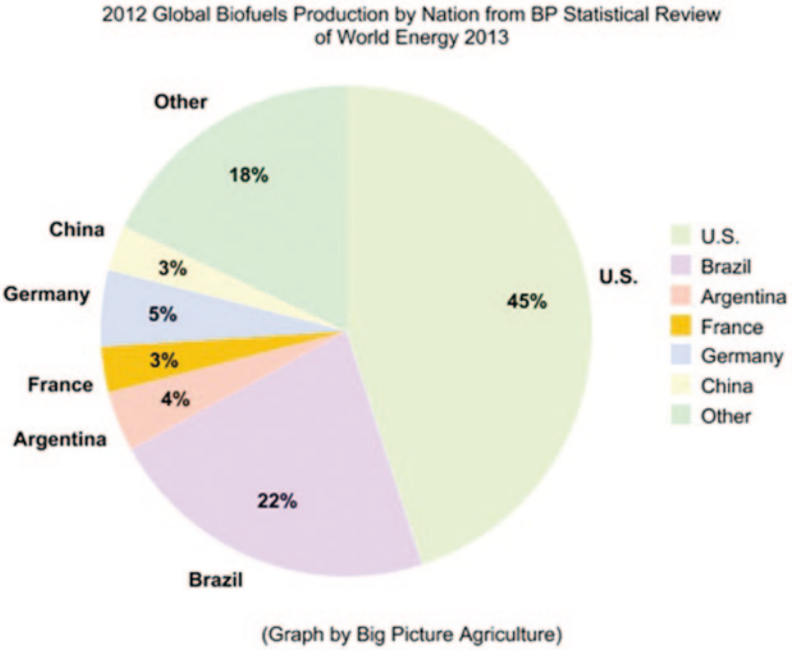

Fig. 5 Representation of 2012 global biofuels production by nation from BP statistical review of world energy 2013

of net exports. Brazil's production rose 3 % to 21.6 billion liters, partly because of a drop in sugar prices. The other top producers account for far smaller volumes; China's output, for instance, totaled 2.1 billion liters in 2012, while Canada's totaled 1.8 billion liters. The European Union (EU) as a whole produced 4.6 billion liters of fuel ethanol in 2012.

The USA also led in biodiesel production, with 3.6 billion liters, while Argentina took second place with 2.8 billion liters, and Germany and Brazil had roughly the same output at 2.7 billion liters apiece. China's biodiesel production, at only 200 million liters in 2012, lags far behind its output of fuel ethanol. Several European nations produce biodiesel, and the EU as a whole still accounted for 41 % of global biodiesel output despite a decline of 7 % in 2012. Worldwide, biodiesel production grew at an average annual rate of 17 % from 2007 through 2012, although the rate of growth slowed considerably.

Biofuel demand is strongly driven by blending mandates and supported by subsidies. Seventy-six states, provinces, or countries had such mandates on the books in 2012, up from 72 the previous year. Global subsidies for liquid biofuels were estimated in 2012 to be well over US $ 20 billion. Mandates or targets have been established in 13 countries in the Americas, 12 in the Asia-Pacific region, and 8 in Africa. In Europe, the EU-27 group of countries is subject to a Renewable Energy Directive (RED) that called for 5.75 % biofuel content in transportation fuels in 2012. The USA and China have established and Brazil has already achieved targets of between 15 and 20 % no later than 2022; India has also mandated 20 % ethanol by 2017.

Whether these targets are stable and will be met is an open question, however. India, for example, is said to have an uneven record of meeting its own mandates. The EU's RED came under strong challenge in 2012 as a result of concerns over the effect that biofuel feedstock cultivation was having on food prices and changes in land use. In response, the European Commission proposed limiting conventional biofuels (those derived from food crops) to a 5 % share of all transport fuels.

Barriers to the Development of Biofuels

The potential of biofuels to serve as a sustainable engine for economic growth is not in question. Yet they are not without their attendant problems and trade-offs. Here, we summarize and discuss some of these factors.

Net GHG Emissions

GHG emissions of corn ethanol and soy biodiesel often thought to be at least modestly lower than petroleum gasoline and diesel may be underestimated by conventional models. Most biofuel lifecycle accounting (LCA) models, which provide the bases for GHG impact estimates, are incomplete in a number of significant ways. For example, most assume a fixed, rather than dynamic, world and thus fail to capture important interactions such as those between changes in production and consumption of energy and materials, and changes in prices of major goods and services throughout the global economy (Phipps et al. 2007). In addition, most conventional LCAs do not adequately account for many pollutants that affect climate, such as nitrogen oxide, CO, and aerosols; do not account for the carbon cycle and bio-geophysical impacts of land-cover changes; and do not adequately represent the nitrogen cycle. Some recently developed LCA models, which have attempted to account for some of these factors, suggest that future average corn ethanol and soy biodiesel systems could have similar or greater GHG emissions than future gasoline or diesel fuel, although the uncertainty in these estimates is large (Delucchi 2006). Robust, comprehensive LCA models that fully capture and account for the factors listed above are urgently needed. Ethanol's local air quality impact also may be underestimated. While ethanol is commonly believed to be a cleaner burning fuel relative to gasoline, ethanol in fact may not provide any local air quality advantage over gasoline. New research suggests that while vehicles powered with E85 (85 % ethanol, 15 % gasoline) generally emit less toluene, xylene, and nitrogen oxides compared with gasoline-powered cars, they emit more acetaldehyde, formaldehyde, and total organic gas (Phipps et al. 2007). These conditions increase ozone and decrease ozone slightly, relative to gasoline, causing an overall increase in population-weighted ozone health problems in the world.

Thus, replacing gasoline with a high-ethanol blend may result in no improvement in local air quality and its associated health effects; substituting E85 for gasoline could result in a roughly equivalent—or possibly greater—number of cases of air-pollution-related asthma, respiratory disease, and premature death in the USA (Jacobson 2007).

Deforestation and Loss of Biodiversity

Besides contributing to GHG emissions, biofuel-driven agricultural expansions can also lead to land-use conflicts among different stakeholders. Indeed, environmentalists have become increasingly concerned about the impacts of rapidly expanding feedstock agriculture in the tropics. For example, several nongovernmental organizations (NGO) have accused oil palm growers in Southeast Asia of destroying large tracts of tropical forests and threatening the survival of many native species, including the orangutan (Koh and Wilcove 2007). In response, oil palm producers have accused NGOs of unfairly targeting the oil palm industry in Southeast Asia while ignoring biofuel feedstock agriculture in other regions, such as soybean cultivation in South America. Producers also argue that oil palm cultivation is not a threat to biodiversity because only disturbed forests or preexisting croplands have been converted to oil palm with minimal disturbance to pristine habitats.

Furthermore, it was reported that the conversion of either primary or secondary (logged) forests to oil palm would result in significant biodiversity losses (Koh and Wilcove 2007). Similarly, the conversion of diverse agroforestry systems within forested landscape mosaics to oil-palm-dominated stands represent further losses of diversity and the isolation of remnant patches of forested habitats (e.g., across many parts of Indonesia (Casson 1999); because palm oil is widely used both as food (e.g., for frying) and fuel (i.e., biodiesel), the spread of oil palm agriculture is a particularly worrisome threat to tropical biodiversity. On a global scale, deforestation has generally been assumed to be a key factor in altered weather patterns, soil degradation, and erosion. While some proponents of biofuels have promoted the cultivation of biomass as a means to green the earth, the logic behind this is flawed. The cultivation of palm trees is a poor alternative to the preservation of primeval forest.

According to Schneider and Mearns (2000) and Firbank (2005), local climate change as a result of deforestation stemming from biomass production could have irreparable effects on local climates, particularly with regard to decreasing levels of rainfall. Indeed, these factors, it is argued, will make it nearly impossible to plan for future land usage (Anderson and Fergusson 2006).The possibility remains, therefore, that regions currently enjoying suitable levels of precipitation may not be able to support extensive agricultural efforts (including the growing of biomass) in the future.

Impact on Food Prices

The promotion of biofuels may lead to the aggravation of problems currently faced by developing nations. If a large global demand for first-generation biofuels ensues, vast stretches of arable land could be switched from the production of foodstuffs to the cultivation of cash crops to be sold to OECD countries for use in biofuel production (Anderson and Fergusson 2006). Aside from reducing the pool of available food at a regional or national level in these largely agrarian-based economies, this would lead to an increase in the price of such food that still manages to find its way to market (Runge and Senauer 2007).

The underlying causes of rising food prices are many and complex. They include factors such as adverse weather conditions that affect crop productivity, speculative or precautionary demand for food commodities, and inappropriate policy responses such as export bans of foods (Josserand 2008; Rahman 2008). More important are structural factors that include rising energy costs, stagnation in crop productivity, policy inadequacies, or failures that constrain agricultural development, climate change, rising demand for higher value and grain-intensive foods (e.g., meat), and diversion of crops or croplands to biofuel production. Among these factors, biofuels have borne the brunt of the blame due largely to the media's sensationalization of the food versus fuel debate. A popular allegory to illustrate the impacts of biofuels on food equates the grain required to fill the tank of a sports utility vehicle to grain that could otherwise feed a person for an entire year (Byerlee 2008).

Although biofuels may have received a disproportionate amount of the blame for increased food prices, it clearly does deserve some of the blame: The use of corn to produce bioethanol in the USA has increased from 6 % of total corn production to 23 % over the past 3 years (Rahman 2008), and this has undoubtedly contributed to tightening food supplies and rising food prices.

Competition for Water Resources

Set against the backdrop of the energy and food crises—presumably precipitated by biofuels, is yet another unfolding and arguably more insidious threat to human survival and well-being—that of a water crisis. Agricultural expansion for biofuels may compete with other uses for water and thus contribute to rising water demands (Pickett 2008). The extent to which the use of biofuels will exacerbate the water crisis depends on how much irrigation is required to grow biofuels crops, which will vary with the type and location of the crop being cultivated. In the USA, irrigation accounts for the majority of the nation's consumptive use of water (i.e., water that does not become available for reuse). Biofuel production could have significant regional and local impacts where water sources are already stressed (Schnoor 2008). For example, the displacement of soybean by corn (to produce corn-based bioethanol) will result in greater water usage.

In other regions of the world, such as Malaysia or Indonesia, abundant rainfall supplies much of the water needed for agriculture. In these regions, drainage is a greater concern for farmers than irrigation, and the production of biofuel crops (e.g., oil palms for biodiesel) is not expected to have a dramatic impact on water availability (Corley and Tinker 2003). However, feedstock agriculture is not the only process in biofuel production that requires water. According to Phillips (2007), it is estimated that biorefineries consume 4 gallons of process water per gallon of bioethanol produced (gal/gal), largely from evaporative losses during the distillation of ethanol following fermentation. This means that a biorefinery producing 100 million gallons of bioethanol per year would use the equivalent of the annual water supply for a town of 5000 people. In comparison, water use in petroleum refining is about 1.5 gal/gal (Pate et al. 2007).

Conclusion

The promotion of biofuels can be seen as a politically attractive tool for governments eager to demonstrate responses to global warming, unsustainable demands for hydrocarbon-based energy, declines in agriculture-related employment, and the diminishing economic value of certain agricultural products. However, much of the shift toward biofuels systems is occurring without careful consideration of the social, economic, and environmental implications of such systems around the world. The advanced biofuel production technologies including lignocellulosic ethanol, microalgal biodiesel, and Fischer–Tropsch fuel have a good technical potential to substantially replace fossil fuels in the future. Lignocellulosic materials such as agricultural residues, woods, and grasses are abundant in most land areas of the world and their generation does not necessarily compete for arable land against food and feed production. Microalgae can produce a huge amount of oil on a small footprint, hundreds or thousands of times higher yield than most oil plants. It is technically possible to produce a high volume of biodiesel that is equivalent or higher than the current level of diesel consumption using microalgae as a feedstock that are grown on a small portion of land areas in the world. Biomass has a large energy potential. A comparison between the available potential with the current use shows that, on a worldwide level, about two fifths of the existing biomass energy potential is used. In most areas of the world, the current biomass use is clearly below the available potential. Only for Asia does the current use exceed the available potential, i.e., nonsustainable biomass use. Therefore, increased biomass use, e.g., for upgrading is possible in most countries. A possible alternative is to cover the future demand for renewable energy, by increased utilization of forest residues and residues from the wood processing industry, e.g., for production of densified biofuels.

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Power Reservoirs of Jumble-Based Biomass in Asia

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Abstract Technology-based efforts towards the treatment of unwanted bugs rejected by the human population which cause unhealthy lifestyle need to be restored as renewable energy. Available data for the utilization of biomass are from bagasse 6 %, sugarcane residues 12 %, rhizomic crops residues 9 %, cone residues 20 %, wheat residues 25 % and rice residues 28 %, which accounts for bioenergy potential of 1550 PJ/year from sugarcane residues, 407 PJ/year from rhizomic crops residues, 2614 PJ/year from cone residues, 3299 PJ/year from wheat residues and 3407 PJ/year from rice residues. The current scenario of the scarcity of energy sources raises the curtains on other resources where Asian countries like India, Myanmar, Pakistan, Nepal, Bhutan, etc. are having population-based jumbles (municipal rejection, domestic garbage, faecal matter of railway toilet flush, hospital effluents, etc). These jumbles must be added to the power catalogue as promising power reservoirs, especially when the prices of fuels are increasing from the past few decades at a global level. This channelization scheme not only creates the power reservoirs; rather, we can restore the lost sight of a green belt. Also, other power resources are bringing forward problems like oil depletion and global warming. This is the reason why many government agencies including the private sectors are endorsing the ideas for expanding the use of biofuels derived mainly from biomass. Biomasses from rich lands of Asian countries are promising reservoirs of energy that need to be exchanged where India can be the

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biggest tunnel. Use of such thin and convenient bioenergy reservoirs will alter the rigorous and costly approach of mechanical and physical conversion, and we can create a long-lasting avenue. The “rejection to selection” approach of such energy reservoirs will create a noble gateway for developing countries in Asia. Utilization of such a process in entrepreneurship through small- and large-scale municipal stationary tanks will help in increasing the living standards, energy security, health security and economic status of Asian countries. Generating a database system which maintains the records of the faecal matter generation sources (industry, railway stations, hospitals, municipal, etc.) and utilization at national levels will keep statistical information on each country’s contribution. Biomass from safari land which is the source of worthy trees must not be sacrificed for ample amounts of cellulose, hemicellulose, lignin, starch, proteins and other organic and inorganic components, though the conversion approach costs us million dollars and makes the bioenergy mission impossible. Here, the authors have suggested the connecting links for power generation from the jumble tanks, thus trying to create a green, healthy and powerful Asia.

Keywords Biomass · Reservoirs · Cellulose · Green belt · Industry · Faecal

Introduction

Biomass refers to the diverse materials obtained from plants and animals, which can be used as raw materials for the creation of useful energy in various forms and for diverse purposes (Sambo 2005). Biomass comes in a variety of forms, but can be classified broadly in terms of end use into fuel biomass, feed biomass, fibre biomass, organic fertilizer biomass and chemical biomass (Ogwo 2012). The versatility of biomass can be measured by the fact that the storage is easy and is transferable to energy (electricity, heat). Biomass can also be utilized as a raw material for the procuring fuel and chemical feedstock. Depending upon the availability of the biomass, either small-scale or large-scale units can be set up (few kilowatts to megawatts), and thus the utilization of biomass will contribute to energy policies. However, there are certain technological constraints which keep the production costs high and prevent the large-scale use of biofuels. It is being debated and research is going on for the suitable conversion technology for a particular biomass. The conventional energy generation from the fossil fuels poses serious environmental problems by emitting greenhouse gas (GHS). The use of alternative renewable energy sources will help reduce the consumption of fossil fuels and the pollution throughout the world. Currently, green energy resources contribute a little amount of the total energy to cater to the demands of the people, highlighting biomass as the most predominant source, that accounts for about 12 % of total energy requirement. This source of bioenergy includes agricultural waste, municipal solid waste (MSW) and forest residues. Biomass being abundantly available in nature can be utilized as a source of energy for the production of heat and electricity for rural and urban areas. Besides, it also promotes rejuvenation of biomass vegetation to avoid environmental deterioration with deprivation of agricultural land necessary for the

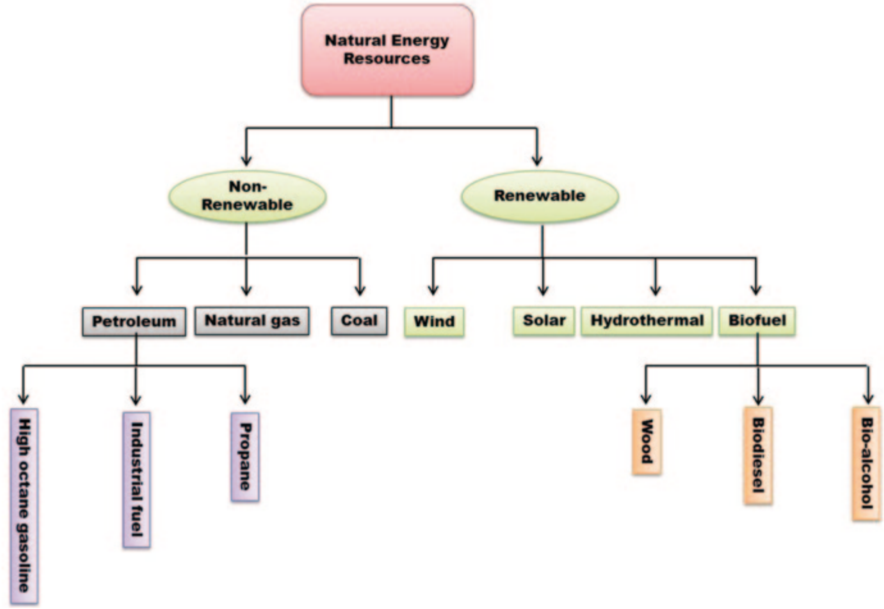

Fig. 1 Ligand: Comparative structure of the natural energy sources present on the planet earth.

livelihood of the rural population. Paliwal et al. (2010) reported that rejuvenation of biomass also maintains equilibrium between CO_2 generation during combustion and its uptake during photosynthesis. Figure 1 gives a comparative structure of the natural energy sources present on earth.

There is a huge gap between the requisite influx of energy and dependent population at a global stage; this crisis needs to be overcome by alternative energy sources which must be eco-friendly and affordable for developing countries. "One man's trash is another man's treasure". Asia is richly endowed with alternate energy resources—solar, wind biomass and small hydros that are widely distributed across the country. These sources can be utilized through commercially viable technologies to generate energy to provide fuel security, without endangering the environment. Various government and private organizations have been making efforts to popularize alternate energy technologies—improved chulahs, biogas plants, biomass gasifiers, solar photovoltaic systems, energy recovery from urban, industrial effluents, mobilizable faecal waste from domestic, municipals, Indian railways, etc. Moreover, a waste management system also plays a vital role in reducing the deleterious environmental effects through various methods. The adopted bioenergy technology flowchart is well described and shown in Fig. 2. Waste management is a challenging problem in all countries more so in developed countries. The main sources of organic waste such as agricultural waste, household food waste and human and animal waste are produced by humans, and these wastes can be decomposed under aerobic or anaerobic condition. But some unscientific methods followed in disposing of organic wastes lead to loss of organic matter and also cause environmental pollution.

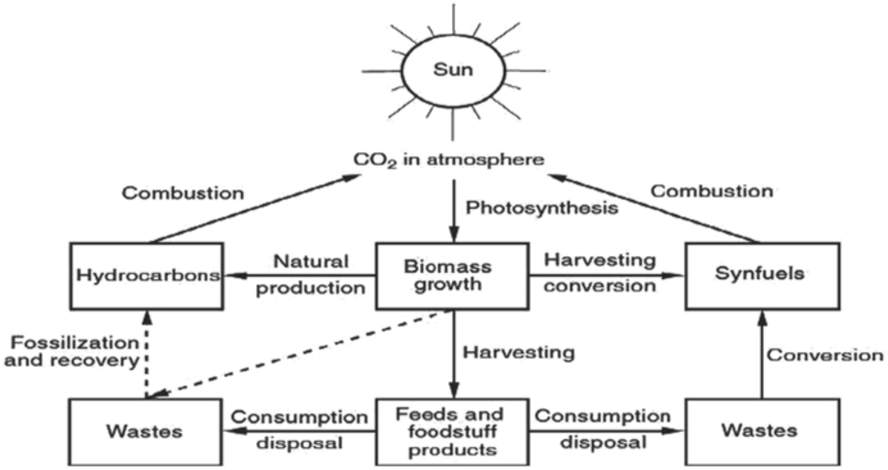

Fig. 2 Bioenergy technology flowchart. (Klass 2004)

Biomass, such as woody biomass and energy crops, is currently an important source of bioenergy to cater to the energy demands in various parts of the world. This bioenergy source possesses tremendous potential to provide the alternative and attractive source of energy mainly in developing nations. However, exploitation of this potential is only permissible if there are promising economic and/or environmental effects. One of the essential aspects is the evaluation of the potentials and estimation of resources in the locale of targets and restriction for their practical utilization. International biofuel trade is going to be an essential factor in the near future. These facts are propitious while considering the production of densified biofuels based on biomass. In most areas of the world, the current biomass use is clearly below the available potential. Only for Asia does the current use exceed the available potential, i.e. non-sustainable biomass use. Therefore, increased biomass use is possible in most countries. Proper utilization of forest and other biomass residues seems to be a promising alternative to cover the future demand for green and sustainable energy (MattiParikka 2004). Figure 3 well represents the biomass resources and their utilization.

Sources of Biomass

Biomass is present throughout the planet in different forms.

Agricultural Biomass

Agricultural biomass plays a vital role in the bioenergy sector to cater to energy demands. However, its capability to generate bioenergy without any effect on climate

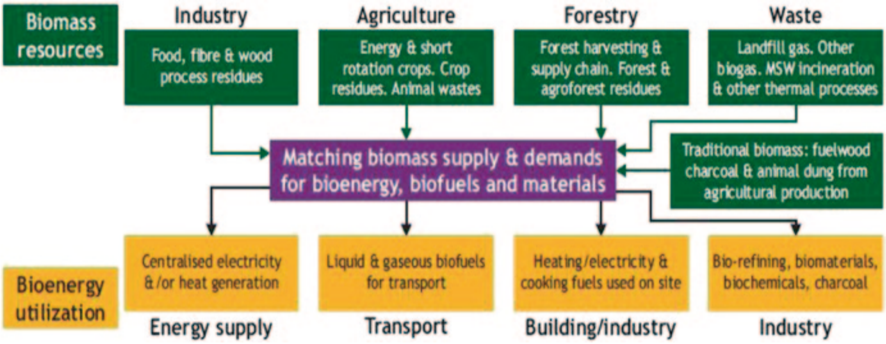

Fig. 3 Biomass resources and bioenergy utilization

or food security lies mainly in the use of abandoned agricultural lands. Nowadays, agricultural land is declining at a very fast pace. Although yields will probably continue to enhance, so will pressure for food and grazing land, driven by a combination of increasing human population and enhancing demands for a meat-based diet.

At a scale persistent with the obtainable resources, the bioenergy sector presents a range of exciting opportunities for enhancing energy independence and sustainability and decreasing the forcing of climate change. But deployed at a larger scale, it could threaten food security and aggravate climate change (Field et al. 2007).

Municipal Waste

The generation of MSW has been increasing around the world due to the various interconnected reasons such as industrialization, urbanization, economic growth and population growth. There is a positive correlation between the MSW generations in terms of kilogram per capita per day with the economic development around the world. The growth of the industries has resulted in the migration of people from the rural areas leading to a rapid increase in population, and thus the waste generation increases proportionally to the increase in population. In the urban areas, the increase in per capita generation has led to changes in the lifestyle with the result that people tend to spend more and thus the MSW generation per capita increases tremendously. This increase poses a challenge for disposal since more and more land is required for dumping. Moreover, due to the changing pattern of the waste it has become imperative that the MSW be segregated for better waste management at the operation facilities (Kaushal et al. 2012).

Most of Asian developing countries face solid waste (SW) generation problems, the main constraints being weak organization and limited budget allocation for solid waste management (SWM). So, their SW reduction is conducted from the source up to the landfill sites. SW generation is between 0.4 and 1.62 kg/capita/day; the composition of biodegradable organic waste is in the range of 42–80.2 %. No separation at source, complicated collection processes, open dumped landfill and no control of gas emissions and leachate in landfill are among the common problems faced. Alternative solutions of SWM in Asian developing countries use social and technical approaches. Social approaches are changing the public behaviour by improving community through training, and encouraging partnerships with decentralized SWM. The technical approaches are reducing biodegradable SW at source, converting waste to energy and using simple technology. These approaches are expected to improve the sustainability of SWM in Asian developing countries (Dhokhikah and Trihadiningrum 2012).

Sewage

The sewage sludge is a mixture which is composed of primary and microbiological sludge, and it contains nontoxic organic compounds, inorganic material and some toxic components. Sludge management has many options for the treatment of sludge of which energy production is also an option. There are many procedures for sludge treatment such as anaerobic digestion (AD), co-digestion and incineration in combination with energy recovery and co-incineration in coal-fired power plants (Kolat and Kadlec 2013).

Forestry

Forests, one of the important sources of fuelwood, have been meeting the energy requirement of most of the rural poor. Due to continued depletion of forest cover and density, the sustainability of fuelwood is questioned; whereas, the ever-increasing demand and poor return of the forest has to be catered with innovative technology and judicious use of fuelwood. Various developmental programmes and societies like National Afforestation Program (NAP), Green India Mission and Joint Forest Management committee should be commenced in both developed and developing countries, to ensure the maximum and fruitful utilization of these rich energy reservoirs (Madguni and Singh 2013).

Woodfuel

The Asia-Pacific Forestry Sector Outlook Study (APFSOS) is an organization affiliated to the Food and Agriculture Organization (FAO) which gathers information regarding the forests. Its role is to examine the information, review and give the outlook regarding the key issues related to forest growth. It has been ascertained that by the year 2050 the world carbon emissions would need to be at the 2000 level or even lesser, even though the energy demands would also increase over this period. There are no simple solutions for delivering this change; however, a mix of conservative approaches of energy usage would help in lowering the carbon intensity. For treading towards the sustainable energy path, there is a need to change the supply and demand pattern. These changes would require time and foundations have been laid for this process because it is a matter of great urgency. Some business communities around the world have shown keen interest in achieving this goal.

Wastes from Hospitals

There are stringent regulations around the world for the hospital waste management, and due to this it is receiving attention as waste generation in this sector ranges between 0.5 and 2.0 kg/bed/day. The SW generated from the health sector consists of various items such as plastics (7–10 %), disposable syringes (0.3–0.5 %), glass (3–5 %), bandages, linen, other infectious waste (30–35 %) and other general wastes (40–45 %). These wastes can also be further utilized as energy sources (Babu et al. 2009).

Biofuels

Biogas

Biogas is another bioenergy source composed of methane, carbon dioxide and other gases (hydrogen sulphide). Production of biogas is mainly influenced by various parameters such as temperature, pH, substrate, loading rate, hydraulic retention time (HRT), carbon/nitrogen ratio and mixing. At the small-scale level, distinct digesters are used in many rural areas to cater to their energy needs as they are cost-effective and easy to handle. The biogas produced is utilized in cooking and heating, in the form of biogas stoves, fertilizers and for lighting and power generation (Rajendran et al. 2012). Various models of biogas plants used in India are floating drum (Indian) digester, fixed-dome (Chinese) digester, Deenbandhu model, Appropriate Rural Technology Institute (ARTI) biogas plant, water kiosk biogas plant, Bangladesh Council of Scientific and Industrial Research (BCSIR) biogas plant, Malaprabhu biogas plant, fixed-dome biogas plant and institutional biogas plant. Various types of dung give varying amounts of gas production, e.g. 0.023–0.04 gas/kg from cattle, 0.04–0.059 from pigs, 0.065–0.116 from poultry and 0.02–0.028 from human faeces.

Biodiesel

Biodiesel, another green energy option, generally comprises monoalkyl esters and was previously derived from vegetable oils or animal fats via the transesterification process. Biodiesel production from pure vegetables or seed oils is not cost-effective and constitutes about 70–85 % of the overall biodiesel production cost; besides, municipal sewage sludge that contains significant amount of lipids has gained worldwide attention as a cheap lipid feedstock for the production of biodiesel. There are numerous ways for biodiesel production which include alkali- or acid-based transesterification; however, alkali-based transesterification is a rapid process and thus is used commercially. Moreover, the biofeedstock that constitutes more than 1 % free fatty acids (FFAs; sludge), mainly acid catalysis followed by base catalysis is recommended because of soap formation with alkali-catalysed transesterification and high FFA. In order to enhance biodiesel production, it is recommended that wastewater operators utilize novel microorganisms that possess oil-producing capabilities. Besides, these microorganisms also possess the ability to resist obnoxious chemicals present in the sludge (Kargbo 2010).

Bioethanol

Asia has a great potential for bioethanol production from biomass (crop residues and wasted crops), and could produce up to 291 GL/year of bioethanol. The most available feedstocks in Asia are rice straw, wheat straw and corn stover. On the global level, there is a potential of bioethanol production from the feedstock of wasted major crops (crops lost in distribution) such as corn, barley, oat, rice, wheat, sorghum and sugarcane. Tables 1 and 2 provide an outline of the bioenergy produced by the wasted grains in Asia (Kim and Dale 2004). Figure 4 shows the biomass consumption in Asian countries. The sustainable biomass production in many countries such as China, India, Malaysia, Philippines, Sri Lanka and Thailand is from plantations and is estimated to be in the range of 182.5–210.5, 62–310, 0.4−1.7, 3.7–20.4, 2.0−9.9 and 11.6–106:6 Mt/year, respectively. Further, it has been calculated that by using the advanced technologies the annual electricity generation potentials from the green biomass resources are estimated to be about 4.5, 114, 27, 79, 254 and 195 % of the total electricity generation in the year 2000 in Malaysia, India, China, Philippines, Sri Lanka and Thailand, respectively (Bhattacharya 2003).

Table 1 Bioethanol production in Asia from wasted grains. (Kim and Dale 2004)

Grain	From wasted grain	From grain replaced by DDGS*	From grain stover/straw/ bagasse (sugarcane)	Total bioethanol (GL)	Gasoline equivalent (GL)
Corn	4.41	2.41	9.75	16.6	11.9
Barley	0.50	0.32	0.61	1.44	1.03
Oat	0.03	0.02	0.07	0.12	0.08
Rice	10.5	3.87	186.8	201.2	144.5
Wheat	4.16	2.62	42.6	49.32	35.42
Sorghum	0.24	0.13	–	0.37	0.27
Sugar cane	0.82	–	22.1	22.1	15.9

[*] *DDGS* Distiller’s dried grains with solubles

Table 2 Potential bioethanol production from grain in Asia. (Kim and Dale 2004)

From waste crop (GL)		From lignocellulosic biomass (GL)	
Corn	6.82	Corn stover	9.75
Barley	0.83	Barley straw	0.61
Oat	0.04	Oat straw	0.07
Rice	14.4	Rice straw	186.8
Wheat	6.78	Wheat straw	42.6
Sorghum	0.37	Sorghum straw	–
Sugar cane	0.82	Bagasse	21.3
Subtotal (A)	30.1	Subtotal (B)	261.0
Total	291.0		

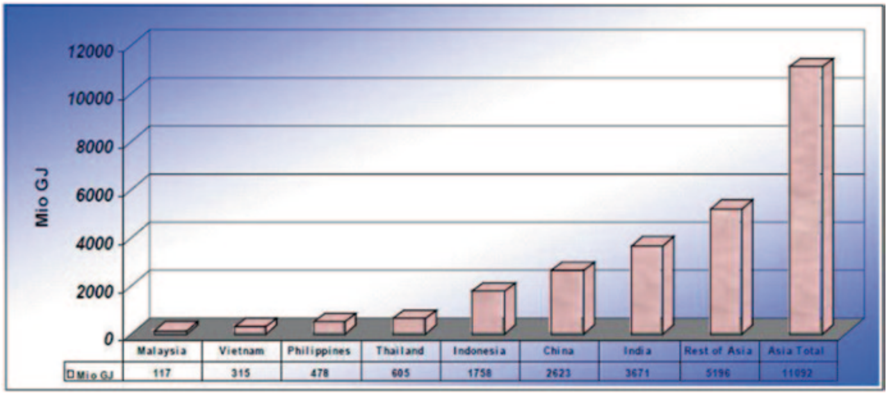

Fig. 4 Biomass consumption in Asian countries

Bioenergy Conversion Techniques

Several processes available for the conversion of biomass to usable energy forms include physical conversion of biomass (firewood, pelletizing, particleboard production), thermochemical conversion of biomass (combustion, gasification, pyrolysis, carbonization, hydrothermal gasification, hydrothermal liquefaction, biodiesel production) and biochemical conversion of biomass (biomethane, ethane fermentation, acetone–butanol fermentation, hydrogen fermentation, lactic acid fermentation, silage, composting).

There are various factors which influence the choice of bioenergy conversion processes such as the biomass feedstock type and quality, requirement or desired energy form, economic conditions, environmental standards and project specific factors (McKendry 2002). Generally, on a large scale, the biomass conversion to energy is attempted using thermochemical, biochemical (biological) and the mechanical extraction (coupled with esterification) processes, even though the cost of biodiesel production is high in comparison with fossil fuel and is thus uncompetitive. This situation may change in the near future as there is an increased awareness among masses about the environment and much research is being conducted for the improvements in technologies.

Thermochemical Conversion

Three main processes used for the thermochemical conversion of biomass are as follows.

Combustion

Combustion involves burning of the biomass at 850 °C that leads to the production of energy (heat, mechanical power or electricity). It involves numerous equipment such as boilers, stoves, turbogenerators, furnaces, steam turbines, etc. These combustion plants consist of boilers that capture heat and then convert it into electricity. Moreover, these are also associated with extensive air pollution control systems that clean the combustion gases to comply with regulatory emission limits before they ooze out into the atmosphere through a chimney. These plants varies from small scale (domestic heating) up to large scale (industrial plants in the range 100–3000 MW) and possess the capacity to use about 50,000–300,000 t of biomass per year. In coal-fired power plants, co-combustion technology is a promising alternative because of the high conversion efficiency of these plants. However, the net bioenergy conversion efficiency for biomass combustion power plants varies from 20 to 40 %. Higher energy efficiency is obtained with systems more than 100 MWe or when the biomass is co-combusted in coal-fired power plants. A heat engine cycle, the Stirling cycle, uses combustion to provide shaft power directly but the development of the cycle is presently limited to small power outputs.

Gasification

During the process of gasification, the partial oxidation of biomass at the temperature range of 800–900 °C yields combustible gaseous mixtures. The “syngas” produced can be utilized for energy production or can be used for producing methane, chemicals, biofuels or hydrogen. The “syngas” has a low calorific value (CV; 4–6 MJ/Nm^3) which can be either burnt directly or used as a fuel for gas engines and turbines (Natural Resources Institute 1996). There is one integrated concept called the biomass integrated gasification/combined cycle (BIG/CC) by which the gas turbines can convert this “syngas” to electricity with a high conversion efficiency. The important advantage of the above process is that it is compact and the “syngas” is cleaned before combustion in the turbine. Furthermore, the utilization of costly gas cleaning equipment is avoided and there is high conversion efficiency ranging from

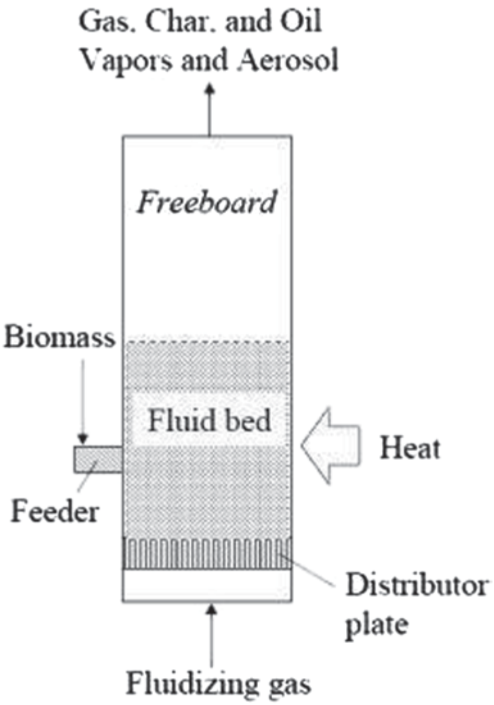

Fig. 5 Pyrolysis: bubbling fluidized-bed reactor. (Jahirul et al. 2012)

40 to 50 % for a plant of 30–60 MWe capacity. However, this BIG/CC technology is not yet commercially available and is at the demonstration stage (Mitsui Babcock 1997; EU 1999; Aston University 1986). The methanol and hydrogen produced from “syngas” are produced by gasification processes (either hydrogen indirect or oxygen blown) and these have a future in transportation. These processes are favoured for methanol and hydrogen because of their higher CV values (9–11 MJ/Nm^3).

Pyrolysis

Pyrolysis involves heating the biomass at around 500 °C in the absence of air and converts it into liquid (bio-oil or bio-crude), solid or gaseous form. Figure 5 depicts the range and possible yields of pyrolysis energy products. Flash pyrolysis is generally utilized for the production of bio-oil enabling the conversion of biomass to bio-crude with an efficiency rate of up to 80 % (Aston University and DK Teknik 1993; EU 1999). Bio-oil finds great application in turbines, engines; besides, it is also used as a feedstock for refineries. However, there are certain limitations associated with the bio-oil such as poor thermal stability and corrosivity. To overcome these limitations, bio-oil undergoes certain processes so as to lower oxygen content and remove alkalis by means of hydrogenation and catalytic cracking of the oil.

Other Processes

Bio-oils are also produced by other processes like hydrothermal upgrading (HTU) and liquefaction. The HTU process generally occurs in wet environment under high pressure and converts the biomass to partly oxygenated hydrocarbons, and currently this process is in its infancy stage. However, liquefaction process is not commonly used because of certain reasons such as complex nature of reactors and fuel feeding system and being more costly. Liquefaction involves conversion of biomass into a stable liquid hydrocarbon at low temperatures and high hydrogen pressures (Warren Spring Laboratory 1993).

Biochemical Conversion

Biochemical conversion involves fermentation and AD, together with a lesser-used process based on mechanical extraction/chemical conversion.

Fermentation

Fermentation involves the production of bioethanol from sugar crops (sugarcane, sugar beet) as well as starch crops (maize, rice). This phenomenon involves the use of certain enzymes produced by microorganisms (yeast) which act on these sugars and then convert it into ethanol Fig. 6. Thermophilic microorganisms are regarded as special candidates for bioethanol production at the commercial scale because they bare the capacity to resist high temperature and toxic by-products formed during the fermentation process (Pirzadah et al. 2014). It is estimated that about 1 t of dry corn produces about 450 l of bioethanol. Besides, the residue produced during the fermentation process is used as cattle feed; however, in the case of sugarcane, the by-product (bagasse) is used in combined heat and power programmes (CHP; Coombs 1996). Nowadays, lignocellulosic biomass is used as a feedstock for bioethanol production.

Anaerobic Digestion

Under AD, organic matter is converted into gaseous form generally termed as biogas (mixture of methane and carbon dioxide with small amount of other gases such as hydrogen sulphide; EU 1999). This phenomenon is carried out by various microorganisms such as bacteria with an energy content of about 20–40 % of the lower heating value of the feedstock. It is an efficient technology especially for treating biomass with high moisture content ranging from 80 to 90 %. Biogas has a direct application in spark ignition gas engines (s.i.g.es) and gas turbines and can be upgraded to higher quality, i.e. natural gas quality, by the removal of CO_2. It can also be used in s.i.g.e. as an energy source to generate electricity only; however, the overall conversion efficiency from biomass to electricity is approximately about 10–16 %.

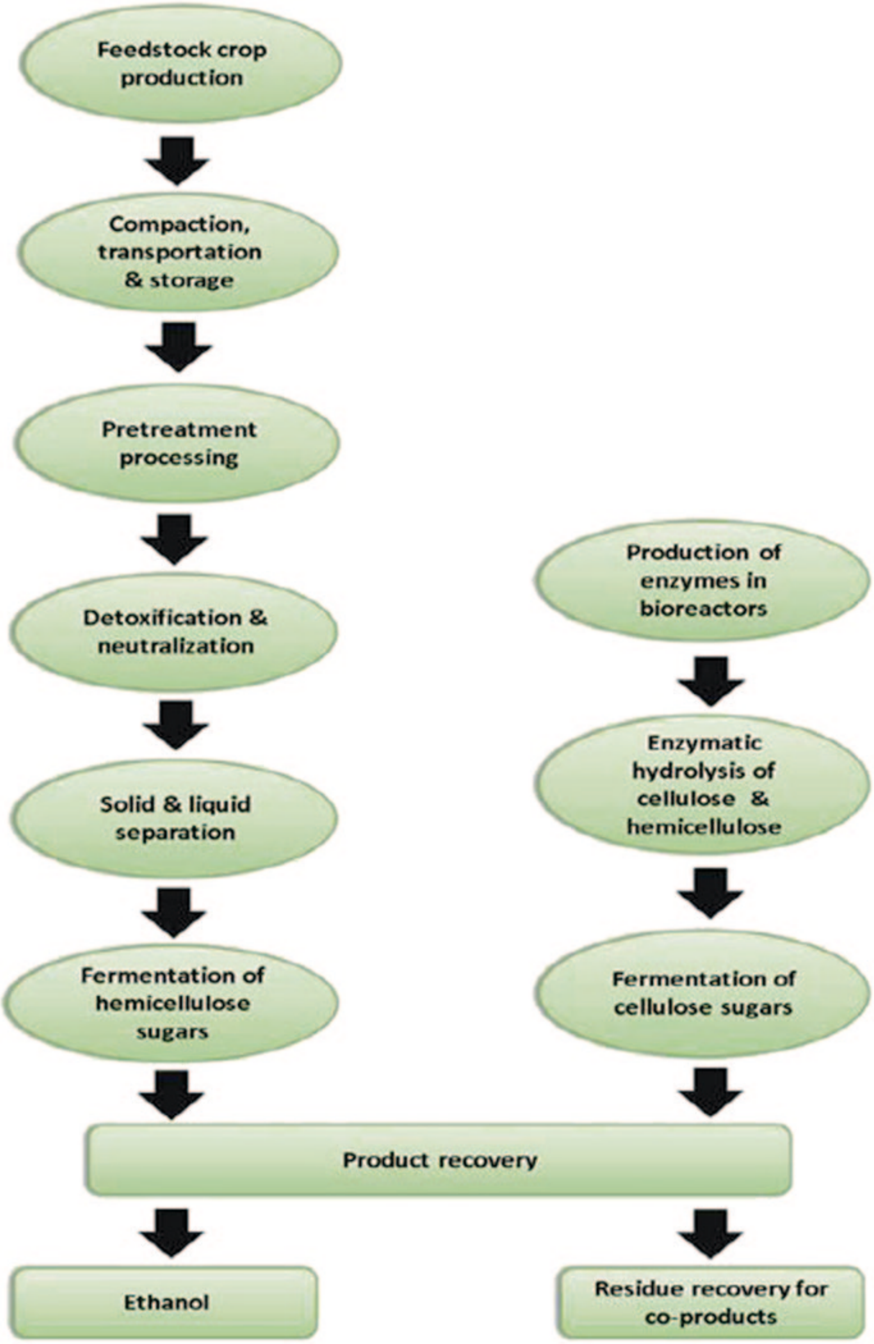

Fig. 6 Flowchart of cellulosic ethanol production from lignocellulosic biomass. (Source: Pirzadah et al. 2014)

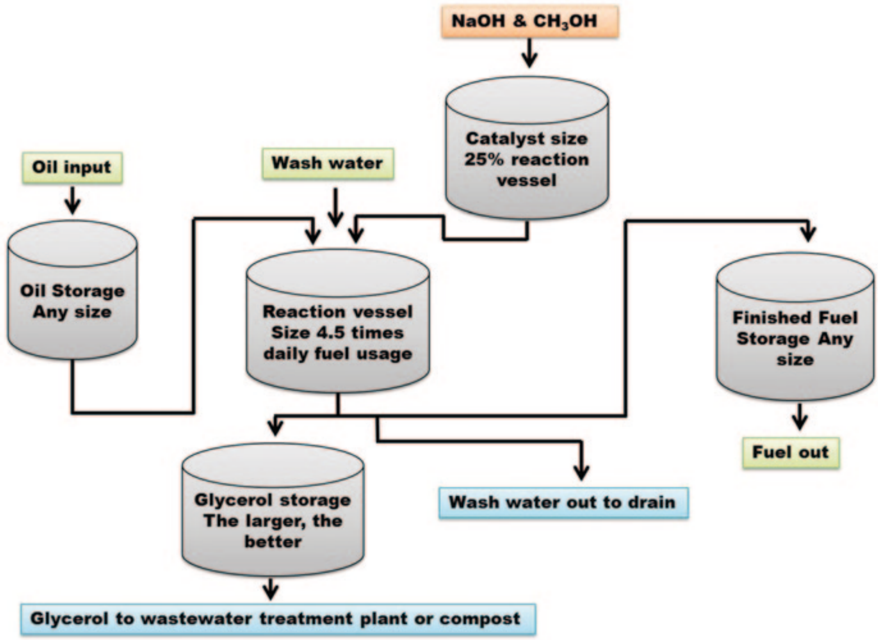

Fig. 7 Biodiesel processor layout and design for transesterification

As with any type of power generating system using an internal combustion engine as the prime mover, waste heat from the engine oil and water-cooling systems and the exhaust could be recovered using a combined heat and power system.

Mechanical Extraction

This phenomenon involves extraction of oil from the seeds of bioenergy crops like *jatropha* nut, groundnut, *Pongamia,* etc. Besides, the residue produced during this process is used as animal feed. It has been estimated that about 3 t of rapeseed are required to produce 1 t of oil. This rapeseed oil then undergoes further processing (esterification) resulting in the formation of rapeseed methyl ester (RME) also known as biodiesel (Warren Spring Laboratory 1993). In some European countries, it is also used as a supplementary transport fuel. Figure 7 depicts a generalised flow sheet for the production of methyl ester biodiesel and the by-product glycerine.

Biomass Energy Programmes

Programmes related to green energy offer many advantages but achieving them requires significant management policies. There are various government and private organizations that work for the efficient production of bioenergy from biomass.

The International Energy Agency (IEA) is one of the autonomous bodies (established in November 1974) within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme (OECD/IEA 2007). The main focus of these organizations include: employment generation to uplift socio-economic status of the people, saving foreign exchange, environmental security, energy security, achievement of climate change communities and acceleration of the green energy. Moreover, the government should provide subsidies to local farmers for biomass cultivation at a large scale. The importance of developing green energy in a sustainable way should be universally recognized; however, no such internationally sustainability assurance system exists for bioenergy or biofuels more broadly. Sustainability requirements will eventually need to be agreed upon internationally, applied locally and to all biomass regardless of end use, if leakage effects or impact shifting is to be avoided. Research and development (R&D) programmes regarding biofuels or bioenergy should be greatly encouraged.

Conclusion

With the changing climatic conditions and escalation in oil prices, current research is focusing towards alternative and promising green approach of energy by using clean technologies utilizing organic waste. Bioenergy from jumble-based biomass which is abundantly available and evenly distributed in nature not only reduce the dependence on petroleum resources but also contribute to sustainable development by diminishing GHG emissions. Currently, the major hindrance in the conversion of jumble-based biomass to bioenergy involves biomass feedstock, conversion technology, hydrolysis process and fermentation. With respect to biomass feedstock, major hindrances are supply, cost, handling and harvesting. The major obstacles associated with the conversion technology involve processing of biomass, convenient and cost-effective pretreatment process to detach hemicellulose and cellulose from their complexity with lignin. Another objection is to develop an adequate and economical hydrolysis process for depolymerization of cellulose and hemicellulose present in the biomass to generate higher levels of simple sugars. Enzymatic hydrolysis is considered as a potent phenomenon for saccharification of complex polymer. Currently, only few commercial technologies are available for the conversion of jumble-based biomass into biofuels. In order to commercialize this technology at a large scale, much research is needed to make this technology accessible and cost-effective.

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Chemical Processes and Reaction By-products Involved in the Biorefinery Concept of Biofuel Production

Mohammad Faruq, Tanvir Arfin and Nor Azah Yusof

Abstract With an increase in population, the demand for energy and impending depletion of fossil fuels have led to the research and development of sustainable technologies which make use of the naturally available biomass resources. When it comes to energy production, the distinct components and different processing technologies associated with biomass require significant amount of investment and is costly to perform everyday operations. From a business point of view, only energy generation with the biomass may not be a profitable industry unless some marketable intermediates and chemicals are produced in addition to energy. Since the major components of biomass include cellulose, hemicellulose and lignin, during its processing for energy, it can form valuable by-products that can find applications in pharmaceutical, food and fertilizer industries. When continuous heat is applied to carbohydrates, such as cellulose and hemicelluloses, it dissociates into products having low molecular weight, which can be useful in the production of ethanol, methane and syngas. Similarly, the burning of lignin forms carbonaceous residue which can act as a source for bio-oil and biofuel, as they are the degraded products of biomass obtained from living materials such as plants, grains, vegetable oils, animal-based oils, etc. For that, the technique of biorefinery system can be followed where it consumes biomass as the major processing input and converts fully into usable end products. The biorefinery system serves as the basic concept by providing sophisticated platform for the co-production of biofuels, value-added chemicals and energy from biomass. The biorefinery concept uses a number of chemical routes where the initial biorenewable feedstock can be useful for the production of solid fuel, or converted into liquid or gaseous forms for the generation of electric power, heat and chemicals. The chief attention on the general processes of chemical conversion of biomass-derived residues from agricultural and forest wastes, self-sufficiently, increases the utilities in daily life, if it is integrated with

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the biorefinery system. The present chapter basically provides an overview of the biorefinery concept and how it can be useful for the industrial usage of by-products formed during the production processes of biofuels and/or energy. The potentials of biomass residues in today’s world energy demand and the basic chemical reactions involved in the processing of agricultural biomass for biofuel production are deeply discussed. The authors make an attempt to organize this chapter for a variety of readers who are interested in the topic of by-products from biomass technologies, including the students and professionals.

Keywords Biorefinery concept · Biomass-derived products · Anaerobic digestion · Pyrolysis · Enzymatic hydrolysis

Introduction

In recent years, the rapid increase in the everyday usage of energy-based technologies led to some apparent changes in the demand and requirements for alternative fuels. In order to meet such demands while balancing the economy and environment, the quest for alternative sources of energy (specially, bioenergy contained in biomass) with sustainability has been increased (Olabi 2013). It is still an undergoing task for many researches to implement more eco-friendly technologies which lessens the negative influences of current energy production processes onto the environment, as new challenges are being faced while meeting the balance of economy, fuel demands and the environment. For sustainability, researchers mainly focus on the processes, mechanisms, tools and techniques which are eco-friendly and can exhibit ample standard of living in the present scenario to the world and can promote for the future generations (Olabi 2012). It has been seen that the fuel production from biomass, which includes the agriculture and crop residues, animal wastes, forest and mill residues, wood and wood wastes, livestock operation residues, aquatic plants and municipal and industrial wastes, can serve as potential for maintaining the sustainability in a renewable way. Some of the factors such as the cost of biomass over the natural coal, limited availability, production time and carbon-trading laws are not fully supporting the use of biomass to its maximum potentials (Campbell et al. 2010). The modern types of bioenergy carriers such as wood pellets, logs, wood gas or biogas and agriculture wastes are also used as various stable rendering agents to meet the fuel challenges in a range of needs. It is also estimated that on the earth about 200 billion tonnes of biomass has been produced every year for the generation of energy content approximately 30,000 EJ (1 EJ = 1 exajoule = 1×10^{18} J).

Nowadays, the primary and secondary metabolites prepared from plants through the extraction of CO_2 and water by the process of photosynthesis serve as the hefty industrial chemical. The two secondary metabolites present in high volume in the biomass such as carbohydrates (simple sugar, cellulose, hemicellulose, starch) and

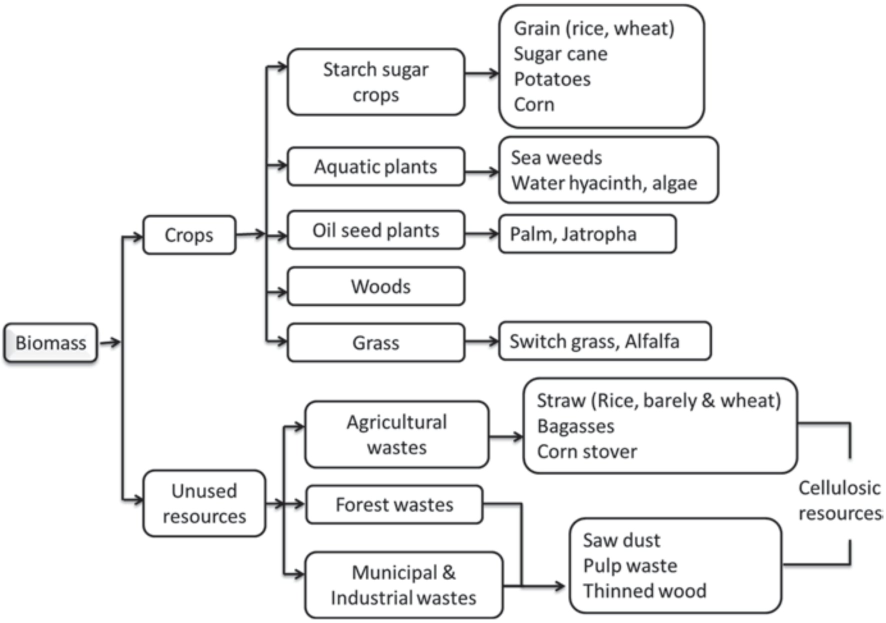

Fig. 1 Biomass as renewable feedstock for biorefineries

lignin (called lignocellulose as well) can be converted into biofuels. In comparison to the secondary metabolites, the primary metabolites of plants are in low volume but with high biochemical values such as gums, resins, rubber, waxes, terpenes, terpenoids, steroids, triglyceride, tannin, plant acids and alkaloids (Clark 2007). By implementing the integrated processing technique, the primary metabolites extracted from plants are employed in the preparation of highly useful products and valued intermediates such as food flavours, feeds, pharmaceuticals, cosmoceuticals and nutraceuticals. However, the secondary metabolites of plant residues and organic wastes are highly applicable to minimize the burning effects of fossil fuels and further production of CO_2 in the environment by serving as feedstock. The produced biofuels are capable of slicing the CO_2 emissions as they are made from CO_2 of plants during their growth and photosynthesis process (Kitani and Hall 1989). On the other hand, the production of biofuels along with its products genuinely increases the economic aspects as well as the employment opportunities in rural areas, in addition to the social aspects of sustainability. The new upcoming era is drifting forward to use the alternate industrial feedstock and is implementing green processes for the production of various chemicals from renewable biomass resources that are available (Stevens and Verhe 2004). The biomasses generated from trees, agroforest residues, grasses, plants, aquatic plants and crops and municipal and industrial wastes can captivate and distract the renewable management of chemical industries. The various processes and products that can be generated from the biomass are clearly depicted in Fig. 1.

Biorefinery Concept/System

For the production of multiple bio-based products, the biorefinery system which is dependent on biomass as the major processing input and converts fully into usable end products can be taken into account. The biorefinery system serves as the basic concept by providing a sophisticated platform for the co-production of biofuels, value-added chemicals and energy from biomass. In addition, it can also serve as a system for the possibility of gasifying biomass to form syngas, a mixture of CO and H_2, for the subsequent synthesis of hydrocarbons, alcohols and other chemicals (Bridgwater 2012). The main problem associated with the use of fossil fuels for energy production is the uncontrollable production of greenhouse gases into the environment which also includes carbon dioxide (CO_2). One of the pathways for the control of CO_2 emissions is the use of greenhouse-gas-mitigating technology such as bioenergy production with carbon capture and storage (BECCS), where it produces negative carbon emissions by combining biomass use with carbon capture and storage (CCS). However, the concerns associated with CCS technology such as the problems of CO_2 leakage can be minimized by the replacement of an alternative technology based on a biorefinery concept called carbon capture and utilization (CCU). By making use of the CCU technology based on the biorefinery concept, the CO_2 and other greenhouse gases formed during the processing of biomass for biofuel production can be utilized for improving the vegetable crop yields (as CO_2 enrichment results in improved crop production), methanol production by means of CO_2 hydrogenation, etc. (Quadrelli et al. 2011). Similar to CO_2 usage, the biorefinery concept was also explored for the conversion of direct fish waste into low-volume, high-value omega-3 fatty acids and fish protein hydrolase, while the fatty acid extraction (fish sludge) was used for the production of low-value, high-volume biogas through a process called anaerobic digestion (Mbatia et al. 2010). Figure 2 shows the flowchart of the biomass conversion processes to form biofuels and other by-products, namely physical, chemical, biological and thermal along with some combination processes.

Physical Conversion Products

Mechanical Extraction

The mechanical extraction procedure is mainly carried to shred large or unsuitable items and to remove recyclables and contaminants. In some instances, materials such as exudates (meaning that liquid or solid fuels) are directly obtained from the cutting or grinding of stems/trunks of living plants and/or freshly harvested materials. For example, in the production of rubber latex from the *Euphorbia* species plant gives some low molecular weight hydrocarbons than rubber, which can serve as petroleum substitutes and turpentine. Similarly, the mechanical extraction

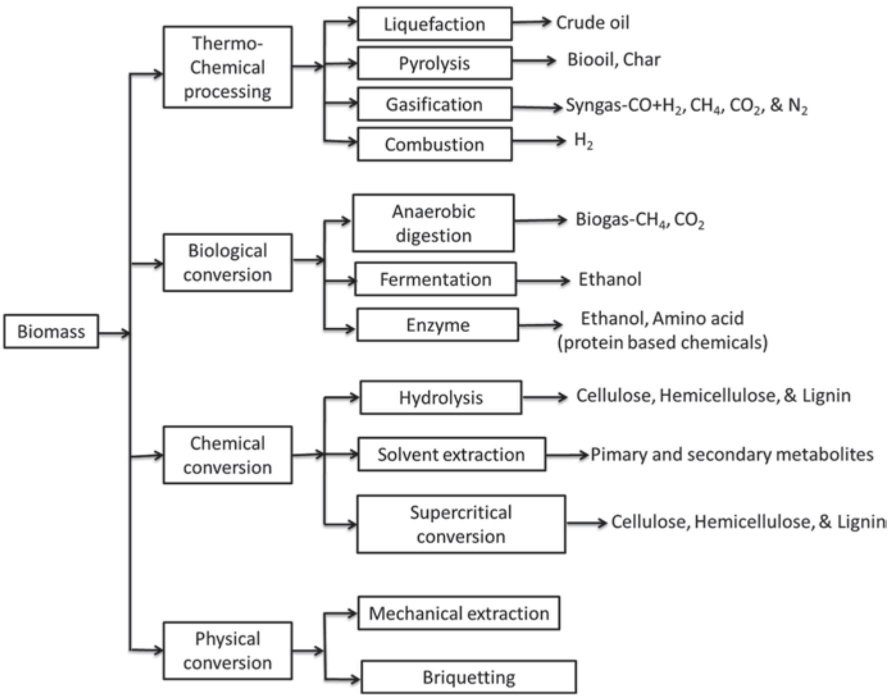

Fig. 2 Biomass conversion processes for the production of biofuels and valued chemicals, in addition to energy

of vegetable plants produces concentrated oils that can be used as fuel for diesel engines; however, the limitations of this oil include the high viscosity and combustion deposits as compared to mineral oils at low ambient temperature conditions, which can be overcome by conversion into esters (biodiesel) (Kalita 2008). The mechanical extraction of plant residues such as nuts (oil palm, coconut copra), seeds (rape, sunflower and soya bean), fruits (olive, castor), leaves (eucalyptus) and tapped exudates (rubber latex and jojoba) by means of transesterification ultimately produces biodiesel.

Briquetting of Biomass

The biomass densification techniques such as pelleting or briquetting allow for an easy way of handling, transporting and storing of agricultural wastes such as rice husk, coffee husk, coir pith, jute sticks, bagasse, groundnut shells, mustard stalks, cotton stalks, etc. For the application of biomass as solid fuel, the two available briquetting technologies include screw press and piston press and the formed briquettes can be used as inputs for the industrial/domestic energy production. The briquetting is usually performed using hydraulic, mechanical or roller presses, and the formed briquettes exhibit density twice (900–1300 kg/m^3) to that of common fuelwood due to its non-porous nature, and the char produced by combustion has higher density than wood or biomass charcoal. The biomass briquetting process is carried at higher pressure and temperature conditions, and the biomass particles self-bond to form a briquette due to thermoplastic flow; for example, lignin due to its natural binding capacity can form high-density briquettes. The commonly used binders in biomass briquetting include lignosulphonates (for animal feeds), bentonite (for feed pelleting), in addition to cooked starch and natural proteins. Thus, formed briquettes produce clean fire and find application in various industries as energy generating agents, such as in boilers for steam generation, in food processing industry as distilleries, in bakeries for drying, in textile industry for drying and bleaching, in the gasification process as the fuel for gasifiers, etc. (Al-Widyan et al. 2002; Ndiema et al. 2002).

Chemical Conversion Products

For the production of liquid fuels from woody biomass, the three major reactions involved are the chemical hydrolysis, solvent extraction and supercritical fluid processing. Both the hydrolysis and supercritical conversion reactions are primarily responsible for the formation of cellulose, hemicellulose and lignin, while the solvent extraction is for primary and secondary metabolites production.

Chemical Hydrolysis

A very important step in biomass processing, chemical hydrolysis is majorly carried out to break down large compounds (lignocellulose) into simpler molecules, and depending upon the technology, the reaction is carried out at high temperature, high pressure and/or acidic conditions. The hydrolysis reaction is influenced by basic factors such as surface to volume ratio of biomass, acid concentration, reaction time and temperature. Among these factors, understanding the biomass surface to volume ratio is of extreme importance as it is useful to judge whether effective hydrolysis to yield significant amounts of sugars at the end has occurred or not by means of an enhanced reaction rate (Jensen et al. 2008). The three components of lignocellulose contained in biomass that needs to be processed by the chemical hydrolysis reaction are cellulose, hemicellulose and lignin.

Cellulose

Cellulose is a form of long crystalline microfibrils and is the main component of secondary cell wall in woody biomass, which is parallel to the fibre axis and is the anisotropic conduct of wood materials. The chemical structure of cellulose is $C_6H_{12}O_6$ and is formed from the long chain of glucose monomer units and has the net calorific value of approximately 17.52 MJ/kg (Bossel 1980). Due to the crystalline structure of cellulose, the cellulose degradation takes place specifically in a high temperature range of 300–340 °C. The hydrolysis of cellulose produces glucose and short cellulose chains, and the rate of this conversion is strongly inhibited by the presence of glucose formed as part of the reaction. Therefore, the conversion of glucose into ethanol as soon as it is formed using a simultaneous saccharification and fermentation technique maintains the concentration of glucose to be low and contributes to enhanced ethanol production (Kim et al. 2001).

Hemicellulose

The woody biomass contains about 25 wt.% of hemicelluloses and its chemical properties are almost similar to cellulose with an exception of crystalline microfibrils formation having backbones of 1,4-β-linked major sugar units. Also, the hemicellulose has small monomeric units which cannot occur acutely in cellulose, and the basic sugar components found in hemicelluloses are pentose, D-xylose, L-arabino and hexose sugars (D-glucose, D-mannone and D-galactose). The hemicelluloses are thermally unstable biomass components yet known, and their degradation generally increases with the raise of temperature and the heat residence time occurs between 100 and 200 °C. They possess lower polymerization capacity than cellulose, are soluble in alkali and are readily hydrolysed (Bourgois et al. 1989).

Lignin

Lignin is a complex reticulated phenolic polymer occurring in the xylem of terrestrial plants, and it is the second most abundant polymeric component of woody biomass in nature which corresponds to around 30 % of the biosphere organic carbon. Lignin is highly significant and plays an indigenous role in industrial bioethanol production as it is composed of high carbon content of about 60 % and of 30 % oxygen. Lignin contributes about half of combustible energy from naturally occurring renewable sources, and depending upon the sources, the thermal decomposition starts above 280 °C. The chemical properties and functions are not completely recovered from lignin and hemicelluloses. The black liquor resulted from the combustion of lignin was used as the energy source, and this contains about half of the wood dissolved components, i.e. the dissolved organic compounds are present in the degraded lignin hemicelluloses and degraded cellulose. The pharmacological properties, including antiviral inhibitor (anti-HIV), make the phenols derived from biomass valuable and useful chemicals. The organic compounds having good antioxidant activity are used for preserving food from lipid peroxidation and oxidative damage that generally occurs in the living systems (Martínez et al. 1996; Mahugo et al. 2009; Nenkova et al. 2011). The loss of food colour, flavour and active vitamin content is prevented by antioxidants by rendering the stability of the molecules involved in various characteristics which are used for producing adhesives and for the synthesis of polymer.

Clark (1983) stated that, after cellulose, lignin is the second largest structural component of biomass based on benzene rings that is located on the subunits of phenylpropane. Lignin is the aromatic component of wood, highly insoluble and act as an adhesive. Lignin is the one which is differentiated into softwoods and hardwoods. Softwood lignin contains only the guaiacyl units, and the hardwood lignin contains both guaiacyl and syringyl units. The molecular weight of softwood lignin is more than the hardwood lignin. The softwoods contain 25–35 % lignin and hardwoods contain 18–25 % lignin. It was observed that cellulose has less energy content than lignin which is generally 25.5 MJ/kg. The lignin is thermally stable and is the major component of cell wall; as such, the lignin degrades and stretches at a temperature of 180 °C (Clark 1983; Hill 2006).

Solvent Extraction

The different unit operations involved in the solvent extraction procedure includes the following: extraction of oil from the oilseeds by employing hexane as one of the solvents, evaporation of the solvent, distillation of the oil–hexane mixture which is also called as miscella and toasting of the de-oiled meal. In some of the prevailing cases, different self-sufficient solvents are used such as halogenated solvents which are mostly dichloromethane, acetone, ethanol or isopropanol, in addition to supercritical CO_2 for the analysis (Stevens and Verhe 2004). Extraction is defined as the process where the expected substance can be gently removed from the raw material and making the substance dissolve into the solvent and even re-enhancing the ample substance from the solvent. The extraction and separation processes are very essential for extracting the respective substances from the biomass. Recently, Dewarte et al. (2007) and Clark et al. (2006) suggested an integrated straw-based biorefinery, and by using this, they isolated high-value chemicals such as waxes, polycosanol and sterol by employing the supercritical CO_2 which is used for the extraction of aromatic woods, namely cedarwood, sandalwood, pinewood, to isolate the extractives. The product formed as extracted lignocellulosic biomass can later be used for the hydrolysis and fermentation of biofuels (Stevens and Verhe 2004).

In general, the procedure for the extraction is dependent on the nature of the natural material and the components which are to be isolated. There are two important conventional extraction procedures such as liquid–liquid extraction and liquid–solid extraction. The two varieties of solvents such as water–dichloromethane and water–hexane are often used for liquid–liquid extraction. The major demerits of the extraction procedure include the use of toxic solvents, expensive and flammable system (Kaufmann and Christen 2002).

Supercritical Water Conversion of Biomass

The substances which are found to be above vapour liquid critical point at temperature and pressure conditions are said to be supercritical fluids, and it is noticed that

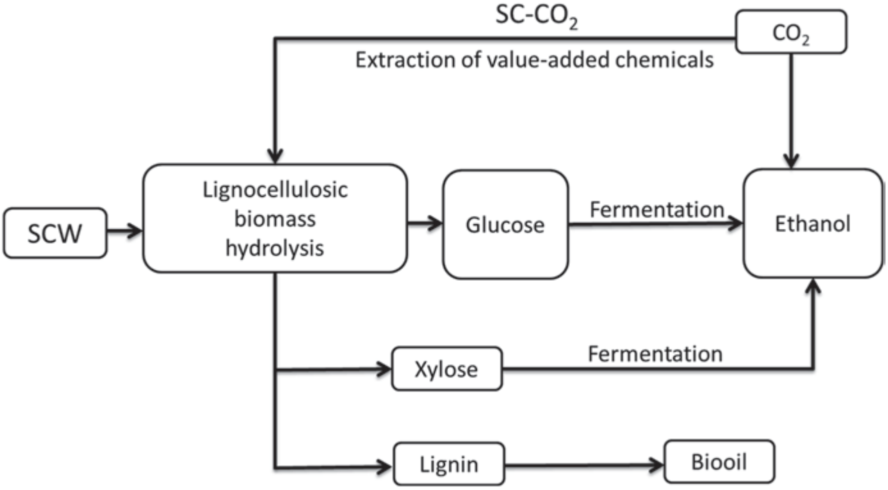

Fig. 3 SCW conversion of biomass. *SCW* supercritical water

it is 644 K and 22 MPa for water and 304 K and 7.4 MPa for CO_2. The fluids are not boiled by decreasing the pressure at constant temperature which resembles that it is neither liquid nor gas, and even it will not condense by cooling at constant pressure also found at supercritical condition (Saka et al. 2006). The substitute pathway, such as acid hydrolysis and enzymatic hydrolysis of cellulose to sugars, is represented by supercritical fluid processing of biomass to chemicals. Acid hydrolysis acid recovery is expensive and even has the issue related to pollution as well. The enzymatic saccharification generally requires the pretreatment of lignocellulosic biomass. The supercritical water (SCW) has the capability to convert cellulose to sugar and biomass into a mixture of oil, organic acid, alcohol and methane very fast as expected. The acid (H^+) and base components (OH^-) of water are disintegrated in supercritical (i.e. 300–644 K; pressure 200–250 bar) and near critical state (523–573 K) where it dissolves also. The small sugar molecules, glucose, xylose and oligosaccharide, are fabricated from the dissolved SCW and lead to breakage of the bonds of cellulose and hemicellulose (Sasaki et al. 1998).

The SCW has optimistic property which makes it an outstanding reaction medium without the use of catalyst for the biomass conversion to value-added products. Figure 3 shows the scheme of SCW conversion of biomass and the integral utilization side streams of the conversion process. The SCW gasification technology was demonstrated for conversion of cellulose into glucose at the specific range of 10–20 s and above which at 45 s pyrolysis starts randomly. The SCW behaves as a strong oxidant when the temperature is increased to 873 K which is SCW becomes a strong oxidant and results in a complete disintegration of the substrate structure usually as the transfer of oxygen from water to carbon atoms. The hydrogen is formed as the hydrogen atom of water is set free. The cellulosic bonds are broken down by SCW which also forms the gaseous products. The schematic overall reaction for biomass is given below (Serani et al. 2008):

$$2C_6H_{12}O_6 + 7H_2 0 \rightarrow CO_2 + 2CH_4 + CO + 15H_2$$

Biological Conversion Products

The biological conversion of biomass is of greater importance in terms of carbon cycle and occurs by means of anaerobic digestion, fermentation and enzymatic conversion.

Anaerobic Digestion

The anaerobic digestion of biomass has gained increasing attention over the years in both developed and developing nations due to the possibility of creating the fuel with the help of a waste treatment method, and the recycling of nutrients to agricultural land can also be created. In addition, the costs associated with its technology, commonly available microbial consortia involved in the process to degrade a wide range of feedstock, easy transportation of fuels, etc. are also driving the sector (Bruni et al. 2010). Despite the advantages, the drawbacks of this technology include the low methane production, incomplete bioconversion and process stability, to mention a few. The process involves the breaking down of biomass and other biodegradable matter by the microorganisms in the absence of oxygen. In this, the animal waste, agriculture and crop residues, municipal solid waste and municipal/industrial sewage sludge are processed to recover energy in the form of biogas which mainly consists of CH_4 and CO_2 (Asam et al. 2011). The formed methane gas can serve as the biofuel source for the generation of electricity. The general pathway is composed of four main steps: hydrolysis, acidification/acidogenesis, acetogenesis and methanogenesis.

Hydrolysis

The first step in the anaerobic digestion process involves the hydrolysis of biomass containing large organic polymers into water-soluble monomers and simple polymers, which are otherwise unusable. The hydrolysis of biomass containing large polymers such as proteins, carbohydrates and fats forms smaller molecules like amino acids, monosaccharides and fatty acids, respectively, by the enzymes produced by microorganisms (obligate or facultative anaerobes). The unbroken large molecules can still be forwarded to the acidogenesis step for their breakdown into simple molecules (Kalyuzhnyi et al. 2000).

$$(C_6H_{10}O_5) + nH_2O \rightarrow n(C_6H_{12}O_6) + nH_2$$

Acidification/Acidogenesis

In this step, the fermentation of small molecules such as amino acids, fatty acids and sugars in the presence of acidogenic microorganisms forms acetic acid as the main end product along with some volatile fatty acids, CO_2 and H_2. The other acidogenesis stage products formed in this reaction include NH_3, H_2, CO_2, H_2S, propionic acid, butyric acid, formic acid, lactic acid, carbonic acid, ethanol and methanol. The following are typical acidogenic reactions, where glucose is converted to ethanol, propionic acid and acetic acid, respectively. These three products without participating in the acetogenesis step can be directly involved in the production of biogas by the methanogenesis bacteria of the fourth step (Jeison et al. 2008):

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$$

$$C_6H_{12}O_6 + 2\ H_2 2CH_3CH_2COOH + 2\ H_2O$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH$$

Acetogenesis

In this step called acetogenesis (creation of acetate), the remaining products formed in the acidogenesis reaction such as propionic acid, butyric acid and alcohols are transformed into H_2, CO_2 and acetic acid. This reaction is facilitated by the presence of hydrogen-scavenging bacteria (acetogens and the hydrogenotrophic methanogens) which are known to maintain the low hydrogen partial pressure (10^{-4} and10^{-6} atm) so as to allow thermodynamic conversion of all acids into acetates. The following are the reactions commonly involved for the conversion of propionic acid, glucose and ethanol into acetic acid (Kim et al. 1994):

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

$$CH_3CH_2OH + 2\ H_2O \leftrightarrow CH_3COO^- + 2\ H_2 + H^+$$

Methanogenesis

Methane gas and water are formed in this step by the conversion of acetate, formaldehyde, H_2, CO_2 and some intermediate products from hydrolysis and acidogenesis.

The two frequently used methanogenic groups include the acetotrophic and hydrogenotrophic, where about two thirds of the methane is produced by the acetotrophic group methanogen. In certain conditions where acetotrophic methanogen becomes inhibited, such as high concentration free ammonia containing environments, a new group of microorganism called syntrophic acetate-oxidizing bacteria can be useful and is known to split acetate into H_2 and CO_2. Under thermophilic and high concentrations of free ammonia conditions, hydrogenotrophic methanogenesis and syntrophic acetate-oxidizing bacteria can contribute to about 90 % of methane production (Qu et al. 2009). The general pathways involved for the production of methane biofuel in methanogenesis by the methanogens bacteria are shown below:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$2C_2H_5OH + CO_2 \rightarrow CH_4 + 2CH_3COOH$$

$$2CH_3(CH_2)_2COOH + 2H_2O + CO_2 \rightarrow CH_4 + 4CH_3COOH$$

Fermentation

The microbial fermentation of biomass containing sugars produces ethanol and higher-chain alcohols which are volatile liquids and can serve as refined petroleum. The fermentation of sugars as feedstock for ethanol is considered as the cleanliest approach for liquid fuel production alternative to fossil fuels as CO_2 is formed as the by-product which can be used in other ways by biorefinery system. Ethanol is produced by the fermentation of food plant resources such as corn (in the USA), sucrose (in Brazil) and other non-food plant residues such as corn stover, sugar cane waste, wheat or rice straw, forestry and mill discards, paper portion of municipal wastes (Lin and Tanaka 2006). Molasses is the most widely used sugar for the fermentation of ethanol, as it contains about 50 wt.% of sugar and about 50 wt.% of organic and inorganic compounds, including water. The thick black-coloured liquid formed in the refinement of sugar when adjusted to a pH of 4–5 with mineral acid and inoculated with yeast or bacteria at a temperature of 20–32 °C for 1–3 days produces the bioethanol. However, microbial technologies are required for the processing of agriculture biomass containing starch such as corn (maize), wheat, oats, rice, potato and cassava for ethanol fermentation. The fermentation of starch is a somewhat complex procedure compared to sugar fermentation, as starch needs to be converted to sugar first before undergoing ethanol formation. The procedure requires starch saccharification effectively by the hydrolysis of starch first catalysed by α-amylase at a temperature of around 140–180 °C, and further conversion into glucose by the addition of glucoamylase. In the following, dextrose is fermented to ethanol in the presence of microorganisms, producing CO_2 as a co-product (Kadam and McMillan 2003; Lin and Tanaka 2006). Furthermore, the fermentation of lignocellulose is more complex than starch, as it contains a mixture of carbohydrate polymers (cellulose and hemicellulose) and lignin. In this, the carbohydrate polymers are tightly bound to the lignin by covalent as well as hydrogen bonds, and for that reason, the fermentation of lignocellulose for ethanol production requires the following steps in series: (1) delignification to liberate cellulose and hemicellulose, (2) formation of free sugars by the depolymerization of carbohydrate polymers and (3) ethanol production by the fermentation of mixed hexose and pentose sugars. In the fermentation of biomass for ethanol production, two types of microorganisms are mainly involved. One is directly involved in the conversion of fermentable sugars into ethanol, while the other is responsible for the production of enzymes that catalyse chemical reactions for the hydrolysis of complex components of biomass residues into simpler molecules (Lin and Tanaka 2006).

Enzymatic Reaction

The enzymatic conversion of biomass residues plays a crucial role in a biorefinery system by reducing the strain imported on the food industry by means of forming the fermentable sugars with the use of any cellulose containing organic matter, rather than utilizing the food crops. The enzymatic conversion of biomass offers high-yield products, higher selectivity, low energy costs and milder conditions as compared to chemical processes. The potential products of this reaction include the bioethanol, acetic acid, lactic acid, amino acids, antibiotics and other chemicals. Several microorganisms such as yeasts of *Saccharomyces cerevisiae,* bacteria of *Zymomonas, Zymomonas mobilis, Escherichia coli* and fungi of *Monilia* sp., *Neurospora crassa, Neurospora* sp., *Zygosaccharomyces rouxii, Aspergillus* sp., *Trichoderma viride, Paecilomyces* sp., etc. have been used to produce biomass-degrading enzymes (cellulase, hemicellulase, pectinase and proteinase) to act as catalysts or can mediate for the direct conversion of CO_2 into ethanol. The purpose of this enzymatic reaction is to decompose cellulose and other carbohydrate containing polymers into fermentable sugars such as glucose and oligomers, where they can further be processed to form valuable products (Yang et al. 2011).The unique application of this enzyme-catalysed reaction was observed during the hydrolysis of starch where it produces sugar syrups of well-defined physical and chemical properties and significantly lessens the unwanted side reactions (Hsu 1996). Similarly, for the hydrolysis of lignocellulose containing polyphenolics and other extractables, the *Trichoderma reesei* fungi was very much useful where it is known for its cellulolytic enzyme production such as α-1,4 glucanases and α-1,6 glucanases (Lin and Tanaka 2006; Suhara et al. 2012). However, the major disadvantage of this procedure was observed during the conversion of cellulose to ethanol where the process is very much time consuming (3–12 days) with a yield of only 0.8–60 g/l of ethanol due to the formation of acetic acid and lactic acid by-products (Wu et al. 1986). Also, it was observed that the removal of hemicelluloses and lignin in the pretreatment process significantly improved the enzymatic digestion of celluloses, as the pretreatment causes the deacetylation of hemicellulose chains and depolymerization of lignin, respectively. The presence of soluble lignin or its derivatives, in addition to slowing down the digestion process, also found to inhibit the activity of enzymes such as cellulases and β-glucosidases due to the involvement of phenols, furans, formic acid and low molecular weight acids (Yang et al. 2011).

Thermochemical Conversion Products

Thermochemical conversion is the chemical reforming process of biomass, where heat and other chemical processes are applied under pressurized and oxygen-deprived conditions to break solid biomass containing long-chain hydrocarbons into short-chain hydrocarbons such as syngas or heavy oil. This includes the subcategories of liquefaction, pyrolysis, gasification and combustion. In thermochemical conversion of biomass, the combustion process is carried in the presence of excessive air, while partial air and no air are required for gasification and pyrolysis processes, respectively. The in-depth discussion about these processes is summarized in the following subsections.

Liquefaction

In liquefaction or hydrothermal liquefaction process, the reduction of biomass in the presence of water at temperatures lower than 400 °C produces direct liquid oil (crude oil) and other liquid/gaseous chemicals as by-products. The unique advantage of this process is that the direct production of crude oil can be possible, which is known for its higher energy content than syngas or alcohol. Unlike other thermochemical processes, liquefaction does not require the biomass to be dried, as the drying process typically consumes significant levels of energy and is time consuming as well. The presence of water in biomass acts as a catalyst and is responsible for the carrying out of several organic chemical reactions such as condensation, cleavage and hydrolysis easily, in addition to affecting the selective ionic chemistry which is not accessible thermally (Kruse and Gawlik 2003). In some instances, the acidic and basic nature of hot water itself acts as catalyst by driving the reactions and can be responsible for the fragmentation of high molecular weight hydrocarbons of residual biomass components. In a study, for example, the average elemental analysis of crude oil obtained from various biowaste streams provide the information that it contains about 62.7 ± 6.4 % and 9.6 ± 0.4 % of carbon and hydrogen, respectively. The other elements of nitrogen (3.9 ± 0.3 %) and sulphur (0.3 ± 0.1 %) were also investigated. In addition to crude oil, the other aqueous products of biomass liquefaction include the volatile organic compounds of primary ketones (acetone) and benzyl compounds such as benzene, ethylbenzene, toluene and styrene. The other gaseous products of CO_2 (98 %) and CO (2 %), along with some combined concentrations of methane and ethane at 299 ppmv, were also detected (Ocfemia et al. 2006).

Pyrolysis

The pyrolysis process has been known for thousands of years, but it is only in the recent years that flash pyrolysis has become of considerable interest because of its operation at moderate temperatures of around 500 °C and for a very short reaction times of up to 2 s only. In the flash pyrolysis, the small dried biomass particles are transformed into liquid fuel (biocrude) with high yields of liquids of up to 75 wt%, and at this temperature, the cellulose and starch break down into sugars for the subsequent fermentation (Bridgwater 2012). In pyrolysis, the thermochemical conversion of biomass directly produces liquid oil such as methanol and syngas along with some possible formation of chemical and food by-products. The process involves the direct heating of biomass in the absence of oxygen or by the partial combustion of some of the biomass in a restricted air or oxygen environment to form gases, vapours, liquid oil, solid char and ash. The typical wood-derived oil, bio-oil, obtained from pyrolysis is found to exhibit 25 % moisture content, 17 MJ/Kg of higher heating value (HHV) and has the composition of about 56 % carbon, 6 % hydrogen, 38 % oxygen and 0.1 % nitrogen (from water, acids, carbonyl compounds and sugars). The bio-oil or crude pyrolysis liquid is composed of a complex mixture of oxygenated hydrocarbons along with significant water in both moisture and reaction product form. The bio-oil exhibits higher density than any other convention fossil fuels and possess the heating value of half of the mineral oil and can easily undergo polymerization on heating. Because of its high carbon content, the bio-oil can serve as a substituent for fuel oil or diesel in many static applications, including boilers, furnaces, engines and turbines, for the generation of electric power (Czernik and Bridgwater 2004). The upgrading of bio-oil to biofuel by means of chemical or catalytic methods allows the formation of number of valuable products such as alcohols, methane, kerosene, gasoline and diesel. Also, the intermediates derived from it can be potential as food flavourings, specialities, resins, agrochemicals, fertilizers and emission controlling agents. For the conversion of bio-oils to usable products, the chemical methods like hydro treating, catalytic vapour cracking, esterification and related processes, gasification to syngas followed by hydrocarbons or alcohol synthesis can be applied (Bridgwater 2012). Pyrolysis is considered as an incomplete gasification process where the type of product formed depends on the applied temperature and pressure, type of input material and also varies depending on the oxidizing or reducing media. In other words, high temperatures and longer residence times increase biomass conversion to gas, while the moderate temperatures and short vapour residence time produces liquids. If gas is the main product of the combustion output, the process is called gasification.

Gasification

Gasification or thermochemical gasification is the process by which the raw carbaneous solid residuals get converted into fuel gas (methane) or chemical feedstock gas (syngas, $CO+H_2$) by providing heat. Similar to pyrolysis, this process also requires dried biomass such as charcoal or wood as feedstock and the reaction occurs at temperatures typically higher than 600 °C with the generation of electric power or heat and gases (syngas, CO_2, CH_4 and N_2) as by-products. The average chemical composition of syngas from a gasifier contains about 22.16 % CO, 17.55 % H_2, 11.89 % CO_2, 3.07 % CH_4, with N_2 and other gases to balance (Wei et al. 2009). The catalytic mediation of syngas formed in this further allows the formation of a number of chemicals such as acetic acid, ethanol, methanol, ammonia, formaldehyde, olefins and gasoline. For example, the syngas conversion by means of the Fischer–Tropsch process in presence of either Fe, Co or Ru catalyst allows the formation of products such as waxes, diesel, olefins and gasoline (Hu et al. 2012).

Combustion

The biomass combustion process is carried out in the presence of excessive oxygen conditions, i.e. a heat-generating oxidation reaction where carbon, hydrogen, combustible sulphur and nitrogen react with oxygen. The different form of combustion processes for solid biomass includes the evaporation combustion, decomposition combustion, surface combustion and smouldering combustion. In industries, the decomposition combustion and surface combustion are the main processes for the production of biomass-based power generation and heat production (i.e. combined power and heat), and the commonly used input materials include paddy husk, bagasse, waste wood, oil palm waste, poultry chicken droppings, etc. The char produced along with the heat by the burning of biomass in evaporation and combustion processes are further processed by surface combustion, where it is only used for the components composed of carbon containing little volatile portions such as charcoal and CO_2. The advantage of using the biomass combustion process for heat production is that the generation of pollutants by the burning of fossil fuels, such as NO*x*, SO*x*, HCl and dioxin, is very low. The energy stored in the biomass is converted into kinetic energy by means of heating in the combustion process (González et al. 2013; Gani and Naruse 2007).

Conclusion

In conclusion, in this chapter, we provide the information about the usage of the biorefinery concept for the production of valuable intermediates and industrial chemicals in addition to energy from the biomass residues derived from plants, agriculture and animal wastes. In developing countries, this can serve as a sustainable technology for the usage of biomass residues with energy production and simultaneous production of valuable chemicals. In this, the biological conversion of the anaerobic digestion process forms syngas and biogas as products without any emissions and can serve as the clean technology. The biorefinery concept of biomass residues and waste processing technology produces electricity, in addition to bioethanol, biodiesel, bio-oil in liquid form and other industrial chemicals such as ammonia, acetic acid and aromatic hydrocarbons. In addition, the promotion of this technology significantly reduces the release of highly toxic aromatic hydrocarbons into the environment from the burning of coal-derived fossil fuels for energy production. Thus, the formation of products from multiple routes while meeting the energy demands can fulfil the investment/equipment costs and operational charges along with the creation of jobs in urban areas.

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Chemical Modifications and Properties of Coir Fibers Biocomposites

**Md. Saiful Islam, Zainal Abidin Talib, Abul Kalam Azad
and Ahsanul Kaiser**

Abstract In this chapter, several types of chemical modifications toward coir fibers (CF) reinforcement polymer biocomposites are described, and their effects on the various properties of the resulting composites are also discussed. Chemical treatments are intended to improve at least one property of the composites. They can however have a positive or negative impact on other composite properties. Interaction, adhesion, and compatibility between the CF and the polymer are the main concern of chemical treatment. Furthermore, chemical modification reduces –OH groups from the cellulose fiber surface. Among various chemical treatments, alkali treatment with NaOH solution is often chosen to modify cellulose-based materials since NaOH reacts with –OH groups of fiber, reduces hydrophilicity, and improves the compatibility between fiber and the polymer matrix. Consequently, significant improvement in mechanical and morphological properties of composite are noticed for the alkali-treated biocomposite materials. Benzenediazonium salt is also an important chemical, which reacts with cellulose in fiber and produces 2, 6-diazocellulose by a coupling reaction. This chapter also discusses some other possible chemical reaction with CF and its physical and mechanical properties of composites. Generally, the physical and mechanical properties are found to be improved on the treatment.

Keywords Coir fiber biocomposites · Alkali treatment · Mechanical strength · Scanning electron microscope

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Introduction

In recent years, natural fiber-based polymer composites have drawn a lot of interest due to their wide range of applications. The natural fibers contain much individuality with many advantages and environmental friendliness which could be easily modified by chemical treatments. It is also abundantly available and come from renewable sources which makes it very interesting for utilizing (Haque et al. 2009). In improving the properties of composites and fulfilling the market demand, conventional polymers are mixed with various reinforcing natural fillers (Zaman et al. 2010). An incredible research is moving in the direction of natural fibers as reinforcement fillers (Rahman et al. 2009b). Natural fibers such as coir, kenaf, jute, palm, etc. are lightweight, biodegradable, inexpensive, and are generally more competent compared to synthetic fibers. (Wambua et al. 2003).

Since natural fiber has many advantages properties, it is widely being used as a reinforcements filler in the polymer composites. However, green fibers have some negative properties and are normally hydrophilic and are not compatible with polymer matrix as polymer is hydrophobic in nature. The main problem of utilizing natural fibers into polymer matrix is the weak chemical interfacial bonding among the fibers and polymer. Coir fibers (CF) are absolutely new in reinforcing polymer compared to other green fibers (Karmakar et al. 2007; Bledzki and Gassan 1999). A comparison of physicochemical and physico-mechanical properties of CF with other natural fibers is illustrated in Table 1. Generally, natural fibers are rough and are time-honored as effective reinforcing filler in polymers matrix. CF has high weather and water resistance because of its three polymeric components cellulose, lignin, and hemicellulose.

Compared to other synthetic polymers, polypropylene (PP) has many outstanding properties such as low density, sterilizability, better flex life, and surface hardness with excellent abrasion resistance (Kabir et al 2010). However, already it has been accepted that PP and its matrix do not form strong bonds with cellulose fibers. Weak chemical bonding and poor interfacial interactions between fibers and polymer are of the most vital factors of bond breakdown. Thus, natural fibers and polymer are simply combined together without having strong interaction between them. It can therefore be concluded that if bonding were to take place among the polymer and the natural cellulose fibers, the overall properties of composite may be further improved (Baysal et al. 2004). Chemical treatments with suitable chemical could be a promising way to create better adhesion and compatibility of fiber-reinforced polymer composite (Hoque et al. 2009). In order to improve the bonding strength between polymer and cellulose fiber, several types of chemical treatment have been carried out on cellulose fibers. Among them, some are very effective in improving the adhesion and compatibility of cellulose fiber to polymer composite (Islam et al. 2011).

In the present chapter, various types of chemical modifications onto CF surfaces are described and their effects on the structural and mechanical properties of the resultant biocomposites are also discussed.

Table 1 Physicochemical and physico-mechanical properties of CF compared with other natural fibers

Properties/fibers	Coir	Flax	Hemp	Jute	Ramie	Sisal
Density (g/m^3)	1.25–1.5	1.4	1.48	1.45	1.5	1.26–1.33
Diameter (μm)	100–450	100	25	60	40–50	100–300
Cellulose content (%)	36–43	62–72	67–75	59–71	68–76	74–75.2
Hemicellulose content (%)	0.2	16–18	16–18	12–13	13–14	10–13.9
Lignin content (%)	41–45	2–2.5	2.8–3.3	11.8–12.9	0.6–0.7	8–12
Microfibrillar angle (°)	30–45	10	6.2	7–9	7.5–12	10–20
Tensile strength (MPa)	105–175	800–1500	550–900	400–800	500–870	600–700
Young's modulus (GPa)	4–6	60–80	70	10–30	44	38
Elongation at break (%)	17–47	1.2–2.4	1.6	1.16–1.8	1.2	3.64–5.12
Moisture absorption (%)	10	7	8	12	12–17	11

CF coir fibers

Alkali Treatment

Alkali treatment with sodium hydroxide (NaOH) has been widely utilized to modify natural fibers (Ndazi et al. 2007; Islam et al. 2012). This treatment can increase the hydrophobicity and reduce the waxy substances from the fiber surfaces. Thus the interfacial interaction and bonding between fiber and polymer could be increased sufficiently after treatment. Usually, 2–5 % NaOH solution has been used for alkali treatment. Sodium hydroxide removes impurities such as fats and waxes from the natural fiber which improve adhesion and compatibility between fibers and polymer. The dismissal of the surface impurities from the natural fibers results in better surface roughness of the fibers by removing more –OH groups and other functional groups from the surface. It is established that NaOH reacts with fiber –OH groups and removes impurities from the fiber (George et al. 2001).

$$\mathrm{CF{-}OH + NaOH \rightarrow CF{-}O^{-}\,Na^{+} + H_2O} + \text{impurities}$$

Nam et al. (2011) investigated the effect of NaOH treatment on the various properties of CF/poly(butylene succinate) (PBS) composites (Nam et al. 2011). In their study, the CF was treated with 5 % NaOH solution at room temperature. The NaOH-treated CF/PBS composite showed significant improvement in mechanical properties compared to the raw composite. In their research, optimum mechanical strength was found for the NaOH-treated CF/PBS composite where tensile strength

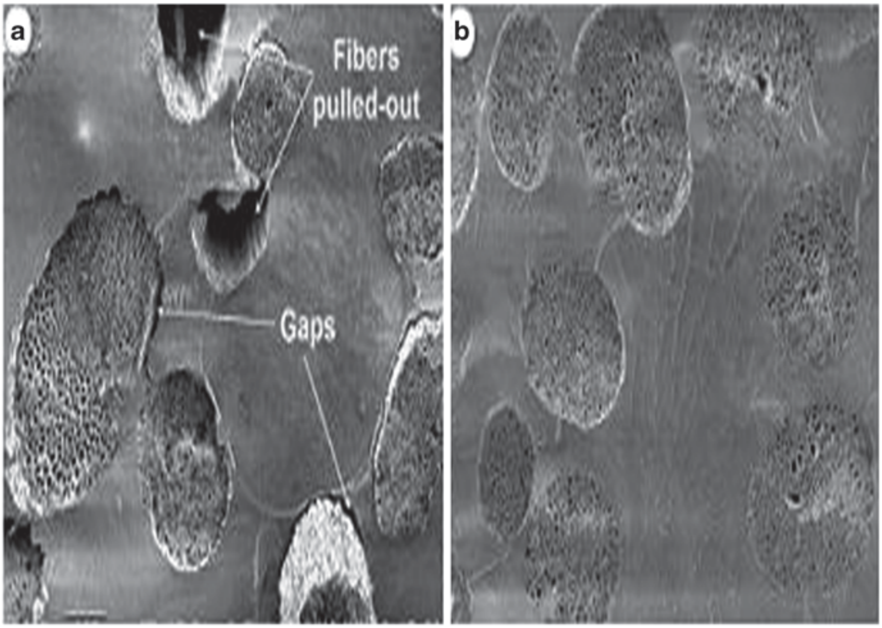


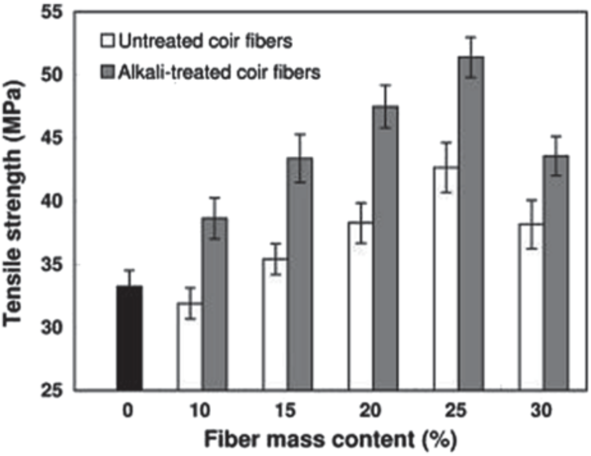
Fig. 1 SEM micrograph of coir/PBS composite of **a** untreated coir fibers and **b** alkali-treated coir fibers. *SEM* scanning electron microscope, *PBS* poly(butylene succinate) (Nam et al. 2011)

increased by 54.5 %, tensile modulus by 142 %, flexural strength by 45 %, and flexural modulus by 97 % as compared to pure PBS resin.

After NaOH treatment, fiber surface and fractured surface morphologies of composites exhibited an improvement in interfacial adhesion and compatibility in coir composites. They observed that alkali treatment improved fiber–matrix adhesion as the removal of impurities from the cellulose fiber surface (Valadez et al. 1999). NaOH treatment improves the surface roughness resulting in rising mechanical interconnection (Rahman and Khan 2007). As a result, the development of a new surface morphology improves the adhesion and compatibility of fiber-to-polymer matrix which significantly improves mechanical properties of resulting composites.

The study reported the surface morphologies of treated and untreated composites and is shown in Fig. 1a, b. From Fig. 1a, it can be seen that raw fiber composites contain several holes. Gaps between cellulose fibers and PBS matrix were obvious; thus, poor interfacial adhesion among the cellulose fiber and polymer was observed. Nevertheless, the gaps are nearly moved out because of NaOH-treated CF (Fig. 1b, confirming better bonding of PBS and fiber, thus improving the overall properties of the composites. Raw CF is able to freely move from the interfacial region with poor interaction, resulting in fast collapse of the CF/PBS composite. On the other hand, treated CF provide a better act of sticking with PBS matrix and helping to the improve the mechanical properties of CF/PBS. Thus, this result shows that alkali

Fig. 2 Tensile strength of untreated and alkali-treated coir fiber/PBS biodegradable composites. *PBS* poly(butylene succinate) (Nam et al. 2011)



treatment of CF is very important to increase the interfacial adhesion and compatibility to polymer matrix before being composite manufactured.

The study also reported the tensile properties of the CF/PBS composites. Tensile properties of treated and untreated composites with various fiber contents are shown in Figs. 2 and 3). The tensile strength and modulus of composites were increased with the increase of fiber loading; however, these properties reduced with 30 % fiber loading. These results indicated that the CF control the external load in PBS matrix, thus enhancing the strength and modulus as compared to those of PBS matrix. It can be said that CF have the ability to improve the mechanical strength in the PBS system. In accordance with the composite concept, mechanical strength of composites depends on three things: (i) cellulose fiber and the matrix, (ii) the fiber content, and (iii) orientation.

Fig. 3 Tensile modulus of untreated and alkali-treated coir fiber/PBS biodegradable composites. *PBS* poly(butylene succinate) (Nam et al. 2011)

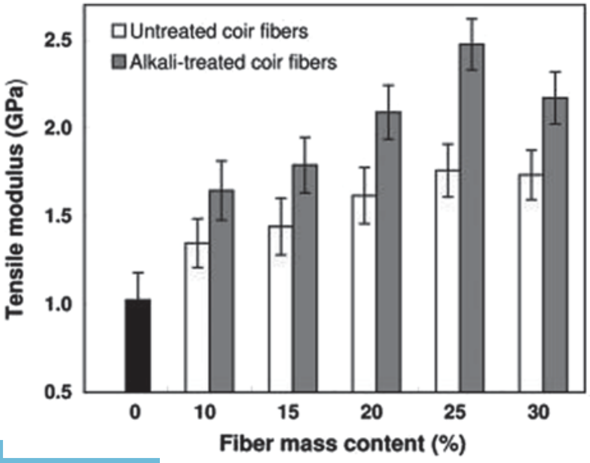
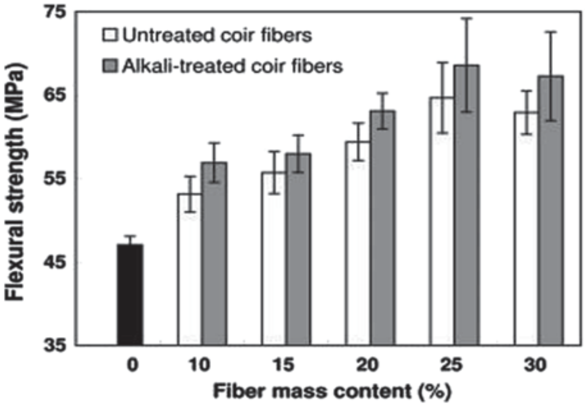
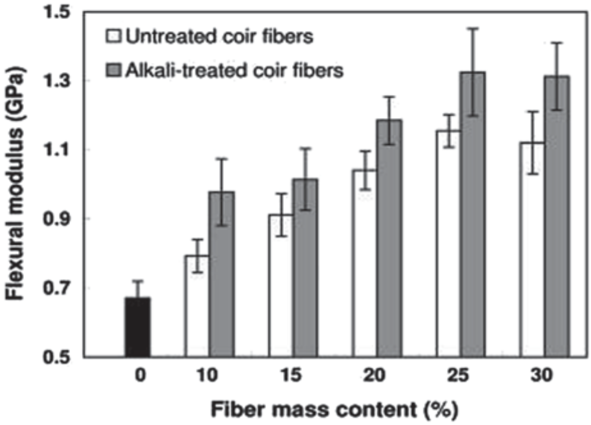


Fig. 4 Flexural strength of untreated and alkali-treated coir fiber/PBS composites. *PBS* poly(butylene succinate) (Nam et al. 2011)



Flexural properties of CF/PBS were also studied by the same researchers (Nam et al. 2011). By their study, it was presented that the flexural properties were increased with increasing fiber loading (Figs. 4 and 5). The alkali-treated composites produced better properties than the PBS matrix and untreated composites. Alkali treatment enhanced fiber–matrix adhesion, thus enhancing flexural properties. However, the finest fiber loading keeps changing with the character of cellulose and polymer matrix. The ratio of fiber, interfacial adhesion between fiber and matrix, processing technique, and agglomeration of fiber also play a vital role in composites (Liu et al. 2009).

Fig. 5 Flexural modulus of untreated and alkali treated coir fiber/PBS composites. *PBS* poly(butylene succinate) (Nam et al. 2011)

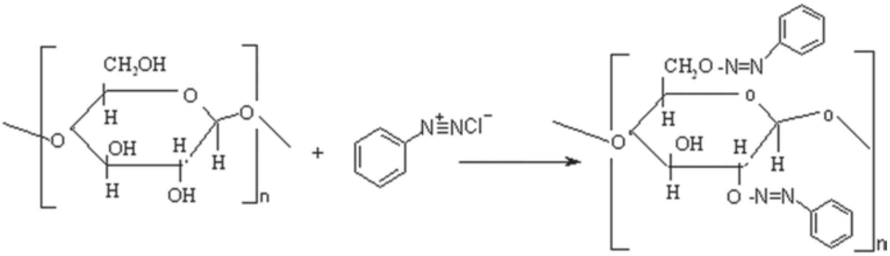


Benzenediazonium Salt Treatments

Recently, benzenediazonium salt has been widely used in the chemical treatment of natural fiber and improving physical, mechanical, and thermal properties of composites. Benzenediazonium produced 2,6-diazocellulose by the coupling reaction with diazonium salt. The mechanical properties of treated CF were enhanced after treatment. Significant changes in morphological properties were also found for this treatment.

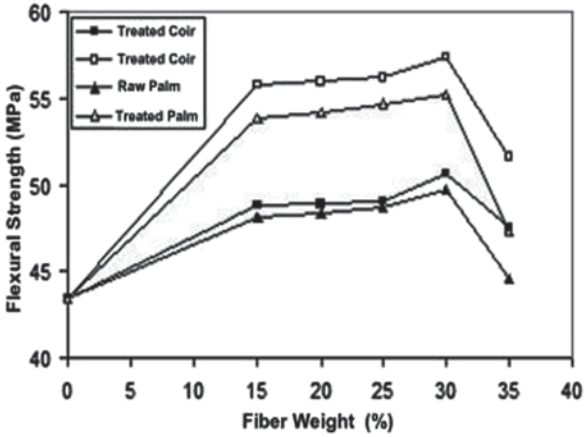
Haque et al. (2010) reported that the physical and mechanical properties of CF- and palm fiber (PF)-reinforced polymer composites were improved significantly by benzenediazonium salt treatment. They reported that the compatibility between fiber and polymer improved much after treatment. Various fiber loading also observed and reported that the mechanical properties increased with increase in fiber loading. Treated fiber-reinforced composites presented higher mechanical properties than raw composite fibers.

The –OH group in cellulose fiber is liable for water sorption and low interaction among fiber and polymer. Hydroxyl groups (–OH) changed after chemical treatment with diazonium salt and produced 2,6-diazocellulose compound. The Fourier transform infrared (FTIR) spectroscopy confirmed this result by changing the absorption spectrum from 1500 to 1650 cm^{-1} and from 1300 to 1000 cm^{-1}. Treated fiber also showed an absorption band near 1400 and 1454.6 cm^{-1}, which confirmed the abovementioned reaction (Matuana et al. 2001). The following reaction scheme could be present for the above reaction.



The effect of fiber loading and chemical treatment on tensile strength of raw and treated CF-reinforced polymer biocomposites was also investigated by their study. For raw fiber, tensile strength of composites seems to decrease with fiber loading (Yang et al. 2007). As the fiber load increased, the poor interfacial area between fiber and polymer matrix increased; thus, when fiber loading increased, the tensile strength was decreased. Benzenediazonium salt treatment improved the compatibility of fiber-to-PP matrix. Therefore, treated composites with 15 % fiber loaded had improved strength compared to PP matrix itself. This result suggests that improved

Fig. 6 Variation of flexural strength at different fiber loading

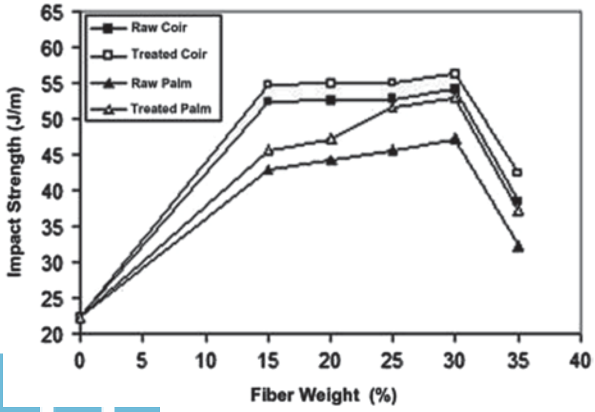


interfacial bonding could transfer stress from the matrix to the cellulose, resulting in better products with enhanced mechanical properties. The Young's modulus of CF composites was also improved by the benzenediazonium salt treatment and with fiber loading. The Young's modulus was found to be improved for treated CF composites than those of the raw and treated PF composites, respectively; the reason was stated earlier.

The flexural strength of various raw and treated composites was shown in Fig. 6. It was found from the figure that the flexural strength increased initially with fiber loading but started decreasing with increasing finer loading (from 30 to 35 %). The same result is also obtained for the flexural modulus. This result indicates that the higher fiber content maintains superior stress to deform. Improved fiber–matrix adhesion was able to support stress share between fiber and polymer matrix. Conversely, fiber loading decreases the adhesion between fiber and polymer matrix, thus reducing the flexural strength of composites.

Figure 7 shows Charpy impact strength results for various treated and raw fiber composites. It was found from the figure that the impact strength of composites

Fig. 7 Variation of impact strength at different fiber loading



was increased when fiber content increased. However, the reverse result was found for higher-fiber-content composites. Thus, it can be said that the impact strength depends on fiber nature and its content and interfacial bonding between fiber and polymer matrix. It can also be said that higher fiber content increases agglomeration of surfaces, resulting in crack propagation. From the figure, it can be found that the impact strength increased with fiber content of all composites. This result is expected because fiber was absorbed energy due to improved interfacial interaction of fiber–polymer matrix. Treated CF composites showed better strength compared to raw composites one, and the reason behind this was explained early.

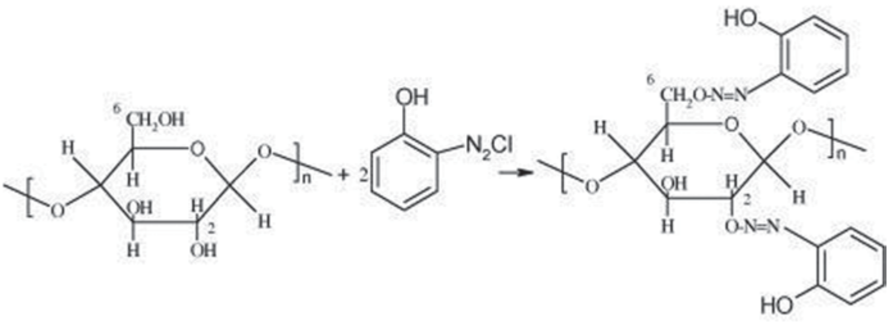
From the hardness result, it was found that the average hardness was improved for treated fibers composites. Fiber loading also affects these properties; however, hardness increased initially with increase in fiber loading. This is expected due to improvement in the stiffness of composites. It was also observed that the water absorption of composites was increased with the increase in fiber loading (Yang et al. 2006). It is suspected that OH group in fiber is responsible for higher water absorption. The OH groups in the composites were increased at higher fiber loading, thus increasing the water absorption of composites. Treated composites show lower water absorption compared to raw composites which indicates reduction of OH group after treatment.

A raw fiber composite shows agglomeration in the composite surfaces as seen in a scanning electron microscope (SEM). The image also indicates the fibers and polymer matrix interfacial interaction are very poor. In contrast, a smoother surface texture could be obtained for treated fiber composites. This result indicates that the benzenediazonium salt is effective to improve interfacial adhesion and interaction between fiber and polymer matrix in the composites.

O-Hydroxybenzene Diazonium Salt Treatment

The properties of CF-reinforced PP composites treated with o-hydroxybenzene diazonium salt have been investigated by Islam et al. (Islam et al. 2009). After treatment with o-hydroxybenzene diazonium salt, CF composites improve its mechanical properties. Treated CF composites exhibit better tensile properties compared to untreated CF composites (Fig. 8). The morphology of fracture surface composites shows significant change after treatment.

This chemical treatment removes OH groups from CF surfaces and produces 2,6-diazocellulose as confirmed through FTIR analysis. Raw CF clearly shows the absorption band near 1734 cm^{-1}, due to -CO group in the fiber, whereas treated CF shows the absorption band near 1700–1600 cm^{-1} and 1300–1000 cm^{-1} corresponding to N–O and C–O stretching (Fig. 9). This result confirmed the reaction between CF and o-hydroxybenzene diazonium salt and produced 2,6-diazocellulose. Therefore, it was expected by this study that the interfacial interaction and adhesion between CF and polymer matrix were significantly improved by the treatment of CF with o-hydroxybenzene diazonium salt.



This study also investigates the fractured surface morphology of CF-reinforced PP composites through SEM (Fig. 10). From SEM images, it was found that the agglomerations between fiber and PP were due to poor fiber–PP interaction in the raw CF composites, whereas, treated CF–PP composites show smoother surfaces texture in their surfaces, proving better interfacial interaction after treatment. The above result indicates that the physico-mechanical properties of CF-reinforced PP composites were significantly increased by o-hydroxybenzene diazonium salt treatment.

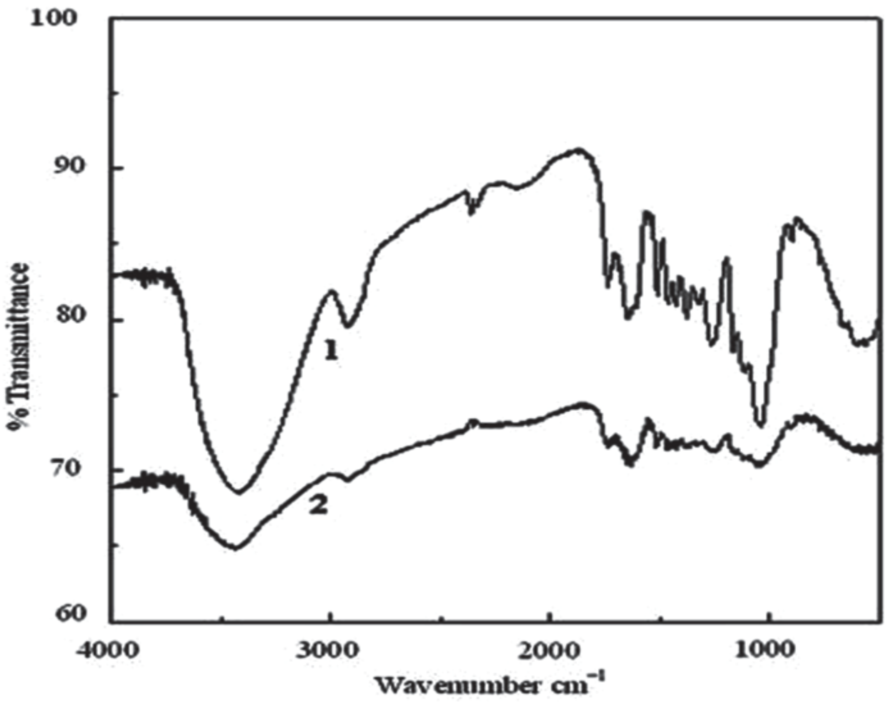


Fig. 8 Variation of tensile strength with filler loading for *1* untreated and *2* treated coir-reinforced PP composites. *PP* polypropylene

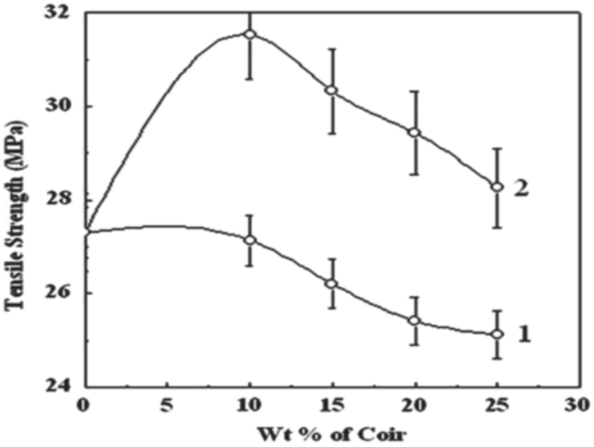


Fig. 9 IR spectra of (**a**) untreated and (**b**) treated coir. *IR* infrared

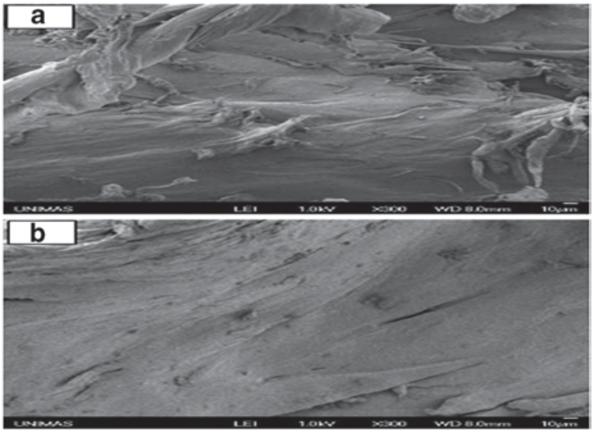
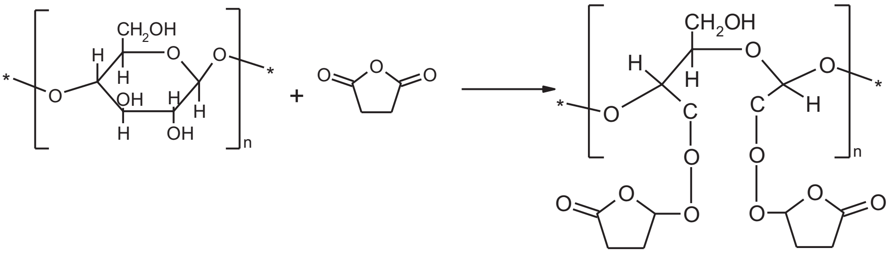


Fig. 10 SEM images of 20 % coir-reinforced PP composites (**a**) untreated coir and (**b**) treated coir PP composites. *SEM* scanning electron microscope, *PP* polypropylene

Some Other Possible Chemical Modification of Coir Fiber

Succinic Anhydride Treatments

Reaction between succinic anhydride and cellulose unit in CF is shown below. This chemical modification could also be effective to improve the overall properties of CF-reinforced composites.



Acrylonitrile Treatment

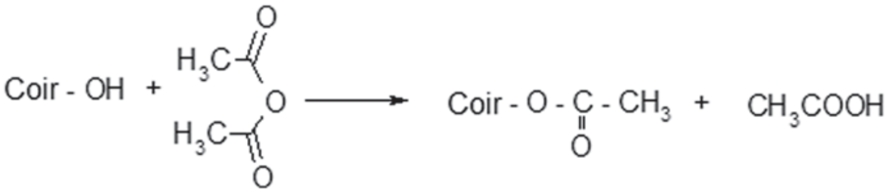
CF could also be reacted with acrylonitrile solution and is also able to increase its hydrophobicity and compatibility between CF and PP matrix.

The coir and acrylonitrile performed the following reaction:

$$\text{Coir}-\text{OH} + \text{CH}_2 = \text{C}-\text{CN} \qquad\qquad \text{Coir}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CN}$$

Maleic Anhydride Treatment

Reaction of acetic anhydride with CF–OH groups forms an ester bond, and acetic acid is formed as a by-product. Reaction without catalyst was conducted at 70 °C (Bongers and Beckers 2003).



$$\text{Coir-OH} + (\text{H}_3\text{C-CO})_2\text{O} \longrightarrow \text{Coir-O-}\underset{\substack{\| \\ \text{O}}}{\text{C}}\text{-CH}_3 + \text{CH}_3\text{COOH}$$

Epoxide Treatment

The reaction of fiber with an epoxide leads to the formation of an ether linkage and a new OH group. Therefore, graft polymerization reactions are possible (Kumar 1994):

$$\text{Coir}-\text{OH} + \text{R}-\text{CH}(-\text{O}-)\text{CH}_2 \rightarrow \text{Coir}-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{R}$$

Several epoxides have been used in the past decades for fiber modification purposes. They include ethylene oxide, propylene oxide, and butylene oxide (Norimoto et al. 1992). Usually, the reaction is catalyzed under mild basic conditions.

Alkyl Halide Treatment

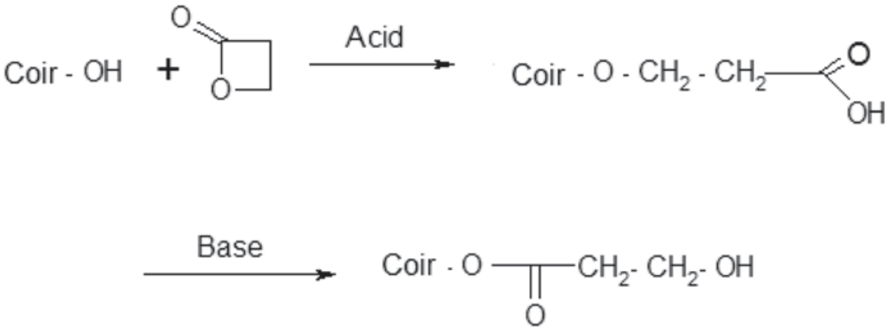
The alkyl halides in the presence of a strong base can be used for fiber etherification:

$$\mathrm{CF-OH\ +\ NaOH \rightarrow CF-ONa\ +\ R-X \rightarrow CF-O-R}$$

Reactions of fiber with crotyl chloride, methyl iodide, and butyl chloride have led to an improvement in physical property.

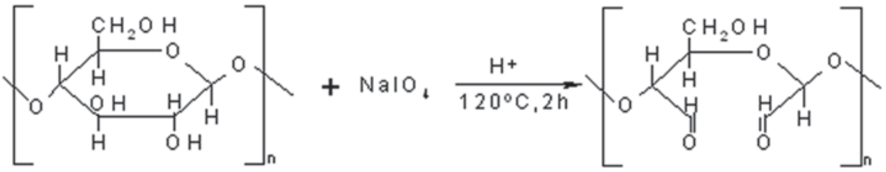
β-Propiolactone Treatments

The reaction of β-propiolactone with fiber can be catalyzed by acids or bases to yield two different products.



Oxidation of Coir Fiber

Cellulose-based natural fiber can be oxidized using an oxidizing agent with acidic catalyst. Oxidation reactions are applied to cellulose in fiber for chemical modifications. Oxidation reactions occur on cellulose selectively at a particular position. The reaction of sodium metaperiodate with cellulose in fiber in the presence of sulfuric acid catalyst at 120 °C and 85 KPa produced an oxidized product. Sodium metaperiodate reacts with OH groups of fiber and produces dialdehyde cellulose compound which improves the overall properties of fiber composites (Rahman et al. 2009a).



Conclusion and Future Perspective

Chemical modification with suitable chemicals provides a noble and facile route for the development of intrinsic negative properties of CF-based composites. Although the chemical treatments sometimes improved the certain properties of composites, the negative effect is also observed in natural fiber-based composites. All chemical modification as mentioned in this chapter is more or less effective to improve the overall properties such as physical, mechanical, and morphological of coir composites. Alkali treatments improved adhesion and compatibility between fiber and polymer matrix much more compared to other chemical treatments. In addition, alkali treatment of CF improves the interfacial interaction and adhesion of fiber–PP matrix, thus increasing the mechanical interlocking between the fiber and polymer matrix in the composites. However, CF structures degrade at high concentration of alkali treatment. Many new chemicals could be effective for CF modification. Therefore, more research on several chemicals is required to investigate their effects on the CF-based biocomposite materials.

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