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# Green composites and coatings from agricultural feedstocks

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**Green composites and coatings from agricultural feedstocks**

by

**Daniel P. Pfister**

A dissertation submitted to the graduate faculty  
in partial fulfillment of the requirements for the degree of

**DOCTOR OF PHILOSOPHY**

Major: Organic Chemistry

Program of Study Committee:  
Richard C. Larock, Major Professor  
Malika Jeffries-EL  
Klaus Schmidt-Rohr  
John Verkade  
Yan Zhao

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To Melissa, Grace, Trey and Ty  
for all your sacrifices and support

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## LIST OF ABBREVIATIONS

AESO	acrylated epoxidized soybean oil
BFE	boron trifluoride diethyl etherate
BMA	<i>n</i> -butyl methacrylate
CCORN	conjugated corn oil
CFO	conjugated fish oil
CLIN	conjugated linseed oil
CS	corn stover
CSOY	conjugated soybean oil
DDGS	distillers dried grains and solubles
DMA	dynamic mechanical analysis
DVB	divinylbenzene
ESG	extracted spent germ
HDPE	high-density polyethylene
LDPE	low-density polyethylene
MA	maleic anhydride
NMR	nuclear magnetic resonance
PLA	poly(lactic acid)
PP	polypropylene
PTFE	polytetrafluoroethylene
SG	spent germ
ST	styrene
SWG	switchgrass

TBPO	<i>t</i> -butyl peroxide
TGA	thermogravimetric analysis
TUN	tung oil
WPC	wood-plastic composite
WS	wheat straw
$\varepsilon$	elongation at break
$E$	Young's modulus
$E'$	storage modulus
$\sigma$	tensile strength
$T_{10}$	temperature at 10% weight loss
$T_{50}$	temperature at 50% weight loss
$T_g$	glass transition temperature
$T_{max}$	temperature at maximum degradation

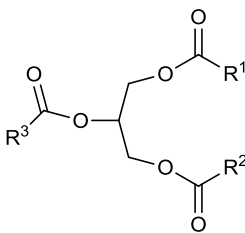
## CHAPTER 1. GENERAL INTRODUCTION

A portion of this introduction was taken from a minireview submitted to ChemSusChem.

Plastics play a vital role in our everyday lives and have become indispensable, being essential to clothing, shelter, transportation and communication, as well as the every day conveniences of modern living. The world's annual production of plastics has increased from less than 2 million tons in 1950 to more than 270 million tons in 2008.<sup>[1]</sup> It was in 1982 that plastics production surpassed that of steel worldwide. This rapid growth in plastics consumption can be attributed to the following advantages: a) high versatility and ability to be tailored to specific technical needs; b) little or no finishing, painting or polishing is required; c) plastics possess a lower density than competing materials; d) excellent thermal and electrical insulation properties; and e) good safety and hygiene properties for food packaging.<sup>[2]</sup> Today, nearly all polymers are produced from petroleum sources and the utilization of fossil fuels in their manufacture accounts for roughly 7% of worldwide oil and gas consumption.<sup>[3]</sup> Recently, high crude oil prices and concerns over petroleum supplies and the environment have triggered a search for biorenewable feedstocks for the production of plastics. Several biorenewable materials, including cellulose, starch, proteins, natural oils and sugar, have garnered a lot of attention as potential feedstocks and, of these, vegetable oils are among the most promising.<sup>[3,4]</sup>

Vegetable oils are made up of triglycerides, which are esters formed from glycerol and three fatty acids (structure shown in Scheme 1). The fatty acid chains can contain anywhere from 8 to 24 carbons and 0 to 5 carbon-carbon double bonds, which are most often non-conjugated and possess a *cis* configuration. The structures of the most common fatty





**Scheme 1.** Triglyceride structure, where  $R^1$ ,  $R^2$ , and  $R^3$  are fatty acids.

acids found in vegetable oils are given in Table 1. What distinguishes one vegetable oil from another is their fatty acid composition. Nearly all of the most common vegetable oils contain significant amounts of palmitic, stearic, oleic, linoleic and linolenic acids. Ricinoleic acid is the major constituent of castor oil, a vegetable oil of significant importance to industry. Table 2 gives the fatty acid composition of selected vegetable oils, as well as the number of carbon-carbon double bonds per triglyceride and the annual worldwide production.

**Table 1**  
**The most common fatty acids found in vegetable oils.**

Fatty Acid	Structure
Palmitic (C16:0)	$\text{HO}_2\text{C}$
Stearic (C18:0)	$\text{HO}_2\text{C}$
Oleic (C18:1)	$\text{HO}_2\text{C}$
Linoleic (C18:2)	$\text{HO}_2\text{C}$
Linolenic (C18:3)	$\text{HO}_2\text{C}$
Ricinoleic (C18:1 OH)	$\text{HO}_2\text{C}$

Vegetable oils have been utilized for a number of years in the production of agrochemicals, coatings, inks, lubricants and plasticizers. They have attracted interest in

various industries, because they tend to be inexpensive, are annually renewable and are available in high purity and vast quantities. In 2002, the worldwide production of vegetable oils was approximately 90 million tons and their production is estimated to grow at a rate of 3.3% per year. While most of the vegetable oils produced are used for human consumption, approximately 15% are used as precursors to the synthesis of new chemical commodities and materials.<sup>[5]</sup> Over the past several years in industry and academia, much attention has been given to the preparation of vegetable oil-based polymeric materials using various polymerization methods. The carbon-carbon double bonds present in both the original and modified vegetable oils have been utilized in cationic, free radical or olefin metathesis polymerizations to give thermosetting resins.<sup>[4c,6]</sup> In order to produce polyurethanes, a variety of different vegetable oil-based polyols have been reacted with di- or polyisocyanates.<sup>[4b]</sup> To a lesser extent, epoxy resins, polyesters and polyamides have also

**Table 2**  
**Degree of unsaturation, fatty acid composition,**  
**and annual production of common vegetable oils.**<sup>[4c,5]</sup>

Oil	Double bonds <sup>[a]</sup>	Fatty Acid Composition (%)					Avg. Annual Production (10 <sup>6</sup> tons)	
		C16:0	C18:0	C18:1	C18:2	C18:3	2001-2005	2009 <sup>[b]</sup>
Castor <sup>[c]</sup>	3.0	1.5	0.5	5.0	4.0	0.5	0.56	0.54
Coconut	-	9.8	3.0	6.9	2.2	-	3.74	3.52
Corn	4.5	10.9	2.0	25.4	59.6	1.2	2.30	2.39
Cottonseed	3.9	21.6	2.6	18.6	54.4	0.7	4.49	4.82
Linseed	6.6	5.5	3.5	19.1	15.3	56.6	0.83	0.61
Olive	2.8	13.7	2.5	71.1	10.0	0.6	2.52	2.95
Palm	1.7	42.8	4.2	40.5	10.1	-	23.53	43.86
Palm kernel	-	8.8	2.4	13.6	1.1	-	2.95	5.19
Peanut	3.4	11.4	2.4	48.3	31.9	-	5.03	5.00
Rapeseed/canola	3.8/3.9	4/4.1	2/1.8	56/60.9	26/21.0	10/8.8	15.29	20.45
Sesame	3.9	9	6	41	43	1	0.76	0.82
Soybean	4.6	11.0	4.0	23.4	53.3	7.8	26.52	35.70
Sunflower	4.7	5.2	2.7	37.2	53.8	1.0	10.77	11.87

<sup>[a]</sup> Number of C-C double bonds per triglyceride

<sup>[b]</sup> Data taken from USDA figures and Oil World Annual 2009

<sup>[c]</sup> Composed of 87.5% ricinoleic acid

been produced from a variety of vegetable oil-based monomers.<sup>[7]</sup>

In an effort to improve the strength and stiffness of vegetable oil-based polymeric materials, fillers or fibers have been incorporated. Natural fibers have gained a lot of interest, because they are biorenewable, biodegradable, very inexpensive, and yet have a high strength and stiffness despite being light in weight. Hemp and flax have garnered the most attention, but other cellulose-based fillers/fibers, including distillers dried grains and solubles, kenaf and wood flour, have been utilized as a reinforcement.<sup>[8]</sup>

### Dissertation Organization

This dissertation is divided into six chapters. The first chapter focuses on the synthesis and characterization of green composites prepared from a free radically-cured tung oil-based resin and spent germ, a particulate natural filler. The second, third and fourth chapters cover the use of agricultural fibers, corn stover, wheat straw and switchgrass, respectively, as reinforcements for free radically-cured conjugated soybean oil- or conjugated linseed oil-based resins. The fifth chapter discusses the effect of the natural oil, corn, soybean, fish, and linseed oil, and the effect of the agricultural fiber, corn stover, wheat straw and switchgrass, on the properties of cationically-cured green composites. The sixth chapter talks about the challenges involved in preparing hybrid latexes from cationic soybean oil-based waterborne polyurethane dispersions and vinyl monomers.

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## CHAPTER 2. PREPARATION AND PROPERTIES OF TUNG OIL-BASED COMPOSITES USING SPENT GERM AS A NATURAL FILLER

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### Abstract

Novel biocomposites have been prepared by the free radical polymerization of a tung oil-based resin using spent germ, the co-product of wet mill ethanol production, as a filler. The effect of filler particle size, amount of filler, amount of crosslinker, and molding pressure on the resulting composites has been investigated. When compared to the pure resin, an increase in storage modulus is observed when filler is added to the matrix. The thermal stabilities of the resulting composites lie between the stabilities of the resin and the spent germ. Decreasing the particle size results in an increase in both the storage modulus and the mechanical properties of the composites. As the amount of crosslinker, divinylbenzene, increases, an improvement in the thermal stabilities and mechanical properties is observed. The composites prepared are mainly composed of renewable resources, possess good thermal and mechanical properties, and have potential applications in the construction and automotive industries.

### Introduction

The growing use and demand for petroleum-based plastics has caused environmental concerns and increased our dependence on foreign oil.<sup>1</sup> The persistence of these

indestructible materials in the environment, a shortage of landfill space, concerns over emissions during incineration, and increasing oil prices have encouraged the development of biodegradable polymers and plastics from biorenewable resources.<sup>2</sup> Biopolymers from renewable natural resources have gained much attention because they are inexpensive and readily available.<sup>3</sup>

Natural oils are among the most promising renewable resources to be used for the production of biopolymers. Considerable recent research on the development of polymeric materials from these oils has been conducted. Wool *et al.*<sup>4,5</sup> and Borrajo *et al.*<sup>6</sup> have prepared rigid polymers from the free radical copolymerization of soybean oil monoglyceride maleates and linseed oil monoglyceride maleates, respectively, with styrene. Hazer *et al.*<sup>7,8</sup> have reported the preparation of new biodegradable materials by the graft copolymerization of polymeric linseed and soybean oil-peroxides with styrene, methyl methacrylate, and *n*-butyl methacrylate. Polyurethane thermosets have been developed by Petrović *et al.*<sup>9,10</sup> and Galià *et al.*<sup>11</sup> by reacting various soybean oil polyols and epoxidized methyl oleate-based polyether polyols, respectively, with isocyanates. The preparation of epoxy resins has also been reported using epoxidized linseed,<sup>12</sup> soybean,<sup>12,13</sup> and castor oils.<sup>13</sup> Work in our group has mainly focused on the preparation of crosslinked networks by polymerization of the unfunctionalized double bonds in natural oils. Thermosets from regular and conjugated soybean oil,<sup>14,15</sup> corn oil,<sup>16</sup> linseed oil,<sup>17,18</sup> tung oil,<sup>19</sup> fish oil,<sup>20</sup> and various other vegetable oils<sup>21</sup> have been prepared by cationic, thermal, and free radical polymerizations.

Fillers are often added to polymers to decrease cost and increase dimensional stability, strength, toughness, and environmental resistance.<sup>22</sup> Composite materials have found many applications in the automobile, aircraft, military, sporting goods, and marine

industries. The term biocomposites is broadly defined and can be used to describe composites resulting from bio-based resins and synthetic fibers, petroleum-based resins and natural fibers, or bio-based resins and natural fibers. The latter are often referred to as “green composites”.<sup>2</sup> Corn and soybean oil-based biocomposites have been successfully prepared using glass fibers as a phase reinforcer.<sup>23-25</sup> The mechanical properties of the resulting materials are significantly improved, making these materials suitable for applications in automobile construction. Natural fibers, as a replacement for synthetic fibers, have gained much attention in the past several years, because of their low cost, low density, acceptable specific strength, renewability, and biodegradability.<sup>2</sup> Petroleum-based polymers reinforced with wood fibers have been extensively investigated in the past and these materials have found many applications in the automotive and construction industries. More recently, wood fibers have been replaced by agricultural fibers, underutilized agricultural co-products, and crop residues. For example, flax and kenaf have been used to reinforce polypropylene (PP),<sup>26,27</sup> high-density polyethylene (HDPE) composites have been prepared with cornstalks and corncobs,<sup>28</sup> and wheat straw, big blue stem grass, soybean hulls, and distillers dried grains and solubles (DDGS) have been used to reinforce both PP and HDPE.<sup>26,28,29</sup> DDGS has also been used as a filler with a phenolic resin.<sup>30</sup> Recently, Wool *et al.*<sup>31,32</sup> and Aranguren *et al.*<sup>33</sup> have reported the preparation of natural fiber composites using an acrylated epoxidized soybean oil (AESO), a modified AESO, or a linseed oil monoglyceride maleates-based matrix and wood flour, flax, hemp, cellulose, or pulp as a fiber or filler. When compared with the pure resin, considerable improvements in the physical and mechanical properties have been observed by the addition of fibers.

Tung oil, a triglyceride oil consisting primarily (~84%) of alpha-elaostearic acid (*cis*-9, *trans*-11, *trans*-13-octadecatrienoic acid), is an excellent drying oil typically used in the preparation of paints and varnishes.<sup>19</sup> The high number of fatty acid side chains containing a conjugated triene makes it reactive towards free radical polymerization. DDGS and spent germ (SG) are the co-products of dry mill and wet mill ethanol production, respectively. With the increased demand for ethanol as a fuel additive, the production of DDGS and SG are expected to increase dramatically. Finding new uses for these underutilized agricultural co-products will increase their value and help offset ethanol production costs.<sup>34</sup> In this work, we report the preparation of tung oil-based composites using SG as a natural filler by a pressure molding process. The effect of filler particle size, amount of filler, amount of crosslinker, and the molding pressure on the structure and properties of the resulting composites have been investigated.

### Experimental

**Materials.** The tung oil (TUN), divinylbenzene (DVB, technical-grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), and *t*-butyl peroxide (TBPO) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The ground spent germ (SG) was provided by Grain Processing Corporation of Muscatine, IA. The polytetrafluoroethylene (PTFE) release agent MS-122DF was purchased from Miller-Stephenson Chemical Co. (Morton Grove, IL).

Seven different particle sizes of SG were obtained using U.S. standard sieves. Unsieved means that the SG was used as received and mesh sizes of >20, >40, >60, and >80 correspond to particles that pass through a 20 (particles <850  $\mu\text{m}$ ), 40 (particles <425  $\mu\text{m}$ ), 60



(particles <250  $\mu\text{m}$ ), and 80 (particles <180  $\mu\text{m}$ ) mesh sieve, respectively. The mesh size 40  $\times$  60 corresponds to particles that pass through a 40 mesh sieve and are retained by a 60 mesh sieve (particles 250-425  $\mu\text{m}$ ), and 60  $\times$  80 corresponds to particles that pass through a 60 mesh sieve and are retained by an 80 mesh sieve (particles 180-250  $\mu\text{m}$ ).

The SG was also extracted to remove relatively unreactive corn oil before being used as a filler. The >80 mesh SG was extracted for 24 hr by Soxhlet extraction with refluxing methylene chloride as the solvent. This extracted SG was then used as a filler under the standard conditions listed below and the resulting composite is designated as ESG.

**Preparation of TUN-based Resin and Composites.** The TUN-based resin was prepared by bulk free radical polymerization. The designated amounts of TUN, BMA, and DVB were added together and stirred vigorously. The TBPO initiator was then added in the amount of 5 wt % of the total resin weight. This mixture was poured into a glass vial and cured at 130 °C for 12 hr and 140 °C for 12 hr. The following nomenclature is used: TUN represents tung oil and BMA and DVB represent the *n*-butyl methacrylate and divinylbenzene comonomers, respectively. For example, TUN50-BMA35-DVB15 corresponds to a resin prepared from 50 wt % TUN, 35 wt % BMA, 15 wt % DVB and 5 wt % of this total weight was the amount of TBPO initiator used.

The composites were prepared using a compression molding process. The SG was dried in a vacuum oven at 70 °C for 18 hr. The designated amounts of TUN, BMA, DVB, and TBPO were mixed and cured using the above cure sequence. Just prior to the gel point (approximately 2 hr), the resin was removed from the oven and added to the SG. This mixture was stirred until all the SG was wetted and was then placed in the cavity of the preheated (130 °C) steel mold coated with the PTFE release agent. The mold was closed and

cured at 130 °C under the designated pressure for 4 hr. The mold was then moved to an oven and cured under atmospheric pressure. Because an undetermined amount of resin and SG was forced out of the mold during the cure process, the reported amounts of SG are based on the initial amounts of SG and resin used. For example, for the composite containing 60% SG, 50 g of resin was added to 75 g of SG. The resin/SG mixture was forced out to ensure that no air bubbles were present in the sample and only a small amount of material was lost. The standard composition and conditions used for preparing the composites were TUN50-BMA35-DVB15, >80 mesh particle size, 50% SG, and 3000 psi molding pressure. When one variable was changed, the rest were held constant. In all cases, the matrix composition was TUN50-(BMA + DVB)50. For example, a composite designated DVB 20 refers to TUN50-BMA30-DVB20, >80 mesh particle size, 50% SG, and 3000 psi molding pressure.

**Characterization.** Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structures of the polymer resin and the resulting composites. A 4.5 g sample was extracted for 24 hr with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70 °C overnight before weighing. <sup>1</sup>H-NMR spectroscopic analysis of the soluble substances was carried out in CDCl<sub>3</sub> using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz.

A Q50 TGA (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 20 °C/min. Generally, a 10-12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the resin and the resulting composites were obtained on a TA Instruments Q800 DMA using a three-point bending mode. A rectangular specimen of about 22 mm × 8.5 mm × 1.5 mm (length × width × thickness) was cut from the samples. Each specimen was cooled to -60 °C and then heated at 3 °C /min to 250 °C at a frequency of 1 Hz under air.

The tensile tests were conducted at 25 °C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type – I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

Three-point bending tests were conducted at 25 °C according to ASTM D790-93 using an Instron universal testing machine at a crosshead speed of 10 mm/min. A rectangular specimen of 65 mm × 14 mm × about 4.5 mm (length × width × thickness) was cut from the samples.

## Results and Discussion

**Soxhlet Extraction Analysis.** The microstructures of the resin and resulting composites were examined using Soxhlet extraction with methylene chloride as the refluxing solvent. Table I gives the percentage of soluble materials for the resin, SG, and composites. Because of the multiple reactive C-C double bonds present in TUN and DVB, the resin is a highly crosslinked thermoset with a low amount of soluble materials. TUN is a triglyceride oil primarily composed of a fatty acid containing a conjugated triene, but also contains fatty acid side chains with non-conjugated double bonds. The wide range of chemical shifts for the vinylic protons (5.2-6.5 ppm) indicates that the carbon-carbon double bonds present in TUN are mostly conjugated (Fig. 1.f). The <sup>1</sup>H-NMR spectrum of the soluble portion of the resin

(Fig. 1.c) shows that it is primarily composed of unreacted tung oil. The oil appears to be non-conjugated, because of the small range of chemical shifts (5.3-5.4 ppm) evident for the vinylic protons. There also seems to be a very small amount of unreacted BMA or oligomers of BMA and TUN present in the soluble material. Because of the absence of peaks in the aromatic region, all the DVB was incorporated into the thermoset.

**TABLE I**  
**Thermal Properties and Extraction Data of the Resin, Spent Germ, and Composites**

Entry	Sample Composition	DMA		TGA			Soxhlet Extraction	
		$T_g$ (°C)	$E'$ (MPa) <sup>a</sup>	$T_{10}$ (°C)	$T_{50}$ (°C)	$T_{max}$ (°C)	% soluble	% insoluble
1	Resin <sup>b</sup>	48	587	346	434	457	3	97
2	Spent Germ <sup>c</sup>	-	-	252	316	298	14	86
3	Unsieved	20	661	266	417	430	5	95
4	>20 Mesh	27	720	267	419	434	3	97
5	>40 Mesh	27	744	267	419	433	5	95
6	>60 Mesh	25	841	267	419	430	5	95
7	>80 Mesh <sup>d</sup>	26	1003	271	423	432	3	97
8	40 × 60 Mesh	26	1013	270	417	433	4	96
9	60 × 80 Mesh	21	880	271	419	434	5	95
10	40% SG	37	989	276	425	433	2	98
11	45% SG	37	1086	270	424	432	2	98
12	55% SG	16	586	267	418	429	5	95
13	60% SG	12	772	259	411	430	6	94
14	DVB 10	19	465	268	416	425	4	96
15	DVB 20	23 (61)	1096	270	426	438	3	97
16	DVB 25	21 (57)	1024	266	430	441	3	97
17	1000 psi	20	745	271	420	431	4	96
18	2000 psi	23	803	273	421	432	3	97
19	ESG	37	1434	264	423	431	0	100

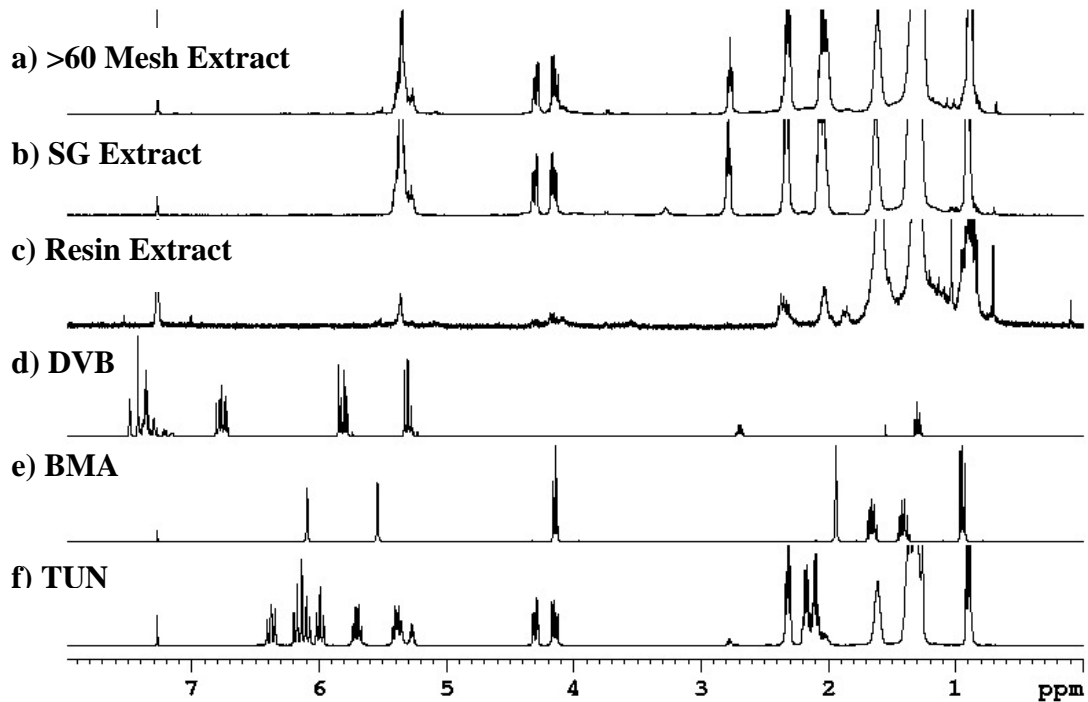
<sup>a</sup> Storage modulus at 25 °C

<sup>b</sup> TUN50-BMA35-DVB15

<sup>c</sup> >80 Mesh

<sup>d</sup> Represents the standard composition: 50% SG, DVB 15, and 3000 psi

All the composites produced had a low amount of soluble materials ranging from 2-6% (Table I). The <sup>1</sup>H-NMR spectrum of the soluble portion of the >60 mesh composite is shown in Fig. 1.a. The soluble material is mainly composed of the crude corn oil present in the SG (Fig. 1.b). The >80 mesh SG used in this study contained 14% corn oil (Table I,



**Figure 1**  $^1\text{H-NMR}$  spectra of a) extract of  $>60$  mesh composite, b) extract of  $>80$  mesh SG, c) extract of the resin TUN50-BMA35-DVB15, d) DVB, e) BMA, f) TUN

entry 2). This oil has a low degree of unsaturation ( $\sim 3.9$  C-C double bonds per triglyceride) compared to tung oil ( $\sim 7.9$  C-C double bonds per triglyceride) and the double bonds present in corn oil are non-conjugated. For these reasons, the corn oil is unreactive towards free radical polymerization. The soluble portion of the composite also contains a very small amount of unreacted BMA and possibly low molecular weight oligomers of BMA or TUN. The  $^1\text{H-NMR}$  spectrum of the extracted  $>60$  mesh composite is representative of the soluble materials obtained from all composites (Fig. 1.a).

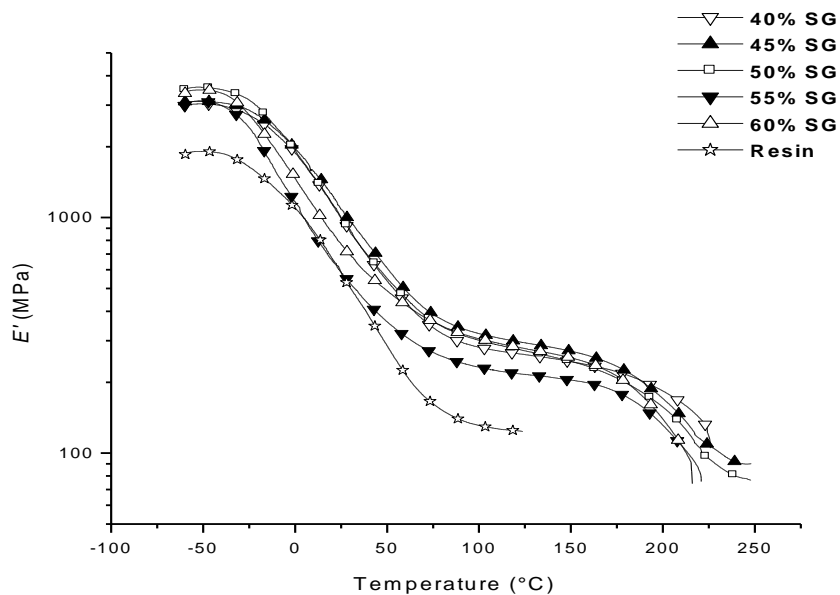
The particle size of the filler (Table I, entries 3-9) appears to have no effect on the % soluble material extracted from the resulting composites with the soluble fractions varying

from 3-5%. There seems to be a trend in the % soluble materials as the amount of SG is increased (entries 10-13). The % soluble materials increases from 2% for the 40% SG composite to 6% for the 60% SG composite. This was expected, because as more SG is added, more of the unreactive crude corn oil is present to be extracted. Another possibility for the increase in % soluble materials is that as more filler is added to the resin, the diffusion of the initiator or chain propagation is inhibited and the result is less crosslinking and a loose network structure. Similar results have been observed elsewhere.<sup>23</sup> As more DVB is added to the resin, the % soluble materials from the resulting composites decreases ever so slightly (entries 14-16). DVB is used as an effective crosslinker and as more DVB is added, the matrix becomes more highly crosslinked reducing the amount of soluble materials. The same trend is observed as the pressure is increased (entries 17 and 18). If the pressure is decreased, while holding the filler concentration constant, incomplete wetting of the filler by the resin is expected, resulting in an increase in voids and filler-filler agglomerations.<sup>33</sup> This makes the filler particles more accessible and the oil contained in the SG is more easily extracted. For the ESG composite (entry 19), most of the oil present in the SG was extracted prior to the preparation of the composite. Therefore, the corn oil that was extracted in all of the previous composites was absent and the resulting composite had 0% soluble materials.

**Dynamic Mechanical Analysis.** The room temperature storage moduli ( $E'$ ) and glass transition temperatures ( $T_g$ ) for the resin and composites are given in Table I. The  $T_g$  data have been obtained from the peak position of the  $\tan \delta$  curve. For the resin and all composites, the typical drop in  $E'$  at the glass transition temperature was observed. With the exception of the 55% SG and DVB 10 composites, the addition of SG increased the  $E'$  value of the composites over the entire temperature range studied. This increased stiffness is likely

the result of the reduced mobility and deformation of the matrix caused by the addition of a filler.<sup>23</sup>

As the larger particles are removed from the filler, it can be seen that  $E'$  increases (entries 3-7).  $E'$  increases from 661 MPa for the unsieved composite to 1003 MPa for the >80 mesh composite. As the particle size in a composite decreases, the filler dispersion and matrix-filler interaction, although it may be weak, should increase.<sup>35</sup> The increased interaction and interfacial adhesion would result in the higher modulus observed. But this trend was not observed when the fine particles were removed from the filler (entries 8 and 9). For the more uniform particle sizes,  $E'$  decreased from 1013 MPa for the 40 × 60 mesh composite to 880 MPa for the 60 × 80 mesh composite. Figure 2 shows the storage modulus as a function of temperature for the resin and the composites prepared with different amounts of SG. As described earlier, it is evident that as SG is added to the matrix,  $E'$  increases over



**Figure 2**  $E'$  of the resin and composites prepared with differing amounts of SG.

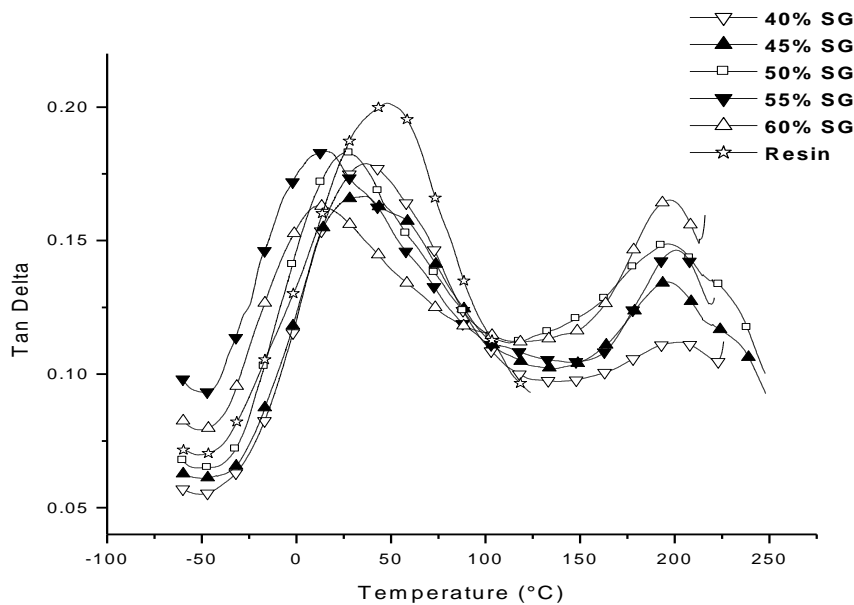
the entire temperature range. The room temperature storage modulus initially increases when the amount of SG is increased from 40% to 45%. As the amount of SG is further increased,  $E'$  decreases from 1086 MPa to a low value of 586 MPa. Initially, the amount of crosslinker appears to have a dramatic effect on  $E'$ . When the amount of DVB increases from 10 (entry 14) to 15 wt % (entry 7),  $E'$  increases from 465 MPa for the DVB 10 composite to 1003 MPa for the DVB 15 composite, but increases very little when the amount of DVB is increased further. As expected, increasing the pressure caused an increase in  $E'$  from 745 MPa (entry 17) to 1003 MPa (entry 7). Increasing the pressure, while holding the amount of filler constant, should result in increased wetting of the filler and better filler-matrix interactions. The highest  $E'$  was observed for the ESG composite. By removing the corn oil from the SG, the resin is more easily absorbed into the filler, which could account for the increased stiffness. It is also possible that the corn oil present in the SG is having a plasticizing effect on all of the composites.

The  $T_g$  is considerably effected when SG is added to the resin. The resin has a  $T_g$  of 48 °C and the resulting composites have glass transition temperatures ranging from 12 to 37 °C. This decrease in  $T_g$  is likely the result of a poor interaction between the filler and the matrix. The TUN and petroleum-based comonomers are hydrophobic in nature and the filler, with a large concentration of hydroxyl groups, is hydrophilic. Figure 3 illustrates the loss factor ( $\tan \delta$ ) as a function of temperature for the resin and composites containing different amounts of SG. For all of the composites, two peaks in the  $\tan \delta$  curve are observed. The first peak (lower temperature) corresponds to the primary relaxation process of the matrix and the second peak (higher temperature) is believed to correspond to the onset of degradation of the filler. Two reasons for this belief are: 1) the peak height increases as the



amount of SG is increased, and 2) the onset of degradation of the filler/composites obtained from the TGA curves was observed to be  $\sim 200$  °C. With all of the variables changed, there appeared to be no trend in the peak heights of the lower temperature  $\tan \delta$  peak for the resulting composites.

As with the % soluble materials, there appears to be no effect on the  $T_g$  as the size of the particles is varied. When the amount of SG is increased from 40% to 60%, the  $T_g$

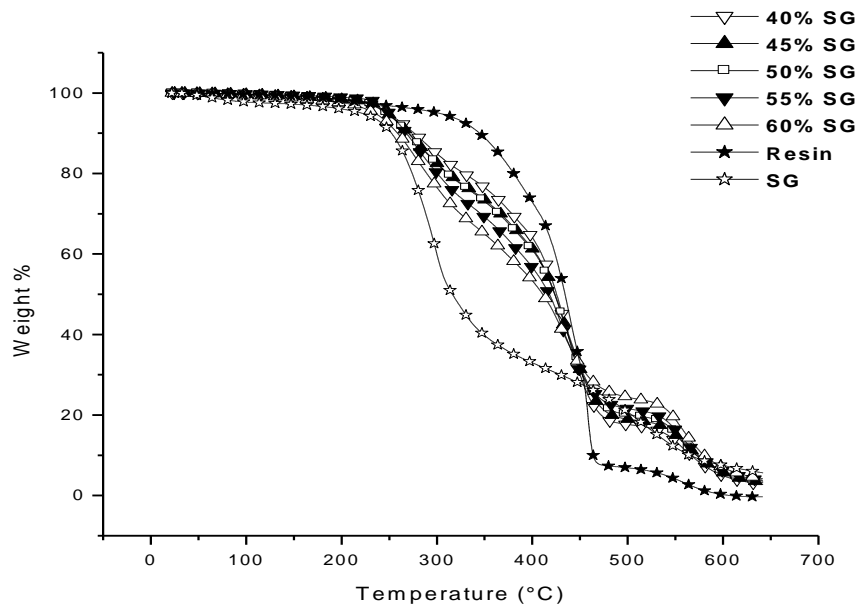


**Figure 3**  $\tan \delta$  curves for the resin and composites prepared with differing amounts of SG.

decreases from 37 to 12 °C. There are two possible explanations for this result. One is that the initiator diffusion and chain propagation could be increasingly inhibited as the amount of filler particles increase, resulting in less crosslinking. Another possibility is that the unreactive corn oil present in the SG could have a plasticizing effect on the matrix. The  $T_g$  increases when the amount of DVB is increased from 10 to 15 wt % due to increased

crosslinking. But as more DVB is added, two relaxation processes (peaks) are observed for the matrix in the  $\tan \delta$  curve. The reactivity of the oil and the comonomers used in the matrix are very different. For the DVB 20 and DVB 25 composites, the large amounts of the more reactive DVB present at the beginning of the reaction may result in a homopolymerization or copolymerization with BMA to form a “DVB-rich” phase. When the amount of DVB decreases, more oil is incorporated into the polymer to form an “oil-rich” phase. These two phases each have their own distinct relaxation processes: the “oil-rich” phase with a  $T_g$  of  $\sim 20$  °C and the “DVB-rich” phase with a  $T_g$  of  $\sim 60$  °C. Similar results have been observed in previously work.<sup>21,23</sup> The  $T_g$  increases from 20 to 26 °C as the pressure is increased from 1000 to 3000 psi, most likely due to a decrease in voids and increased filler-matrix interactions discussed earlier. When the corn oil is removed from the SG, the  $T_g$  of the resulting composite increased from 26 °C (entry 7) to 37 °C (entry 19). As discussed earlier, this could be a result of the increased absorption of the matrix by the filler or the corn oil acting as a plasticizer.

**Thermogravimetric Analysis.** Figure 4 shows the TGA curves of the resin, SG, and composites prepared with different amounts of SG. The curves of the composites with different amounts of SG are representative of all composites. The thermal degradation of the resin, SG, and composites can be separated into three stages. For the resin, the first stage, from 25 to 300 °C, corresponds to the loss of unreacted oil and soluble materials. The second stage, from 300 to 475 °C, likely involves degradation of the crosslinked insoluble resin and the last stage, from 475 to 650 °C, involves oxidation of the char. No residue was left above 650 °C. The first stage of degradation of the SG, from 25 to 125 °C, represents the loss of water. The starch, protein, corn oil, and hemicellulose portions are lost in the second stage in



**Figure 4** TGA curves for the resin, SG, and composites prepared from differing amounts of SG.

the temperature range of 125 to 400 °C.<sup>36-38</sup> In the third stage, 400 to 650 °C, the degradation of cellulose is observed and approximately 5 wt % of residue is left after 650 °C. For the composites, the first stage ranges from 25 to 350 °C and corresponds to the loss of soluble materials, starch, protein, and hemicellulose. The second stage of degradation, from 350 to 500 °C, represents loss of the crosslinked matrix. The final stage, from 500 to 650 °C, is a result of the loss of cellulose and the oxidation of char. Approximately 4 wt % of residue remains after 650 °C. Figure 4 indicates that the first and third stages of degradation for the composites are dictated by the filler. As more SG is added to the composite, an increase in the mass loss from 25 to 350 °C and 500 to 650 °C is observed.

The temperatures at 10% weight loss ( $T_{10}$ ), temperatures at 50% weight loss ( $T_{50}$ ), and temperatures at maximum degradation ( $T_{max}$ ) are given in Table I for the resin, SG, and

the resulting composites. It can be seen from the data that the resin is far more thermally stable than the SG. The degradation of the resin doesn't actually begin until 300 °C, whereas the SG has lost nearly 60% of its mass by 350 °C. As the particle size of the filler decreases (entries 3-9), the thermal stability tends to increase. When the particle size is changed from unsieved to >80 mesh,  $T_{10}$  increases from 266 to 271 °C and  $T_{50}$  increases from 417 to 423 °C, but  $T_{max}$  seems to be unaffected. There is a large drop in the  $T_{10}$  and  $T_{50}$  values when the amount of SG is increased.  $T_{10}$  and  $T_{50}$  values decrease from 276 to 259 °C and 425 to 411 °C, respectively, when the amount of SG is increased from 40 to 60%. The  $T_{max}$  value also decreased, but to a lesser extent. As the amount of DVB increases (entries 14-16), the  $T_{50}$  and  $T_{max}$  values are most affected and no trend is observed for the  $T_{10}$  values. The  $T_{50}$  values increase from 416 to 430 °C and the  $T_{max}$  values increase from 425 to 441 °C when the DVB increases from 10 to 25 wt %. This was expected because of the increased crosslinking resulting from the larger amounts of DVB. Increasing the pressure appears to have little affect on the  $T_{10}$ ,  $T_{50}$ , and  $T_{max}$  values, only causing small increases in these values (entries 17 and 18). Extracting the SG prior to preparing the composite (entry 19) has little affect on the thermal stability.

From the TGA data, the  $T_{10}$  values appear to be most affected by the filler, while the  $T_{max}$  values seem to be affected by the resin and  $T_{50}$  seems to be influenced by both the resin and the filler. For example, when the filler is varied, either the size or the amount (entries 3-13), the  $T_{10}$  and  $T_{50}$  values increase or decrease significantly, while little or no trend is observed for the  $T_{max}$  values. But when the resin is changed (entries 14-16),  $T_{50}$  and  $T_{max}$  change the most, while  $T_{10}$  appears to be unaffected. This is expected, because of the low thermal stability of the filler and the higher stability of the resin.

**Mechanical Properties.** The mechanical properties of the composites are given in Table II. With an exception for the composites prepared with more uniform particles sizes (entries 6 and 7), the Young's modulus ( $E$ ) and tensile strength ( $\sigma$ ) increase as the particle size of the filler decreases.  $E$  and  $\sigma$  increase from 310 to 470 MPa and 5.5 to 12.3 MPa, respectively, as the particle size changes from unsieved to >80 mesh (entries 1-5). Similar to the room temperature storage modulus,  $E$  stays relatively constant, while increasing the SG amount from 40 to 45% (entries 8 and 9). But as the amount of SG is further increased,  $E$  drops from

**TABLE II**  
**Mechanical Properties of the Composites**

Entry	Sample Composition	Young's Modulus (MPa)	Tensile Strength (MPa)	Flexural Modulus (MPa)	Flexural Strength (MPa)
1	Unsieved	310 ± 6	5.5 ± 0.2	543 ± 63	5.8 ± 0.2
2	>20 Mesh	421 ± 8	7.3 ± 0.3	657 ± 41	6.3 ± 0.7
3	>40 Mesh	408 ± 11	7.5 ± 0.5	760 ± 22	10.3 ± 0.3
4	>60 Mesh	410 ± 6	8.6 ± 0.4	728 ± 91	10.9 ± 0.9
5	>80 Mesh <sup>a</sup>	470 ± 8	12.3 ± 0.6	991 ± 69	17.8 ± 0.9
6	40 × 60 Mesh	543 ± 11	7.6 ± 0.2	818 ± 82	11.9 ± 0.6
7	60 × 80 Mesh	494 ± 15	7.7 ± 1.4	895 ± 41	13.9 ± 0.9
8	40% SG	516 ± 15	13.1 ± 0.4	763 ± 35	18.6 ± 1.0
9	45% SG	525 ± 8	13.5 ± 0.5	906 ± 66	17.0 ± 0.8
10	55% SG	423 ± 9	9.1 ± 0.3	625 ± 66	10.0 ± 0.6
11	60% SG	335 ± 11	6.7 ± 0.3	938 ± 40	12.2 ± 0.5
12	DVB 10	196 ± 3	7.0 ± 0.4	295 ± 26	7.7 ± 0.1
13	DVB 20	678 ± 13	13.5 ± 0.6	1045 ± 86	20.2 ± 0.1
14	DVB 25	867 ± 17	12.4 ± 1.0	1228 ± 129	15.4 ± 0.6
15	1000 psi	393 ± 18	8.9 ± 0.7	682 ± 15	12.5 ± 0.6
16	2000 psi	388 ± 3	9.0 ± 0.5	638 ± 13	10.3 ± 0.4
17	ESG	746 ± 22	15.1 ± 1.2	1063 ± 47	24.8 ± 1.2

<sup>a</sup> Represents the standard composition: 50% SG, DVB 15, and 3000 psi

a high value of 525 MPa for the 45% SG composite to 335 MPa for the 60% SG composite (entries 10 and 11). A similar trend is observed in  $\sigma$ , which drops from 13.5 to 6.7 MPa as the amount of SG increases from 45 to 60%. Increasing the amount of DVB from 10 wt % to 25 wt % caused an increase in  $E$  from 196 to 867 MPa (entries 12-14). As the DVB is

increased from 10 to 20 wt %,  $\sigma$  increases from 7.0 to 13.5 MPa, but increasing to 25 wt % causes a decrease in  $\sigma$ . It is possible that higher crosslinking reduces the number of conformations that the matrix can take on, while being under an applied force. When a crack becomes a failure, the matrix can disperse a lesser amount of energy, causing the decrease in  $\sigma$ . Similar results have been observed elsewhere.<sup>23</sup> No affect on  $E$  and  $\sigma$  is observed when the pressure is initially increased, but when the pressure is increased from 2000 to 3000 psi, both  $E$  and  $\sigma$  increase from 388 to 470 MPa and 9.0 to 12.3 MPa, respectively (entries 15 and 16). By removing the unreactive corn oil from the SG, increases in both the modulus and strength are observed (entry 17).

As expected, the flexural modulus and strength increase as the particle size of the SG decreases (entries 1-7). This is most likely the result of better filler dispersion and filler-matrix interactions obtained by using smaller particles. The flexural modulus increases from 543 to 991 MPa and the flexural strength increases from 5.8 to 17.8 MPa as the filler is changed from unsieved to >80 mesh. With the exception of the 55% SG composite, the flexural modulus increases as the SG is increased from 40 to 45 wt %, but stays relatively constant as more SG is added (entries 8-11). The modulus increases from 763 MPa for the 40% SG composite to 991 MPa for the 50% SG composite. For the most part, the flexural strength decreases as more SG is added. The flexural strength decreases from 18.6 to 12.2 MPa as the amount of SG increases from 40 to 60 wt %. As with the Young's modulus, there is a large increase in the flexural modulus as the amount of crosslinker (DVB) increases. The flexural modulus increases from 295 to 1228 MPa when going from DVB 10 to DVB 25 (entries 12-14). The flexural strength also follows the same trend as the tensile strength. As the crosslinking of the matrix increases, the strength increases, but too much

crosslinking results in a decrease in the strength of the composite. The flexural strength increases from 7.7 to 20.2 MPa, when the amount of DVB increases from 10 to 20 wt %, but decreases to 15.4 MPa, when the amount of DVB is further increased to 25 wt %. Increasing the pressure from 1000 to 2000 psi causes a drop in both the flexural modulus and strength (entries 15 and 16), but when going from 2000 to 3000 psi, the modulus and strength increase from 638 to 991 MPa and 10.3 to 17.8 MPa, respectively (compare entries 5 and 16). As described earlier, the thermal and mechanical properties are improved when the corn oil is removed from the SG prior to preparation of the composite (entry 17). It is believed that the observed increase in the absorption of the matrix by the filler leads to a better filler-matrix interaction. The flexural modulus increases from 991 (entry 5) to 1063 MPa (entry 17) and the flexural strength increases from 17.8 to 24.8 MPa.

### Conclusions

“Green composites” have been prepared from a free radical initiated, tung oil-based resin using spent germ (SG) as a natural filler. The matrix used in this study is highly crosslinked, causing the resulting composites to contain a low percent of soluble materials. This soluble portion is primarily composed of the corn oil present in the SG. The composites produced are quite thermally stable with  $T_{max}$  values in the area of 430 °C. In general, the thermal and mechanical properties of the composites are improved by decreasing the size of the filler. This is most likely the result of an enhanced interfacial adhesion and filler-matrix interaction. As more SG is added to the composite, the properties tend to decrease, due to the filler-filler agglomerations and an increase of voids expected when the amount of filler is increased, while holding the pressure constant. Divinylbenzene (DVB) is used as an effective crosslinker and, as expected, the thermal and mechanical properties of the

composites increase as the concentration of DVB in the matrix increases. For the most part, as the pressure during the cure is increased, the properties increase. When decreasing the pressure, while holding the amount of filler constant, incomplete wetting of the filler by the matrix is expected, resulting in poorer properties. By removing the corn oil from the SG prior to composite preparation, an improvement in thermal and mechanical properties is obtained.

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### CHAPTER 3. THERMOPHYSICAL PROPERTIES OF CONJUGATED SOYBEAN OIL/CORN STOVER BIOCOSITES

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#### Abstract

Novel “green composites” have been prepared using a conjugated soybean oil-based resin and corn stover as a natural fiber. Corn stover is the residue remaining after grain harvest and it is estimated that approximately 75 million tons are available annually in the United States. The effect of the amount of filler, the length of the fiber, and the amount of the crosslinker on the structure and thermal and mechanical properties of the composites has been determined using Soxhlet extraction analysis, thermogravimetric analysis, dynamic mechanical analysis, and tensile testing. Increasing the amount of corn stover and decreasing the length of the fiber results in significant improvements in the mechanical properties of the composites. The Young’s moduli and tensile strengths of the composites prepared range from 386 to 1324 MPa and 3.5 to 6.5 MPa, respectively. Water uptake data indicate that increasing the amount and fiber length of the corn stover results in significant increases in the absorption of water by the composites. The composites, containing 20 to 80 wt % corn stover and a resin composed of 50 wt % natural oil, contain 60 to 90 wt % renewable materials and should find applications in the construction, automotive, and furniture industries.

## Introduction

As the global demand for petroleum-based plastics continues to increase, environmental concerns and rising crude oil prices have triggered a search for replacements for these non-biodegradable plastics. The use of biorenewable resources for the production of biopolymers has gained a large amount of interest over the past decade because of their low cost and ready availability (Andjelkovic et al., 2006; Li and Larock, 2005). Natural oils, containing a triglyceride structure with unsaturated fatty acid side chains, are among the most promising natural resources for the production of bioplastics. Considerable research towards the development of these materials from natural oils has been conducted. Rigid thermoset polymers have been prepared by the free-radical copolymerization of soybean oil monoglyceride maleates (Can et al., 2001), linseed oil monoglyceride maleates (Mosiewicki et al., 2005), and modified acrylated epoxidized soybean oil (AESO) (Colak and Kusefoglul, 2007; Lu et al., 2005) with styrene. Soybean oil-based polyols have been reacted with various isocyanates to prepare both cast polyurethane resins and rigid polyurethane foams (Guo et al., 2006). Work has also been done to prepare epoxy resins from various epoxidized natural oils (Jin and Park, 2008; Miyagawa et al., 2005). Our group has mainly focused on using the unfunctionalized double bonds in regular and conjugated natural oils to produce thermosetting materials. Bioplastics ranging from soft and rubbery to hard and brittle have been prepared from various vegetable oils by cationic, thermal, and free radical polymerizations (Andjelkovic et al., 2005; Henna et al., 2007; Li and Larock, 2003; Valverde et al., 2008).

Fibers or particles are typically added to polymers to increase the stiffness and strength of the material. Natural fibers, as a reinforcement for plastics, have gained a lot of

attention over the past several years because of their strength, stiffness, low density, low cost, and biodegradability. Much research has focused on the preparation of thermoplastic, petroleum-based polymers reinforced with natural fibers, and both wood and non-wood fibers have been used in the automotive and construction industries to reinforce petroleum-based plastics (Mohanty et al., 2005).

Research using natural fibers as a filler in natural oil-based resins has been conducted to a lesser extent. These composites are usually termed “green composites” because they are composed of bio-based resins and natural fibers. Epoxidized linseed oil- and epoxidized soybean oil-based biocomposites have been prepared using hemp (Boquillon, 2006), flax (Liu et al., 2006), and kenaf (Tran et al., 2006) fibers as the filler. Hemp fibers have also been employed to reinforce a matrix containing soybean oil methyl ester and epoxidized methyl linseedate (Mehta et al., 2004). Castor oil-based polyurethanes have been used to prepare composites containing sisal and coconut fibers (Silva et al., 2006) and distiller’s dried grains with solubles (Wu and Mohanty, 2007). Various natural fibers, from flax to pulp, have been used as a filler in a AESO-based matrix (O'Donnell et al., 2004). Biocomposites based on a linseed oil monoglyceride maleates-based matrix and wood flour have also been prepared (Mosiewicki et al., 2005). Previous work in our group has focused on biocomposites using spent germ and soybean hulls to reinforce tung oil and conjugated soybean oil-based resins, respectively (Pfister et al., 2008; Quirino and Larock, 2009). Typically, significant improvements in the mechanical properties, when compared to the pure resin, are observed by employing natural fibers as a filler.

Corn stover, the residue remaining after grain harvest, makes up more than half of all crop residues in the United States (Moebius-Clune et al., 2008). Although it is highly

debated, the 2005 “Billion Ton” study estimates that approximately 75 million tons of corn stover are available in the U.S. annually (Perlack et al., 2005; Wilhelm et al., 2007). A lot of attention has been given to the use of corn stover as a feedstock for cellulosic ethanol production, but there is also potential for this vast amount of biomass to be used as a natural fiber for the preparation of biocomposites. Research has been conducted on the preparation of biocomposites from corn stover and waste polyethylene (Thamae et al., 2008) and polypropylene (Panthapulakkal and Sain, 2006). Corn stover has also been used to reinforce starch acetate to produce biodegradable packaging foams (Ganjyal et al., 2004). To our knowledge, no studies have been conducted using corn stover as a filler in natural oil-based composites.

Soybean oil is a triglyceride oil consisting of 11% palmitic, 4% stearic, 23% oleic, 54% linoleic, and 8% linolenic acids. Soybean oil contains approximately 4.5 C-C double bonds per triglyceride and is typically used in the food oil market (Andjelkovic et al., 2005). In this work, we report the preparation of conjugated soybean oil-based “green composites” using corn stover as a natural fiber filler by a compression molding process. The effect of the fiber size, the amount of filler, and the amount of the crosslinker on the structure and thermal and mechanical properties of the resulting composites have been investigated.

### **Materials and Methods**

**Materials.** The soybean oil was purchased in a local supermarket and the linseed oil was supplied by Archer Daniels Midland (Decatur, IL). The oils were conjugated according to our previously published procedure and the conjugation was calculated to be approximately 100% (Larock et al., 2001). The divinylbenzene (DVB, technical-grade; assay 80% by gas chromatography, 20% ethylvinylbenzene) and *t*-butyl peroxide (TBPO) were purchased from

Aldrich Chemical Co. (Milwaukee, WI) and used as received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The release film, Wrightlon<sup>®</sup> 5200, was supplied by Airtech International, Inc. (Huntington Beach, CA). The corn stover (CS) was collected directly from a forage harvester on the Iowa State University Sorenson research farm in Boone County, IA. The CS was then ground to pass through a 0.5, 1, or 2 mm screen using a Wiley mill.

**Preparation of Conjugated Soybean Oil-based Composites.** The composites were prepared using a compression molding process. The designated amounts of 100% conjugated soybean oil (CSOY) or linseed oil (CLIN), BMA, and DVB were added together and stirred. The TBPO initiator was then added in the amount of 5 wt % of the total resin weight. The following nomenclature is used: CSOY and CLIN represent conjugated soybean oil and linseed oil, respectively, and BMA and DVB represent the *n*-butyl methacrylate and divinylbenzene comonomers, respectively. For example, CSOY50-BMA35-DVB15 corresponds to a resin prepared from 50 wt % CSOY, 35 wt % BMA, 15 wt % DVB and 5 wt % of this total weight was the amount of TBPO initiator used. The resin mixture was added to the CS, which was dried in a vacuum oven at 70 °C for approximately 18 hr prior to use. This mixture was stirred until all the CS was wet and was then placed in the cavity of the preheated (140 °C) steel mold covered with the release film. The mold was closed and cured at 140 °C for 3 hr and 160 °C for 3 hr under a pressure of 400 psi. The mold was then moved to an oven and cured under atmospheric pressure at 180 °C for 2 hr. When the mold cooled to room temperature, the composite was removed and post-cured at 180 °C for 1 hr. The reported amounts of CS are based on the initial amounts of CS and resin used. For example, for the composite containing 60% CS, 35 g of resin was added to

approximately 52.5 g of CS. The standard composition used for preparing the composites was CSOY50-BMA35-DVB15, 70 wt % CS, and 2 mm fiber size. When one variable was changed, the rest were held constant. In all cases, the matrix composition was CSOY or CLIN50-(BMA + DVB)50. For example, a composite designated CSOY-DVB10-70-2mm refers to a composite prepared using CSOY50-BMA40-DVB10 as the resin and 70 wt % CS as the filler, where the fiber size is 2 mm.

**Characterization.** Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structure of the resulting composites. A 4.5 g sample was extracted for 24 hr with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70 °C overnight before weighing. <sup>1</sup>H NMR spectroscopic analysis of the soluble substances was carried out in CDCl<sub>3</sub> using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 300 MHz.

A Q50 TGA (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 20 °C/min. Generally, a 10-12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the composites were obtained on a TA Instruments Q800 DMA in tension mode. A rectangular specimen of about 22 mm × 8.5 mm × 1.5 mm (length × width × thickness) was cut from the samples. Each specimen was cooled to -80 °C and then heated at 3 °C /min to 200 °C at a frequency of 1 Hz under air.

The tensile tests were conducted at 25 °C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-

shaped test specimen (type – I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

The water uptake of the composites was measured according to ASTM D570-98. The test specimens, 33 mm × 11 mm × 3 mm (length × width × thickness), were conditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed. The specimens were then immersed in distilled water for four weeks. At specific time intervals, the specimens were removed from the water, quickly wiped dry with a paper towel, weighed, and placed back in the water. The water uptake was calculated as:

$$\text{Water uptake, \%} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

At the end of the four week period, the specimens were reconditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed to determine the amount of soluble matter lost during immersion. The soluble matter was calculated as:

$$\text{Soluble matter, \%} = \frac{\text{conditioned weight} - \text{reconditioned weight}}{\text{conditioned weight}} \times 100$$

## Results and Discussion

**Soxhlet Extraction Analysis.** The % soluble materials from the CS and the resulting composites are given in Table 1. The 2 mm CS (entry 1) used in this study contains less than 1% soluble material. Based on the <sup>1</sup>H NMR spectrum of the soluble portion (Fig. 1(b)), the CS extract appears to be mainly composed of a triglyceride oil. The small range of chemical shifts for the vinylic protons (5.2-5.5 ppm) and the presence of bisallylic protons (2.8 ppm) indicate that the oil present in the CS extract is nonconjugated. For this reason, the oil is relatively unreactive towards free radical polymerization and will most likely not be incorporated into the matrix.



**TABLE 1**  
**Extraction Data and Thermal Properties of the Corn Stover and Composites**

Entry	Sample	Soxhlet	TGA		DMA	
		Extraction % Soluble	$T_{10}$ (°C)	$T_{50}$ (°C)	$T_g$ (°C)	$E'$ (MPa) <sup>a</sup>
1	CS <sup>b</sup>	<1	259	319	--	--
2	CSOY-DVB15-20-2mm	2	314	419	-9, 75	150
3	CSOY-DVB15-30-2mm	3	299	408	-5, 80	170
4	CSOY-DVB15-40-2mm	8	285	385	-3, 82	186
5	CSOY-DVB15-50-2mm	7	281	378	-3, 87	288
6	CSOY-DVB15-60-2mm	7	276	360	-11, 93	524
7	CSOY-DVB15-70-2mm <sup>c</sup>	7	273	352	-17, 95	817
8	CSOY-DVB15-80-2mm	6	264	328	1, 90	354
9	CSOY-DVB15-70-0.5mm	6	271	363	-27, 95	1041
10	CSOY-DVB15-70-1mm	6	278	366	-9, 99	946
11	CSOY-DVB10-70-2mm	6	272	349	-2, 92	571
12	CSOY-DVB20-70-2mm	5	273	359	-13, 96	999
13	CLIN-DVB10-70-2mm	6	274	356	18, 85	743
14	CLIN-DVB15-70-2mm	4	280	360	8, 96	872
15	CLIN-DVB20-70-2mm	5	276	370	-2, 98	1109

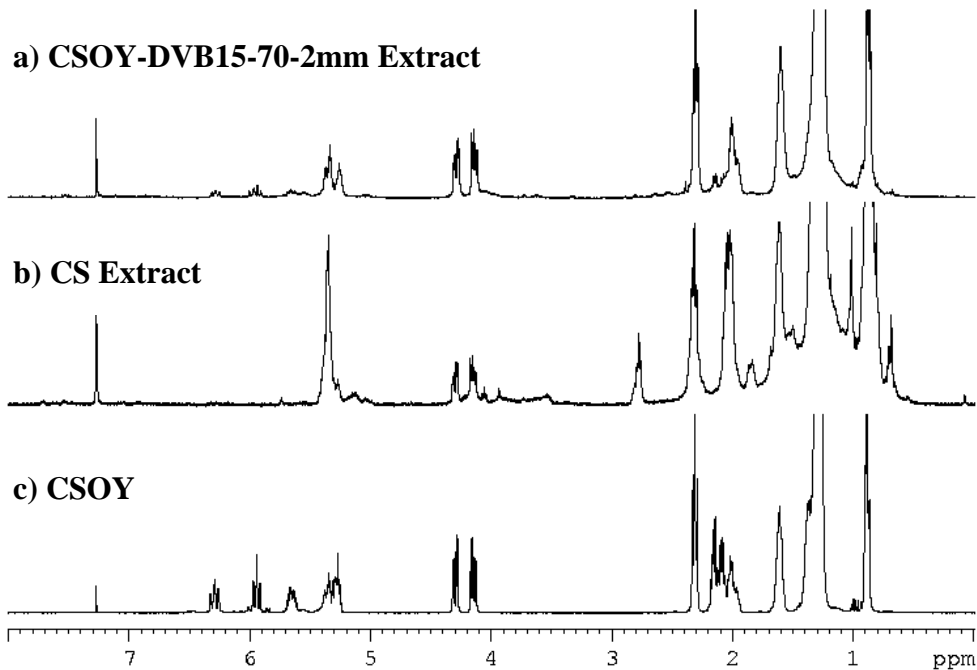
<sup>a</sup> Storage modulus at 150 °C

<sup>b</sup> 2 mm CS

<sup>c</sup> Standard composition: CSOY50-BMA35-DVB15, 70% CS, 2 mm CS

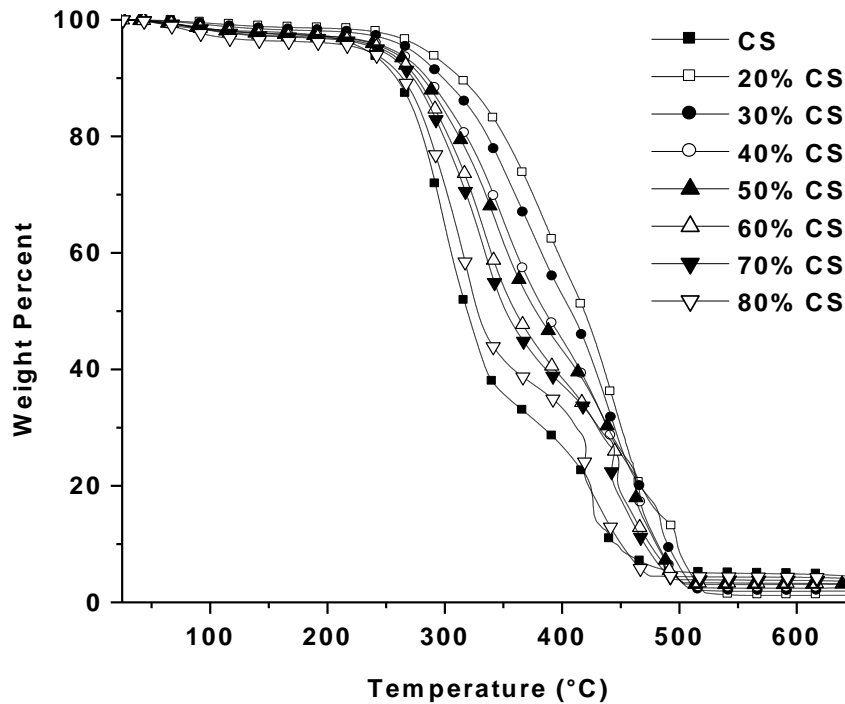
The % soluble materials from the composites prepared range from 2 to 8%. Fig. 1(a) shows the <sup>1</sup>H NMR spectrum of the soluble portion of the composite designated CSOY-DVB15-70-2mm. This spectrum is representative of all composite extracts. The CSOY-DVB15-70-2mm extract is mainly composed of unreacted CSOY.

As the amount of CS in the composites increases from 20 to 80 wt % (entries 2-8), no apparent trend is observed for the % soluble materials. When increasing from 20 to 40 wt % CS, the % soluble increases from 2 to 8%, but little changes in the % soluble materials when the amount of CS is increased to 80 wt %. Varying the size of the CS (entries 9 and 10), the amount of DVB, or the type of oil (entries 11-15) appears to have little effect on the % soluble materials.



**Fig. 1.**  $^1\text{H}$  NMR spectra of (a) extract of CSOY-DVB15-70-2mm composite, (b) extract of 2 mm CS, and (c) CSOY.

**Thermogravimetric Analysis.** Fig. 2 shows the TGA curves for the CS and resulting composites prepared with differing amounts of CS. The thermal degradation for these materials can be separated into three stages. The first stage, from 25 to 250 °C, corresponds to the loss of water and light volatiles. The fiber components of CS (hemicellulose, cellulose, and lignin) and the resin degrade in the final two stages. It is known that hemicellulose, cellulose, and lignin degrade between 200-260 °C, 240-350 °C, and 280-500 °C, respectively, but because the degradation processes of the fiber components are very complex when in an oxidative atmosphere, it is not possible to separate them (Tomczak et al., 2007).

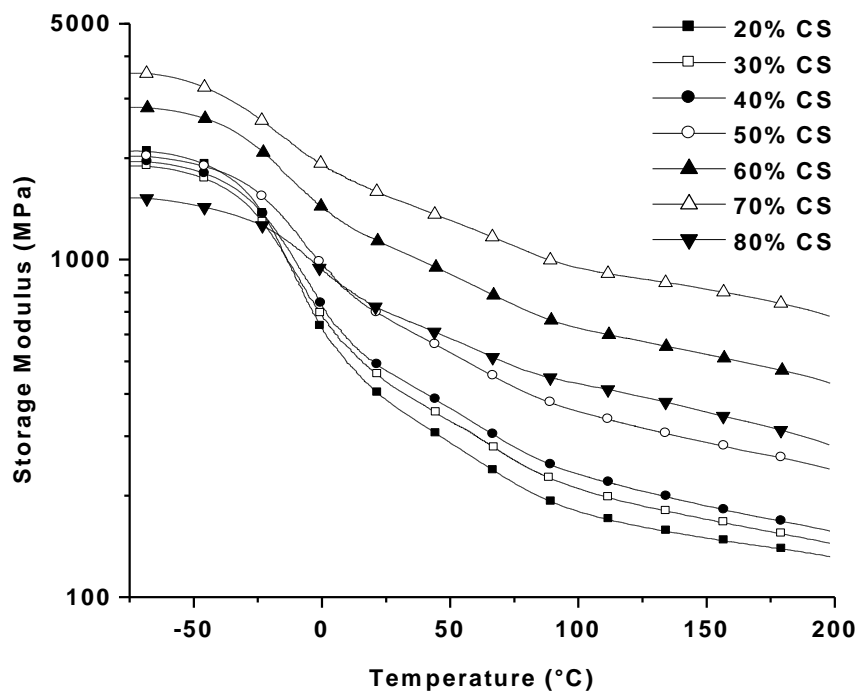


**Fig. 2.** TGA curves for the CS and composites prepared from differing amounts of CS.

The temperatures at 10% weight loss ( $T_{10}$ ) and temperatures at 50% weight loss ( $T_{50}$ ) are given in Table 1 for the CS and composites. From the data, it is observed that the matrix has a higher thermal stability than the CS. As more CS is incorporated into the composite, both the  $T_{10}$  and  $T_{50}$  values decrease. When increasing from 20 to 80 wt % CS (entries 2-8), the  $T_{10}$  and  $T_{50}$  decrease from 314 and 419 °C to 264 and 328 °C, respectively. No apparent trends in the  $T_{10}$  and  $T_{50}$  values are observed when the length of the CS fibers is decreased (entries 9 and 10). As the fiber length is changed from 2 mm to 1 mm, the  $T_{10}$  and  $T_{50}$  values increase from 273 to 278 °C and 352 to 356 °C, respectively, but a decline in both values is observed when decreasing the fiber length further to 0.5 mm. Increasing the amount of DVB, for both the CSOY- and CLIN-based composites (entries 11-15), tends to have little

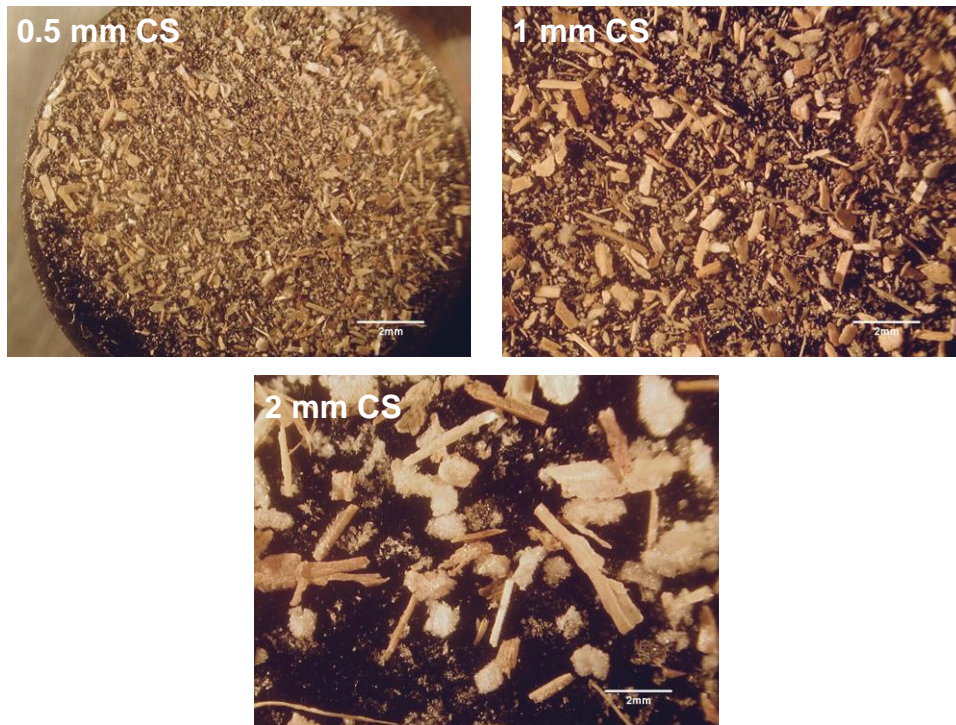
affect on the  $T_{10}$  values, but an increase in the  $T_{50}$  values is observed. This is likely the consequence of a higher crosslinked matrix resulting from the higher concentration of DVB. When CLIN is used as a replacement for CSOY, at all concentrations of DVB (entries 11-15), an increase in the thermal stability is observed, but the effect is most apparent for the  $T_{50}$  values. Linseed oil is a triglyceride oil with a high percentage of linolenic acid (C18:3) containing approximately six C-C double bonds per triglyceride. Because CLIN, when compared to CSOY, contains more double bonds per triglyceride, a more highly crosslinked structure can be formed, resulting in an increase in the thermal stability.

**Dynamic Mechanical Analysis.** The rubbery plateau storage moduli ( $E'$ ) and glass transition temperatures ( $T_g$ ) for the composites are given in Table 1. The  $T_g$  data have been obtained from the peak position of the  $\tan \delta$  curve. From Fig. 3, with the exception of the



**Fig. 3.**  $E'$  of the composites prepared with differing amounts of CS.

composites prepared from 80% CS, it is observed that increasing the amount of CS causes an increase in the storage modulus over the entire temperature range, but particularly in the rubbery plateau. This indicates that the natural fibers impart stiffness to the material by reducing the mobility and deformability of the matrix.  $E'$  increases from 150 to 817 MPa when the amount of CS is increased from 20 to 70 wt %, but a decrease to 354 MPa is observed when increasing the CS further to 80 wt %. The drop in the modulus for the 80% CS composite is the result of the addition of too much CS, which results in incomplete wetting of the fibers by the resin and an inability to effectively bind the fibers together. When the fiber length is decreased from 2 to 0.5 mm, a steady increase in  $E'$  is seen. Typically, for short fiber composites, a decrease in the fiber length or aspect ratio results in composites with lower stiffness and strength (Abdelmouleh et al., 2007; Kalaprasad et al., 2004). Fig. 4 shows images that were recorded using a stereo microscope with oblique lighting of the 0.5, 1, and 2 mm CS. Looking at the 2 mm CS image, there appear to be two different types of material present, fibers and somewhat spherical particles. CS is mainly composed of the leaves and stalks of the corn plant. When milled, the leaves and outer shell of the stalk yield fibrous material, whereas the inner portion of the stalk, or pith, yields particles with a soft and spongy texture (Peterson and Hixon, 1929). As the CS is milled to pass through smaller screens, not only do fiber lengths decrease, but a decrease in the diameter or width of the fibers is also observed, resulting in only minor changes to the aspect ratios of the fibers. If the wt % of the filler is held constant, these smaller fibers and particles have a larger surface area than the larger fibers and particles. In our previous work using particulate agricultural co-product fillers, it was determined that the particle size, and therefore the surface area of the filler, considerably affected the mechanical properties of the

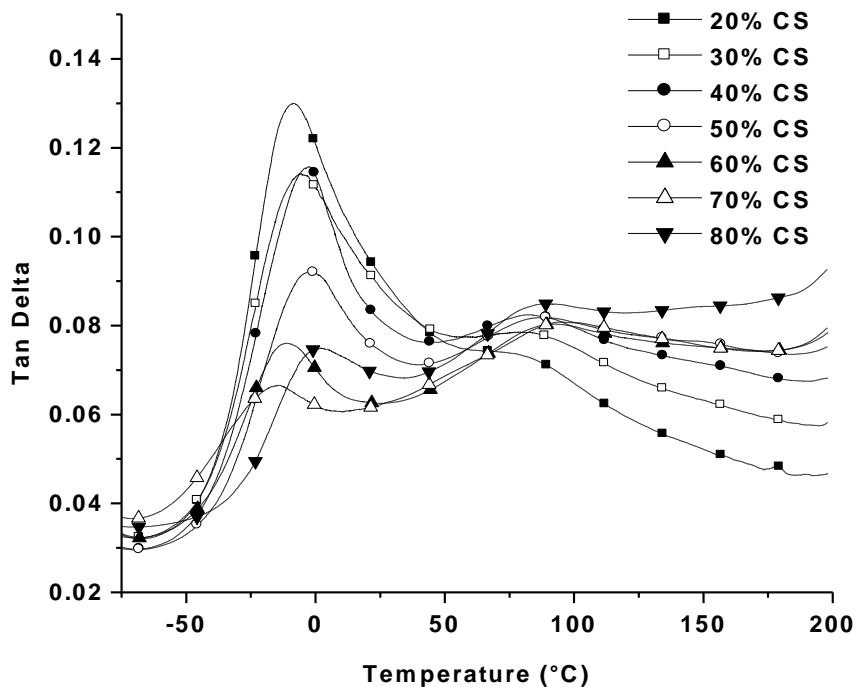


**Fig. 4.** Stereo microscope images of 0.5, 1, and 2 mm CS at 8x magnification.

composites (Pfister et al., 2008; Quirino and Larock, 2009). In fact, significant improvements in the properties can be obtained by decreasing the size of the filler particles. So the improved  $E'$  observed by the reduction in fiber length is likely a consequence of the increased surface area and, therefore, filler-matrix interaction. Increasing the amount of DVB, for both the CSOY- and CLIN-based composites, and replacing CSOY with CLIN, at all concentrations of DVB, results in an increase in  $E'$ . As the amount of crosslinker, DVB, is increased or the CSOY is replaced with a more highly unsaturated oil, CLIN, the matrix becomes more crosslinked, resulting in an increase in the stiffness.

Fig. 5 illustrates the loss factor ( $\tan \delta$ ) as a function of temperature for composites containing different amounts of CS. For all of the composites, two peaks in the  $\tan \delta$  curve

are observed resulting from a phase separation in the matrix. The reactivity of the oil and the comonomers used in the matrix are very different. At the beginning of the polymerization, the more reactive DVB polymerizes first resulting in a homopolymerization or copolymerization with BMA to form a “DVB-rich” phase. As the concentration of DVB monomer decreases, more oil is incorporated into the polymer to form an “oil-rich” phase. Each of these two phases have their own distinct relaxation processes: the “oil-rich” phase with a  $T_g$  of  $\sim -10$  °C and the “DVB-rich” phase with a  $T_g$  of  $\sim 90$  °C. Similar results have been observed in previous work (Pfister et al., 2008). As the amount of CS is increased, the two  $T_g$ s tend to shift away from one another, especially when changing from 40 to 70 wt % CS. It is possible that the addition of CS inhibits chain propagation during the polymerization. This effect may be more dramatic for the higher molecular weight, large oil



**Fig. 5.** Tan  $\delta$  curves for the composites prepared with differing amounts of CS.

molecule resulting in a more phase separated matrix. The  $T_g$ s shift from -9 and 75 °C to -17 and 95 °C respectively when increasing the amount of CS from 20 to 70 wt %. From Fig. 5, it can also be seen that, as the amount of CS is increased, the peak height of the lower temperature peak in the  $\tan \delta$  curve decreases dramatically, but the higher temperature peak is not affected. Again, because of the addition of too much CS, the 80% CS composite does not follow this trend. The fiber length appears to only affect the lower temperature  $T_g$ , but no trend is observed with this change. As expected, because of the high reactivity of DVB, an outward shift of the  $T_g$ s is observed by the addition of more DVB, particularly for the CLIN-based composites. For the CLIN-based composites, the  $T_g$ s change from 18 and 85 °C to -2 and 98 °C when increasing the DVB from 10 to 20 wt %, respectively. Replacing CSOY with CLIN results in considerable changes in the low temperature  $T_g$ . Because of the higher degree of unsaturation for CLIN, the “oil-rich” phase of the matrix should have a higher crosslink density, resulting in a higher  $T_g$ . When CSOY is replaced with CLIN, the “oil-rich” phase  $T_g$  goes from -2 to 18 °C, -17 to 8 °C, and -13 to -2 °C for the resins containing 10, 15, and 20 wt % DVB, respectively.

**Mechanical Properties.** The Young’s moduli ( $E$ ) and tensile strengths ( $\sigma$ ) for the composites are given in Table 2. As the amount of CS is increased from 20 to 70 wt %,  $E$  and  $\sigma$  increase from 291 and 2.7 MPa to 1117 and 4.8 MPa, respectively, but, for reasons mentioned previously, a decrease to 927 and 3.7 MPa is observed when further increasing the CS amount to 80 wt %. Because of the increased surface area and filler-matrix interaction, decreasing the length of the fiber increases both  $E$  and  $\sigma$  considerably. By reducing the fiber length from 2 mm to 0.5 mm,  $E$  increases from 1117 to 1398 MPa and  $\sigma$  increases from 4.8 to 7.0 MPa. As the amount of DVB is increased from 10 to 20 wt %, for both types of oil, a



steady increase in  $E$  is observed. Initially,  $\sigma$  decreases slightly when increasing from 10 to 15 wt % DVB, but significant increases are observed when further increasing to 20 wt %. At all levels of DVB, the use of CLIN, instead of CSOY, gives increases in both  $E$  and  $\sigma$ . The improved mechanical properties observed by the addition of more DVB or the use of CLIN is the result of a higher crosslinked matrix.

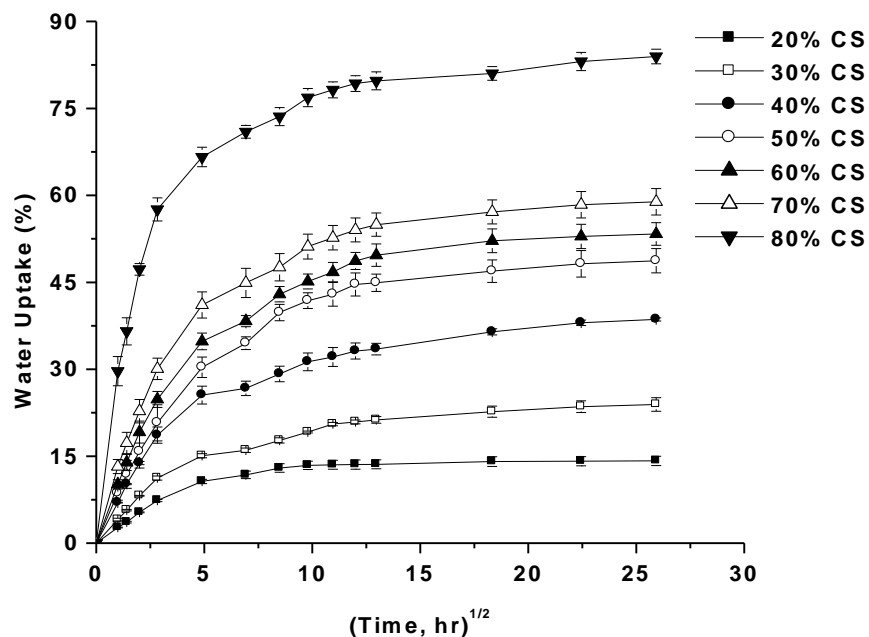
**TABLE 2**  
**Mechanical Properties and Water Uptake Data for the Composites**

Entry	Sample	Tensile Properties		Water Uptake		
				Saturation Water Content (%)	Soluble Matter (%)	Water Absorbed (%)
		$E$ (MPa)	$\sigma$ (MPa)			
1	CSOY-DVB15-20-2mm	291 ± 38	2.7 ± 0.6	14	2.1	16
2	CSOY-DVB15-30-2mm	386 ± 58	3.5 ± 0.7	24	3.0	27
3	CSOY-DVB15-40-2mm	429 ± 67	3.7 ± 0.5	39	4.4	43
4	CSOY-DVB15-50-2mm	601 ± 57	3.7 ± 0.4	49	5.3	54
5	CSOY-DVB15-60-2mm	841 ± 88	4.2 ± 0.5	53	6.1	60
6	CSOY-DVB15-70-2mm <sup>a</sup>	1117 ± 47	4.8 ± 0.4	59	7.3	66
7	CSOY-DVB15-80-2mm	927 ± 79	3.7 ± 0.3	84	9.8	94
8	CSOY-DVB15-70-0.5mm	1398 ± 97	7.0 ± 0.6	39	7.9	47
9	CSOY-DVB15-70-1mm	1324 ± 54	6.5 ± 0.3	48	8.0	56
10	CSOY-DVB10-70-2mm	1045 ± 103	4.9 ± 0.6	64	8.1	72
11	CSOY-DVB20-70-2mm	1290 ± 43	5.9 ± 0.9	59	7.3	66
12	CLIN-DVB10-70-2mm	1205 ± 40	6.6 ± 0.5	58	7.2	65
13	CLIN-DVB15-70-2mm	1213 ± 121	6.2 ± 0.7	55	7.0	62
14	CLIN-DVB20-70-2mm	1366 ± 69	7.4 ± 0.5	54	7.7	62

<sup>a</sup> Standard composition: CSOY50-BMA35-DVB15, 70% CS, 2 mm CS

**Water Uptake.** The saturation water content, soluble matter lost, and total water absorbed for all composites are given in Table 2 and the water uptake vs. square root of time curves are given in Fig. 6 for the composites prepared with differing amounts of CS. The saturation water content was taken from the plateau of the water uptake vs. the square root of time

curve and the total water absorbed is the sum of the saturation water content and the soluble matter lost. From Fig. 6, it can be concluded that the water uptake of these composites is mainly due to the presence of the lignocellulosic CS (our natural oil-based resins, being hydrophobic in nature, should absorb very little water). A dramatic increase in the uptake of water occurs as the amount of CS is increased. As the amount of CS is increased from 20 to 80 wt %, the saturation water content increases from 14 to 84%. From Table 2, it is observed that the soluble matter lost is only affected by the change in CS. The soluble matter increases from 2.1 to 9.8% when going from 20 to 80 wt % CS, respectively. Since the natural oils and comonomers used in the resin are nonpolar and immiscible with water, it is assumed that the water soluble material is being extracted from the CS. The diffusion constant of water in the composite, which is proportional to the initial slope of the water uptake vs. the square root of time curve, also increases as the amount of CS is increased. Although the curves for all



**Fig. 6.** Water uptake vs. the square root of time for the composites prepared with differing amounts of CS.

composites are not shown, the diffusion constant of water follows the same trend as the saturation water content for all of the composites. Reducing the fiber length from 2 to 0.5 mm, results in significant decreases in the saturation water content from 59 to 39%. Decreasing the size of the fibers should result in a better dispersion in the matrix leading to less contact between the fibers. Since the fibers are the main cause of the water uptake, the decreased contact between the fibers should limit the transport of water into the composite, resulting in a lower water uptake. Creating a more highly crosslinked structure, by either increasing the amount of DVB or replacing CSOY with CLIN, causes small decreases in the water uptake of the composites. Absorption of water by a composite typically leads to undesirable effects on the mechanical properties, but it is possible that it may also accelerate the biodegradation of the composite. So, depending on the application, a high uptake of water could be positive or negative. If long term applications, where these materials would possibly be exposed to water, are desired, sealing or coating the composite to reduce or eliminate the water absorption may be necessary.

### **Conclusions**

“Green composites” have been prepared using corn stover (CS) as a natural fiber to reinforce a free radically cured conjugated soybean or linseed oil-based resin. The composites contain approximately 5% soluble materials, which was mainly composed of unreacted conjugated oil. Increasing the amount of CS results in a significant improvement in the mechanical properties of the composites, but a decrease in the thermal stabilities is observed, resulting from the low thermal stability of the CS. The properties of the composites can also be improved by decreasing the fiber length, which is likely a result of the increased filler-matrix interaction caused by the increase in surface area of the fibers.

Divinylbenzene (DVB) is used as a crosslinker and the thermal and mechanical properties are enhanced by increasing the amount of DVB. Conjugated linseed oil, which has a higher degree of unsaturation than conjugated soybean oil, was used to replace conjugated soybean oil and the thermal and mechanical properties increase as a result. Water uptake data suggests that the amount CS is the main factor in the absorption of water by the composites, although significant decreases in the water uptake can be achieved by decreasing the fiber length. The composites prepared in this work are truly “green composites,” containing 60 to 90 wt % materials obtainable from biorenewable resources. Due to the high renewable content of these composites, they should have advantages over the traditional polyethylene-, polypropylene-, and poly(vinyl chloride)-based wood-plastic composites (WPCs) currently used in the construction, automotive, and furniture industries. These natural oil-based biocomposites may be somewhat weaker than the traditional WPCs, but should still find nonstructural applications in the aforementioned industries. The biocomposites produced in this work should thus be good candidates for automotive panels, wall panels, ceiling tiles, furniture, windows, and doors.

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## CHAPTER 4. GREEN COMPOSITES FROM A CONJUGATED LINSEED OIL-BASED RESIN AND WHEAT STRAW

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### Abstract

Green composites have been prepared using a free radically-cured conjugated linseed oil-based resin reinforced with wheat straw. The effect of the amount of the wheat straw; the size of the wheat straw fiber; the matrix crosslink density; the incorporation of a compatibilizer, maleic anhydride; and the molding pressure on the structure, water absorption, and thermal and mechanical properties of the composites has been investigated. In general, increasing the amount of the wheat straw, the crosslink density of the matrix, and the molding pressure leads to improved thermal and mechanical properties. By using maleic anhydride as a compatibilizer, significant improvements in the mechanical properties can be achieved. Results from water uptake experiments indicate that the amount and fiber size of the wheat straw are the major factors influencing the absorption of water in the composite. The composites prepared are composed of 75 to 95 wt % renewable materials and most have properties suitable for industrial applications.

### Introduction



With the recent volatility in the crude oil market and concerns over the environment, there has been a large push towards the replacement of petroleum-based plastics and composites by biorenewable materials. These renewable materials are often available in vast quantities, relatively inexpensive, and produce plastics that are much more biodegradable than traditional petroleum-based plastics.

Natural oils, as a feedstock for thermosetting resins, have gained a lot of attention over the past decade, because of their availability and low cost. Studies on the preparation of soft to rigid thermosetting plastics, foams, and coatings based on functionalized natural oils, such as soybean or linseed oil monoglyceride maleates [1,2], acrylated epoxidized soybean oil (AESO) [3], soybean or canola oil-based polyols [4-7], epoxidized vegetable oils [8,9], fatty acid-based aromatic triols [10], and bicyclic-containing vegetable oils [11] have been studied extensively. Although recently we have prepared plastics by the ring opening metathesis polymerization of functionalized vegetable oils [11], as well as soy polyol-based coatings [5], most of our work has focused on the use of regular and conjugated unfunctionalized vegetable oils for the preparation of thermosetting resins. Bio-based polymers, ranging from soft and flexible to rigid and brittle, have been prepared from regular and conjugated soybean oil [12-14], corn oil [15], linseed oil [16,17], tung oil [18], fish oil [19], and various other vegetable oils [20] by cationic, thermal, and free radical polymerizations.

In order to impart strength and stiffness to natural oil-based materials, reinforcing fillers or fibers are often added. Natural fibers, as a replacement for synthetic fibers, have attracted much interest because of their high strength and stiffness, low density and cost, and biodegradability. Research on the production of high performance composite materials and

biofoam composites has been conducted using flax, hemp, and sisal fibers, wood flour and various other cellulose-based fibers to reinforce free radically-cured linseed oil monoglyceride maleates- or AESO-based resins [21-24]. Epoxidized soybean or linseed oil-based resins have been used as a matrix in hemp, flax, and kenaf composites [25-28]. Distiller's dried grains with solubles (DDGS), the co-product of dry mill ethanol production, coconut fibers, and sisal fibers have been employed as a reinforcement for castor oil-based polyurethanes [29,30].

Work in our group has focused on the use of agricultural residues and co-products produced here in the Midwest as reinforcement for our natural oil-based resins. Spent germ, the co-product of wet mill ethanol production; soybean hulls; and corn stover have been used as fillers for tung oil- and conjugated soybean or linseed oil-based resins [31-33]. Typically, when compared to the pure resin, dramatic improvements in the mechanical properties of these composites have been observed by the addition of natural fibers. These materials should find many applications in the automotive, furniture, and construction industries. It should be noted that the aforementioned composites are often termed "green composites", because both the matrix and reinforcement are obtained from biorenewable resources.

Linseed oil is a triglyceride oil containing approximately six C-C double bonds. It consists of 57% linolenic acid (C18:3), 15% linoleic acid (C18:2), 19% oleic acid (C18:1), and 4% stearic acid (C18:0) and, because of its high degree of unsaturation, is often used as a drying oil for surface coatings [17].

Wheat straw is the residue remaining after wheat harvest. According to the USDA, the United States produced 75 million tons of wheat grain in 2008 and, at a conservative straw-to-grain ratio of 1:1, likely produced approximately 75 million tons of wheat straw

[34,35]. Although there is considerable debate on exactly how much residue can be removed from the field without detrimental effects to the soil, according to the “Billion Ton” study of 2005, approximately 11 million tons of wheat straw are available annually in the US for other purposes [36]. With increases in crop yields, this amount could be increased to 35-57 million tons per year. Over the past several years, there has been increasing interest in the use of wheat straw as a low cost replacement for wood fillers in the production of wood plastic composites (WPC). Thus, extensive research utilizing wheat straw as a reinforcing filler for petroleum-based plastics, such as Novolac resin, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and poly(vinyl alcohol), has been conducted [37-41]. One group has reported the use of wheat straw to reinforce an AESO-based resin, but to our knowledge, no studies have been conducted using wheat straw as a filler in unfunctionalized natural oil-based resins [42].

In this work, we report the preparation of conjugated linseed oil-based “green composites” using wheat straw as a natural fiber filler by a compression molding process. The effect of the fiber size; the amount of the filler; the amount of the crosslinker; the molding pressure; and the use of a compatibilizer, maleic anhydride (MA), on the structure and thermal and mechanical properties of the resulting composites have been investigated.

### Experimental

**Materials.** The linseed oil was supplied by Archer Daniels Midland (Decatur, IL) and was conjugated according to our previously published procedure [43]. The extent of conjugation was calculated to be approximately 100%. The divinylbenzene (DVB, technical grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), maleic anhydride (MA), and *t*-butyl peroxide (TBPO) were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used as

received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The release film, Wrightlon<sup>®</sup> 5200, was supplied by Airtech International, Inc. (Huntington Beach, CA). The wheat straw (WS) was collected directly from the Iowa State University Burkey research farm in Boone County, IA and was then ground to pass through 0.5, 1 or 2 mm screens using a Wiley mill.

**Preparation of Conjugated Linseed Oil/Wheat Straw Composites.** The composites were prepared using a compression molding process. The designated amounts of 100% conjugated linseed oil (CLIN), BMA, and DVB were mixed and stirred. Five wt % of the total resin weight of the TBPO initiator was then added. The following nomenclature is used: CLIN represents conjugated linseed oil and BMA and DVB represent the *n*-butyl methacrylate and divinylbenzene comonomers, respectively. For example, CLIN50-BMA35-DVB15 corresponds to a resin prepared from 50 wt % CLIN, 35 wt % BMA, 15 wt % DVB and 5 wt % of this total weight was the amount of TBPO initiator used. The resin mixture was added to the WS, which was dried in a vacuum oven at 70 °C for approximately 18 hr prior to use. This mixture was stirred until all of the WS was wet and was then placed in the cavity of the preheated (140 °C) steel mold lined with the release film. The mold was closed and cured at 140 °C for 3 hr, followed by 160 °C for 3 hr, under a pressure of 400 psi. The mold was then moved to an oven and cured under atmospheric pressure at 180 °C for 2 hr. Once the mold cooled to room temperature, the composite was removed and post-cured at 180 °C for 1 hr. The reported amounts of WS are based on the initial amounts of WS and resin used. For example, for the composite containing 60 wt % WS, 35 g of resin was added to approximately 52.5 g of WS. The standard composition used for preparing the composites was CLIN50-BMA35-DVB15 and 80 wt % WS of 2 mm fiber size. When one variable was

changed, the rest were held constant. In all cases, the matrix composition was CLIN50-(BMA + DVB + MA)50. For example, a composite designated CLIN-DVB05-80-2mm refers to a composite prepared using CLIN50-BMA45-DVB05 as the resin and 80 wt % WS as the filler, where the WS fiber size is 2 mm.

It should be noted that in our previous work, we have prepared unreinforced, free-radically cured natural oil-based resins, but because of shrinking and cracking problems, these resins are cured for much longer time periods (3 days) and at lower temperatures. Since we are using higher cure temperatures and much shorter times, we are unable to produce the unreinforced resin because of the previously mentioned problems. If the cure temperature was reduced and the time increased in order to produce an unreinforced resin, it would be inaccurate to compare the pure resin to the composites. For these reasons, we are unable to obtain the thermal and mechanical properties of the pure resin.

**Characterization.** Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structure of the resulting composites. A 4.5 g sample was extracted for 24 hr with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70 °C overnight before weighing. <sup>1</sup>H NMR spectroscopic analysis of the soluble substances was carried out in CDCl<sub>3</sub> using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz.

A Q50 TGA (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 20 °C/min. Generally, a 10-12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the composites were obtained on a TA Instruments Q800 DMA in tension mode. A rectangular specimen of about 22 mm × 8.5 mm × 1.5 mm (length × width × thickness) was cut from the samples. Each specimen was cooled to -120 °C and then heated under air at 3 °C /min to 200 °C at a frequency of 1 Hz.

The tensile tests were conducted at 25 °C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

The water uptake of the composites was measured according to ASTM D570-98. The test specimens were conditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed. The specimens were then immersed in distilled water for 4 weeks. At specific time intervals, the specimens were removed from the water, quickly wiped dry with a paper towel, weighed, and placed back in the water. The water uptake was calculated as:

$$\text{Water uptake, \%} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

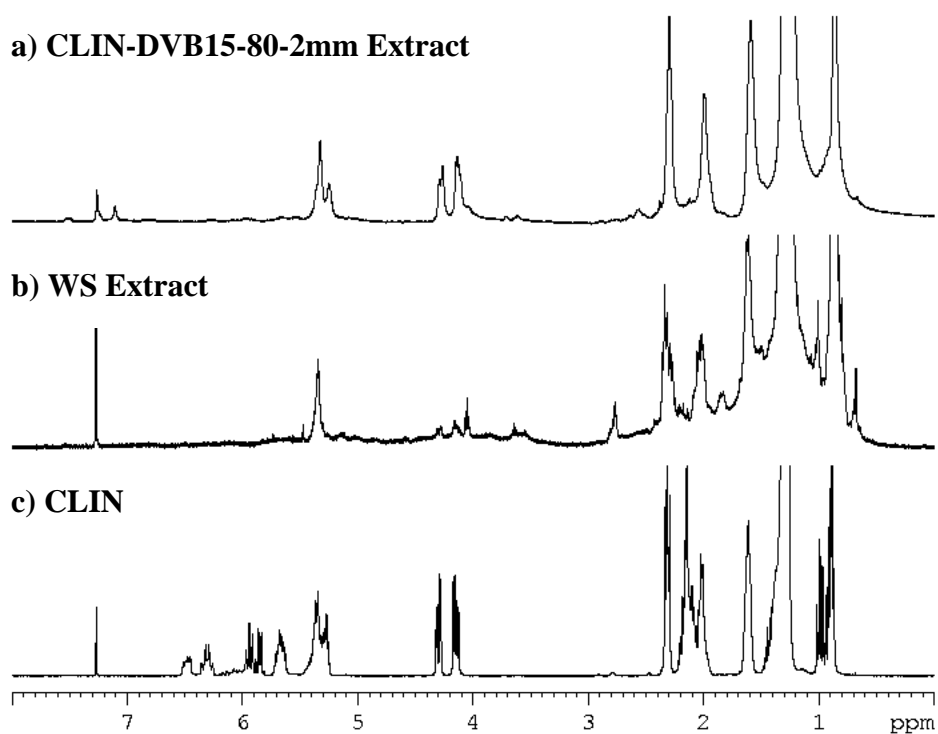
At the end of the 4 week period, the specimens were reconditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed to determine the amount of soluble matter lost during immersion. The soluble matter was calculated as:

$$\text{Soluble matter, \%} = \frac{\text{conditioned weight} - \text{reconditioned weight}}{\text{conditioned weight}} \times 100$$

## Results and Discussion

**Soxhlet Extraction Analysis.** Soxhlet extraction was used to determine the extent of incorporation of the conjugated linseed oil and other comonomers into the thermosetting

matrix. As can be seen from the  $^1\text{H}$  NMR spectrum in Fig. 1a, the soluble materials extracted from the composites appear to be mainly composed of unreacted conjugated linseed oil. There also appears to be a small amount of divinylbenzene or oligomers containing divinylbenzene present. This spectrum is representative of all composite extracts.



**Fig. 1.**  $^1\text{H}$  NMR spectra of (a) extract of the CLIN-DVB15-80-2mm composite, (b) extract of 2 mm WS, and (c) CLIN.

The % soluble materials from the WS and the resulting composites are given in Table 1. The 2 mm WS used in this work contains less than 1% soluble materials. The extract of the WS (Fig. 1b) also appears to be mainly a triglyceride oil. But because of the small range of chemical shifts for the vinylic protons (5.2-5.5 ppm) and the presence of bisallylic protons (2.8 ppm), this oil is nonconjugated and thus not likely to be incorporated into the matrix.

**Table 1**  
**Extraction Data and Thermal Properties of the Wheat Straw and Composites**

Entry	Sample	Soxhlet	TGA	
		Extraction % Soluble	$T_{10}$ (°C)	$T_{50}$ (°C)
1	WS <sup>a</sup>	<1	266	311
2	CLIN-DVB15-50-2mm	6	295	409
3	CLIN-DVB15-60-2mm	6	292	396
4	CLIN-DVB15-70-2mm	4	286	384
5	CLIN-DVB15-80-2mm <sup>b</sup>	4	282	364
6	CLIN-DVB15-90-2mm	4	273	322
7	CLIN-DVB15-80-1mm	3	277	348
8	CLIN-DVB15-80-0.5mm	3	274	341
9	CLIN-DVB05-80-2mm	3	283	353
10	CLIN-DVB25-80-2mm	4	281	379
11	CLIN-DVB35-80-2mm	3	283	388
12	CLIN-DVB45-80-2mm	3	284	393
13	CLIN-DVB15-MA05-80-2mm	2	282	372
14	CLIN-DVB15-MA10-80-2mm	2	281	369
15	CLIN-DVB15-MA15-80-2mm	2	279	373
16	CLIN-DVB15-80-2mm-600psi	2	285	371

<sup>a</sup> 2 mm WS

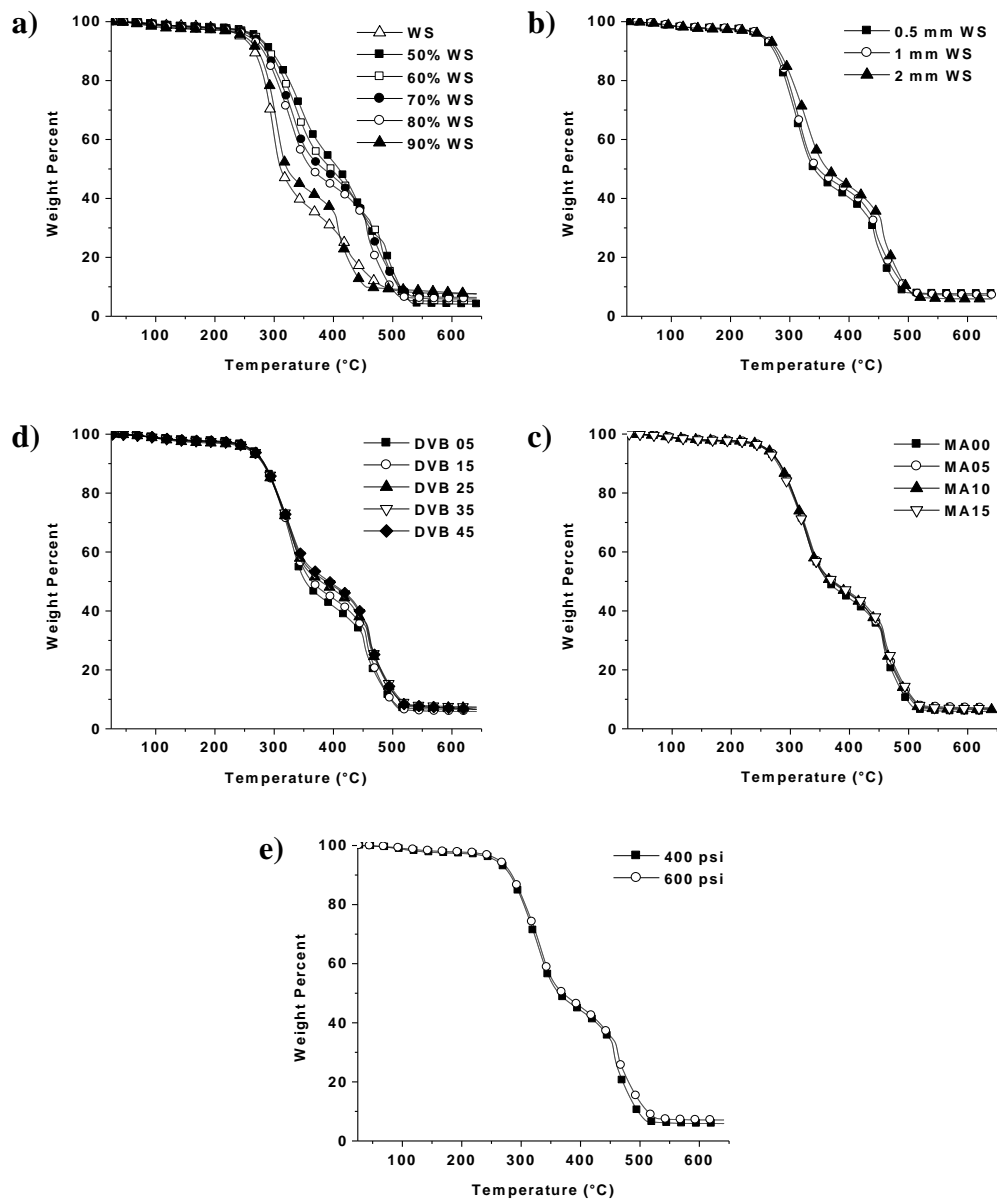
<sup>b</sup> Standard composition: CLIN50-BMA35-DVB15, 80% WS, 2 mm WS, 400 psi

Looking at Table 1, it is apparent that most of the conjugated linseed oil and comonomers are incorporated into the matrix. All of the composites prepared contain a relatively small amount of soluble materials (2-6%) and none of the variables changed seem to have a large effect on the % soluble materials. Increasing the amount of the WS (entries 2-6), decreasing the size of the WS (entries 7 and 8), incorporating MA into the matrix (entries 13-15), and increasing the molding pressure (entry 16) results in only small decreases in the % soluble materials. No change in the % soluble materials is observed when the amount of DVB is varied (entries 9-12).

**Thermogravimetric Analysis.** From Fig. 2, it can be seen that the WS and composites thermally degrade in three stages. The first stage, from 25 to 250 °C, corresponds to the loss of water and other light volatiles. In the final two stages, the resin and hemicellulose,



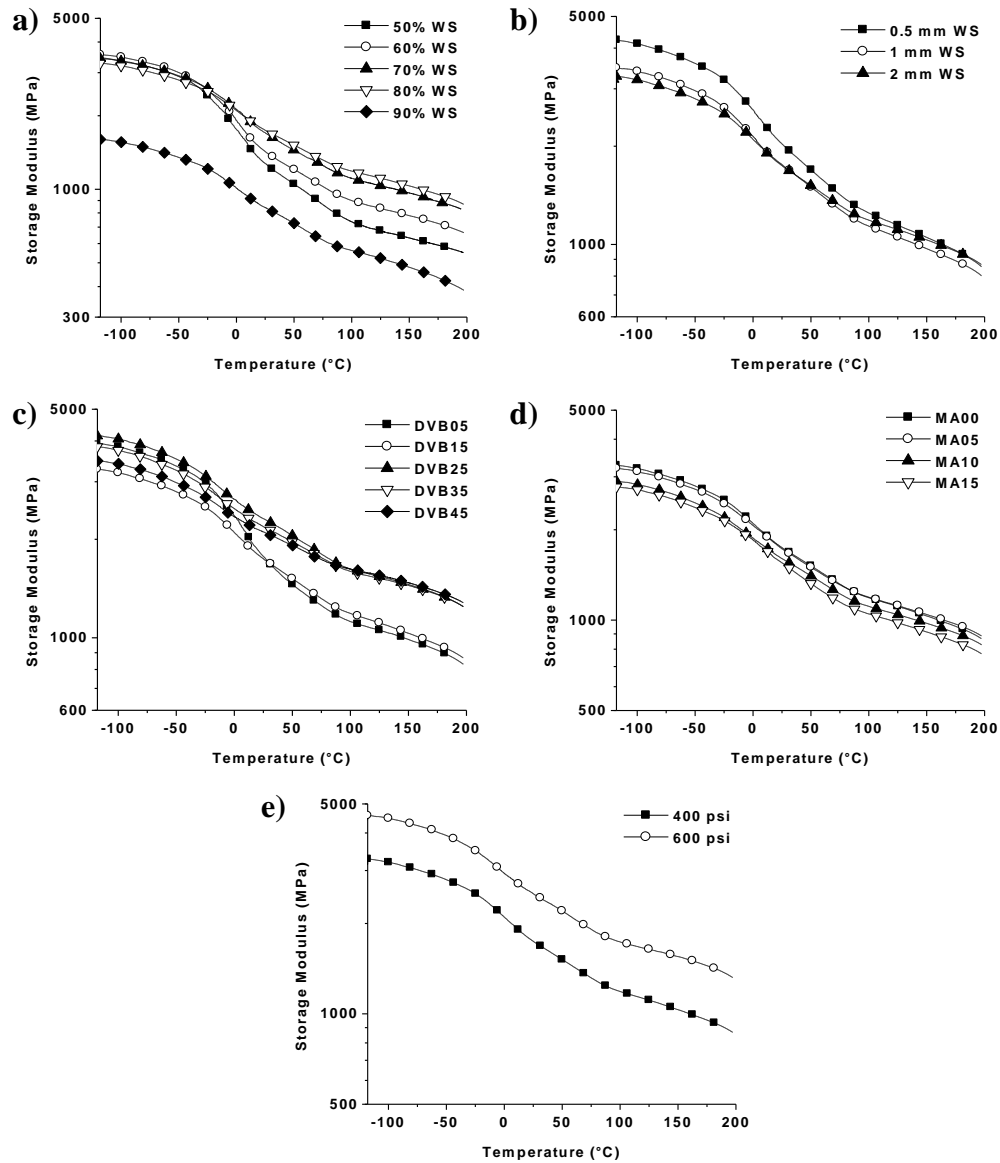
cellulose, and lignin contained in the WS degrade. It is known that hemicellulose, cellulose, and lignin degrade between 200-260 °C, 240-350 °C, and 280-500 °C, respectively, but because the degradation processes of the fiber components are very complex when in an oxidative atmosphere, it is not possible to separate them [44].



**Fig. 2.** TGA curves for the WS and composites prepared from a) differing amounts of WS, b) differing WS fiber sizes, c) differing amounts of DVB, d) differing amounts of MA, and e) differing molding pressures.

The temperatures at 10% weight loss ( $T_{10}$ ) and 50% weight loss ( $T_{50}$ ) are given in Table 1. From both Fig. 2a and the  $T_{10}$  and  $T_{50}$  values given in Table 1, it is apparent that the WS is far less thermally stable than the conjugated linseed oil-based matrix. As more WS is added to the composite, dramatic decreases in the thermal stabilities are observed. When the amount of WS is increased from 50 to 90 wt %, the  $T_{10}$  and  $T_{50}$  values decrease from 295 to 273 °C and 409 to 322 °C, respectively. Decreasing the size of the WS fibers results in a lower thermal stability, which is likely a result of the increased surface area of the fiber.  $T_{10}$  and  $T_{50}$  decrease from 282 to 274 °C and 364 to 341 °C respectively, when the size of the WS fibers is changed from 2 to 0.5 mm. Changing the amount of DVB in the matrix appears to only affect the  $T_{50}$  values. As the amount of DVB is increased from 5 to 45 wt %, the  $T_{50}$  value increases from 353 to 393 °C, while  $T_{10}$  stays relatively constant. This enhanced thermal stability is most likely the result of a higher crosslinked matrix caused by the addition of more DVB. As seen with DVB, the addition of MA to the matrix has no effect on the  $T_{10}$  values and, although there is no trend, a small increase in the  $T_{50}$  values is observed by the addition of MA. Increasing the molding pressure to 600 psi, which should increase the interaction between the filler and the matrix, results in a small increase in the thermal stability. An increase in  $T_{10}$  and  $T_{50}$  from 282 to 285 °C and 364 to 371 °C is seen when the pressure is increased from 400 to 600 psi.

**Dynamic Mechanical Analysis.** Fig. 3 shows the storage modulus as a function of temperature for all of the composites and the rubbery plateau storage moduli ( $E'$ ) and glass transition temperatures ( $T_g$ ) are listed in Table 2. The glass transition temperatures were taken from the peak of the tan delta curves, which are shown in Fig. 4. As can be seen from

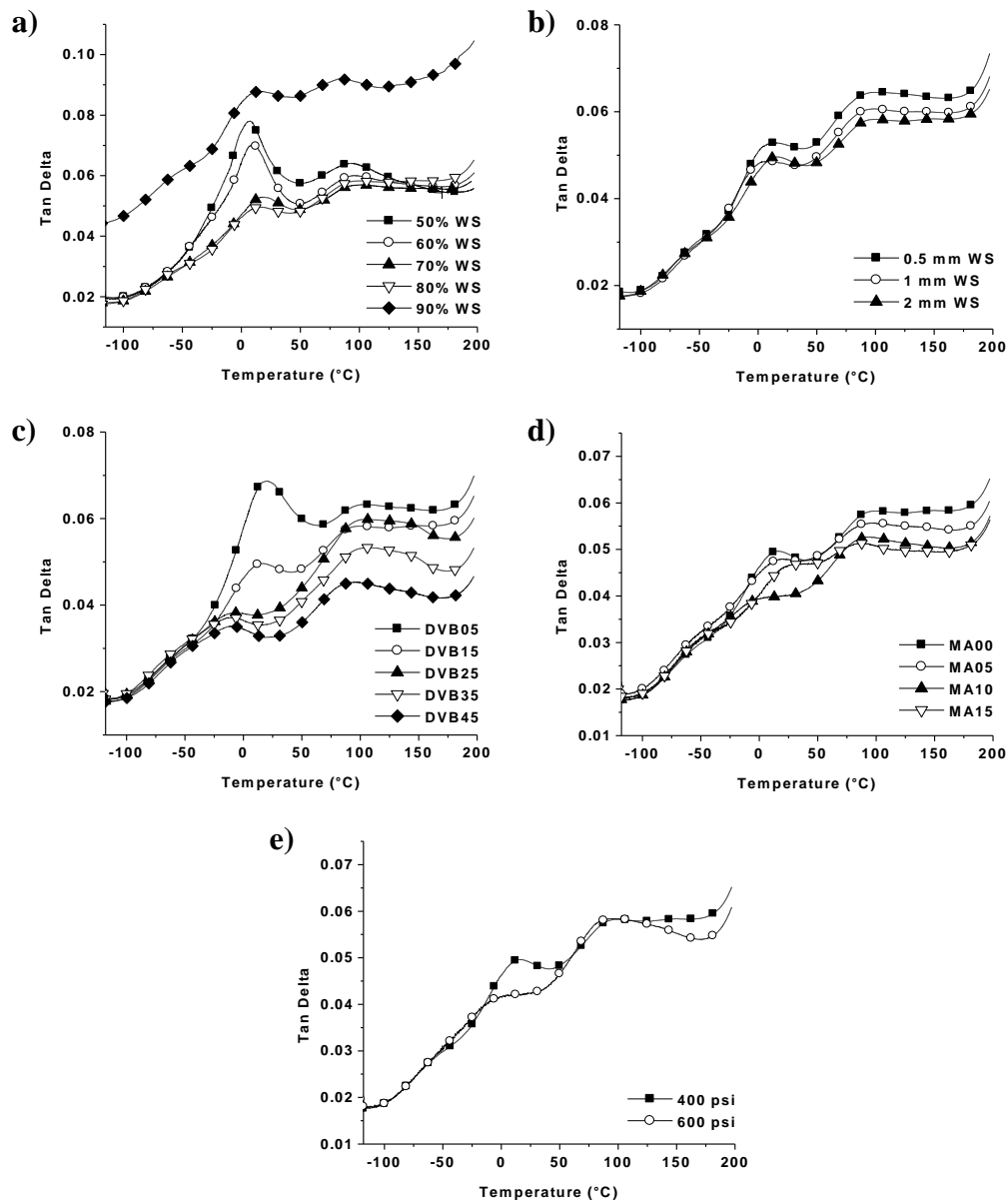


**Fig. 3.**  $E'$  of the composites prepared with a) differing amounts of WS, b) differing WS fiber sizes, c) differing amounts of DVB, d) differing amounts of MA, and e) differing molding pressures.

Fig. 3a, the WS acts as an effective reinforcement resulting in an increase in the storage modulus, particularly in the rubbery plateau. When the amount of WS is increased from 50 to 80 wt %,  $E'$  increases from 632 to 1032 MPa (entries 1-4). Increasing the amount of WS further to 90 wt % results in a dramatic loss in  $E'$ . If too much WS is added to the matrix,

incomplete wetting of the fibers by the matrix results, leading to an inability to effectively bind the fibers together. Varying the size of the WS fibers (entries 6 and 7), appears to have little effect on  $E'$ . Dramatic improvements in  $E'$  can be achieved by the addition of more DVB, a result of the higher crosslinked matrix.  $E'$  increases from 988 to 1456 MPa when the amount of DVB is increased from 5 to 25 wt %, respectively, but further increases in the amount of DVB result in little change in  $E'$  (entries 8-11). Although the effect is small, replacing BMA with MA looks to negatively impact  $E'$ . The addition of 5 wt % MA has no effect on  $E'$  (entry 12), but when the amount is increased to 15 wt % (entry 14),  $E'$  decreases to 913 MPa compared to an  $E'$  of 1032 MPa for the matrix containing no MA (entry 4). Increasing the molding pressure results in significant improvements in  $E'$  (entry 15). When the molding pressure is increased from 400 to 600 psi,  $E'$  increases from 1032 to 1551 MPa.

For all of the composites, two peaks in the tan delta vs. temperature curves are observed (Fig. 4). The two  $T_g$ 's are the result of a phase separated matrix. The conjugated linseed oil and other comonomers, in particular DVB, used in this matrix have very different reactivities. At the beginning of the polymerization, the more reactive DVB homopolymerizes or copolymerizes with BMA to form a "DVB-rich" phase. As the concentration of DVB monomer decreases, more of the conjugated linseed oil is incorporated into the polymer to form an "oil-rich" phase. Each of these two phases has its own distinct relaxation processes: the "oil-rich" phase with a  $T_g$  of  $\sim 10$  °C and the "DVB-rich" phase with a  $T_g$  of  $\sim 100$  °C. Similar results have been observed in previous work on spent germ composites [31]. Increasing the amount of the WS tends to result in an upward shift of the  $T_g$ 's. It may be possible that as the amount of the stiff WS fiber is increased, the mobility of the polymeric chains is further reduced, resulting in an increase in the  $T_g$ . Because of its high



**Fig. 4.** Tan delta curves for the composites prepared from a) differing amounts of WS, b) differing WS fiber sizes, c) differing amounts of DVB, d) differing amounts of MA, and e) differing molding pressures.

reactivity, increasing the amount of DVB causes greater divergence in the two  $T_g$ 's, indicating a more phase separated matrix. The difference between the  $T_g$ 's of the “oil-rich” and “DVB-rich” phases increases from 83 to 105 °C when the amount of DVB is increased

from 5 to 45 wt %, respectively. Varying the size of the WS fibers, adding MA (with the exception of the MA15 composite), and increasing the molding pressure appear to have very little effect on the  $T_g$ 's. When compared to the standard composition (entry 4), if 15 wt % MA is used, the “oil-rich”  $T_g$  and “DVB-rich”  $T_g$  shift from 13 to 33 °C and 99 to 87 °C, respectively. The observed shift of the  $T_g$ 's towards one another indicates that using a large amount of MA makes the matrix more homogeneous or less phase separated, but because the polymerization of the four monomers in the presence of WS is complex, it is unclear why this is the case.

**Mechanical Properties.** The Young's moduli ( $E$ ) and tensile strengths ( $\sigma$ ) for all of the composites are given in Table 2. As can be seen, dramatic improvements in the stiffness and strengths of the composites result from the addition of more WS.  $E$  and  $\sigma$  increase from 958 and 5.4 MPa to 1662 and 7.6 MPa respectively, when the amount of WS is increased from 50

**Table 2**  
**Thermomechanical Properties of the Composites**

Entry	Sample	DMA		Tensile Properties	
		$T_g$ (°C)	$E'$ (MPa) <sup>a</sup>	$E$ (MPa)	$\sigma$ (MPa)
1	CLIN-DVB15-50-2mm	7, 94	632	958 ± 42	5.4 ± 0.4
2	CLIN-DVB15-60-2mm	9, 95	780	1426 ± 80	5.8 ± 1.3
3	CLIN-DVB15-70-2mm	18, 100	966	1398 ± 59	6.7 ± 0.7
4	CLIN-DVB15-80-2mm <sup>b</sup>	13, 99	1032	1662 ± 114	7.6 ± 1.1
5	CLIN-DVB15-90-2mm	15, 91	480	968 ± 96	2.5 ± 0.5
6	CLIN-DVB15-80-1mm	10, 98	970	1456 ± 131	7.3 ± 0.6
7	CLIN-DVB15-80-0.5mm	14, 103	1051	1418 ± 138	8.9 ± 2.5
8	CLIN-DVB05-80-2mm	20, 103	988	1325 ± 135	5.0 ± 1.2
9	CLIN-DVB25-80-2mm	-7, 105	1456	1775 ± 76	8.7 ± 1.2
10	CLIN-DVB35-80-2mm	-12, 106	1446	1869 ± 42	9.8 ± 0.7
11	CLIN-DVB45-80-2mm	-9, 96	1474	1883 ± 173	8.8 ± 1.8
12	CLIN-DVB15-MA05-80-2mm	16, 97	1044	1618 ± 63	9.0 ± 1.0
13	CLIN-DVB15-MA10-80-2mm	13, 95	976	1742 ± 37	10.4 ± 0.5
14	CLIN-DVB15-MA15-80-2mm	33, 87	913	1799 ± 78	10.2 ± 1.1
15	CLIN-DVB15-80-2mm-600psi	10, 97	1551	1747 ± 91	8.8 ± 0.7

<sup>a</sup> Storage modulus at 150 °C

<sup>b</sup> Standard composition: CLIN50-BMA35-DVB15, 80% WS, 2 mm WS, 400 psi

to 80 wt %. Again, because the addition of too much fiber results in incomplete wetting by the resin, the 90% WS composite does not follow this trend. Decreasing the fiber size of the WS tends to have opposite effects on  $E$  and  $\sigma$ . When the size of the WS fiber is decreased from 2 to 0.5 mm,  $E$  decreases from 1662 to 1418 MPa, while  $\sigma$  increases from 7.6 to 8.9 MPa. These differences are not dramatic and are within the experimental error. In our previous work, we typically have seen an increase in the mechanical properties as the size or length of the fibers is reduced [31,33]. The improved properties are likely the result of the increased surface area, leading to a better filler-matrix interaction, caused by the reduction of the fiber size. Since both the length and diameter of the fibers are reduced by milling through a smaller screen, the aspect ratios of the fibers used here are relatively unaffected when the size of the WS is decreased. Increasing the amount of DVB, which is used to increase the crosslink density of the matrix, results in enhanced mechanical properties.  $E$  increases from 1325 to 1883 MPa when the amount of DVB is increased from 5 to 45 wt %, but a peak in  $\sigma$  is observed at 35 wt % DVB. It appears that the addition of too much DVB (45 wt %) results in a very brittle matrix, causing a lower  $\sigma$ . Higher crosslinking reduces the number of conformations that the matrix can take on, while being subjected to an applied force. When a crack becomes a failure, the matrix can disperse a lesser amount of energy, causing the decrease in  $\sigma$ . In order to enhance the filler-matrix interaction, MA was added to the matrix at the expense of BMA. The interaction should be enhanced if MA is both incorporated into the polymer matrix through the C-C double bond and chemically bonded to the WS fiber by ring opening of the anhydride by the hydroxyl groups present in the cellulose-based fiber. It is indeed observed that significant improvements in the mechanical properties, in particular  $\sigma$ , result from the addition of a small amount of MA.  $E$  increases

from 1662 to 1799 MPa when the amount of MA is increased from 0 to 15 wt %. For  $\sigma$ , an optimal value was observed at 10 wt % MA. As the amount of MA is increased from 0 to 10 wt %,  $\sigma$  increases from 7.6 to 10.4 MPa, but no change in  $\sigma$  is observed when increasing the MA content to 15 wt %. Increasing the molding pressure, and, therefore, the filler-matrix interaction, causes a small increase in the mechanical properties.  $E$  increases from 1662 to 1747 MPa and  $\sigma$  increases from 7.6 to 8.8 MPa, when the molding pressure is increased from 400 to 600 psi.

**Table 3**  
**Water Uptake Data for the Composites**

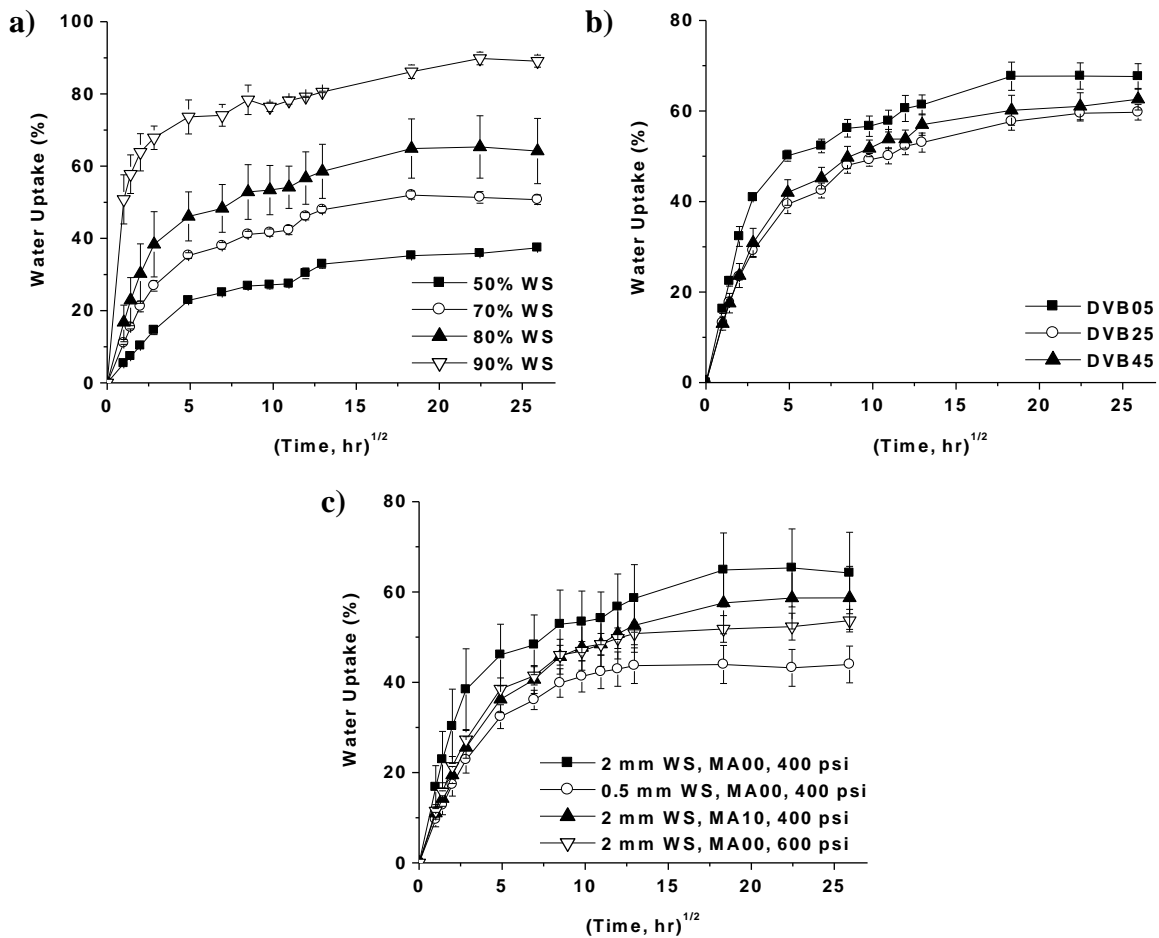
Entry	Sample	Saturation Water Content (%)	Soluble Matter (%)	Water Absorbed (%)
1	CLIN-DVB15-50-2mm	37	4.0	41
2	CLIN-DVB15-70-2mm	51	5.3	56
3	CLIN-DVB15-80-2mm <sup>a</sup>	64	6.3	70
4	CLIN-DVB15-90-2mm	89	7.5	97
5	CLIN-DVB05-80-2mm	68	7.1	75
6	CLIN-DVB25-80-2mm	60	5.4	65
7	CLIN-DVB45-80-2mm	63	6.1	69
8	CLIN-DVB15-80-0.5mm	44	6.4	50
9	CLIN-DVB15-MA10-80-2mm	59	3.6	62
10	CLIN-DVB15-80-2mm-600psi	54	6.2	60

<sup>a</sup> Standard composition: CLIN50-BMA35-DVB15, 80% WS, 2 mm WS, 400 psi

**Water Uptake.** The saturation water content, soluble matter lost, and total water absorbed for selected composites are given in Table 3 and the water uptake vs. square root of time curves are given in Fig. 5. The saturation water content was taken from the plateau of the water uptake vs. square root of time curve and the total water absorbed is the sum of the saturation water content and the soluble matter lost. From Table 3 and Fig. 5, it is observed that the main factors influencing the water uptake of the composites are the amount and size



of the WS fibers. The water absorbed increases from 41 to 97% as the amount of WS is increased from 50 to 90 wt % (entries 1-4). The soluble matter and initial slope of the water uptake vs. square root of time curve, which is proportional to the diffusion constant of water in the composite, also increase significantly as the amount of WS is increased. Since all of the monomers used in the matrix are relatively nonpolar and immiscible with water, the water soluble material from the composites is likely extracted from the WS fibers. Significant reductions in the water absorbed can be achieved by reducing the size of the WS



**Fig. 5.** Water uptake vs. the square root of time for the composites prepared with a) differing amounts of WS, b) differing amounts of DVB, and c) differing WS fiber sizes, amounts of MA, and molding pressures.

fibers. The total water absorbed decreases from 70 to 50% as the size of the WS fibers is decreased from 2 to 0.5 mm (entries 3 and 8). As the size of the WS fibers is reduced, the fibers are better dispersed in the matrix, which should lead to less contact between the fibers. Since the fibers are the major influence on the water uptake in the composites, the decreased contact results in lower water absorption. Similar results have been observed in our previous work on corn stover composites [33]. The diffusion constant of water in the composite is also reduced as a result of the decreased WS fiber size, while the % soluble matter is unaffected. Increasing the crosslink density of the matrix, by increasing the amount of DVB (entries 5-7), and increasing the interaction between the filler and the matrix, by either incorporating MA (entry 9) or increasing the molding pressure (entry 10), results in small decreases in the total water absorbed, the percent soluble matter, and the diffusion constant of water in the composites.

### Conclusions

Green composites have been produced from a conjugated linseed oil-based resin reinforced with wheat straw (WS), the under-utilized residue remaining after wheat harvest. The composites prepared contain approximately 4% soluble materials, which is mainly composed of unreacted conjugated linseed oil. The WS acts as an effective reinforcement and an increase in the amount of WS tends to result in improvements in the thermal and mechanical properties of the composites. But because of the low thermal stability of the WS, increasing the amount of the WS causes significant decreases in the thermal stability of the composites. Increasing the crosslink density of the matrix, by increasing the amount of divinylbenzene, results in considerable increases in the thermal and mechanical properties. Improvements in the thermal and mechanical properties can also be achieved by increasing

the filler-matrix interaction, by either incorporating a compatibilizer, maleic anhydride, or increasing the molding pressure. It has been determined that the major factors influencing the uptake of water in the composites are the amount and size of the WS fibers. Increasing the amount or size of the WS fibers causes significant increases in the water absorption of the composites.

Recently, polyethylene-, polypropylene-, and poly(vinyl chloride)-based wood-plastic composites (WPCs) have gained a lot of attention and are currently used in the construction, automotive, and furniture industries. The biocomposites produced here, containing 75 to 90 wt % biorenewable materials, may be slightly weaker than the traditional WPCs used, but have the advantage of having a high renewable content. It is expected that these materials will find nonstructural applications in the previously mentioned industries and may be good candidates for automotive panels, wall panels, ceiling tiles, furniture, windows, and doors. Regarding commercialization of the biocomposites, we are aware of the problems associated with the long cure times used to prepare these materials. Studies are currently underway to look into the effect of the cure time on the thermal and mechanical properties of our natural oil-based biocomposites and promising results are being obtained.

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## **CHAPTER 5. GREEN COMPOSITES USING SWITCHGRASS AS A REINFORCEMENT FOR A CONJUGATED LINSEED OIL-BASED RESIN**

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### **Abstract**

Switchgrass has been used as a filler to produce conjugated linseed oil-based green composites. The effect of the amount of the switchgrass; the matrix crosslink density; and the incorporation of a compatibilizer, maleic anhydride, on the structure, water absorption, and thermal and mechanical properties of the composites has been investigated. The thermal stability of the composites is primarily dependent on the amount of the switchgrass fibers, which are far less thermally stable than the linseed oil-based resin. For the most part, improvements in the mechanical properties can be achieved by increasing the amount of switchgrass (up to 70 wt %), increasing the amount of the crosslinker, and adding maleic anhydride to increase the filler-matrix interaction. The uptake of water in the composites is mostly influenced by the loading of the switchgrass fibers.

### **Introduction**

With the recent push towards the use of environmentally friendly materials, much attention has been given to the use of natural fibers as a replacement for synthetic fibers in the preparation of composites. Natural fibers have the main advantage of being biorenewable

and biodegradable, but are also light in weight, have high strength and stiffness, and can be obtained at a very low cost.

“Green composites” is the term often given to composites prepared from both natural fibers and a bio-based matrix. Of the bio-based matrices often employed in the preparation of green composites, natural oil-based resins are among the most common, because natural oils are available in large quantities and are relatively inexpensive. These natural oils typically contain multiple functional groups per molecule leading to highly crosslinked thermosetting resins with very good thermal and mechanical properties.

Of all the work on the preparation of natural oil-based green composites, most have focused on the use of functionalized natural oils. Early work in this area, conducted by Wool *et al.*, prepared high performance composite materials using flax, hemp, cellulose, and pulp to reinforce an acrylated epoxidized soybean oil-based resin.<sup>1,2</sup> Aranguren *et al.* employed a linseed oil monoglyceride maleates-based resin and wood flour in order to produce green composites.<sup>3</sup> Several groups have utilized resins containing epoxidized vegetable oils to prepare green composites. Epoxide functionalized soybean and linseed oils, and their derivatives have been used to prepare bio-based matrices reinforced with various natural fillers, including hemp, flax, and kenaf fibers and soy proteins.<sup>4-7</sup> More recently, acrylated epoxidized soybean oil has been used in the preparation of biofoam and structural composites with sisal, flax, hemp, and pulp as the natural fibers.<sup>8,9</sup>

Unfunctionalized natural oil-based green composites have been studied to a lesser extent. Composites prepared by Silva *et al.* and Mohanty *et al.* utilize polyurethane resins based on castor oil and, respectively, coconut and sisal fibers<sup>10</sup> and distillers dried grains with solubles (DDGS), the co-product of dry mill ethanol production,<sup>11</sup> as a reinforcement. Work



in our group has focused on agricultural co-products and residues produced here in the Midwest to reinforce unfunctionalized regular and conjugated natural oils. Spent germ,<sup>12</sup> the co-product of wet mill ethanol production, soybean hulls,<sup>13</sup> corn stover,<sup>14</sup> and wheat straw<sup>15</sup> have been used, along with tung, conjugated soybean, and conjugated linseed oil-based resins to prepare green composites. With natural fiber contents as high as 90 wt %, all the aforementioned natural oil-based green composites contain a significant biorenewable content and most have properties suitable for applications in the automotive, construction, and furniture industries.

The present work focuses on the use of switchgrass to reinforce a conjugated linseed oil-based resin. Linseed oil is a highly unsaturated triglyceride oil containing approximately six C-C double bonds per triglyceride. It consists of 57% linolenic acid (C18:3), 15% linoleic acid (C18:2), 19% oleic acid (C18:1), and 4% stearic acid (C18:0) and is typically used as a drying oil for surface coatings.<sup>16</sup>

Switchgrass is a perennial warm-season grass native to North America. A lot of attention has been given to the use of switchgrass as a bioethanol feedstock, because it can be easily integrated into existing farming operations, is highly productive, is suitable for marginal lands, and has low water and nutritional requirements.<sup>17</sup> But there is also potential for the use of switchgrass as a reinforcement in the preparation of composite materials and research in this area has been conducted. Kuo *et al.* produced wood/agricultural fiberboard, which utilized a soy protein-based adhesive to bond wood and switchgrass fibers,<sup>18</sup> and in other work, Van den Oever *et al.* prepared petroleum-based thermoplastic composites containing polypropylene and switchgrass.<sup>19</sup> To our knowledge, research on the use of switchgrass as a reinforcement in natural oil-based green composites has not been reported.

## Experimental

**Materials.** The linseed oil was supplied by Archer Daniels Midland (Decatur, IL) and was conjugated to produce conjugated linseed oil (CLIN) according to our previously published procedure.<sup>20</sup> The extent of conjugation was calculated to be approximately 100%. The divinylbenzene (DVB, technical grade; assay 80% by gas chromatography, 20% ethylvinylbenzene), maleic anhydride (MA), and *t*-butyl peroxide (TBPO) were purchased from Sigma-Aldrich Corporation (St. Louis, MO) and used as received. *n*-Butyl methacrylate (BMA) was purchased from Alfa Aesar (Ward Hill, MA) and used as received. The release film, Wrightlon<sup>®</sup> 5200, was supplied by Airtech International, Inc. (Huntington Beach, CA). The switchgrass (SWG) was supplied by Chariton Valley Resource Conservation and Development Inc. (southern Iowa) and was ground to pass through a 2 mm screen using a Wiley mill.

**Preparation of Conjugated Linseed Oil/Switchgrass Composites.** The composites were prepared using a compression molding process. The designated amounts of 100% CLIN, BMA, and DVB were mixed and stirred. Five wt % of the total resin weight of the TBPO initiator was then added. The following nomenclature is used: CLIN represents conjugated linseed oil and BMA, DVB, and MA represent the *n*-butyl methacrylate, divinylbenzene, and maleic anhydride comonomers, respectively. For example, CLIN50-BMA30-DVB15-MA05 corresponds to a resin prepared from 50 wt % CLIN, 30 wt % BMA, 15 wt % DVB, and 5 wt % MA and 5 wt % of this total weight was the amount of TBPO initiator used. The resin mixture was added to the SWG, which was dried in a vacuum oven at 70 °C for approximately 18 hr prior to use. This mixture was stirred until all of the SWG was wet and was then placed in the cavity of the preheated (140 °C) steel mold lined with the release film.

The mold was closed and cured at 140 °C for 3 hr, followed by 160 °C for 3 hr, under a pressure of 400 psi. The mold was then moved to an oven and cured under atmospheric pressure at 180 °C for 2 hr. Once the mold cooled to room temperature, the composite was removed and post-cured at 180 °C for 1 hr. The reported amounts of SWG are based on the initial amounts of SWG and resin used. For example, for the composite containing 60 wt % SWG, 40 g of resin was added to 60 g of SWG. The standard composition used for preparing the composites was CLIN50-BMA35-DVB15 and 70 wt % SWG. When one variable was changed, the rest were held constant. In all cases, the matrix composition was CLIN50-(BMA + DVB + MA)50. For example, a composite designated CLIN-DVB05-70 refers to a composite prepared using CLIN50-BMA45-DVB05 as the resin and 70 wt % SWG as the filler. It is assumed that the remaining undesigned comonomer is BMA.

It should be noted that in our previous work, we have prepared unreinforced, free-radically cured natural oil-based resins, but because of shrinking and cracking problems, these resins were cured for much longer time periods (3 days) and at lower temperatures. Since we are using higher cure temperatures and much shorter times, we are unable to produce the unreinforced resin, because of the previously mentioned problems. If the cure temperature were reduced and the time increased in order to produce a viable unreinforced resin, it would be inaccurate to compare the pure resin to the composites. For these reasons, we are unable to obtain the thermal and mechanical properties of the pure resin.

**Characterization.** Soxhlet extraction was used to determine the amount of soluble materials in the composites and to characterize the structure of the resulting composites. A 4.5 g composite sample was extracted for 24 hr with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary

evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70 °C overnight before weighing.  $^1\text{H}$  NMR spectroscopic analysis of the soluble substances was carried out in  $\text{CDCl}_3$  using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz.

A Q50 TGA (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 20 °C/min. Generally, a 10-12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the composites were obtained on a TA Instruments Q800 DMA in tension mode. A rectangular specimen of about 22 mm  $\times$  8.5 mm  $\times$  1.5 mm (length  $\times$  width  $\times$  thickness) was cut from the samples. Each specimen was cooled to -120 °C and then heated under air at 3 °C /min to 200 °C at a frequency of 1 Hz.

The tensile tests were conducted at 25 °C according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

The water uptake of the composites was measured according to ASTM D570-98. The test specimens were conditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed. The specimens were then immersed in distilled water for 4 weeks. At specific time intervals, the specimens were removed from the water, quickly wiped dry with a paper towel, weighed, and placed back in the water. The water uptake was calculated as:

$$\text{Water uptake, \%} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

At the end of the 4 week period, the specimens were reconditioned by drying in an oven at 50 °C for 24 hr, cooled in a desiccator, and weighed to determine the amount of soluble matter lost during immersion. The soluble matter was calculated as:

$$\text{Soluble matter, \%} = \frac{\text{conditioned weight} - \text{reconditioned weight}}{\text{conditioned weight}} \times 100$$

## Results and Discussion

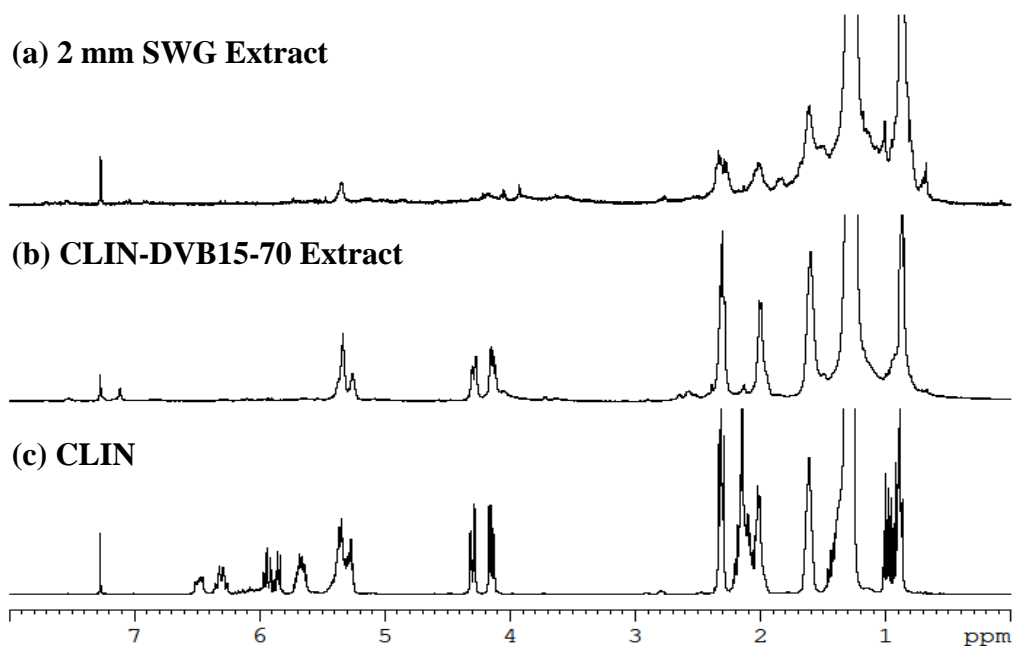
**Soxhlet Extraction Analysis.** The % soluble materials for the SWG and all of the composites are given in Table I. The 2 mm SWG (entry 1) used in this work contains approximately 3% soluble materials. Based on the <sup>1</sup>H NMR spectrum (Fig. 1a), the SWG extract seems to consist mainly of a fatty substance. There appears to be very little triglyceride oil. The extract appears to be a mixture of fatty acids and derivatives.

**Table I.** Extraction Data and Thermal Properties of the Switchgrass and Composites

Entry	Sample	Soxhlet Extraction	TGA	
		% Soluble	<i>T</i> <sub>10</sub> (°C)	<i>T</i> <sub>50</sub> (°C)
1	SWG <sup>a</sup>	3	292	348
2	CLIN-DVB15-50	3	311	425
3	CLIN-DVB15-60	3	305	407
4	CLIN-DVB15-70 <sup>b</sup>	4	302	394
5	CLIN-DVB15-80	3	298	375
6	CLIN-DVB15-90	3	293	351
7	CLIN-DVB05-70	3	302	386
8	CLIN-DVB25-70	3	301	406
9	CLIN-DVB35-70	3	305	423
10	CLIN-DVB45-70	3	306	434
11	CLIN-DVB15-MA05-70	4	300	403
12	CLIN-DVB15-MA15-70	3	298	408
13	CLIN-DVB10-MA05-70	3	300	391
14	CLIN-DVB00-MA15-70	4	296	389

<sup>a</sup> 2 mm SWG

<sup>b</sup> Standard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG

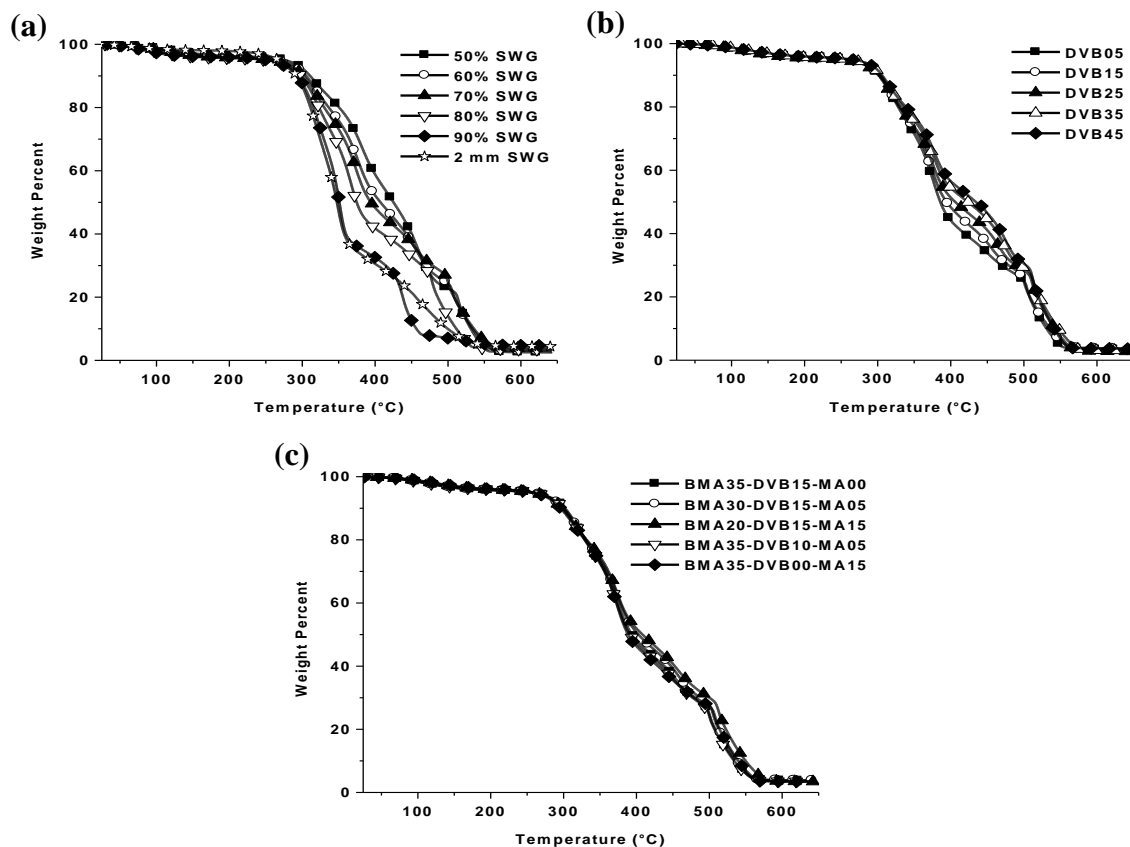


**Fig. 1.**  $^1\text{H}$  NMR spectra of (a) extract of 2 mm SWG, (b) extract of the CLIN-DVB15-70 composite, and (c) CLIN.

Changing the amount of the SWG (entries 2-6); the crosslinker, DVB (entries 7-10); or the compatibilizer, MA (entries 11-14); has little effect on the % soluble materials obtained from the composites. All of the composites, regardless of the composition, have 3 or 4% soluble materials. Fig. 1b shows that the extract is mostly composed of unreacted CLIN or low molecular weight oligomers containing CLIN. This  $^1\text{H}$  NMR spectrum is representative of all of the composite extracts. The small range of chemical shifts in the vinylic region (5.2-5.5 ppm) of the spectrum and the absence of a peak at 2.8 ppm indicate that the extracted oil is not conjugated and contains no bisallylic protons. It may be that the unreacted oil contains significant amounts of saturated or monounsaturated (oleic acid) fatty acid side chains. It is also possible that the oil was incorporated into an oligomer through

one of the carbon-carbon double bonds of a polyunsaturated fatty acid side chain, which would result in a loss of conjugation and eliminate the possibility for bisallylic protons. The presence of a small peak in the aromatic region ( $\sim 7.1$  ppm) also indicates a small amount of DVB, which is most likely part of an oligomer.

**Thermogravimetric Analysis.** The temperatures at 10% ( $T_{10}$ ) and 50% ( $T_{50}$ ) weight loss and the TGA curves for the SWG and all of the composites are given in Table I and Fig. 2, respectively. From the TGA curves, it is seen that the SWG and resulting composites essentially degrade in three stages. The first stage corresponds mainly to the loss of water in



**Fig. 2.** TGA curves for the (a) SWG and composites prepared from differing amounts of SWG, (b) composites prepared from differing amounts of DVB, and (c) composites prepared from differing amounts of MA.

the temperature range of 100 to 150 °C. In the final two stages, the fiber components (cellulose, hemicellulose, and lignin) of the SWG and the resin degrade. Because the degradation of the fiber components, when in an oxidative atmosphere, is very complex, it is not possible to determine when each degrades.<sup>21</sup>

The TGA curves and data show that the SWG is far less thermally stable than the CLIN-based resin.  $T_{10}$  and  $T_{50}$  decrease from 311 to 293 °C and 425 to 351 °C respectively, when the amount of SWG is increased from 50 to 90 wt %. When looking at the TGA curves given in Fig. 2 for the composites prepared with differing amounts of DVB, it is seen that the resin most likely begins to degrade at around 375 °C. It is at this point where a large difference in the TGA curves is observed. Since the resin doesn't begin to degrade until about 375 °C, varying the amount of DVB doesn't have much of an effect on the  $T_{10}$  values, but  $T_{50}$  increases from 386 to 434 °C as the amount of DVB is increased from 5 to 45 wt %. Increasing the amount of DVB should significantly increase the crosslink density of the resin, resulting in an improvement in the thermal stability. Again, changing the resin composition, this time by incorporating a compatibilizer, MA, has little effect on the initial thermal stability of the composites. Replacing BMA (entries 11 and 12) and DVB (entries 13 and 14) with 5 and 15 wt % MA has little or no effect on  $T_{10}$ , but does have more of an effect on  $T_{50}$ . If 15 wt % MA is used to replace BMA, an increase in  $T_{50}$  from 394 to 408 °C is observed, but it appears that the crosslinker, DVB, is more important than the compatibilizer with regards to the thermal stability of the composites. As all of the DVB is replaced by MA,  $T_{50}$  slightly decreases from 394 to 389 °C.

**Dynamic Mechanical Analysis.** The rubbery plateau storage moduli ( $E'$ ) and glass transition temperatures ( $T_g$ ) for the composites are given in Table II. The  $T_g$ 's were obtained



from the peak of the  $\tan \delta$  vs. temperature curves, which are given in Fig. 3 along with the storage modulus vs. temperature curves. From the DMA data and curves, it is observed that the SWG acts as an effective reinforcement to increase the stiffness of the composites.  $E'$  increases from 557 to 1002 MPa as the amount of SWG is increased from 50 to 80 wt % (entries 1-4). But increasing the SWG loading further to 90 wt % (entry 5) results in a dramatic decrease in  $E'$ . Adding too much SWG leads to a weaker material because an insufficient amount of resin is available to wet the fibers and effectively bind them together. As expected, increasing the amount of DVB, and therefore the crosslink density of the resin, results in significant increases in  $E'$ , which increases from 677 to 1690 MPa as the amount of DVB is increased from 5 to 45 wt % (entries 6-9).

**Table II.** Thermomechanical Properties of the Composites

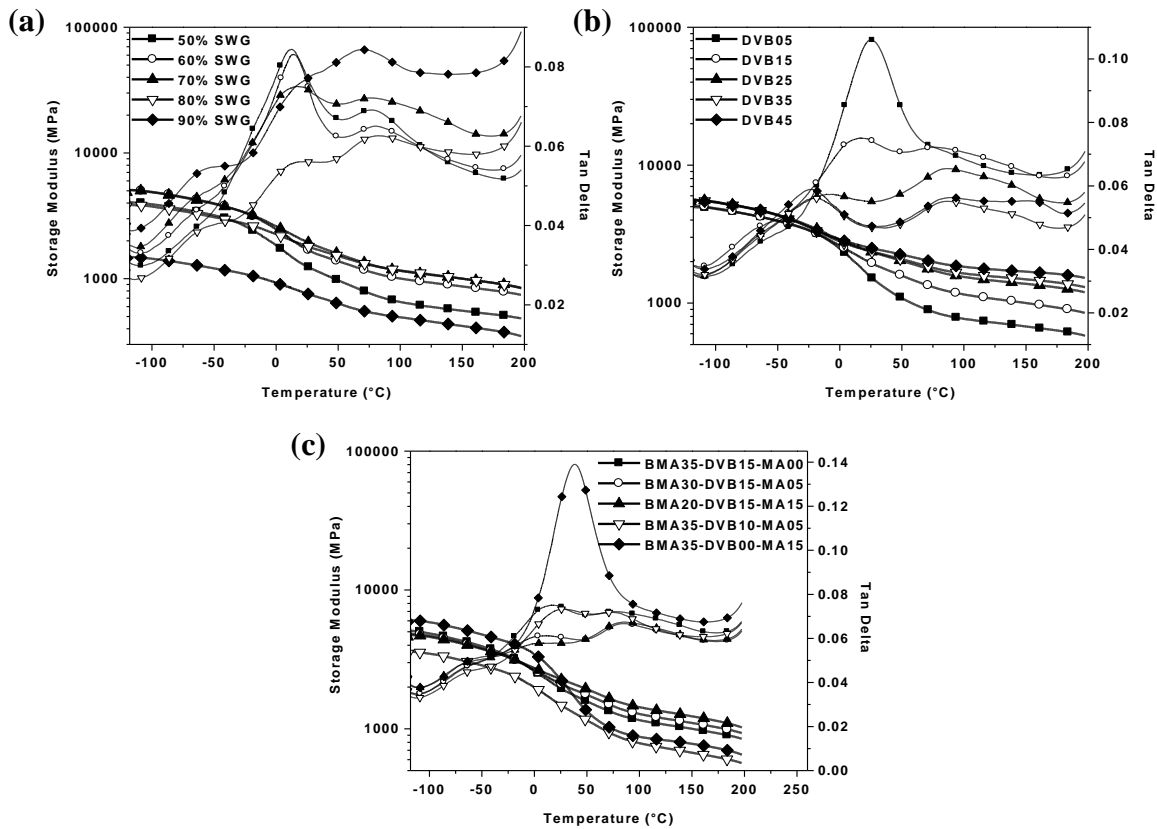
Entry	Sample	DMA		Tensile Properties	
		$E'$ (MPa) <sup>a</sup>	$T_g$ (°C)	$E$ (MPa)	$\sigma$ (MPa)
1	CLIN-DVB15-50	557	12, 77	986 ± 23	7.1 ± 0.5
2	CLIN-DVB15-60	868	15, 80	1190 ± 49	7.2 ± 0.6
3	CLIN-DVB15-70 <sup>b</sup>	1001	18, 76	1247 ± 43	7.6 ± 0.6
4	CLIN-DVB15-80	1002	22, 83	1077 ± 64	4.4 ± 0.6
5	CLIN-DVB15-90	421	72	385 ± 91	0.9 ± 0.4
6	CLIN-DVB05-70	677	25	937 ± 51	5.9 ± 0.5
7	CLIN-DVB25-70	1379	-8, 87	1525 ± 124	9.9 ± 1.2
8	CLIN-DVB35-70	1487	-21, 87	1652 ± 28	9.3 ± 0.7
9	CLIN-DVB45-70	1690	-24, 89	1639 ± 49	9.2 ± 1.0
10	CLIN-DVB15-MA05-70	1103	9, 85	1283 ± 51	8.5 ± 0.5
11	CLIN-DVB15-MA15-70	1231	4, 85	1523 ± 75	10.4 ± 2.1
12	CLIN-DVB10-MA05-70	673	28, 75	1235 ± 62	8.5 ± 0.9
13	CLIN-DVB00-MA15-70	781	39	1070 ± 73	6.6 ± 0.4

<sup>a</sup> Storage modulus at 150 °C

<sup>b</sup> Standard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG

MA is used as a compatibilizer to increase the interaction between the CLIN-based resin and the SWG fibers. It's expected that MA can be incorporated into the matrix through

the C-C double bond and also chemically bind to the fibers through ring opening of the anhydride by the hydroxyl groups present on the lignocellulosic fibers. Seeing that  $E'$  increases from 1001 to 1231 MPa when 15 wt % MA is used to replace BMA (entries 10 and 11), it can be concluded that MA is a useful compatibilizer. But the improvements in  $E'$  gained by the use of MA are not enough to compensate for the removal of DVB. Replacing the crosslinker with either 5 or 15 wt % MA results in a reduction in  $E'$  (entries 12 and 13).



**Fig. 3.**  $E'$  and tan delta curves for composites prepared with (a) differing amounts of SWG, (b) differing amounts of DVB, and (c) differing amounts of MA.

From the  $\tan \delta$  vs. temperature curves given in Fig. 3, it's observed that two peaks ( $T_g$ 's) are present for most of the composites indicating a phase separated matrix. The

reactivity of the vegetable oil and the comonomers used in the matrix are very different. Initially, the more reactive DVB polymerizes resulting in a homopolymerization or copolymerization with BMA to form a “DVB-rich” phase. As the concentration of DVB monomer decreases, more CLIN is incorporated into the polymer to form an “oil-rich” phase. Each of these two phases have their own separate  $T_g$ 's: the “oil-rich” phase with a  $T_g$  of  $\sim 15$  °C and the “DVB-rich” phase with a  $T_g$  of  $\sim 85$  °C. Similar results have been observed in previous work.<sup>12</sup> When the amount of SWG is increased from 50 to 80 wt %, both  $T_g$ 's tend to increase. Based on the shoulder peak at approximately  $-60$  °C that becomes more evident as the amount of SWG is increased, the increase in the  $T_g$ 's may be the result of a more phase separated matrix. As the amount of SWG is increased, the mobility of the larger oil molecule may decline, limiting its ability to be incorporated into the polymer. This could lead to another phase in the matrix that is even more “rich” in CLIN. If more oil is incorporated into this phase and not in the other two phases, that would explain the observed increase in the  $T_g$ 's.

Increasing the amount of DVB in the matrix causes a dramatic outward shift in the  $T_g$ 's, resulting from a more phase separated matrix. If only 5 wt % DVB is used, a homogeneous matrix results with a  $T_g$  of 25 °C, but as the amount of DVB is increased from 15 to 45 wt %, the  $T_g$ 's shift from 18 and 76 °C to  $-24$  and 89 °C respectively.

Adding MA at the expense of BMA tends to make the resin more phase separated. The lower temperature  $T_g$  decreases from 18 to 4 °C and the higher temperature  $T_g$  increases from 76 to 85 °C as BMA is replaced by 15 wt % MA. But, as might be expected, replacing the highly reactive DVB with 5 wt % MA causes the two  $T_g$ 's to shift towards one another,

indicating a more homogeneous matrix. If all of the DVB is replaced with MA, a homogeneous resin is obtained with a  $T_g$  of 39 °C.

**Tensile Properties.** The Young's moduli ( $E$ ) and tensile strengths ( $\sigma$ ) for the composites are given in Table II. As the amount of SWG is initially increased from 50 to 70 wt %,  $E$  and  $\sigma$  increase from 986 to 1247 MPa and 7.1 to 7.6 MPa respectively, but, because of an insufficient amount of resin to bind the fibers together, increasing the amount of SWG further to 90 wt % results in a significant decrease in both  $E$  and  $\sigma$ .

Increasing the crosslink density of the matrix, by increasing the amount of DVB, tends to improve the mechanical properties.  $E$  increases from 937 to 1652 MPa as the amount of DVB is increased from 5 to 35 wt % and stays relatively constant when further increasing to 45 wt %. However,  $\sigma$  peaks at 25 wt % DVB and decreases slightly when more DVB is added. The tensile strength increases from 5.5 to 9.9 MPa when the amount of DVB is changed from 5 to 25 wt % and decreases to 9.2 MPa at 45 wt % DVB. The drop in  $\sigma$  above 25 wt % DVB is most likely a result of a more brittle matrix caused by too much crosslinking.<sup>14</sup>

Significant improvements in  $E$  and  $\sigma$  can be obtained by using a small amount of a compatibilizer, MA, in place of BMA. As a compatibilizer, the MA increases the filler-matrix interaction by chemically binding the SWG fibers to the resin. Approximately 22% and 37% increases in  $E$  and  $\sigma$  respectively were observed by replacing 15 wt % BMA with MA.

DVB is used as an effective crosslinker to improve the thermal and mechanical properties of the composites, but it is also quite expensive. Limiting its use in the resin will make the composites more economically advantageous, when finding applications in

industry. When 5 wt % DVB is substituted with MA, the mechanical properties of the composites are retained.  $E$  decreases very little from 1247 to 1235 MPa and  $\sigma$  improves from 7.6 to 8.5 MPa, but replacing all of the DVB with MA results in a reduction in both the strength and stiffness.

**Table III.** Water Uptake Data for the Composites

Entry	Sample	Saturation Water Content <sup>a</sup> (%)	Soluble Matter <sup>b</sup> (%)	Water Absorbed <sup>c</sup> (%)
1	CLIN-DVB15-50	31	2.1	33
2	CLIN-DVB15-70 <sup>d</sup>	42	3.1	45
3	CLIN-DVB15-90	94	5.8	100
4	CLIN-DVB05-70	46	3.5	50
5	CLIN-DVB25-70	40	3.1	43
6	CLIN-DVB45-70	41	2.9	44
7	CLIN-DVB15-MA15-70	37	2.8	40
8	CLIN-DVB00-MA15-70	40	3.4	43

<sup>a</sup> Saturation water content was taken from the plateau of the water uptake vs. square root of time curve

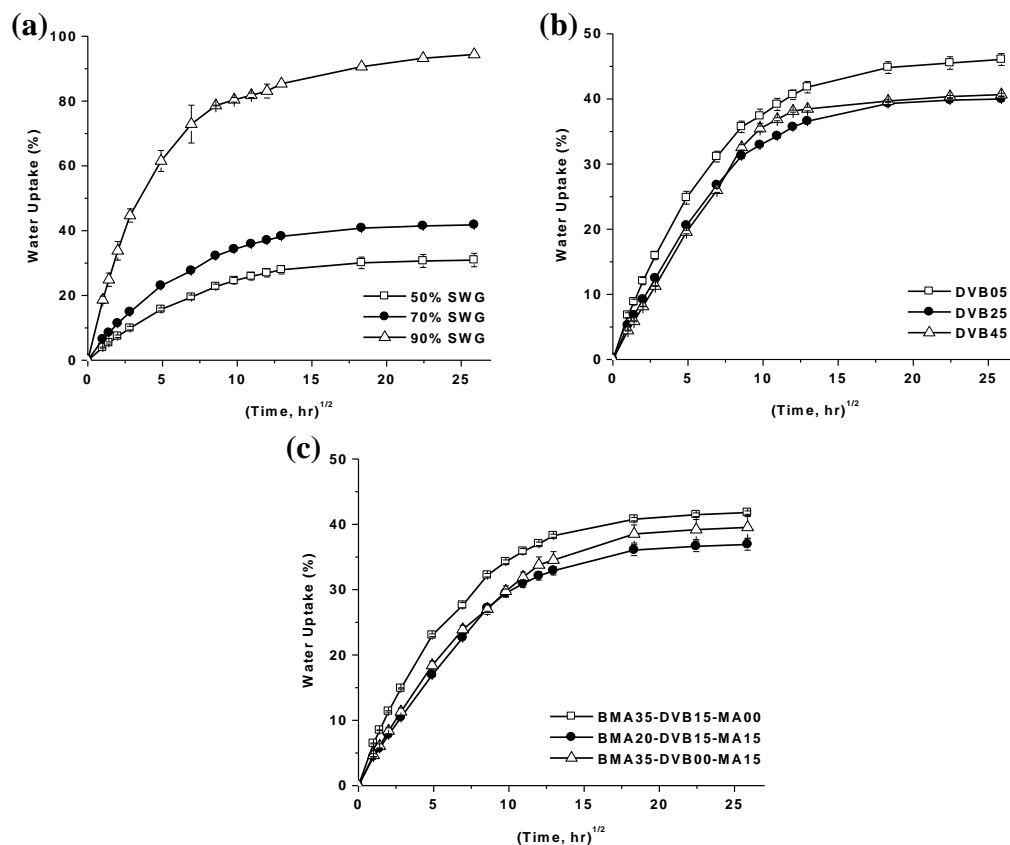
<sup>b</sup> Soluble matter is the percent mass lost during immersion

<sup>c</sup> Water absorbed is the sum of the saturation water content and the soluble matter lost

<sup>d</sup> Standard composition: CLIN50-BMA35-DVB15-MA00, 70 wt % SWG

**Water Uptake.** The saturation water content, soluble matter lost, and total water absorbed and the water uptake vs. square root of time curves are given in Table III and Fig. 4, respectively, for selected composites. As expected and seen in the data and the curves, the hydrophilic lignocellulosic SWG fibers have the largest influence on the water uptake of the composites. The total water absorbed increases from 33 to 45% when increasing the amount of SWG from 50 to 70 wt % (entries 1 and 2), but more than doubles to 100% when further increasing the fiber loading to 90 wt % (entry 3). The diffusion constant of water in the composite, which is proportional to the initial slope of the water uptake vs. square root of time curve, and soluble matter also increase significantly as the amount of SWG is increased. Since all of the monomers are quite hydrophobic and immiscible in water, it's expected that

the soluble matter is extracted from the SWG fibers. Changing the composition of the resin, by either varying the amount of the crosslinker or incorporating a compatibilizer, has a much lower effect on the water uptake of the composites. Increasing the amount of DVB tends to result in slight decreases in the soluble matter, water absorbed, and the diffusion constant of the water (entries 4-6). Whether MA replaces 15 wt % BMA or DVB (entries 7 and 8), decreases in the water absorbed and diffusion constant of the water are obtained. This is likely the result of the increased filler-matrix interaction and, therefore, “shielding” of the fibers by the resin caused by the use of MA.



**Fig. 4.** Water uptake vs. the square root of time for composites prepared with (a) differing amounts of SWG, (b) differing amounts of DVB, and (c) differing amounts of MA.

## Conclusions

Green composites have been prepared using switchgrass (SWG) as a reinforcing filler for a bio-based resin containing conjugated linseed oil. The composites, with a biorenewable content of 75 to 95 wt %, have thermal stabilities up to 300 °C and Young's moduli and tensile strengths ranging from 385 to 1652 MPa and 0.9 to 10.4 MPa, respectively. Increasing the amount of SWG up to 70 wt % leads to improved mechanical properties, but because of the low thermal stability of the fibers, increasing the amount of SWG also results in composites with a lower thermal stability. Divinylbenzene (DVB) is used as an effective crosslinker and the thermal and mechanical properties are enhanced by increasing its concentration. By incorporating a compatibilizer, maleic anhydride (MA), to increase the filler-matrix interaction, an improvement in the mechanical properties can be obtained.

Water uptake in the composites is primarily influenced by the amount of the hydrophilic SWG fibers. Dramatic increases in the water absorbed results from an increase in the amount of the SWG, although slight decreases in the water absorbed can be obtained by increasing the amount of DVB or incorporating MA. A high water uptake of the composites could be good or bad depending on the intended application of the material. The water will likely compromise the mechanical properties of the composites, but should also accelerate the biodegradation of the SWG fibers. If the mechanical properties are crucial to the application, it may be necessary to coat or seal the composite to deter the absorption of water.

Polyethylene-, polypropylene-, and poly(vinyl chloride)-based wood-plastic composites (WPCs) have found many applications in the automotive and construction industries. Although slightly weaker than traditionally used WPCs, the green composites

produced here have the advantage of having a high annually renewable content and should find nonstructural applications as automotive panels, wall panels, ceiling tiles, furniture, windows, and doors.

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**CHAPTER 6. CATIONICALLY-CURED  
NATURAL OIL-BASED GREEN COMPOSITES:  
EFFECT OF THE NATURAL OIL AND THE AGRICULTURAL FIBER**

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**Abstract**

Green composites have been produced from various cationically-cured natural oil-based resins and agricultural fibers. The natural oils and agricultural fibers of interest include corn, soybean, fish, and linseed oils and corn stover, wheat straw, and switchgrass fibers. The effect of the type of the natural oil and the agricultural fiber on the structure and thermal and mechanical properties of the composites has been studied using Soxhlet extraction, thermogravimetric and dynamic mechanical analysis and tensile testing. The green composites, with agricultural fiber loadings of 75 wt %, have thermal stabilities up to 275 °C. The Young's moduli and tensile strengths of the composites range from 1590 to 2300 MPa and 5.5 to 11.3 MPa, respectively. In general, an increase in the degree of unsaturation of the natural oil results in improvements in the thermal and mechanical properties of the composites. The wheat straw fibers tend to give composites with the best thermal and mechanical properties.

**Introduction**

The recent volatility in the crude oil market and concerns over the environment has encouraged many industries to focus on the production of greener materials. The plastics and composites industries are no exception. Although poly(lactic acid), PLA, has gained the most attention in the plastics industry, there is also a lot of interest given to the use of natural oils as a feedstock for plastic materials.<sup>1-3</sup> Natural oils have a triglyceride structure with a high functionality per molecule leading to crosslinked thermosetting resins and are annually renewable, available in large quantities, and have historically been very inexpensive. In the composites industry, natural fibers are seen as a viable replacement for synthetic fibers, because they are biorenewable, biodegradable, very inexpensive, and yet have a high specific strength and stiffness.

“Green composites” is the term often given to composites prepared from both a bio-based filler and a bio-based matrix. Work concentrating on the use of functionalized natural oils to prepare green composites has been carried out extensively in the past. Most researchers have utilized acrylated or methacrylated epoxidized soybean oil (AESO), vegetable oil monoglyceride maleates, or epoxidized vegetable oils to produce bio-based resins and reinforced these materials with various lignocellulosic fibers, generally hemp, flax, or kenaf.<sup>4-12</sup> Research on the preparation of green composites from unfunctionalized natural oils has either taken advantage of the double bonds already present in the oil to produce thermosetting resins or made use of the hydroxyl groups present in castor oil to produce polyurethanes, which have been reinforced with natural fibers.<sup>13,14</sup>

The green composites produced in our group have utilized a range of agricultural fibers to strengthen bio-based resins prepared by the free radical copolymerization of conjugated vegetable oils through the carbon-carbon double bonds present in the triglyceride.

Spent germ,<sup>15</sup> the co-product of wet mill ethanol production, soybean hulls,<sup>16</sup> corn stover,<sup>17</sup> and wheat straw<sup>18</sup> have all been used to reinforce tung oil-, conjugated soybean oil-, or conjugated linseed oil-based resins. The present work also uses corn stover, wheat straw, and switchgrass as a natural fiber reinforcement, but instead focuses on resins produced by the cationic copolymerization of conjugated natural oils, such as corn, soybean, fish, and linseed oil. Plastics produced by the cationic copolymerization of these oils with styrene and divinylbenzene have been studied in the past by our group<sup>19-22</sup> and biocomposites have been prepared by reinforcing some of these resins with glass fibers<sup>23,24</sup> or clays.<sup>25,26</sup> These previously prepared cationically-cured natural oil-based plastics and composites were produced at low temperatures using long cure times, whereas the composites produced in this work are cured at much higher temperatures in order to reduce the cure time. To this date, no green composites have been prepared from cationically-cured natural oil-based resins and natural fibers.

Corn stover and wheat straw are the residues remaining after the corn and wheat grain harvest and the 2005 “Billion Ton” study estimates that 75 and 11 million tons of each, respectively, are available annually in the U.S.<sup>27</sup> Switchgrass is a perennial warm-season grass native to North America. A large amount of interest has been given to these fibers, particularly corn stover and switchgrass, as a feedstock for cellulosic ethanol production, but they are also being looked into as a reinforcement for plastics. Nearly all of the research in this area has focused on producing composites from petroleum-based thermoplastics or thermosets, but some have used these fibers as a reinforcement for soy protein-, starch-, and AESO-based plastics.<sup>28-37</sup> The fiber composition and ash content of the corn stover, wheat

straw, and switchgrass are given in Table 1. As can be seen, the fiber composition of the agricultural fibers varies little, but there are notable differences in the ash content.

**Table 1**  
**Composition of the Agricultural Fibers Used\***

<b>Agricultural Fiber</b>	<b>Cellulose (% mass)</b>	<b>Hemicellulose (% mass)</b>	<b>Lignin (% mass)</b>	<b>Ash (% mass)</b>
Corn Stover	35	23	19	12
Wheat Straw	33	26	18	5
Switchgrass	33	23	17	10

\* Taken from the U.S. Dept. of Energy Biomass Feedstock Composition and Property Database

The annual global production of soybean, corn, fish, and linseed oil is approximately 26.5, 2.3, 1.1, and 0.8 million tons, respectively.<sup>3</sup> The main use of corn and soybean oil is in the food industry, but more recently they are also being used as a feedstock for biodiesel production. Fish oil is typically used in aquaculture. However, with its nutritional benefit, fish oil is increasingly finding direct use in human foods and capsules.<sup>38</sup> Being highly unsaturated, linseed oil is most often used as a drying oil for surface coatings.<sup>39</sup> In this work, we study the effect of varying the natural oil and the agricultural fiber on the structure and thermal and mechanical properties of the resulting cationically-cured composites.

## Experimental

**Materials.** The soybean and corn oil was purchased in a local supermarket. The Menhaden fish oil was supplied by Omega Protein (Houston, TX) and the linseed oil was supplied by Archer Daniels Midland (Decatur, IL). All oils were conjugated to produce conjugated corn oil (CCORN), conjugated soybean oil (CSOY), conjugated fish oil (CFO), and conjugated linseed oil (CLIN) according to our previously published procedure.<sup>40</sup> The extent of conjugation was calculated to be in the range of 95-100%. The styrene (ST), divinylbenzene (DVB, assay 80% by gas chromatography, 20% ethylvinylbenzene), and boron trifluoride

diethyl etherate (BFE) were purchased from Sigma-Aldrich Corporation (St. Louis, MO) and used as received. The release film, Wrightlon<sup>®</sup> 5200, was supplied by Airtech International, Inc. (Huntington Beach, CA). The corn stover (CS) was collected directly from a forage harvester on the Iowa State University Sorenson research farm in Boone County, IA. The wheat straw (WS) was collected directly from the Iowa State University Burkey research farm in Boone County, IA. The switchgrass (SWG) was supplied by Chariton Valley Resource Conservation and Development Inc. (southern Iowa). These three agricultural fibers were ground to pass through a 2 mm screen using a Wiley mill.

**Preparation of the Natural Oil-based Resins and Composites.** The natural oil-based resins were prepared by bulk cationic polymerization. The monomer mixture was prepared by adding 45 wt % of the conjugated natural oil, 25 wt % of ST, and 25 wt % of DVB together and stirring vigorously. Prior to the initiator being added, the resin mixture was cooled in a dry ice/acetone bath. The BFE initiator was modified to ensure a homogeneous polymerization by mixing 3 wt % of the initiator with 5 wt % of the conjugated oil. The modified-BFE initiator was then added to the monomer mixture and this mixture was stirred, poured into a glass mold, and cured at 180 °C for 4 hr. In all cases, the composition of the resin is 50 wt % conjugated natural oil, 25 wt % ST, and 25 wt % DVB. The following nomenclature is used: a polymer designated CSOY corresponds to a resin prepared from 50 wt % CSOY, 25 wt % ST, 25 wt % DVB and 3 wt % of this total weight was the amount of BFE initiator used.

The composites were prepared using a compression molding process. The resin was mixed as described earlier and then added to the agricultural fiber, which was dried in a vacuum oven at 70 °C for approximately 18 hr prior to use. This mixture was stirred by hand

until all of the agricultural fiber was wet and was then placed in the cavity of the steel mold lined with the release film. The mold was closed and cured at 180 °C for 4 hr under a pressure of 400 psi. Once the mold cooled to room temperature, the composite was removed and post-cured at 180 °C for 1 hr. In all cases, the matrix composition was 50 wt % conjugated natural oil, 25 wt % ST, and 25 wt % DVB and the agricultural fiber loading was 75 wt %. For example, a composite designated CFO-WS refers to a composite prepared using a resin containing 50 wt % CFO, 25 wt % ST, and 25 wt % DVB and 75 wt % WS as the filler.

**Characterization.** Soxhlet extraction was used to determine the amount of soluble materials in the agricultural fibers, pure resins, and composites and to characterize the structure of the resulting composites. A 4.5 g sample was extracted for 24 hr with 110 mL of refluxing methylene chloride using a Soxhlet extractor. After extraction, the resulting solution was concentrated on a rotary evaporator and both the soluble and insoluble materials were dried in a vacuum oven at 70 °C overnight before weighing. <sup>1</sup>H NMR spectroscopic analysis of the soluble substances was carried out in CDCl<sub>3</sub> using a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz.

A Q50 TGA instrument (TA Instruments, New Castle, DE) was used to measure the weight loss of the samples under an air atmosphere. The samples were heated from room temperature to 650 °C at a heating rate of 20 °C/min. Generally, a 10-12 mg sample was used for the thermogravimetric analysis.

The dynamic mechanical properties of the resins and the resulting composites were obtained on a TA Instruments Q800 DMA in tension mode. A rectangular specimen of about 25 mm × 8.5 mm × 1.5 mm (length × width × thickness) was cut from the samples. Each

specimen was cooled to  $-120\text{ }^{\circ}\text{C}$  and then heated under air at  $3\text{ }^{\circ}\text{C}/\text{min}$  to  $200\text{ }^{\circ}\text{C}$  at a frequency of 1 Hz.

The tensile tests were conducted at  $25\text{ }^{\circ}\text{C}$  according to ASTM D638 using an Instron universal testing machine (model 4502) at a crosshead speed of 10 mm/min. The dogbone-shaped test specimen (type I specimen in ASTM D638M) had a gauge section with a length of 57 mm, a width of 12.7 mm, and a thickness of about 4.5 mm.

## Results and Discussion

**Fatty Acid Composition of the Natural Oils.** As mentioned before, natural oils are made up of triglycerides and what distinguishes one from another is their fatty acid composition. Table 2 gives the fatty acid composition and the number of C-C double bonds per triglyceride for corn, soybean, fish, and linseed oil. The vegetable oils used in this work (corn, soybean, and linseed oil) tend to be rich in palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. Fish oil, on the other hand, has a

**Table 2**  
**Fatty Acid Composition of the Natural Oils Used**

Natural Oil	C=C Bonds <sup>a</sup>	Fatty Acid Composition (%)									
		C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:4	C20:5	C22:5	C22:6
Corn	4.0	<1	11	2	25	60	1	--	--	--	--
Soybean	4.5	<1	11	4	23	54	8	--	--	--	--
Fish <sup>b</sup>	5.7	10	20	3	9	2	2	2	13	3	8
Linseed	5.9	<1	5	4	19	24	47	--	--	--	--

<sup>a</sup> Number of carbon-carbon double bonds per triglyceride

<sup>b</sup> Contains <2% of several other fatty acids

relatively low amount of C18 fatty acids and instead contains significant amounts of saturated fatty acids and long chain, highly unsaturated fatty acids. The different fatty acid composition for each oil leads to a variation in the degree of unsaturation. Corn oil, with



significant amounts of oleic and linoleic acids and very little linolenic acid, has a relatively low degree of unsaturation (~4.0 C-C double bonds), whereas linseed oil, with nearly 50% linolenic acid, has a higher degree of unsaturation (~5.9 C-C double bonds). The different levels of C-C double bonds results in resins with different crosslink densities, which should affect the thermal and mechanical properties of the pure resins and resulting composites. Typically, we have seen that more highly unsaturated oils give plastics and composites with improved thermal and mechanical properties.<sup>17,22-24</sup> Fish and linseed oils both have approximately the same number of C-C double bonds per triglyceride, but you can see that their fatty acid compositions are very different. The C-C double bonds in linseed oil are fairly evenly distributed throughout the triglyceride molecule, while fish oil has significant amounts of saturated fatty acids and then longer chain fatty acids with four or more C-C double bonds. Although the degree of unsaturation for these two oils is the same, the crosslinking in the resulting resins should be considerably different. The large amount of saturated fatty acid side chains in fish oil will not get incorporated into the polymer chains and will thus act as a plasticizer, which should give a softer material than materials derived from linseed oil.

**Soxhlet Extraction Analysis.** The % soluble materials from the agricultural fibers, pure resins, and composites are given in Table 3. The agricultural fibers used in this work generally to contain a low amount of soluble materials (entries 1-3). Although the <sup>1</sup>H NMR spectra are not shown, the extracts are mainly composed of a fatty substance (triglyceride oil, fatty acids, *etc.*).

With the exception of the resin prepared from CFO, the % soluble materials changes very little as the natural oil is varied (entries 4-7). It decreases slightly from 15% for the

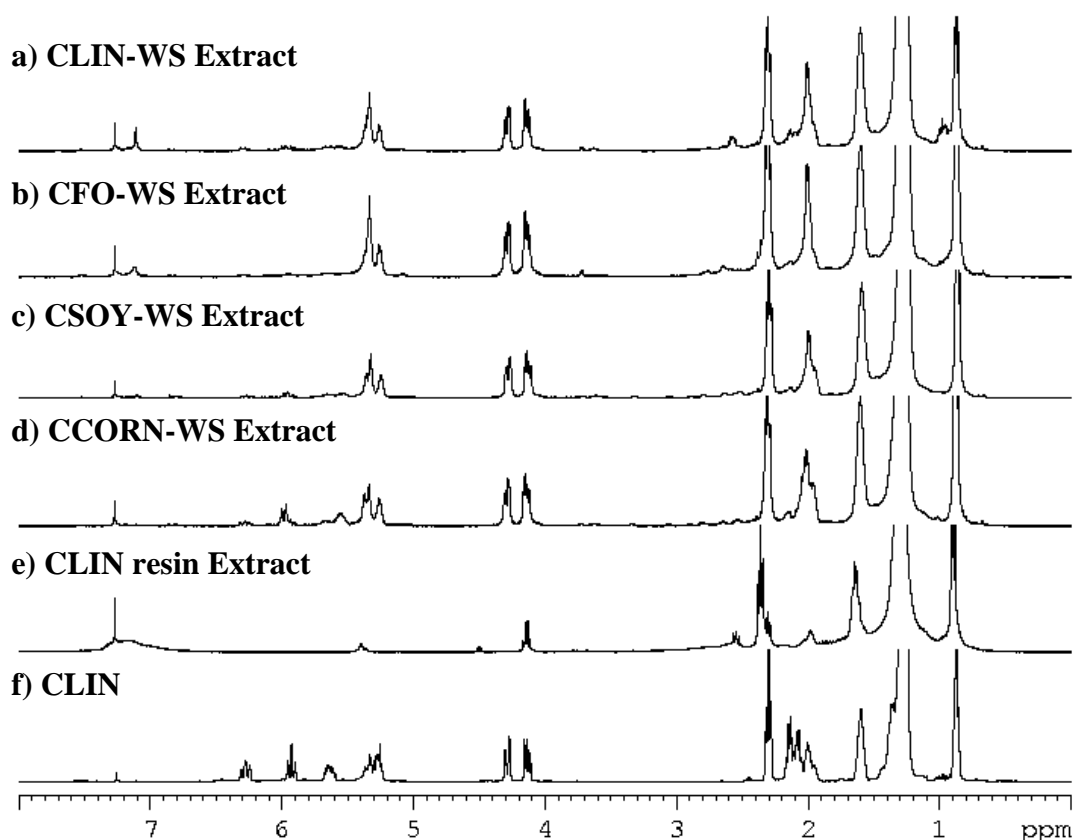
CCORN-based resin to 13% for the resin from CLIN. The higher amount of soluble materials for the CFO-based resin (19%) is likely the result of the high saturated fatty acid content present in CFO. Since more than a third of the fatty acid chains in CFO are saturated, it is likely that some of the triglyceride molecules contain two saturated fatty acid side chains. These molecules, with a low potential to crosslink, should more readily form oligomers that are soluble in methylene chloride. A representative  $^1\text{H}$  NMR spectrum of the extract from the CLIN-based resin is given in Figure 1. Regardless of the natural oil, the  $^1\text{H}$  NMR spectra of the resin soluble extracts are alike and are also similar to the spectra of soluble extracts from cationically-cured natural oil-based resins previously prepared in our group.<sup>20,22</sup> Earlier studies indicate that the extracts mainly contain unreacted oil, initiator fragments (peak at 4.1 ppm), and oligomers composed of oil and the aromatic comonomers (broad peak above 7 ppm).

**Table 3**  
**Extraction Data and Thermal Stability of the Resins and Composites**

Entry	Sample	Soxhlet Extraction	TGA <sup>a</sup>	
		% Soluble	$T_{10}$ (°C)	$T_{50}$ (°C)
1	2 mm CS	<1	259	319
2	2 mm WS	<1	266	311
3	2 mm SWG	3	292	348
4	CCORN resin	15	386	472
5	CSOY resin	15	383	471
6	CFO resin	19	297	466
7	CLIN resin	13	399	471
8	CCORN-CS	8	291	370
9	CSOY-CS	8	294	377
10	CFO-CS	7	294	378
11	CLIN-CS	5	299	390
12	CCORN-WS	9	297	403
13	CSOY-WS	9	297	407
14	CFO-WS	7	295	403
15	CLIN-WS	6	299	423
16	CCORN-SWG	7	299	381
17	CSOY-SWG	7	299	389
18	CFO-SWG	7	300	378
19	CLIN-SWG	5	300	394

<sup>a</sup>  $T_{10}$  = temperature at 10% weight loss;  $T_{50}$  = temperature at 50% weight loss

The composites contain between 5 and 9% soluble materials. From the data in Table 3, it can be seen that the amount of soluble materials in the agricultural fibers appears to have little effect on the amount of soluble materials in the resulting composites. For example, the 2 mm SWG has the highest amount of soluble materials, yet the composites reinforced with SWG tend to have the lowest % soluble materials. Also, when taking into account the % soluble materials of the individual components (fibers and resin), the composites tend to have a higher than expected amount of soluble materials. This is particularly true for the CS and WS composites. The higher than expected % soluble materials for the composites is likely



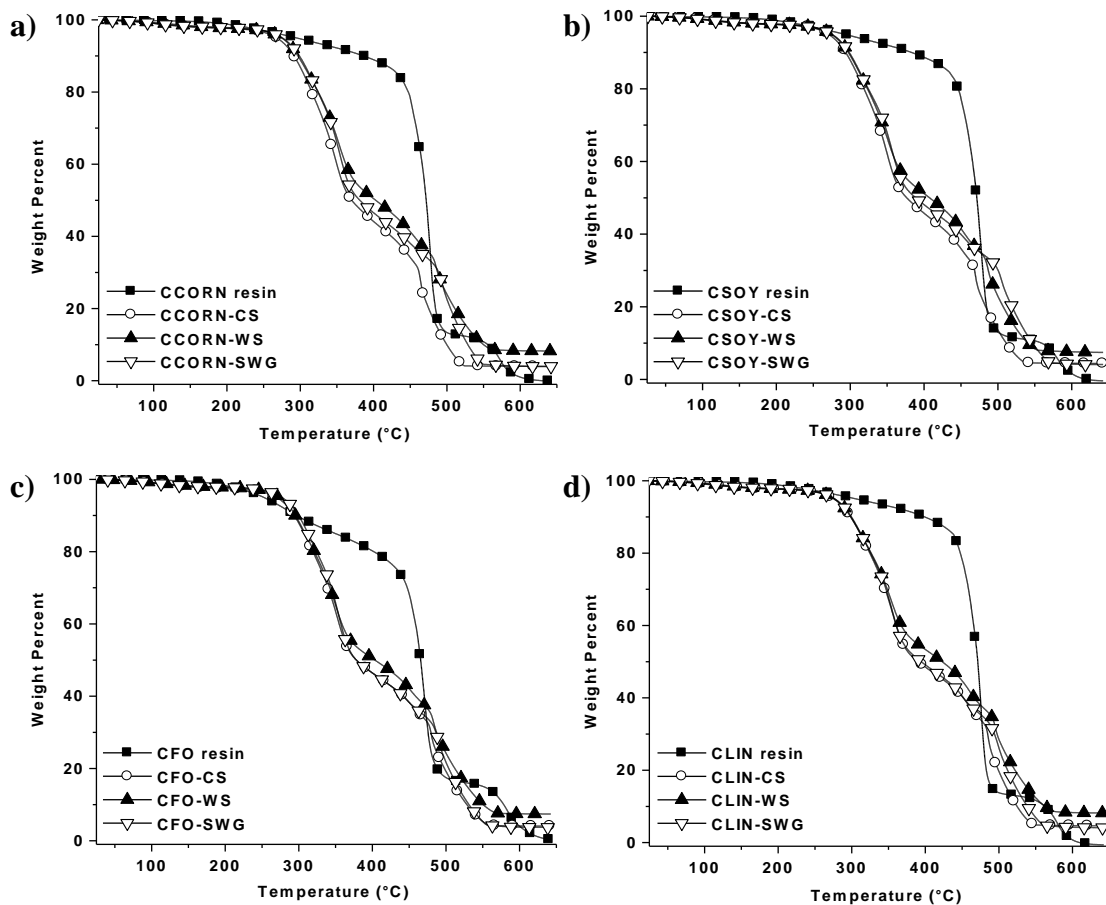
**Figure 1**  $^1\text{H}$  NMR spectra of the extracts from a) the CLIN-WS composite, b) the CFO-WS composite, c) the CSOY-WS composite, d) the CCORN-WS composite, e) the CLIN resin, and f) CLIN.

the result of a lower crosslinked resin. It is likely that the addition of fibers inhibits chain propagation during the polymerization, resulting in less crosslinking.

While the % soluble materials varies little for the composites and may be within the experimental error, the overall trend appears to be that a more highly unsaturated natural oil gives a lower % soluble materials. For example, with the CS composites, the % soluble materials stays constant at 8% for the CCORN- and CSOY-based composites (entries 8 and 9), decreases to 7% for the CFO-based composite (entry 10), and decreases further to 5% for the CLIN-based composite (entry 11). With regards to the fiber, the WS composites tend to have the highest amount of soluble materials, followed by CS, and then SWG. For the CCORN-based composites, the composite reinforced with WS contains 9% soluble materials, the CS composite contains 8%, and the SWG composite contains 7%. From the  $^1\text{H}$  NMR spectra of the soluble extracts from the composites (Figure 1a-d), it is seen that the soluble material is essentially unreacted natural oil or oligomers mostly composed of natural oil. All of the spectra of the composite extracts are not shown, but it has been observed that the composition of the extracts is only dependent on the type of the natural oil and not on the agricultural fiber. While the spectra for extracts from the composites prepared from different oils are very similar, the peak in the aromatic region at 7.1 ppm becomes more prominent as the number of C-C double bonds in the oil increases. These aromatic protons are from ST or DVB comonomers most likely contained in low molecular weight oligomers, along with the natural oil.

**Thermogravimetric Analysis.** The temperatures at 10% ( $T_{10}$ ) and 50% ( $T_{50}$ ) weight loss for the agricultural fibers, pure resins, and composites are given in Table 3 and the TGA curves for the pure resins and composites are given in Figure 2. From the TGA curves, it is

observed that the pure resins are far more thermally stable than the resulting composites and that both the resins and composites essentially degrade in three stages. For the resins, the first stage, up to  $\sim 450$  °C, corresponds to loss of the unreacted oil and low molecular weight oligomers. The second stage, from 450 to 500 °C, corresponds to degradation of the crosslinked resin and char formation and the char is oxidized in the final stage,  $>500$  °C. With the exception of the CFO-based resin, the TGA data in Table 3 suggests that the initial thermal stability of the resins is somewhat dependent on the degree of unsaturation of the



**Figure 2** TGA curves for the pure resins and composites prepared from a) CCORN, b) CSOY, c) CFO, and d) CLIN.

natural oil, while no effect is observed at higher temperatures.  $T_{10}$  remains relatively constant at 386 and 383 °C for the CCORN- and CSOY-based resins, respectively, and increases to 399 °C for the resin prepared from CLIN, but  $T_{50}$  stays constant at ~471 °C regardless of the vegetable oil. The lower thermal stability for the CFO-based resin, particularly at the lower temperatures, is likely the result of the high amount of saturated fatty acids contained in CFO. This leads to a higher amount of soluble materials in the CFO-based resin, which is lost at lower temperatures.

One of the drawbacks of natural fibers is their low thermal stability (Table 3, entries 1-3). By replacing 75 wt % of the resin with agricultural fibers, a decrease of about 100 °C for the  $T_{10}$  and  $T_{50}$  values is observed. As seen in Figure 2, the first stage of degradation for the composites occurs up to 275 °C and corresponds to the loss of water, unreacted oil, and low molecular weight oligomers. In the final two stages, the resin and fiber components (cellulose, hemicellulose, and lignin) of the lignocellulosic fillers decompose, but because the degradation of the fiber components is very complex when in an oxidative atmosphere, it is not possible to determine where each degrades.<sup>41</sup> With regards to the natural oil, the composites tend to become more thermally stable as the degree of unsaturation increases. The CFO-WS and CFO-SWG composites are exceptions to this rule. For example, for the CS composites,  $T_{10}$  and  $T_{50}$  increase from 291 to 299 °C and 370 to 390 °C, respectively, as the natural oil is changed from CCORN to CLIN (entries 8-11). Again, the lower than expected thermal stability for the CFO-based composites is likely the result of the high saturated fatty acid content in CFO and, therefore, the likelihood of forming low molecular weight oligomers.

Figure 2 shows a comparison of the thermal stability of the composites as the agricultural fiber is changed, while keeping the natural oil-based resin constant. As with the % soluble materials, the thermal stability of the agricultural fibers does not affect the thermal stability of the resulting composites. Even though the thermal stability varies significantly for each agricultural fiber (entries 1-3), initially, changing the fiber has little effect on the thermal stability of the composites. At higher temperatures, the WS composites tend to be the most stable, followed by SWG, and then CS. For example, with the CLIN-based composites,  $T_{50}$  decreases from 423 °C for the WS composite to 394 °C for the SWG composite, and further to 390 °C for the CS composite. Meanwhile, for the same CLIN-based composites,  $T_{10}$  basically stays constant at 300 °C.

**Dynamic Mechanical Analysis.** The room temperature and rubbery storage moduli ( $E'$ ) and glass transition temperatures ( $T_g$ ) for the pure resins and the resulting composites are given in Table 4. As seen from the storage modulus vs. temperature curves given in Figures 3a-d, the pure resins exhibit dynamic mechanical properties typical of our thermosetting natural oil-based plastics.<sup>42</sup> While in the glassy state at lower temperatures, the modulus remains relatively constant. At about 0 °C, a large decrease in  $E'$  is observed corresponding to the onset of segmental mobility in the polymer network, but because the samples yielded at higher temperatures, the resins did not exhibit the typical rubbery plateau. The room temperature storage moduli of the resins tend to be directly related to the degree of unsaturation of the natural oil.  $E'$  increases from 1030 to 1520 MPa as the oil is changed from CCORN (~4.0 C-C double bonds) to CLIN (~5.9 C-C double bonds).

The addition of agricultural fibers to the resins causes an increase in  $E'$  over the entire temperature range, but particularly at higher temperatures. The dramatic increase in  $E'$  in the

**Table 4**  
**Thermomechanical Properties of the Resins and Composites**

Entry	Sample	DMA <sup>a</sup>			Tensile Properties <sup>b</sup>		
		$T_g$ (°C)	$E'$ at 25 °C (MPa)	$E'$ at 150 °C (MPa)	$E$ (MPa)	$\sigma$ (MPa)	$\varepsilon$ (%)
1	CCORN resin	82	1030	- <sup>c</sup>	460 ± 20	13.9 ± 0.5	22 ± 4
2	CSOY resin	84	1040	- <sup>c</sup>	470 ± 10	14.7 ± 0.3	25 ± 2
3	CFO resin	108	1230	- <sup>c</sup>	630 ± 110	18.8 ± 0.2	10 ± 3
4	CLIN resin	97	1520	- <sup>c</sup>	920 ± 120	25.1 ± 1.0	10 ± 4
5	CCORN-CS	-23, 97	1970	1310	1590 ± 70	7.0 ± 0.7	1 ± 0
6	CSOY-CS	-15, 97	1950	1280	1790 ± 70	8.2 ± 0.2	1 ± 0
7	CFO-CS	9, 94	2120	1330	1870 ± 100	8.6 ± 0.7	1 ± 0
8	CLIN-CS	-14, 98	2290	1490	1960 ± 100	11.3 ± 0.8	1 ± 0
9	CCORN-WS	-18, 98	2410	1610	2050 ± 110	8.1 ± 0.9	1 ± 0
10	CSOY-WS	-32, 101	2580	1750	2160 ± 100	8.3 ± 0.8	1 ± 0
11	CFO-WS	-12, 96	2810	1810	2300 ± 170	8.4 ± 0.4	1 ± 0
12	CLIN-WS	-15, 97	2970	1930	2280 ± 120	10.7 ± 0.7	1 ± 0
13	CCORN-SWG	-13, 99	1950	1230	1710 ± 160	6.7 ± 1.6	1 ± 0
14	CSOY-SWG	-11, 100	2170	1400	1800 ± 90	6.5 ± 0.6	1 ± 0
15	CFO-SWG	97	2310	1400	1850 ± 170	5.5 ± 0.9	1 ± 0
16	CLIN-SWG	-6, 101	2480	1570	1920 ± 90	8.5 ± 0.9	1 ± 0

<sup>a</sup>  $T_g$  = glass transition temperature;  $E'$  = storage modulus

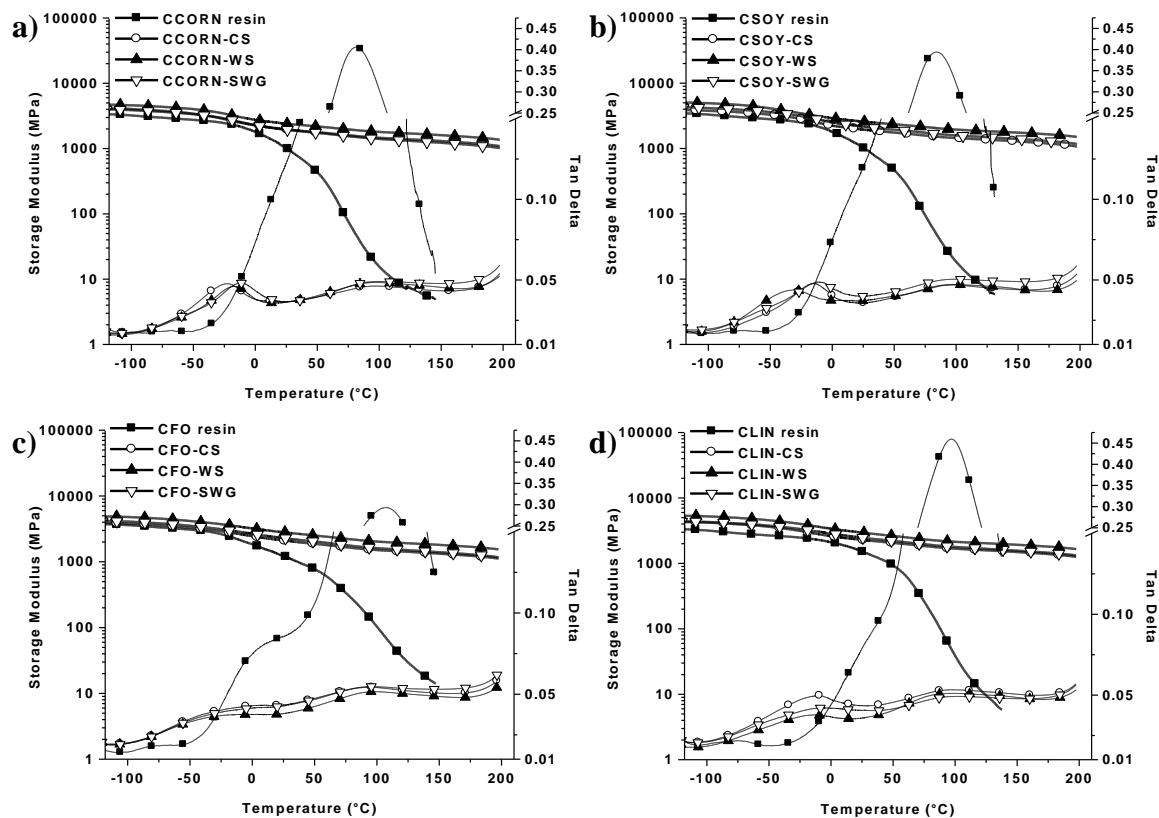
<sup>b</sup>  $E$  = Young's modulus;  $\sigma$  = tensile strength;  $\varepsilon$  = elongation at break

<sup>c</sup> The pure resin DMA specimens broke below 150 °C

rubbery region is a result of the reduction in the mobility and deformability of the resin caused by the stiff lignocellulosic fibers.<sup>43</sup> Increasing the number of C-C double bonds in the natural oil, and therefore the crosslink density of the matrix, leads to an increase in the stiffness of the composites over the entire temperature range. For the composites reinforced with WS (entries 9-12), the room temperature and rubbery plateau moduli increase from 2410 and 1610 MPa for the CCORN-based composites to 2970 and 1930 MPa for the CLIN-based composites. From the storage modulus curves in Figure 3, it can be seen that the WS fibers lead to composites with the highest stiffness. The SWG composites tend to be slightly more rigid than the CS composites, but both these fibers give composites with significantly lower storage moduli than the composites from WS. For example, the room temperature and rubbery storage moduli for the composite designated CFO-WS are 2810 and 1810 MPa,



respectively (entry 11). When the WS fibers are replaced with SWG, the same moduli decrease to 2310 and 1400 MPa (entry 15), while the CFO-CS composite has room temperature and rubbery storage modulus values of 2120 and 1330 MPa (entry 7).



**Figure 3**  $E'$  and tan delta curves for the pure resins and composites prepared from a) CCORN, b) CSOY, c) CFO, and d) CLIN.

The  $T_g$ 's listed in Table 4 were taken from the peaks of the tan delta vs. temperature curves, which are given in Figure 3. It should be noted that a break in the y-axis was inserted to account for the large difference in the peak heights for the pure resins and composites. For the most part, increasing the degree of unsaturation of the natural oil increases the  $T_g$  of the resulting plastic. The  $T_g$  of the pure resin increases from 82 to 97 °C as the natural oil is

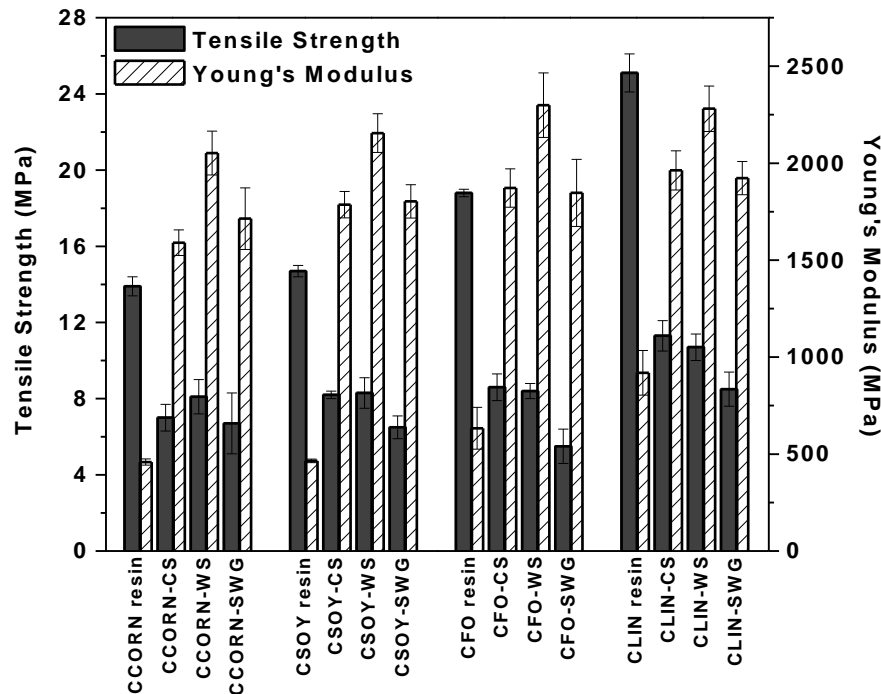
changed from CCORN to CLIN. The higher  $T_g$  for the CFO-based resin appears to be the result of a phase separation in the resin. When looking at Figure 3c, a strong shoulder peak at around 0 °C is observed in the tan delta curve for the CFO-based resin that is not present in the curves of the other natural oil-based resins. This indicates a slight phase separation in the CFO-based resin and may be a result of the difference in reactivities of the saturated and highly unsaturated fatty acid side chains present within CFO. The CFO molecules with a significant amount of saturated fatty acid side chains will be far less reactive toward polymerization than the natural oil molecules with highly unsaturated side chains. The more reactive, highly unsaturated CFO molecules should get incorporated into the polymer chains first leading to a highly crosslinked, rigid phase. As their concentration decreases, more of the highly saturated CFO molecules will get incorporated giving a softer phase with a lower crosslink density.

Adding agricultural fibers to the resin results in dramatic decreases in the tan delta peak heights and also causes a phase separation in the matrix. The large decrease in the peak height could be a result of two things: 1) the reduced mobility of the polymer chains caused by the addition of stiff agricultural fibers and 2) since the peak height is a relative measure of the amount of polymeric material taking part in the transition, a reduction is expected as the resin is replaced by the fibers.<sup>43,44</sup> The phase separation in the matrix is most likely a result of the agricultural fibers inhibiting the mobility of the monomers and propagation of the polymer chains. This inhibition should be more dramatic for the larger, high molecular weight natural oil molecules limiting their ability to be incorporated into the polymer chains. This would lead to a rigid phase that is rich in the ST and DVB comonomers and a softer phase that is rich in the natural oils. Each of these phases has its own  $T_g$ : the oil-rich phase

with a  $T_g$  of  $\sim 15$  °C and the ST/DVB-rich phase with a  $T_g$  of  $\sim 100$  °C. Similar results have been observed in our previous work on composites.<sup>17,18</sup> From Figure 3, it can be observed that, with the exception of the CFO-based composites, all of the tan delta curves for the composites appear pretty similar. With the CFO-based composites, there is no strong peak for the oil-rich phase, but instead more of a shoulder. The  $T_g$ 's vary somewhat for all of the composites, but no real trend was observed as the natural oil or agricultural fiber was varied.

**Mechanical Properties.** The Young's moduli ( $E$ ), tensile strengths ( $\sigma$ ), and elongations at break ( $\epsilon$ ) for the resins and composites are given in Table 4.  $E$  and  $\sigma$  are also displayed graphically in Figure 4. The pure natural oil-based resins display tensile properties typical of rigid plastics. Increasing the number of C-C double bonds in the natural oil increases the strength and stiffness of the resulting plastic, but also makes it more brittle.  $E$  increases from 460 to 920 MPa,  $\sigma$  increases from 13.9 to 25.1 MPa, and  $\epsilon$  decreases from 22 to 10% as the number of C-C double bonds per triglyceride is increased from  $\sim 4.0$  in CCORN to  $\sim 5.9$  in CLIN.

When the agricultural fibers are added to the resins, a nearly threefold increase in the stiffness of the materials is observed, but the strengths are approximately halved and the materials became much more brittle. The enhanced stiffness of the composites can be attributed to the stiff lignocellulosic fibers, while the decreased strength and brittle nature of the composites is likely a result of the poor interfacial interaction between the hydrophobic natural oil-based matrix and the hydrophilic lignocellulosic fibers. For the most part, increasing the crosslink density of the matrix, by increasing the degree of unsaturation of the natural oil, causes an increase in the stiffness and strength of the composites. For example, with the CS composites,  $E$  and  $\sigma$  increase from 1590 to 1960 MPa and 7.0 to 11.3 MPa,



**Figure 4**  $E$  and  $\sigma$  for the pure resins and composites.

respectively, when changing from a CCORN-based resin to a CLIN-based resin (Table 4, entries 5-8). Regardless of the type of natural oil or the agricultural fiber,  $\varepsilon$  stayed constant at 1%. From Figure 4, we can better see the effect of the agricultural fiber on  $E$  and  $\sigma$ , while the natural oil is held constant. The WS fibers definitely give composites with the highest modulus, while the composites from CS and SWG fibers have about the same stiffness. For example, for the CFO-based composites,  $E$  decreases from 2300 MPa for the WS composite to 1870 and 1850 MPa for the CS and SWG composites, respectively. With regards to  $\sigma$ , the CS and WS fibers give composites with approximately the same strength and the SWG fibers give the weakest composites. The CFO-CS and CFO-WS composites have  $\sigma$  values of 8.6 and 8.4 MPa respectively, while  $\sigma$  decreases to 5.5 MPa for the CFO-SWG composite.

## Conclusions

Cationically-cured corn, soybean, fish, and linseed oil-based resins have been reinforced with corn stover, wheat straw, and switchgrass fibers to produce green composites. The composites prepared are much more brittle and have lower tensile strengths than the pure resins, but the addition of fibers also results in a roughly threefold increase in the stiffness when compared to the pure resins. Because of the low thermal stability of the agricultural fibers, the composites have a lower thermal stability than the natural oil-based pure resins, but are still stable up to 275 °C. Natural oils with a higher number of C-C double bonds per triglyceride typically give composites with improved thermal and mechanical properties. Of the three agricultural fibers studied, the composites prepared using wheat straw as a reinforcement tend to have the best thermal and mechanical properties.

Although some of the mechanical and thermal properties of the composites are inferior to the properties of the pure resins, it is important to note that the biorenewable content of the composites is ~88% compared to 50% for the resins. The high annually renewable content of these composites should make them appealing to the automotive, construction, and furniture industries. While these composites are somewhat weak, it is expected that they should still find nonstructural applications, such as automotive panels, wall panels, ceiling tiles, window frames, furniture, and doors, in the previously mentioned industries.

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## CHAPTER 7. SOYBEAN OIL-BASED CATIONIC WATERBORNE POLYURETHANE/VINYL POLYMER HYBRID LATEXES

### Introduction

Polyurethanes are among the most important class of specialty polymers and, due to the very broad range of monomers employed in their synthesis, are perhaps the most versatile polymers with regards to the wide variety of materials which can be produced.<sup>[1]</sup> Polyurethanes are typically employed as rigid and flexible foams, but over the past several years, coatings and adhesives applications have grown significantly.<sup>[2]</sup> These polyurethane materials typically contain significant amounts of organic solvents and possibly free isocyanate groups. Environmental and health concerns have encouraged research into waterborne polyurethanes, making them one of the most rapidly developing and active branches of polyurethane chemistry and technology.<sup>[3]</sup> Waterborne polyurethanes not only eliminate volatile organic compounds, but also have viscosity and flow properties that are independent of their molecular weight and have good film forming properties.<sup>[1b]</sup>

Acrylic polymer latexes are among the most common materials produced by emulsion polymerization and are widely used for coatings and other applications.<sup>[4]</sup> To further enhance the performance of waterborne polyurethanes, hybrid latexes with acrylics have been produced. These hybrid emulsions are expected to provide the advantages of both systems, such as the excellent weather resistance and affinity to pigments, as well as the lower cost of acrylics, and the superior mechanical stability, adhesion, solvent and chemical resistance, and toughness of polyurethanes.<sup>[5]</sup> Several techniques, for instance batch, semibatch, and surfactant-free emulsion and miniemulsion polymerizations, have been utilized to polymerize acrylics in the presence of polyurethanes to give a variety of materials,



including core-shell and grafted hybrid latexes and interpenetrating polymer networks.<sup>[5,6]</sup> These single component hybrid emulsions tend to have properties superior to physical blends, because of the incompatibility between the polyurethane and acrylic dispersions.<sup>[6]</sup>

As with most plastics consumed today, nearly all polyurethane materials are produced entirely from petroleum feedstocks. However, concerns over the environment and petroleum costs and supply have many looking to biorenewable feedstocks to prepare polyurethanes. Of the potential renewable materials, vegetable oils have gained a considerable amount of interest, because they are available in vast quantities and tend to be very inexpensive. A very broad range of polyols and even a few isocyanates have been prepared from vegetable oils leading to a wide variety of polyurethane materials ranging from flexible and rigid foams to soft elastomers to ductile and hard plastics.<sup>[1a,7]</sup>

Vegetable oil-based waterborne polyurethanes have been studied to a much lesser extent. Work in our research group has used methoxylated soybean oil polyols with various hydroxyl content to produce both anionic<sup>[8]</sup> and cationic<sup>[9]</sup> waterborne polyurethanes. The hydroxyl content plays an important role in controlling the mechanical properties of the resulting polyurethane films, as significant improvements in the strength, stiffness and toughness are obtained by increasing the hydroxyl content. Similarly, anionic soybean oil-based polyurethanes have been prepared using 2-hydroxyethyl methacrylate as a chain-terminating agent.<sup>[10]</sup> In order to improve the poor mechanical properties and water sensitivity of pure starch films, anionic waterborne polyurethanes, based on castor oil or a rapeseed oil-based polyol, have been blended with plasticized starch.<sup>[11]</sup> When the polyurethane is 20% or lower, the blends exhibit high miscibility and better mechanical properties and water resistance.

Our research group has also prepared hybrid latexes, with and without a surfactant, from anionic soybean oil-based polyurethanes and vinyl monomers.<sup>[3,12]</sup> When a surfactant is used, miscible hybrid latexes are obtained, while a core-shell structure (polyurethane shell and vinyl polymer core) is obtained when no surfactant is used. In both cases, when compared to the pure polyurethanes, significant improvements in the thermal and mechanical properties result from the addition of vinyl polymers. Herein, we report on the challenges involved in preparing cationic soybean oil-based polyurethane/vinyl monomer hybrid latexes.

### Experimental

**Materials.** The soybean oil was purchased at the local supermarket and used directly without further purification. Methoxylated soybean oil polyols (MSOLs) were prepared according to our previous procedure.<sup>[8]</sup> Isophorone diisocyanate (IPDI), *N*-methyl diethanol amine (NMDA), cetyltrimethylammonium bromide (CTAB), styrene (ST), butyl acrylate (BA), and ammonium persulfate (APS) were purchased Sigma-Aldrich Corporation (St. Louis, MO). Glacial acetic acid (AcOH), potassium persulfate (KPS), sodium dodecyl sulfate (SDS), and methyl ethyl ketone (MEK) were purchased from Fisher Scientific Company (Waltham, MA). All materials were used as received without further purification.

**Synthesis of the Soybean Oil-Based Polyurethane Dispersions (SPUs).** The MSOL (10 g), IPDI and NMDA were added to a flask equipped with a mechanical stirrer. Unless otherwise specified, the molar ratio of the NCO groups of the IPDI, the OH groups of the MSOL, and the OH alcohol groups of the NMDA was held at 2.0 : 1.0 : 0.95. The reaction was carried out at 80 °C for 1 hr and then MEK was added to reduce the viscosity of the system. After an additional 2 hr reaction, the reactants were cooled to room temperature and then neutralized by the addition of AcOH, followed by dispersion at high speed with distilled

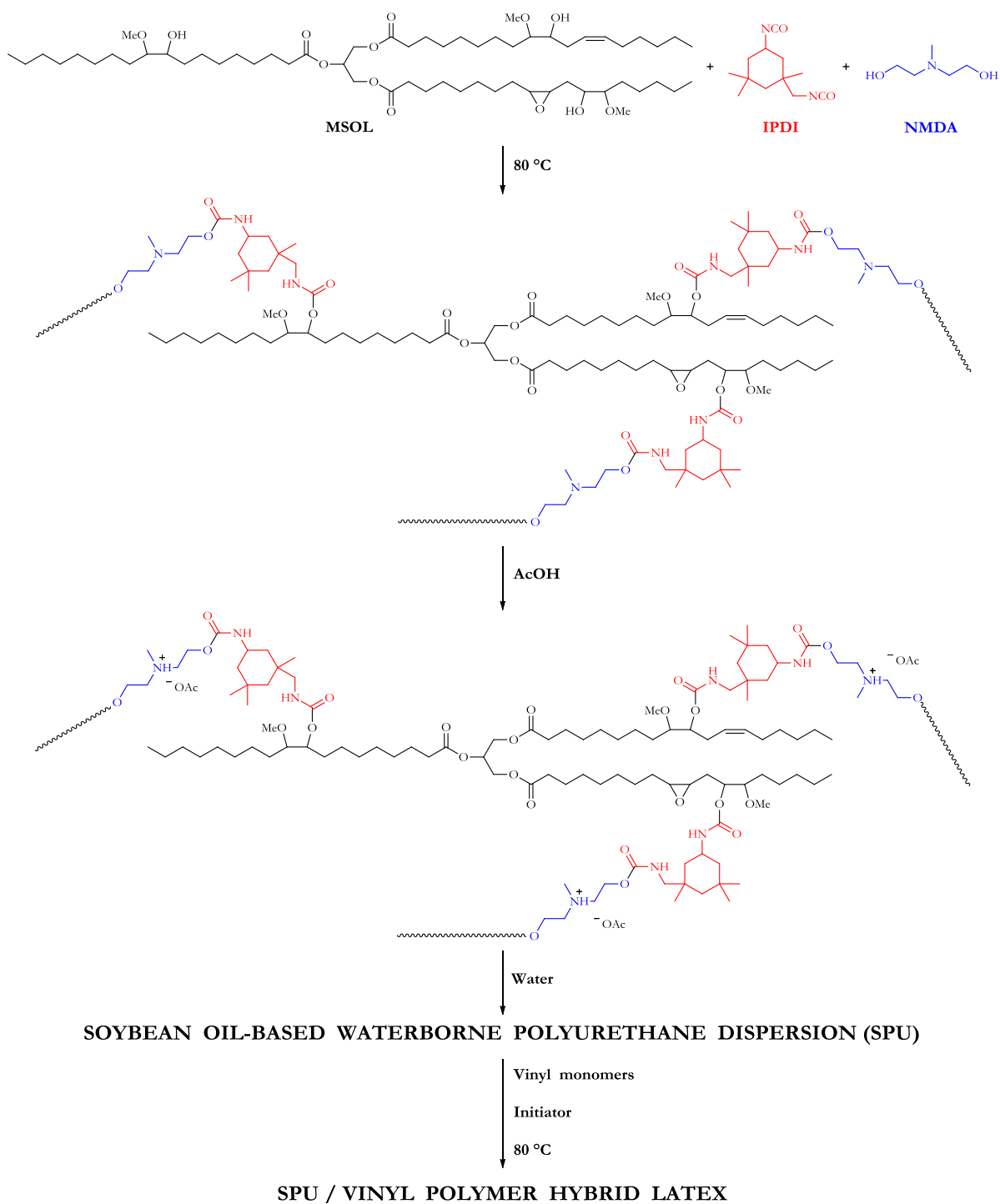
water, to produce the SPU dispersions with a solid content of about 15 wt % after removal of the MEK under vacuum.

**Synthesis of the SPU/Poly(Vinyl Monomer) Hybrid Latexes.** The preparation of the hybrid latexes is illustrated in Scheme 1. When a surfactant was used, the following procedure was used. The surfactant (SDS or CTAB, 3 wt % of vinyl monomers) and the initiator (KPS or APS, 1 wt % of vinyl monomers) were dissolved in distilled water. A mixture of ST and BA in a ratio of 70:30 by weight was then added to the above aqueous solution with vigorous stirring to obtain the pre-emulsions. The desired weight of the SPU and the acrylate pre-emulsion was placed in a flask and stirred for 30 min at room temperature under an argon atmosphere and then brought to the polymerization temperature of 80 °C for 4 hr to obtain the hybrid emulsion.

When no surfactant was used, the following procedure was employed. The desired amount of ST and BA in a ratio of 70:30 by weight was added to the SPU. The resulting reactants were stirred at room temperature under an argon atmosphere for 2 hr, and then brought to the polymerization temperature of 80 °C for 4 hr to obtain the hybrid emulsion, using KPS or APS (1 wt % of vinyl monomers) as an initiator.

### **Results and Discussion**

An effort has been made to produce cationic SPU/vinyl polymer hybrid latexes. Due to the presence of quaternary ammonium groups in the backbone of the polyurethane, it is reasonable to expect that these hybrid latexes may exhibit antimicrobial activities and therefore find unique applications. As mentioned previously, anionic SPU/vinyl polymer hybrid latexes have successfully been prepared with vinyl polymer contents as high as 60 wt



**Scheme 1.** Preparation of soybean oil-based polyurethane (SPU)/vinyl polymer hybrid latexes.

% for the surfactant-free latexes and 75 wt % for the latexes employing a surfactant. However, significant challenges have been encountered when trying to prepare the cationic hybrid latexes, both with and without a surfactant. Initially, attempts were made to prepare surfactant-free hybrid latexes with 50 wt % vinyl monomers with little success. After heating the hybrid emulsion in order to initiate the polymerization, the hybrid emulsion became unstable, as spots began to form on the upper interior walls of the flask. The amount of vinyl monomers was then reduced to 20 wt %, but similar results were obtained.

It is assumed that these unstable hybrid emulsions are the result of the inability of the cationic SPUs to effectively stabilize the vinyl monomers. Cationic surfactants are known to have poor detergency and suspending power, when compared to anionic and nonionic surfactants, and are rarely used in industry.<sup>[13]</sup> They also act as poor emulsifiers and are rarely used for emulsion polymerizations. In an effort to increase the stability of the hybrid emulsions, the ionic content of the SPU was increased. Two methods were used to increase the ionic content in the SPU: 1) the NMDA content was increased from 8.8 wt % (2.0 mol IPDI NCO : 1.0 mol MSOL OH : 0.95 mol NMDA OH) to 10.5 wt % (2.25 : 1.0 : 1.2) to 12.0 wt % (2.47 : 1.0 : 1.45) to 13.8 wt % (2.75 : 1.0 : 1.7) and 2) the amount of AcOH used to neutralize the NMDA in the standard SPU (2.0 : 1.0 : 0.95) was increased from 1.5 times to 3 times to 5 times the number of moles of NMDA. The latter method is more appealing, since the biobased content of the SPU remains high (>50 wt %). For both methods, it was apparent that the ionic content in the SPU was increased, as the particle size of the dispersion progressively decreased as the amount of NMDA or AcOH was increased, which was observed by the increasing clarity of the SPU emulsion. However, these SPUs were still not effective at stabilizing the vinyl polymers, because hybrid emulsions with vinyl polymer

contents higher than 30 wt % could still not be prepared. Even at 30 wt % vinyl polymers, the hybrid emulsions became unstable after a couple of hours, as small particles began to precipitate.

Other methods to stabilize the hybrid emulsions have also been examined. Surfactants, either cationic (CTAB) or anionic (SDS), were employed at 3 wt % based on the vinyl monomers. The resulting hybrid latexes are expected to be composed of particles containing only SPU, only vinyl polymers, and a mixture of SPU and vinyl polymers, rather than the core-shell structure of the surfactant-free hybrid emulsions. However, the addition of a surfactant appeared to have no effect on the stability of the hybrid emulsions, as stable emulsions with high vinyl polymer contents could still not be obtained. Also, acrylic acid was used as a replacement for AcOH. When used in a large excess, the acrylic acid could copolymerize with the other vinyl monomers and, with the presence of the carboxylic acid, help stabilize the polymer particles, but hybrid emulsions with vinyl polymer contents higher than 30 wt % were still not stable.

### **Conclusions**

Although the future of cationic SPU/vinyl polymer hybrid latexes at this stage looks bleak, other attempts to successfully prepare stable hybrid emulsions are probably worthwhile. Because of its simplicity, batch emulsion polymerization was used to prepare the hybrid emulsions described here. Semibatch emulsion polymerization is another process commonly used to prepare PU/vinyl polymer hybrid emulsions and is much more versatile. The variables for the semibatch process include the composition of the initial charge, the time or reaction state when the flow of the remaining ingredients is started, the rate of ingredient additions, and the composition of input streams as a function of time. Proper

manipulation of these variables allows one to control the reaction and product characteristics.<sup>[5]</sup> It would also be interesting to use nonionic surfactants or long chain vinyl pyridinium salts to stabilize the hybrid emulsions. The pyridinium salt could make up a significant portion of the vinyl monomers and also act as an antimicrobial surfactant.

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## CHAPTER 8. GENERAL CONCLUSIONS

This dissertation discusses the preparation and properties of green composites produced from natural oils and agricultural co-products or residues. A variety of natural oil-based resins, both free radically- and cationically-cured, and agricultural filler/fiber reinforcements have been utilized in their production. These novel composites contain anywhere from 60 to 95% renewable materials and have properties suitable for nonstructural applications, such as automotive panels, wall panels, ceiling tiles, window frames, furniture and doors, in the automotive, construction and furniture industries.

In Chapter 2, composites from a tung oil-based resin and spent germ, the co-product of wet mill ethanol production, are discussed. When compared to the pure resin, the addition of spent germ significantly improves the stiffness, as nearly all composites have a higher storage modulus than the unreinforced resin. Unfortunately, increasing the amount of spent germ negatively impacts the thermal and mechanical properties of the composites. Increasing the molding pressure causes an increase in the filler-matrix interaction, resulting in better properties. By removing the unreactive corn oil present in the spent germ prior to composite preparation, considerable improvements in the composite properties are obtained.

The focus of Chapter 3 is on composites from conjugated soybean or linseed oils and corn stover. Corn stover is a widely available, abundant natural fiber and has been proven to be an effective reinforcement for natural oil-based resins. Reducing the fiber length of the corn stover has little effect on the aspect ratio of the fibers, but notably increases the mechanical properties of the composites. Conjugated linseed oil, being more highly



unsaturated than soybean oil, gives a higher crosslinked resin leading to composites with enhanced properties.

Chapter 4 looks into composites prepared from wheat straw and conjugated linseed oil. Wheat straw is another widely available agricultural fiber and composites with as much as 90 wt % wheat straw have been prepared, with the highest mechanical properties occurring at 80 wt % wheat straw. Increasing the amount of divinylbenzene, an effective crosslinker, results in significant improvements in the thermal and mechanical properties of the composites.

In Chapter 5, switchgrass is utilized as a reinforcement for a conjugated linseed oil-based resin in the preparation of green composites. Switchgrass was once plentiful across North American prairies, but a large portion has been plowed under for other agricultural crops. With the recent interest in switchgrass as a feedstock for cellulosic ethanol production, there is potential for vast quantities of switchgrass to become readily available in North America in the near future, which will open the door for other value-added applications, including reinforcing fibers. Switchgrass has been shown to be an effective reinforcement, as composites with up to 90 wt % switchgrass have been prepared. In order to increase the interaction between the fiber and resin, maleic anhydride has been employed as a compatibilizer and the addition of 15 wt % maleic anhydride results in 22 and 37% increases in the Young's modulus and tensile strength, respectively.

The water absorption of these corn stover, wheat straw and switchgrass composites has also been studied. In general, the major factors influencing the uptake of water in the composites are the amount and size of the agricultural fiber, while varying the resin composition has a lesser effect on the water uptake.

Chapter 6 discusses composites prepared from various cationically-cured natural oil-based resins and agricultural fibers. The effect of the type of the conjugated natural oil, corn, soybean, fish and linseed oil, and the agricultural fiber, corn stover, wheat straw and switchgrass, on the thermomechanical properties of the resulting composites has been studied. Generally, the natural oils with a higher number of carbon-carbon double bonds give composites with superior properties. With regards to the agricultural fiber, the composites prepared with wheat straw as the reinforcement tend to have the best properties.

While the agricultural-based green composites described in this dissertation are interesting and have a promising future, some challenges do exist. Economics are always a large hurdle when trying to commercialize bio-based materials. These composites have a big advantage of being largely composed, in some cases 70 or 80 wt %, of very cheap (on the order of cents per pound) agricultural residues or co-products. However, the resin has some limitations, even though it's composed of 50 wt % natural oil. Due to a higher reactivity towards both free radical and cationic polymerizations, conjugated oils are needed in the preparation of these green composites. These conjugated oils are not commercially available at present and must be synthesized in the lab. This process involves the use of an expensive rhodium catalyst, which is consumed in the reaction. In an effort to make the conjugation procedure more economical, work is currently being conducted in our laboratories looking at ways to recycle the rhodium catalyst. Until this is possible, the use of these conjugated natural oils is not very practical. It may also be desirable to look into other methods of conjugating natural oils. At one point, Archer Daniels Midland produced conjugated linseed oil using a ruthenium catalyst, but apparently, a lack of market forced them to discontinue

production of this material. A method of conjugating natural oils using an iodine catalyst has also recently been developed in Professor John Verkade's laboratories.

The long cure times associated with producing these green composites and the use of divinylbenzene in the resin also raise economic concerns. Currently, studies are in progress to reduce the cure time of these materials and preliminary results indicate that the cure time can be reduced drastically with little negative effect on the properties of the composites. Divinylbenzene is used as a highly reactive, efficient crosslinker, but is quite expensive (~\$3 per pound). It has been shown that a portion of divinylbenzene can be replaced by maleic anhydride, a compatibilizer, with little effect on the properties of the composites, but one starts to see decreases in the mechanical properties when the divinylbenzene is completely replaced. Dicyclopentadiene, a very inexpensive crosslinker, should perhaps be looked into as a replacement for divinylbenzene. However, dicyclopentadiene has a much lower reactivity and it is expected that the cure times would need to be increased significantly, therefore adding cost to the material.

While, at the moment, the green composites discussed here may not be economically competitive with petroleum-based composites, as crude oil prices continue to rise and petroleum becomes more scarce, these materials will become more appealing. With continued effort and time dedicated to the production of green composites, there is little doubt that they will continue to find more and more applications in various industries.

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