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Review Article

Polymer Composites Reinforced by Nanotubes as Scaffolds for Tissue Engineering

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The interest in polymer based composites for tissue engineering applications has been increasing in recent years. Nanotubes materials, including carbon nanotubes (CNTs) and noncarbonic nanotubes, with unique electrical, mechanical, and surface properties, such as high aspect ratio, have long been recognized as effective reinforced materials for enhancing the mechanical properties of polymer matrix. This review paper is an attempt to present a coherent yet concise review on the mechanical and biocompatibility properties of CNTs and noncarbonic nanotubes/polymer composites, such as Boron nitride nanotubes (BNNTs) and Tungsten disulfide nanotubes (WSNTs) reinforced polymer composites which are used as scaffolds for tissue engineering. We also introduced different preparation methods of CNTs/polymer composites, such as in situ polymerization, solution mixing, melt blending, and latex technology, each of them has its own advantages.

1. Introduction

Tissue engineering, an important emerging topic in biomedical engineering, has shown tremendous promise in creating biological alternatives for harvested tissues, implants, and prostheses [1]. Tissue engineering may be defined as the application of biological, chemical, and engineering principles toward the repair, restoration, or regeneration of living tissues using biomaterials, cells, and factors alone or in combination [2]. Scaffold is one of the key components in the tissue engineering paradigm in which it can function as a template to allow new tissue growth and also provide temporary support while serving as a delivery vehicle for cells and/or bioactive molecules structure [3, 4]. The scaffold should be porous and permeable to permit the ingress of cells and nutrients and should exhibit the appropriate surface structure and chemistry for cell attachment. Ideal scaffold should possess a suitable combination of physical properties to match those of the replaced tissue with good biocompatibility. Various synthetic alternatives such as metal, alloys, ceramics, polymers, and biocomposites have been researched as scaffold for bioapplications. Among those scaffold biomaterials, the polymers and polymers composites occupy significant position. Polymer materials are playing an increasingly important part in a diverse range of applications; polymer systems can be used for a variety of applications, such as drug delivery, diagnostics, tissue engineering and "smart" optical systems, switching surfaces and adhesives, and protective coatings that adapt to the environment, as well as biosensors, microelectromechanical systems, coatings, and textiles [5]. Nowadays, synthetic degradable polymers, such as polycaprolactone (PCL), polyglycolic acid, polyvinyl alcohol (PVA), and polylactic acid (PLA), have been evaluated extensively as scaffold biomaterials [6]. However, the results of research show that their mechanical properties and biocompatibility are unsatisfactory for the tissue engineering of load-bearing bone. Several strategies for improving the mechanical properties (compression and flexural) of polymeric scaffolds have been reported, with a focus towards developing nanomaterials reinforced polymeric composites [6].

Nanomaterials, which are materials with basic structural units, grains, particles, fibers, or other constituent components smaller than 100 nm in at least one dimension, have

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evoked a great amount of attention [7]. Nanomaterials have special mechanical, electrical magnetic, optical, chemical, and other biological properties because of their high aspect ratio and surface area. Among nanomaterials, the nanotube material attracted wide attention of researchers. Nanotubes, with structures that resemble tiny drinking straws, large inner volumes can be filled with sundry chemicals and biomolecules, ranging in size from small molecules to proteins [8, 9]. After carbon nanotubes (CNTs) were discovered by lijima in 1991, noncarbonic nanotubes were manufactured by different routes: in 2000, Rothschild et al. discovered Tungsten disulfide nanotubes (WSNTs) by vapor-solid growth method; Nath et al. composited MS_2 nanotube in 2001 by vapor phase method; Kinenkamp et al. synthesised ZnS nanotube by restoring sulfurization process [10–12]. Then a variety of noncarbonic nanotubes has been synthesized, such as boron nitride nanotubes (BNNTs) [13], Bi_2S_3 nanotube [14], NbS_2 nanotube [15], $NbSe_2$ nanotube [16], AIN nanotube [17], GaN nanotube [18], InP nanotube [19], SiO_2 nanotube [20], and ZnO nanotube [21]. CNTs, one of the most concerned nanomaterials, with unique electrical, mechanical, and surface properties, such as high aspect ratio, high strength-to-weight ratio, extraordinary mechanical properties (their axial elastic modulus and tensile strength were theoretically predicted to be as high as 1-2 TPa and 200 GPa, resp.), have held great interest with respect to biomaterials, particularly those to be positioned in contact with bone such as prostheses for arthroplasty, plates or screws for fracture fixation, drug delivery systems, and scaffolding for bone regeneration, whose outstanding properties have sparked an abundance of research [22–31]. In recent years, some reports have showed that functionalized CNTs even can improve cell compatibility of matrix material, promote tissue regeneration, and inhibit the formation of glial scar and fibrous tissue [32, 33]. These results suggest that CNTs might hold great promise for synthesizing new kinds of multifunctional nanocomposites in biomedical applications and might be used as reinforcements to improve biological properties of polymer. Noncarbonic nanotubes are important members in quasi-one-dimensional family, because they have a high volume percentage of surface area, which show a high chemical activity and unique physical properties. Through modifying by physical and chemical methods, giving nanotubes new features, such as in the information element, biosensors, molecular field of ion channel machine, smart drugs, microtools, and advanced technology materials in aerospace have important applications. To noncarbonic nanotubes, their research has been focused on the discussion of their manufacturing method and properties, and few reports have investigated the application of their reinforce polymer in tissue engineering; only BNNTs and WSNTs as reinforcement factor with polymer composites have been reported.

In this paper, we will present a comprehensive review about the preparation and processing and the properties of polymer composites reinforced by carbon and noncarbonic nanotube that used or potentially could be used as scaffolds in tissue engineering.

2. Preparation of Nanotubes

CNTs were discovered in the late 1950s while the synthesis of CNTs was first reported in 1991 by Iijima [23] and Bacon [42]. Right now, there are several methods to produce CNTs including arc discharge, laser ablation, chemical vapor deposition (CVD), catalyst chemical vapor deposition (CCVD), and template-directed synthesis [43]. Although arc discharge is a common method for CNTs synthesis, it is difficult to control the morphology of CNTs, such as length, diameter, and number of layers. Compared with arc-discharge and laser-ablation methods, CVD is most widely used for its low setup cost, high production yield, and ease of scale-up. There are two main types of nanotubes existing: the single-walled nanotubes (SWNTs) which are composed by a rolled monolayered graphene sheet and the multiwalled nanotubes (MWNTs) which possess several graphitic concentric layers. In the high-temperature methods, multiwalled carbon nanotubes (MWCNTs) can be produced from the evaporation of pure carbon, but the synthesis of single-walled carbon nanotubes (SWCNTs) requires the presence of a metallic catalyst. The CVD approach requires a catalyst for both types of CNTs but also allows the production of carbon nanofibers [44].

In recent years, people from compounds of graphite, boron nitride which have layered structure synthesized nanotubes. Methods of noncarbonic nanotubes mainly are arc discharge, chemical vapor deposition, laser ablation, carbothermal reduction, carbon nanotubes as a template, pyrolysis, a ball mill, and a relatively low temperature of decomposition [13, 45–51]. Recently, the mechanism of nanotubes has a new understanding, breaking conventional wisdom that only layered materials can form nanotubes. Scientists have developed new ideas of synthesis and proposed a new mechanism of into the tube and from the nonlayered material prepared nanotubes. For example, from chalcogenide MX_2 (M = Mo, W, Nb, X = S, Se) prepared nanotubes. Methods preparing chalcogenide nanotubes are direct vulcanization MO_3 method, decomposition MX_3 method, decomposition $(NH_4)MS_4$ method, carbon tube template method, a hydrothermal synthesis method, and so on. In 2000, Rothschild et al. prepared nanoscale diameter of WS_2 nanotubes by vapor-solid growth method [10].

BNNTs represent V compound nanotubes that can be obtained through a variety of methods, such as arc discharge, chemical vapor deposition, laser ablation, carbothermal reduction, carbon nanotube template method, pyrolysis method, ball milling method, and hydrothermal synthesis method [13, 45–51]. In 2000, Lourie et al. synthesized BNNTs by chemical vapor deposition method [13]. Xu et al.'s team prepared BNNTs by hydrothermal synthesis method in 2003 [51]. After obtaining BNNTs, a number of groups used BNNTs, by filling heterogeneous substances into the pipe body cavity to get the nanotubes reinforced composites, hoping to obtain superior characteristics.

3. Preparation of Polymer Composites Reinforced by Nanotubes

Preparing nanotubes/polymer composites must solve two major problems: favorably dispersed of nanotubes in the

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Table 1: Comparison of CNTs/polymer composites with various fabricating methods.

Method	Advantages	Disadvantages
Solution mixing	Wider applicability, better dispersion	Low stability, residual solution
Melt blending	Wide applicability, good dispersion	Poor dispersion, large residual stress, and low interfacial bonding strength
In situ polymerization	Widest applicability, best dispersion	Residual monomer, matrix strength decline, and large residual stress
Latex technology	Versatile, reproducible, and reliable	Mechanical properties of the material were not significantly improved

matrix and the interface binding with the polymer and nanotubes. Due to small diameter and high surface energy, nanotubes tend to agglomerate easily, which affect their dispersion in the polymer uniformly. Therefore, the primary problem in the preparation of nanotubes/polymer composites is to solve the uniform dispersion of nanotubes in a polymer matrix. In recent years, ultrasound treatment as an important method of dispersing nanotubes, which benefits its dispersion and activation and initiates the polymerization, can effectively solve the problem of nanotubes dispersion in the polymer [6]. In order to improve the adhesion of the interface between the polymer and the nanotubes, it is possible to introduce functional groups into the surface of nanotubes or using the plasma treatment (e.g., NH_3) [52].

The common fabricating methods of nanotubes/polymer composites are solution mixing, melt blending, latex technology, and in situ polymerization method. These methods and their features are briefly described in Table 1. Solution mixing is the most common method for the fabrication of nanotubes/polymer nanocomposites because it is amenable to small sample sizes. In solution mixing, nanotubes are generally dispersed in solvent and then mixed with polymer solution by mechanical mixing, magnetic agitation, or high energy sonication. Subsequently, the nanotubes/polymer composites can be obtained by vaporizing the solvent at a certain temperature [53–55]. Many researchers, such as Xu et al. and Lau et al., have fabricated the CNTs/epoxy composite using this method [56, 57]. For laboratory studies, the solution blending method is a simple way, often to achieve the desired results, but for insoluble polymers, this method is not applicable. It is also not suitable for large-scale industrial preparation. Because this method the process is long and complicated to operate, the consumption of solvents, and complete removal of the solvent are difficult [58]. Melt blending is a versatile and commonly used method to fabricate polymeric materials, especially for thermoplastic polymers. Melt blending uses a high temperature and a high shear force to disperse nanotubes in a polymer matrix [59–61]. The major advantage of this method is that no solvent is employed to disperse nanotubes. Its well-known disadvantage is that nanotubes can easily be damaged to a certain extent or broken in some cases [44, 62–64]. Latex technology is a relatively new approach to incorporate nanotubes into a polymer matrix. By using this technology, it is possible to disperse nanotubes in most of polymers that are produced by emulsion polymerization or that can be brought into the form of an emulsion. The advantages of this technique are obvious: the whole process is easy, versatile, reproducible, and reliable [53–55]. The solvent used for nanotubes dispersion is water; thus, the process is a safe, environmentally friendly, and low-cost. In situ polymerization is considered as a very efficient method to significantly improve the nanotubes dispersion and the interaction between nanotubes and polymer matrix. Generally, nanotubes are firstly mixed with monomers, either in the presence or absence of a solvent, and then these monomers are polymerized via addition or condensation reactions with a hardener or curing agents at an elevated temperature. One of the major advantages of this method is that covalent bonding can be formed between the functionalized nanotubes and polymer matrix, resulting in much improved mechanical properties of composites through strong interfacial bonds [65–67]. To improve the processability, electrical, magnetic, and optical properties of nanotubes, some conjugated or conducting polymers are attached to their surfaces by in situ polymerization. It enables grafting of polymer macromolecules onto the convex walls of nanotubes. This then provides a better nanotubes dispersion and formation of a strong interface between the nanotube and the polymer matrix. Epoxy-based nanocomposites comprise the majority of reports using in situ polymerization methods [68–75]. Song et al. successfully covalently grafted biocompatible poly (L-lactic acid) (PLA) onto the convex surfaces and tips of the MWNTs by one step based on in situ polycondensation of the commercially available L-lactic acid monomers [76].

4. Properties of Polymer Composites Reinforced by Nanotubes as Scaffold for Tissue Engineering

4.1. Polymer Composites Reinforced by Carbon Nanotubes. Recently, polymers have received broad attention in the field of biomedicine. However, their respective problems, such as insufficient mechanical properties and biocompatibility, can directly affect their performance in vivo. For example, although PGA and poly-L-lactic acid (PLLA) can provide a proper plasticity and controlled biodegradation, the biocompatibility is not as satisfactory as that of other biomaterials and the mechanical properties of them seem like insufficient when they are used for large bone defect repair. Conversely, natural polymers, such as collagen, chitosan, and natural extracellular matrix (ECM), exhibit excellent biocompatibility, biodegradable properties; however, their weak mechanical properties have limited their clinical applications [77]. An ideal composite with proper mechanical properties for biomedical applications must be biodegradable and biocompatible and promote cell growth and proliferation. For instance, polymers, which include natural polymer and synthesized polymer, when they are fabricated as CNTs/polymer composites, some of them demonstrate excellent biocompatibility and bioactivity due to the high aspect ratio and

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surface area of nanostructure. Nanostructured surfaces of CNTs show high (bio- and cyto-) compatibility, by promoting protein adsorption and enhancing subsequent cellular adhesion and tissue growth more than on traditional biomaterials' surfaces such as ceramics, titanium alloy, and biopolymers. Many experimental results have shown that the combination of CNTs offers an attractive route to introduce new mechanical properties. The use of CNTs/polymeric biomaterial composites as scaffolds for bone engineering has recently become a subject of interest. Scaffolds for tissue regeneration require properties such as rigidity to bear external force, biodegradability and absorption, the ability to promote the adhesion and proliferation of cells, and the ability to be penetrated by blood vessels and body fluids. To date, CNTs have been used to reinforce the weak points of existing scaffold materials. In 2011, Zhang synthesized a series of poly (lactic-co-glycolic acid) (PLGA)/MWNTs composite scaffolds for tissue engineering [34]. Compared to the pure PLGA scaffold, the tensile stress of the PLGA/0.25% MWNTs scaffolds was increased by 54% (from 5.88 to 9.08 MPa), Young's modulus was increased by 8% (from 163.53 to 176.83 MPa), and the elongation at break was increased by 49% (from 27.14% to 40.39%). It is evident that even a small amount of MWNTs would significantly improve the tensile strength of the composites. Thermal characterization showed that the incorporation of MWNTs into the PLGA matrix increased the thermal stability of the composite scaffolds. After 24 hours of rat bone marrow-derived mesenchymal stem cells (BNSCs) culture, compared to the pure PLGA scaffolds, cells on the PLGA/MWNTs composites were spread more with long filopodia. In addition, cells on the PLGA/1.25% MWNTs scaffolds had started to migrate through the pores and grow inside the fiber network. The cells that came in contact with each other through filopodia integrated with the surrounding fibers to form a 3D cellular network, indicating better adhesion on the PLGA/1.25% MWNTs scaffolds. Therefore, the mechanical and biological properties of PLGA reinforced by MWNTs have improved significantly and the PLGA/MWNTs composite scaffolds fabricated by electrospinning may be potentially useful in tissue engineering applications, particularly as scaffolds for bone tissue regeneration. In 2013, Vozzi et al. microfabricated three-dimensional (3D) scaffolds by mixing PLLA and MWCNTs for bone tissue engineering [35]. In the test, their mechanical properties are measured and their biocompatibility with human fetal osteoblasts (hFOB) is studied. The 3D microfabricated PLLA/MWCNTs nanocomposite scaffolds showed higher stiffness and cell viability than the pure 3D microfabricated PLLA scaffolds. The result of nanoindentation test suggested that the presence of CNTs increased the elastic modulus. The results showed that the PLLA/MWCNTs nanocomposite structures exhibited an improvement in the mechanical properties that could be tailored through changes in the topology of the structure. Cell test showed that all of the composite films possess good cell compatibility, with a value from the viability test of higher than 75% with respect to the control (**Figure 1(a)**). At different times, the cell density statistically increased (**Figure 1(b)**), so this result suggests that the cells on the PLLA/MWCNTs scaffold were more viable. In 2013, Chen et al. synthesized Chitosan-multiwalled carbon nanotubes/hydroxyapatite nanocomposites (CHI-MWCNTs/HA) for bone tissue engineering (**Figure 2**). The mechanical properties of the composites were evaluated by measuring their compressive strength and elastic modulus [36]. The result showed that elastic modulus and compressive strength increased sharply from 509.9 to 1089.1 MPa and from 33.2 to 105.5 MPa with an increase of multiwalled carbon/chitosan weight ratios from 0 to 5%, respectively. Biological results suggested that no matter on the CHI-HA composites or on the CHI-MWNTs/HA composites with different MWNTs/CHI weight ratios, the cells were spread out and had some filopodia. Meanwhile, the cells presented fusiform and polygonal morphology. These results demonstrate that preosteoblast MC3T3-E1 cells attachment and adhesion on the surface of the CHI-MWNTs/HA composites are good and the CHI-MWNTs/HA composites possess noncytotoxicity. Using CCK-8 assay to quantify cell proliferation, the result showed that MC3T3-E1 cell proliferation on CHI-HA or CHI-MWNTs/HA surface at 7 days of culture is higher than that at 3 days of culture, indicating good in vitro biocompatibility of CS-HA and CHI-MWNTs/HA nanocomposites.Abarrategi et al. studied the use of MWCNTs/CHI scaffolds, with a well-defined microchannel porous structure, has been shown biocompatible and biodegradable supports for culture growth, which was suitable for biomedical applications [78]. Zawadzak et al. developed porous polyurethane foams coated with CNTs by depositing CNTs on the surfaces of polyurethane foams using electrophoretic deposition (EPD), with the overall objective of creating a new family of functional bone tissue engineering scaffolds with nanostructured surface topography shown in **Figure 3**. The scaffolds retained their high porosity and interconnected pore structure after CNTs coating [79]. Furthermore, the CNTs coating was thought to promote the scaffolds osteoconductivity and mineralization potential as well as provide not only a nanostructured surface but also an electric conductivity function, suggesting that the polyurethane foams with CNTs coating have the potential to be used as bioactive scaffolds in bone tissue engineering due to their high interconnected porosity, bioactivity, and nanostructured surface topography. Shi et al. [80] studied the fabrication of highly porous scaffolds made of three different materials: poly (propylene fumarate (PPF) polymer, an ultrashort single-walled carbon nanotube (US-tube) nanocomposite, and a dodecylated US-tube (F-US-tube) nanocomposite. To assess the influence of the different composition and porosity of materials on the properties of scaffolds, scanning electron microcopy, microcomputed tomography, and mercury intrusion porosimetry were used to analyze the pore structures of scaffolds. The results indicate that the good performance of the functionalized ultrashort SWCNTs nanocomposite, which is tunable porosity and mechanical properties, may be a promise candidate of the ideal materials for scaffolds applied for the bone tissue engineering applications.

4.2. Polymer Composites Reinforced by Noncarbonic Nanotubes.

The first inorganic nanotubes WSNTs were discovered in 1992 by Tenne and coworkers [81]. The study

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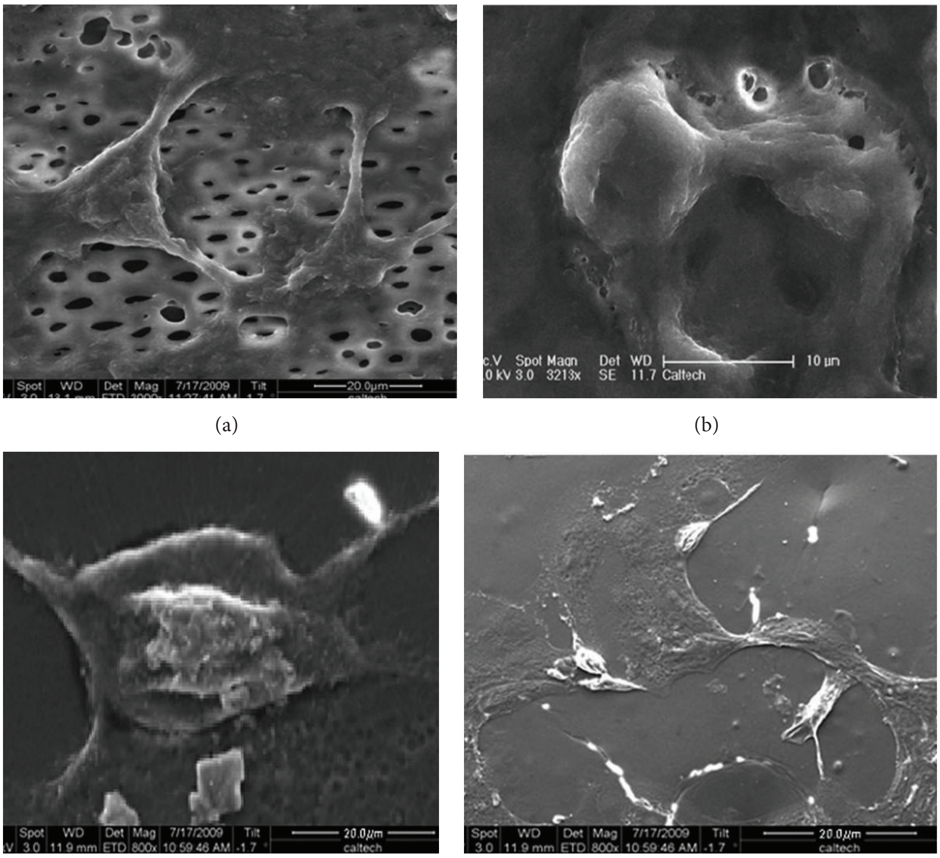

(a) (b)

(c) (d)

Figure 1: SEM micrographs of hFOB 1.19 cells cultured on the (a) PLLA/CNT spun film, (b) PLLA spun film, (c) PLLA/CNT 3D bonelike PAM scaffold, and (d) PLLA 3D bonelike PAM scaffold [35].

observed closed polyhedral and cylindrical crystals of tungsten disulphide semiconductor compound. WSNTs possess high mechanical properties (Young's modulus ≈150 GPa, bending modulus ≈217 GPa) [82, 83] and functional groups make it possible to disperse in organic solvents, polymers, epoxy, and resins [84]. In comparison to CNTs [85–93], few reports have investigated the mechanical properties of WSNTs-reinforced polymeric nanocomposites [39, 94]. Zohar et al. [39] evaluated the effect of embedding inorganic nanotubes (INT) of tungsten disulfide (WS_2) in an epoxy matrix, on the mechanical, thermal, and adhesion properties of the resulting nanocomposites and reported ≈49%, ≈39%, and ≈85% improvements in fracture toughness, shear strength, and peel strength of epoxy composites (compared to pristine epoxy controls) at 0.5 wt.% loading of WSNTs. Reddy et al. reported an ≈22-fold improvement in the elastic modulus and 30–35% improvements in the tensile strength and toughness of electrospun PMMA fiber composites (compared to pristine PMMA fiber controls) at 2 wt.% loading of WSNTs [40]. The study shows that the mechanical properties of polymeric nanocomposites can be significantly enhanced at very low loading concentrations of WSNTs. Lalwani et al. investigated the efficacy of WSNTs as reinforcing agents to improve the mechanical properties of PPF composites as a function of nanomaterial loading concentration (0.01–0.2 wt.%), compared with SWCNTs and MWCNTs, and crosslinked PPF composites [41]. TEM result showed that WSNTs (Figures 4(c) and 4(d)) existed as individually dispersed sharp needle-like nanotubes with mean outer diameter of ≈100 nm and a length of ≈1–15 lm. TEM was performed on 50–100 nm thick sections of crosslinked PPF nanocomposites to assess the dispersion of nanostructures in the polymer matrix (Figure 4). WSNTs were well dispersed as individual nanotubes. Mechanical testing (compression and three-point bending) shows a significant enhancement (up to 28–190%) in the mechanical properties (compressive modulus, compressive yield strength, flexural modulus, and flexural yield strength) of WSNTs-reinforced PPF nanocomposites compared to the crosslinked PPF composites. In general, WSNTs showed mechanical reinforcement better than (up to 127%) or equivalent to that of carbon nanotubes (SWCNTs and MWCNTs). Sol fraction analysis showed significant increases in the crosslinking density of PPF in the presence of WSNTs (0.01–0.2 wt.%). The results taken together indicate that PPF nanocomposites were fabricated at low loading concentrations (0.01–0.2 wt.%) of WSNTs towards the fabrication of biodegradable polymeric implants possessing improved mechanical properties. And none of

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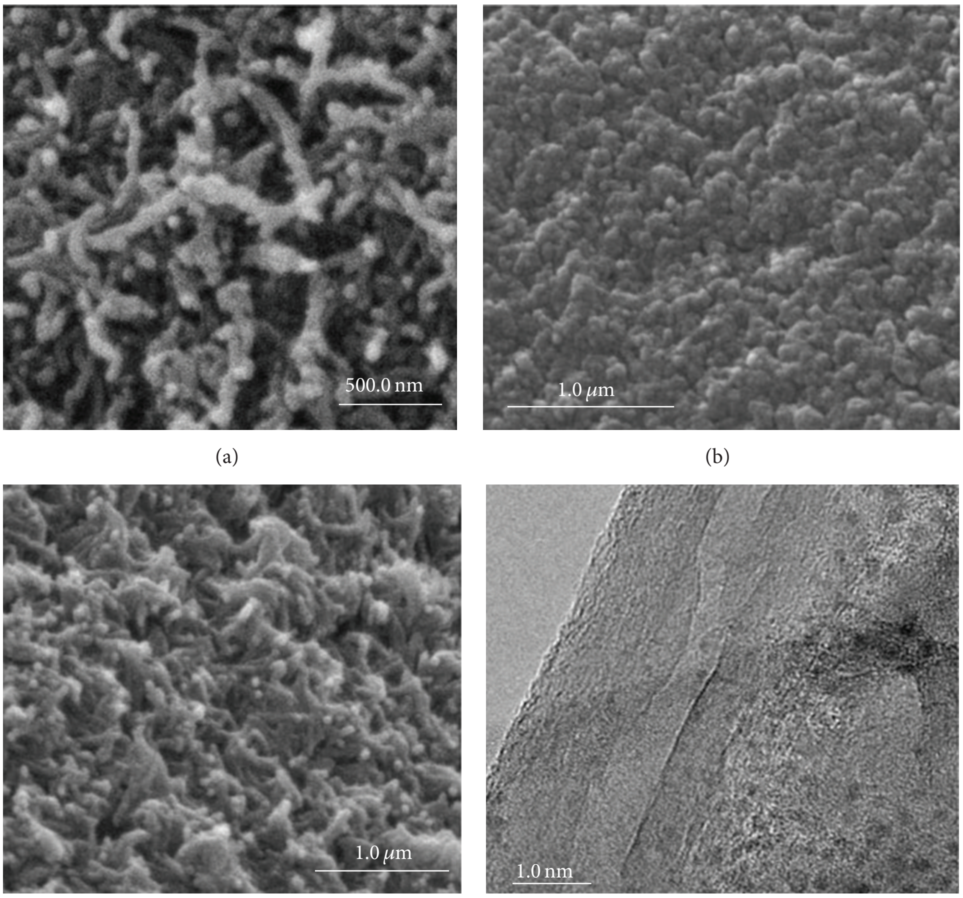

(a) (b) (c) (d)

Figure 2: SEM micrographs of (a) MWNTs, (b) the CS/HA composite, (c) the CS-MWNTs/HA composite, and (d) TEM micrographs of the CS-MWNTs/HA composites [36].

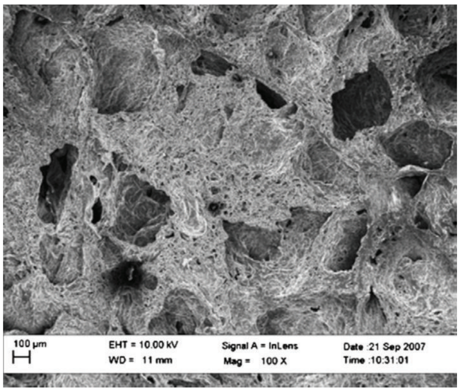

Figure 3: SEM image showing the macroscopic pore structure of a polyurethane foams coated with CNTs by EPD (deposition voltage: 20 V) [79].

these studies have focused on biomedical applications or have made direct comparisons between carbon and inorganic nanotubes as reinforcing agents.

BNNTs, other important noncarbonic nanotubes, were predicted theoretically in 1994 and they were synthesized shortly thereafter [45, 95, 96]. Boron nitride is isoelectronic to carbon and has a stable hexagonal structure analogous to that of graphite and possesses chiralities [46] (Figure 5). BNNTs have excellent elastic modulus of 1.22 TPa (similar to CNTs) and tensile strength similar to CNTs, which makes it a potential candidate as reinforcement. In addition to their structural similarity, BNNTs and CNTs have similar mechanical properties and thermal conductivity [97, 98]. However, BNNTs are distinct in several key aspects. First, BNNTs are wide band gap semiconductors whose electrical properties are independent of geometry, while CNTs may be metal or semiconducting depending on chirality and diameter. Second, BNNTs are more chemically inert and structurally stable than CNTs [99]. Hence, their reinforcement will not adversely affect the ductility of the scaffolds. BNNTs have higher chemical stability than CNTs in oxidative atmosphere, with their oxidation starting at 1223 k compared to CNTs at 773 k. The flexible and elastic nature of BNNTs and its ability to withstand heavy deformation could be helpful in preventing damage to itself during high pressure application. High temperature oxidation resistance of BNNTs is better than CNTs, which makes it more suitable for high temperature processing. BNNTs are noncytotoxic to osteoblasts and

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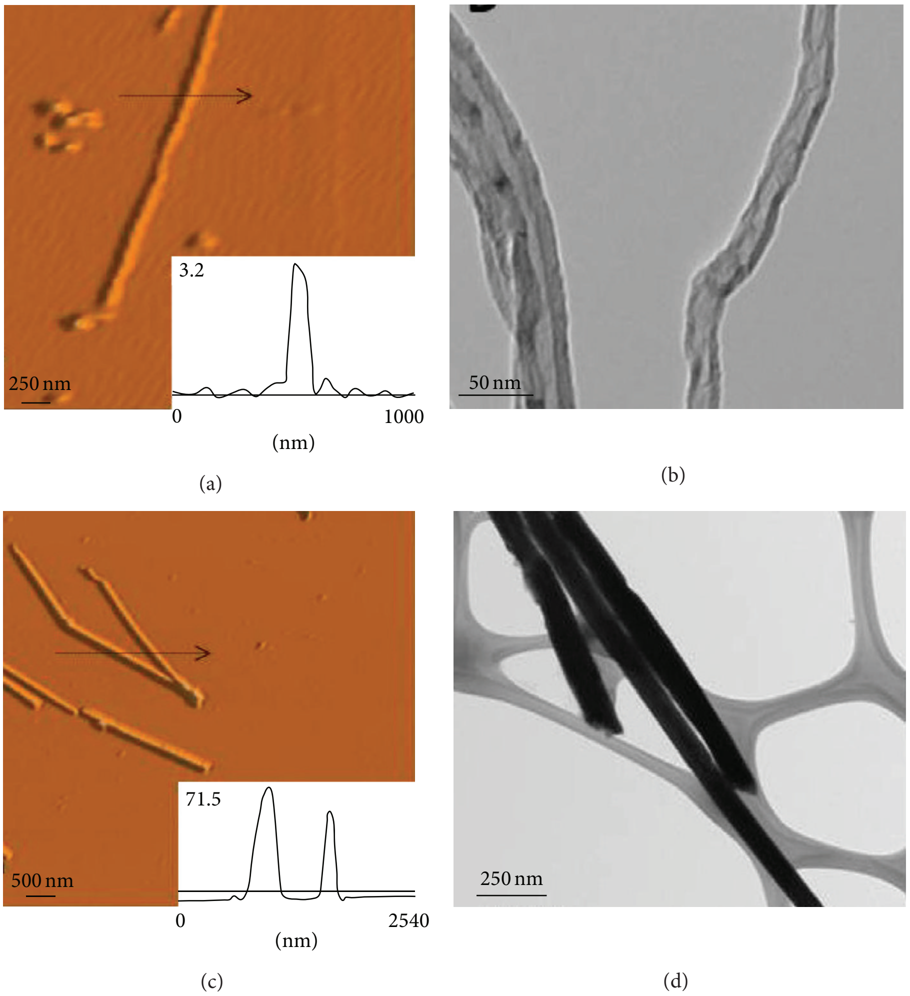

(a) (b)

(c) (d)

Figure 4: AFM and TEM images of MWCNTs ((a) and (b)) and WSNTs ((c) and (d)). The insets in (a) and (c) show the corresponding height (Z) profiles [41].

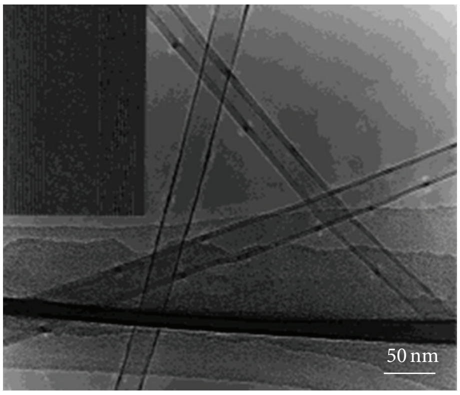

Figure 5: TEM images of BN straight cylindrical nanotubes. The inset shows the perfect ordering of BN tubular layers [46].

macrophages. BNNTs are also found to be noncytotoxic to human embryonic kidney cells and human neuroblastoma cell line. BNNTs are relatively new in the field of composites with very few studies on them being available. BNNTs-reinforced polymer composites have shown improvement in thermal, mechanical, and optical properties [37, 100–104]. In 2005, By Zhi et al. fabricated BNNTs-reinforced composites by using poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(vinyl butyral) (PVB), or poly(ethylene vinyl alcohol) (PEVA) as the matrix and their thermal, electrical, and mechanical properties are evaluated by Vickers microhardness tests [105]. More than 20-fold thermal conductivity improvement in BNNTs-containing polymers is obtained, and such composites maintain good electrical insulation. The coefficient of the thermal expansion of the BNNTs-loaded polymers is dramatically reduced comparing the breakdown electric fields of neat polymers with those of their BNNTs composites including PMMA, PS, PVB, and PEVA. Only in the case of PS dose the breakdown electric field decreases, while in the other three cases, it marginally increases. In any case, all the materials remain insulating and possess a high breakdown electric field. The Vickers hardness of PEVA, PS, and PMMA was only slightly affected when they were loaded with the BNNTs. This indicated that there is no

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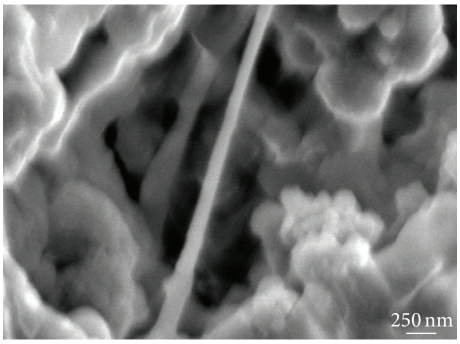

Figure 6: SEM image of the fracture surface of PLC-5BNNT composite showing polymer coated BNNTs of varying diameters [37].

obvious negative effect on the mechanical properties of the composites.

Lahiri et al. [37] studied the cytocompatibility of BNNTs reinforced polylactide-polycaprolactone (PLC) copolymer composite with osteoblasts and macrophages in vitro in 2010. The results show that the BNNTs addition to PLC enhances the tensile strength and also resulted in an increase in the expression levels of the Runx2 gene, the main regulator of osteoblast differentiation. Stress-strain behavior shows a gradual increase in the tensile strength with the addition of BNNTs from 2.67 MPa in PLC to 4.98 and 5.59 MPa for PLC-2BNNTs and PLC-5BNNTs, respectively. Tensile strength at 2.4 strain increases by 87% and 109%, with addition of 2 and 5 wt.% BNNTs, respectively. SEM images of the fracture surface of PLC-5BNNTs (Figure 6) show the BNNTs bridges within PLC matrix. Dangling BNNTs with the other end fully embedded in the polymer matrix. Cytotoxicity assay of bare BNNTs on osteoblast and macrophage cells shows that presence of BNNTs does not increase the number of dead cells and hence are biocompatible to these cells. Osteoblast cell viability study on polymer films reveals a 30% increase in live to dead cells ratio with BNNTs addition in PLC. Gene expression results indicate accelerated osteoblast differentiation and growth in the presence of BNNTs. Biodegradable PLC-BNNTs composite films, with improved mechanical properties and biocompatibility, have been successfully synthesized for their possible application in orthopedic scaffolds. In the same year, Lahiri et al. propose BNNTs reinforced hydroxyapatite (HA) as a composite material for orthopedic implant application. HA-4 wt% BNNTs composite offers excellent mechanical properties—120% increment in elastic modulus, 129% higher hardness, and 86% more fracture toughness, as compared to HA [38]. HA-BNNTs composite also showed 75% improvement in the wear resistance. Tribological behavior of HA and HA-BNNTs composite is quantified in terms of coefficient of friction (CoF) and wear volume loss. The CoF increases by ~25% with BNNTs reinforcement in HA. The presence of BNNTs decreases the wear volume loss of HA matrix by 75%. Proliferation and viability of osteoblast cells are evaluated on HA and HA-BNNTs surface after in vitro culturing for 1, 3, and 5 days. The population of the osteoblast also increases visibly from 1 to 3 days on both surfaces. This observation indicated that HA and HA-BNNTs surfaces are suitable for osteoblast cell proliferation. Population of osteoblast cells is slightly denser on HA-BNNTs surface than HA after 3 days of culture. Osteoblast proliferation and cell viability showed no adverse effect of BNNTs addition. HA-BNNTs composite is, thus, envisioned as a potential material for stronger orthopedic implants.

We summarized the properties of the polymer composites reinforced by nanotubes mentioned in this paper in Table 2.

5. Conclusion and Future Developments

In this review, we provide an overview of the research on polymer composites reinforced by CNTs and noncarbonic nanotubes. CNTs and noncarbonic nanotubes reinforced polymer composites are an emerging class of high-performance materials with unique and promising properties. CNTs and noncarbonic nanotubes reinforced polymer, in particular, aimed at taking advantage of nanotubes' superior mechanical properties as well as their high aspect ratio and surface area [106, 107]. CNTs and noncarbonic nanotubes/polymer nanocomposites have the advantage of size compatibility between their constituents. Introducing CNTs and noncarbonic nanotubes to polymer matrices modifies mechanical, electrical, thermal, and morphological properties of the produced nanocomposite. The prospect of obtaining advanced nanocomposites with multifunctional features, for example, materials used for structures and electrical conductors, has attracted the efforts of researchers in both academia and industry [108, 109]. Biomedical in particular recognizes many potential applications such as scaffolds for bone and neural tissue engineering materials [110–112].

The most commonly employed synthetic polymers for tissue engineering are biodegradable polyesters. Although they do not possess adequate mechanical stiffness to provide structural support in bone constructs, they are very easy to manufacture and process compared with biopolymers such as collagen, which are highly labile, or ceramics such as hydroxyapatite, which are difficult to melt, dissolve, or extrude. Advanced polymer-based nanocomposite materials have gained popularity for wide engineering applications which have been conducted in vitro and in vivo environments in research in the past few years. Many researches have also demonstrated the use of nanostructural materials as reinforcements to enhance the mechanical properties and thermal stability of biocompatible polymers for artificial joints and scaffolding [113–115]. To keep highly porous structure of scaffolds, which can further provide an ideal environment for the migration and proliferation of cells, they had better supply and adequate mechanical strength during the initial healing state. Moreover, it is shown that many research efforts have been directed towards producing CNTs and noncarbonic nanotubes/polymer composites for functional and structural applications [116–119].

Emergence of carbon nanotubes raises nanotube research boom, and researchers have prepared a variety of noncarbonic nanotubes. Overall, new trends appear in preparation

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Table 2: Property improvements of polymer composites reinforced by nanotubes.

	Reinforcement		Biocompatibility		Mechanical properties		References
Type	Content (%)	Matrix	Method	Improvement	Property	Percentage	
MWNT	>95 wt	PLGA	BMSCs cells culture	Improve cell adhesion and proliferation	Tensile stress	54	[34]
MWCNT	—	PLLA	Human fetal osteoblasts cells	Improve cell compatibility	Elastic modulus	67	[35]
MWNT	—	CHI-HA	CCK-8	Improve cells attachment and cell proliferation	Elastic modulus	53	[36]
BNNT	2 wt	PLC	Osteoblast cell	Accelerated osteoblast differentiation and growth	Tensile strength	87	[37]
BNNT	5 wt	PLC	Osteoblast cell	Accelerated osteoblast differentiation and growth	Tensile strength	109	[37]
BNNT	4 wt	HA	HA-BNNT to osteoblasts	Improve osteoblast proliferation and viability	Elastic modulus	120	[38]
WSNT	0.5 wt	Epoxy	—	—	Peel strength	85	[39]
WSNT	2 wt	PMMA	—	—	Elastic modulus	30	[40]
WSNT	0.01–0.2 wt	PPF	—	—	Compressive modulus	60	[41]

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of noncarbonic nanotubes which is mainly from random growth transition to controlled growth and from disorder growth transition to order growth. Evaluation of the performance will be the main theme of research in the field of noncarbonic nanotubes and exploring the causes of the growth mechanism and the peculiar physical properties are the focus of research from now on. Contacting the noncarbon nanotubes with the next generation of nanodevices also becomes future research development direction in this area.

There are still some challenges to be confronted. It has become clear that issues of dispersion, alignment, and stress transfer are crucial and often problematic at this size scale. Dispersion is often obtained by using unentangled nanotubes, high viscosities, and high shear rates. A degree of alignment has been successfully obtained using shear and elongation as well as, to a lesser extent, magnetic and electrical fields. However, the most critical factor is the production and how to achieve efficient, fast, large, and continuous production of low-cost high purity nanotube is also a need to solve practical problems, such as the progress of research on BNNTs is still limited by the poor availability of BNNT samples for widespread investigation of their properties and applications. The lack of a simple and straightforward production process has made it extremely difficult to perform an accurate biocompatibility investigation [120, 121]. Recently, new techniques have been developed to obtain high-purity BNNTs using common furnaces exploited for CNT synthesis [122, 123]. This will allow an increment of BNNT production and a more sustained availability of good samples for future biological investigations.

In conclusion, the improvement and application of these composites will depend on how effectively we can handle the challenges. The significant progress in the understanding of these composite systems within the past few years points toward a bright future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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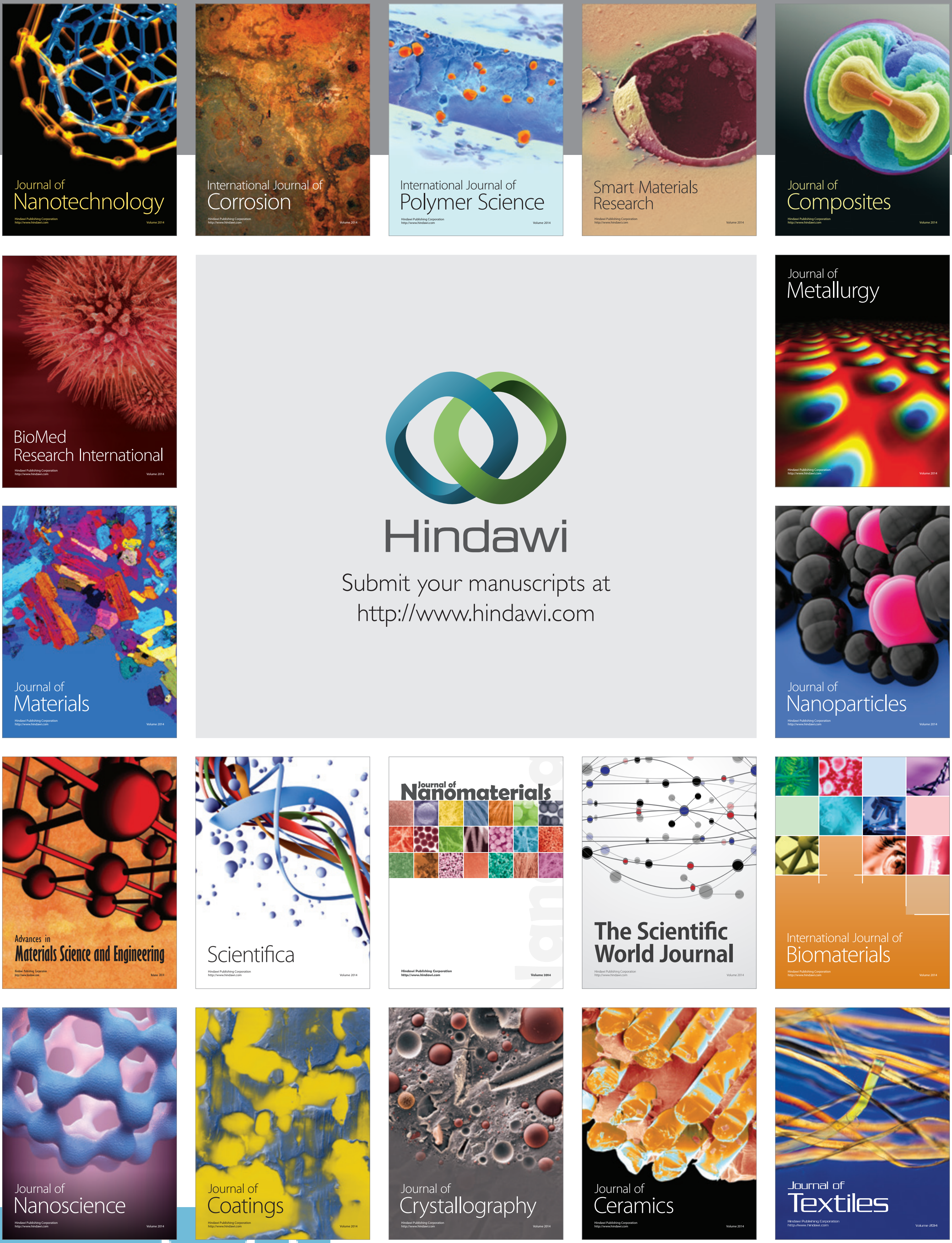

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