Research Article

Mechanical Behavior of Nanostructured Hybrids Based on Poly(Vinyl Alcohol)/Bioactive Glass Reinforced with Functionalized Carbon Nanotubes

H. S. Mansur,¹ M. M. Pereira,¹ H. S. Costa,² and A. A. P. Mansur¹

¹ Center of Nanoscience, Nanotechnology, and Innovation (CeNano) and Department of Metallurgical and Materials Engineering, Federal University of Minas Gerais, 31270-901 Belo Horizonte, MG, Brazil

² Department of Metallurgy and Material Engineering, Centro Federal de Educação Tecnológica de Minas Gerais, Avenida Amazonas 5253, Nova Suíça, 30421-169 Belo Horizonte, MG, Brazil

Correspondence should be addressed to H. S. Mansur, hmansur@demet.ufmg.br

Received 21 August 2012; Revised 26 October 2012; Accepted 6 November 2012

Academic Editor: Tianxi Liu

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This study reports the synthesis and characterization of novel tridimensional porous hybrids based on PVA combined with bioactive glass and reinforced by chemically functionalized carbon nanotubes (CNT) for potential use in bone tissue engineering. The functionalization of CNT was performed by introducing carboxylic groups in multiwall nanotubes. This process aimed at enhancing the affinity of CNTs with the water-soluble PVA polymer derived by the hydrogen bonds formed among alcohol (PVA) and carboxylic groups (CNT-COOH). In the sequence, the CNT-COOH (0.25 wt%) were used as the nanostructure modifier for the hybrid system based on PVA associated with the bioactive glass (BaG). The mechanical properties of the nanostructured hybrids reinforced with CNT-COOH were evaluated by axial compression tests, and they were compared to reference hybrid. The averaged yield stresses of macroporous hybrids were (2.3 ± 0.9) and (4.4 ± 1.0) MPa for the reference and the CNT reinforced materials, respectively. Moreover, yield strain and Young's modulus were significantly enhanced by about 30% for the CNT-COOH hybrids. Hence, as far as the mechanical properties are concerned, the results have clearly showed the feasibility of utilizing these new hybrids reinforced with functionalized CNT in repairing cancellous bone tissues.

1. Introduction

Despite the fact that materials science technology has resulted in clear improvements in the field of bone substitution medicine, no satisfactory bone substitute has been developed yet. As a result, most of the severe injuries related to bone are still unrecoverable or not adequately treated [1, 2]. Regeneration of tissue using the body's own self-healing mechanisms is an ideal approach for bone repair, which is the aim of tissue engineering, that is, to restore diseased or damaged tissue to its original state and function, reducing the need for transplants and replacements. More specifically, bone tissue engineering combines cells and a biodegradable 3D scaffold to repair bone tissue. One of the challenges in tissue engineering is associated with the development of suitable scaffold materials that can act as templates for cell adhesion, growth, and proliferation.

Bioactive glasses are important bioceramic materials and have been used for the repair and reconstruction of diseased bone tissues. Nevertheless, bioactive glasses usually have reduced mechanical properties, especially in a porous form, compared to cortical and cancellous bone. The alternative that is being considered is the development of novel composites materials and hybrid systems. In the last 3 decades, several research groups have developed a variety of biomaterials to act as synthetic scaffolds that may guide and stimulate the three-dimensional tissue growth [3–11].

Our group has been active on researching the synthesis and characterization of organic-inorganic hybrids in the system poly(vinyl alcohol)/bioactive glass (PVA/BaG) [12–15] to be used as scaffolds in tissue engineering applications. PVA/BaG have been prepared by the sol-gel process and the effect of PVA content, degree of hydrolysis, and synthesis conditions on properties of the porous scaffolds,

and on degradation kinetics have been reported [16–19]. The results have clearly shown that it is possible to tailor the hybrids mechanical properties and degradation behavior by engineering the structure of the materials. Nevertheless, the level of mechanical strength attained can be still improved by further nanostructure control and use of additional strengthening mechanisms.

Carbon nanotubes (CNTs) have been used as reinforcement of polymers due to their extremely high strength to weight ratio, with superior mechanical properties. However, it is known that the efficiency of CNTs as polymer reinforcements will depend on their chemical affinity to polymer, which may affect their dispersion in the polymeric phase, and the polymer matrix/CNT interface bonding [20].

Chemical functionalization of CNT is an effective way for preventing aggregation and allowing dispersion and stabilization in the polymer matrix. Among the several studied methods, covalent functionalization can be highlighted [21]. In general, functional COOH or OH groups can be created on CNT surface by oxidation with oxygen, air, sulfuric acid, nitric acid, or mixtures of acids [22, 23].

An increase in the amount of methods available for chemical modification and functionalization of CNTs has made possible their dispersion in water and allowed manipulation and processing in physiological environment [24, 25]. The functionalization of CNTs with carboxylic acid groups is convenient since a variety of reactions can be carried out with this chemical group [26].

Thus, to the best of our knowledge, this is the first report to synthesize and characterize novel macroporous bio-nanocomposite scaffolds designed by combining polymer (PVA) with bioactive glass (BaG) and reinforced with chemically modified carbon nanotubes. These hybrids were produced based on the reaction of the organic and inorganic precursors using the foaming method via sol-gel route and then reinforced by functionalized carbon nanotubes. The mechanical properties of the hybrids were evaluated by compression tests, and the results were analyzed considering the cancellous bone as the target promising application.

2. Materials and Methods

2.1. Synthesis of CNT Reinforced Hybrid Scaffolds. To avoid redundancy with previous researches published by our group [18, 19], the full details for the synthesis and characterization of the hybrids based on PVA and bioactive glass were not included in this study. Here, the major focus was given to the novelty associated with the effect on the mechanical properties by adding the chemically modified carbon nanotubes to the macroporous hybrid nanostructures. So, poly(vinyl alcohol)/bioactive glass (BaG) hybrid scaffolds reinforced with carbon nanotubes (CNTs) were prepared by a sol-gel foaming method, and three hybrid systems were produced: (i) hybrid with composition 70 wt.% polymer and 30 wt.% glass (PVA/BaG); (ii) hybrid with same composition, cross linked with 5% glutaraldehyde (PVA/BaG/GA); (iii) hybrid with same composition, with addition of functionalized CNT (PVA/BaG/CNT).

Purified multiwall CNTs, with 10 to 30 nm external diameter, and 1 to 2 μm length, from SES Research (USA), were functionalized with carboxylic groups before use. The chemical modification was performed by refluxing 1.0 g of CNT's in 50 mL HNO_3 14 mol·L⁻¹ for 15 h at 120°C, followed by filtration using 0.7 μm filter (AP4004700—Millipore). CNTs were then washed with DI water, until filtrate reached pH 5.5 ± 0.1 and dried for 48 hours at $60 \pm 5^\circ\text{C}$.

PVA aqueous solution with concentration 28 wt.% was prepared by dissolving PVA powder (Aldrich-Sigma with degree of hydrolysis DH = 80% and molecular weight Mw = 9,000–10,000 g/mol) in a water bath at 90°C under constant stirring, for 1 h. The pH of the solution was corrected to 2.0 ± 0.1 with hydrochloric acid (HCl) solution 2N. For preparation of the reinforced hybrids, appropriate amount of CNT was added to the PVA solution, in a proportion of 0.25 wt. (%) with respect to PVA.

The starting sol solution with designed composition 58 wt.% SiO_2 -33 wt.% CaO -9 wt.% P_2O_5 was synthesized by mixing tetraethoxysilane (TEOS), DI water, triethylphosphate (TEP), and calcium chloride in presence of hydrofluoric acid solution 2N. The water/alkoxide molar ratio used for was 12:1 (H_2O :TEOS).

An appropriate amount of the glass precursor sol was added to the PVA solution, with and without CNTs added, and the mixture was stirred for approximately five minutes. Then, a surfactant sodium laureate sulfate (SLS, Oxiteno 27% v/v) and a catalyst (HF 10% v/v) were added as foaming and gelling agents, respectively. The mixture was vigorously stirred, and the foams obtained were cast just before gelation in plastic containers, which were then sealed. All samples were aged and dried for 10 days at 40°C. Glutaraldehyde (GA, Sigma 25 wt.% aqueous solution, IUPAC: Pentane-1,5-dial) was added as bifunctional chemical modifier for the preparation of the cross-linked hybrids, in a concentration of 1.0 wt.% with respect to PVA.

2.2. Structural and Mechanical Characterization of Hybrids. For the evaluation of pore morphology and macropore size range, SEM images were taken from organic-inorganic hybrids with a JSM 6360LV (JEOL/NORAN) microscope. Prior to examination, samples were coated with a thin gold film by sputtering. Secondary electrons (SE) images were obtained by using an accelerating voltage of 10–15 kV. CNTs images were assessed using TEM (Tecnai G2-Spirit-FEI) at 120 kV. The samples were by placed onto a holey carbon grid for the TEM analysis.

FTIR spectra were obtained within the range 600–4000 cm^{-1} (Perkin-Elmer, Paragon 1000), using the attenuated total reflectance spectroscopy method (ATR-FTIR). Hybrid samples were placed on the ATR crystal prism (ZnSe), and 64 scans were acquired at 2 cm^{-1} resolution with the subtraction of background.

The mechanical behavior of the hybrids was evaluated by compression tests. Specimens were evenly cut from the most homogeneous region of the strut to form cubic blocks (approximately $10 \times 10 \times 10 \text{ mm}^3$) and tested using equipment EMIC DL 3000, with a crosshead speed of 0.5 $\text{mm} \cdot \text{min}^{-1}$ and a 2.0 kN load cell. At least five replicates

FIGURE 1: FTIR spectra of (a) CNT and (b) CNT functionalized by chemical treatment. Below the magnified spectra from 1850–1500 cm^{-1} . Inset: structures of CNT before and after carboxylic functionalization (CNT–COOH).

($n = 5$) of each hybrid system were measured, and the results averaged.

3. Results and Discussion

Several works in the literature show that carboxylic groups-modified CNTs (CNT–COOH) are very efficient as reinforcing agents in composites. In this work a treatment with HNO_3 was used to functionalize CNT with carboxylic groups. Figure 1 presents the FTIR spectra of CNT before and after the chemical treatment. In the modified CNT spectrum a band at 1745 cm^{-1} can be observed which corresponds to the stretching vibration of carboxyl groups (–COOH) introduced. This result shows that the chemical treatment used was effective to functionalize the CNTs, allowing a good dispersion of CNT's in the PVA solution and their incorporation into the composite scaffold.

In Figure 2 it presents a set of images (from Figure 2(a) to Figure 2(h)) obtained for hybrids made of PVA/BaG (Figures 2(a) and 2(c)) and PVA/BaG modified with CNT–COOH (Figures 2(b), 2(d), 2(e), 2(f), 2(g), and 2(h)). Preliminarily, the visual analysis (digital images, no magnification) has indicated that homogeneous systems were synthesized (Figures 2(a) and 2(b), BaG/PVA and PVA/BaG/CNT–COOH, resp.). It is worth noting that a remarkable color change to “black” was observed in BaG/PVA/CNT–COOH samples as compared to “white” PVA/BAG hybrids due to the CNTs incorporated into the structure but with a uniform and relatively even distribution in the material. The SEM images of the hybrids with CNTs reinforcement (Figure 2(d)) have showed that three-dimensional macropore structures were produced similar to the hybrids without CNTs (Figure 2(c)). Moreover, SEM images of PVA/BaG modified with CNT–COOH at higher

FIGURE 2: Digital (a) and SEM (c) images of porous PVA/BaG hybrid. Digital (b), SEM (d–g), and TEM (h) images of the hybrid material containing CNT–COOH. Inset (top): illustration of cancellous bone tissue macroporous structure.

FIGURE 3: Stress x strain compression curves for (a) hybrid PVA/BaG; (b) hybrid cross linked with 1 wt% glutaraldehyde (PVA/BaG/GA); (c) hybrid with addition of functionalized CNT (PVA/BaG/CNT). Inset: detail of curve at initial deformation region.

magnifications (Figures 2(e), 2(f), and 2(g)) evidenced that fairly homogeneous hybrids systems were produced where no segregation or phase separation was detected. Due to the very low dimensions of carbon nanotubes (purified multiwall CNTs, with 10 to 30 nm external diameters) they were only detected with reasonable resolution by TEM analysis as showed in Figure 2(h).

Typical stress-strain compression curves for the three hybrid systems studied are presented in Figure 3. An increase in strength is observed when the hybrid (PVA/BaG, Figure 3(a)) is cross linked with 1 wt% of glutaraldehyde (PVA/BaG/GA, Figure 3(b)). The addition of functionalized CNTs (PVA/BaG/CNT-COOH), Figure 3(c)) also led to an increase in the mechanical strength compared to the PVA/BAG hybrids, comparable to that obtained by cross linking. The average yield stress was (2.3 ± 0.9) and (4.4 ± 1.0) MPa for the PVA/BAG and CNT reinforced material, respectively, indicating an improvement of about 90%. The yield strain (Y_s) and Young's modulus (Y_m) were also enhanced by approximately 30% for the CNT-COOH hybrids as compared to not reinforced matrices (from PVA/BaG to PVA/BaG/CNT: Y_s = from 7.5 ± 0.3 to $9.6 \pm 1.1\%$; Y_m = from 0.6 ± 0.2 to 0.8 ± 0.3 MPa). These results indicate that the addition of functionalized CNTs were effective as a strengthening mechanism in PVA/BAG hybrids.

Concerning to tissue engineering applications, synthetic materials have to be properly designed to match the mechanical properties to be a suitable alternative for the replacement of cortical or cancellous bones. Thus, the hybrids produced in this work, PVA/BaG and hybrids reinforced with CNT, presented yield stress values within the range normally reported for trabecular bone [19]. Also, as a highly porous material and with 3D architecture the developed hybrid systems showed a similar trend to the trabecular bone concerning the elastic modulus.

To effectively transfer and distribute the applied load (stress), a reasonable dispersion and interface adhesion are necessary. Studies in PVA-based composites with chemically modified CNT have shown that PVA is capable of forming a crystalline coating around nanotubes, maximizing the interfacial load transfer [27–29]. This is one reason for the improved mechanical properties of hybrids when compared with pure PVA. Moreover, functionalization of CNT using HNO_3 solution promotes the addition of hydrophilic moieties to the system like carboxylic, carbonyl, and phenol groups on the surface of CNTs [22]. These groups help the interaction through hydrogen bonding between CNT and PVA molecules, both with hydrophilic character. For low concentrations of (CNT-COOH) the interaction between nanotubes is lower than their interaction with PVA

FIGURE 4: FTIR spectra of PVA/BaG (a) and PVA/BaG/CNT-COOH (b) hybrids in selected ranges of the IR spectrum: (A) 4000–600 cm^{-1} , (B) 4000–2800 cm^{-1} (Region 1), and (C) 1800–1500 cm^{-1} (Region 2). Inset: schematic illustration of hydrogen bonds formed between hydrophilic chemical groups (hydroxyls and carboxyls).

FIGURE 5: Schematic representations of the incorporation of CNT-COOH in the PVA/BaG network.

molecules, allowing their homogeneous dispersion in the PVA matrix and promotion of mechanical reinforcement of the structure [30].

As an additional supporting tool for the characterization of the hybrids, FTIR spectroscopy was performed on the samples for evaluating some of the possible interactions among chemical groups of the components of the hybrids (PVA/BaG matrices and CNTs). In Figure 4(a), it presents the typical FTIR spectra of PVA/BaG and PVA/BaG/CNT-COOH hybrids (Figure 4(A) (a) and (b), resp.). Both spectra are very similar with most bands associated with predominant chemical groups of the major components of the samples, PVA and BaG, and minor contribution from CNT-COOH due to its lower content (0.25 wt%). Nonetheless, based on a more in-depth analysis, focusing on some specific ranges of the FTIR spectra (Region 1 and Region 2, Figure 4(A)), it can be observed some relevant changes related to the addition of functionalized CNT in the hybrids, as presented in Figures 4(B) and 4(C). Essentially, in Figure 4(B), the vibrational bands ranging from 2800 to 3000 cm⁻¹ can be associated with the contribution of alkyl groups (νCH_n) from PVA. Also, bands at 3200–3600 cm⁻¹ are often related to hydroxyl groups (stretching, νOH)

present in CNT-COOH and PVA, with hydrogen bonds (OH...OH) interactions causing some “broadening” of the region in both spectra. In addition, in Figure 4(C) (1500–1800 cm⁻¹) some important contributions can be observed at 1750–1700 cm⁻¹ from carbonyl stretching of acid modified nanotubes ($\nu\text{C=O}$, CNT-COOH) and hydrogen bonds formation (bending, $\delta(\text{OH})$ OH...OH) at 1650–1630 cm⁻¹. Thus, the results have given further evidence that hydrogen bonds were formed between hydrophilic chemical groups, such as hydroxyls and carboxyls (–OH, –COOH) in the hybrids reinforced by functionalized CNT (inset Figure 4), which are expected to play a major role on the overall properties and structure of the systems produced.

In summary, the chemical modification of CNTs used in this work incorporated carboxylic groups (–COOH), giving them a partially hydrophilic character, allowing to dispersion in aqueous media, and promoting hydrogen bonding with alcohol groups (OH, PVA) and maybe with silanols (Si–OH). Figure 5 presents a schematic representation of the interactions between carboxyl-functionalized CNT and PVA hydroxyl groups (not in scale). When prepared with bioactive glass the material will also include the interactions with silanol groups from the glass phase (Figure 5, inset BaG)

resulting in a hybrid material reinforced at the nanostructural level.

4. Conclusions

The chemical treatment in nitric acid led to the functionalization of CNTs with carboxylic groups. The surface modification allowed the homogeneous dispersion of CNTs in PVA solution and in the modified hybrids produced. The average yield stress of the macroporous hybrid reinforced with CNT was (4.4 ± 1.0) MPa, 90% higher than the reference hybrid material PVA/BAG. Yield strain and Young's modulus were enhanced in about 30% for the CNT-COOH hybrids. These values are in agreement with those values reported in the literature for potential application in repairing cancellous bone tissue. In summary, this study has offered a new approach for designing engineered synthetic hybrids aiming at developing nanostructured systems with equivalent mechanical properties of bone tissues.

Acknowledgments

This research was funded by FAPEMIG/CAPES/CNPq Brazilian Agencies. The authors thank the Staff of the Center of Microscopy/UFGM for TEM/SEM analyses.

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