A novel nanocomposite designed for a new generation of biomedical bone cement and implant coatings is reported: the composite material consists of poly(methyl methacrylate) (PMMA)-modified hydroxyapatite (HA) reinforced with multiwalled carbon nanotubes (see figure). The findings suggest that 0.1% of multiwalled carbon nanotubes in the PMMA/HA nanocomposite material gives the best mechanical properties.
Hydroxyapatite Modified with Carbon Nanotube-Reinforced Poly(methyl methacrylate): A Novel Nanocomposite Material for Biomedical Applications

By Manoj Kumar Singh,* Mrs. Tolou Shokuhfar, José Joaquim de Almeida Gracio, António Carlos Mendes de Sousa, José Maria Da Fonte Fereira, Hamid Garmestani, and Said Ahzi

1. Introduction

Carbon nanotubes, because of their small dimensions and high aspect ratio, exhibit exceptional physical and chemical properties.[1–3] No other material can compete with their outstanding combination of mechanical, thermal, and electronic properties, which make them an outstanding reinforcement material for composites.[4–7] The ideal reinforcement material would impart mechanical integrity to the composite at high loadings, without diminishing its bioactivity.

Hydroxyapatite (HA) is the prime constituent of bone cements because of its ability to bond chemically with living bone tissues; this is due to its similar chemical composition and crystal structure to apatite in the human skeletal system. However, the intrinsic brittleness and poor strength of sintered HA restricts its clinical applications under load-bearing conditions.[8,9] Poly(methyl methacrylate) (PMMA) is another material commonly used as bone cement; however, its low mechanical strength makes the use of PMMA problematic. In the present work, a novel nanocomposite material was synthesized comprising multiwalled carbon nanotubes (MWCNTs), PMMA, and HA, which promises to be a superior material for biomedical applications. The selection of PMMA was made for two main reasons: i) PMMA is already used as bone cement and it is highly compatible with HA, and ii) MWCNTs are highly stable in their original form and PMMA can act as a functionalizing and linking material between them and HA.

There are two main goals when preparing the MWCNTs/PMMA/HA nanocomposite, namely: i) to obtain a homogeneous dispersion of the MWCNTs, ensuring uniform properties throughout the composite, and ii) to enhance the interaction between the MWCNTs and mixing material to achieve an appropriate level of interfacial stress transfer. The dispersion of the MWCNTs is probably the most pressing issue. The MWCNTs should be uniformly dispersed to guarantee that they are individually coated with the PMMA-modified HA composite, which is imperative in order to have an efficient load transfer to the MWCNT network. This also results in a more uniform stress distribution and minimizes the presence of loci of high stress concentration. To this purpose, the percentage of MWCNTs in the nanocomposite material should be controlled—a large amount of MWCNTs cause them to bundle up in weakly interacting tubes as a result of the van der Waals attraction,[10] and, moreover, it will decrease the interfacial interaction between the mixing material and the MWCNTs.

Having these issues in mind, a freeze-granulation technique[11] is performed to prepare a novel nanocomposite of PMMA-modified hydroxyapatite with an appropriate percent...
age of MWCNTs. By using this technique it is possible to increase material homogeneity and also enhance the dispersion of MWCNTs in the composite matrix. The phase compositions and the surface morphology of the nanocomposite material were studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and micro-Raman spectroscopy. Additionally, the determination of the elastic modulus and hardness of the nanocomposite was performed by a nanoindentation technique for a wide range of MWCNT concentrations. The tests indicate that 0.1 wt% concentration of MWCNTs in the PMMA-modified HA nanocomposite material yields the best mechanical properties. This novel nanocomposite material could be specifically used in bone cement that requires high strength and bone repair.

2. Results and Discussion

Figures 1–4 show the surface morphology of the MWCNT-reinforced samples for 0, 0.01, 0.1, and 1 wt% of MWCNTs, respectively. From the SEM observations for different concentrations of MWCNT-reinforced samples, it is clearly observed the concentration of 0.1 % of MWCNTs yields the best reinforcement for the PMMA/HA nanocomposite (Fig. 3a and b). For 0.1% MWCNT concentration, an intercalation of the PMMA/HA composite inside the MWCNT distribution does occur (Fig. 3a and b), leading to an increase in the MWCNTs’ dispersion. Below this concentration, the mutual interaction between two adjacent MWCNTs is practically nonexistent, which tends to decrease the homogeneity of the nanotubes inside the PMMA/HA matrix. Figure 2 depicts the surface morphology of the 0.01% MWCNT–PMMA/HA nanocomposite. Higher nanotube concentrations, because less PMMA/HA is available to intercalate into the MWCNT distribution, may lead to weak bonding between the PMMA/HA and MWCNTs, making the composite weak in strength. The SEM image of 1% MWCNT–PMMA/HA composite shows agglomeration of MWCNTs into bundles. This indicates that the PMMA/HA did not intercalate into the bundles. Only the outside nanotubes of a bundle can be bonded to the composite (Fig. 4).

Figure 5 illustrates the XRD patterns of PMMA, HA, and 0.1% MWCNT–PMMA/HA. It is clearly shown that the main constituent phases of the composite are crystalline HA[12,13] (Joint Committee on Powder Diffraction Standards, JCPDS card no.: 09-0432). No MWCNTs peaks were found in the XRD pattern of the 0.1% MWCNT–PMMA/HA compo-
site, most likely because detection of small percentages of MWCNTs is not possible within the sensitivity limit of XRD. Miller indices of the diffraction peaks are given in parentheses in Figure 5. PMMA, which is an amorphous polymer (Meneghetti et al.[14]), shows a broad peak[15] at a 2θ value of 13°. The shape of the most intense broad peak reflects the ordered packing of the polymer chains.[15]

The visible Raman spectra collected from the 0.1% MWCNT-reinforced PMMA/HA sample, (an SEM image of which is shown in Fig. 6a) denoted by a blue line in Figure 6b, shows several distinct features. The feature near 1773 cm⁻¹ is attributed to the C–O bonds and indicates that COO⁻ functional groups in functionalized MWCNTs interact with C–O of PMMA. [16–18] Several other peaks can also be observed at 602 (PO₃⁴), 962 (PO₃⁴), 1592 and 814 (tangential and symmetric CC₄ stretching modes, respectively), 1452 (CH bending), 1123 (C–O stretching), 1724 (–C––O stretching), and 2952 cm⁻¹ (CH stretching), which are attributable to the HA, MWCNTs, and PMMA, as indicated in the figure.[19–23]

In the present work, the nanoindentation technique is employed to study the variation of mechanical properties of a MWCNT-reinforced PMMA/HA composite with different concentrations of MWCNTs. Figure 7 displays the typical load–displacement curves[24,25] at a peak indentation load of 10 mN on the MWCNT-reinforced PMMA/HA composite; it clearly demonstrates that no cracks were formed during indentation [25,26] A considerable amount of creep strain at the peak load was found for all the samples. The holding segment at the peak load is necessary for the dissipation of creep displacement; most polymeric
biomaterials and tissues often exhibit this type of time-dependent or viscoelastic behavior.\cite{27–30}

To study the effect of nanotube dispersion in the PMMA/HA composites, hardness and elastic modulus values are needed for both small and large indentation depths. Thirty-two nanoindentation tests were carried out on each sample, and the experimental errors were \( \pm 0.60 \) GPa for the elastic modulus and \( \pm 0.05 \) GPa for the hardness. These values are presented in Figure 8 as a function of the indentation depth for PMMA/HA and its MWCNT-reinforced samples. The average hardness and elastic modulus for these composites are listed in Table 1.

It can be observed that the hardness and elastic modulus of these composites increase with increasing MWCNT content up to 0.1%. Beyond this value, as can be noted from Figure 8a, an increase in MWCNT content yields a considerable decrease of hardness.

In a previous publication,\cite{31} the authors demonstrated that there are several key requirements for an optimal fiber-reinforced, polymer-based composite system, namely: a) The fibers should be long enough so that the stress developed within them is significantly larger than the nominal stress on the composite; b) The cross-sectional area of the fiber should be as small as possible, as the strength of the fiber is inversely proportional to the square root of its maximum flaw size; therefore, for smaller cross-sectional areas, the appearance of flaws is reduced; c) The spatial arrangement of the fibers in the matrix has to be of a significant order to ensure a unidirectional, maximal reinforcement. Also self-consistent calculations lead to the conclusion that an isotropic arrangement of the fibers will result in the dilution of the reinforcement effect within the polymer matrix. Previously, the law of volumetric mixtures was used to analyze the mechanical behavior of a continuous medium of PMMA/HA with a blend of carbon nanotubes distributed in the matrix. According to the numerical calculations\cite{32} carried out, the Young modulus of the composite increases with increasing MWCNT concentration up to a concentration of around 10%. The present experimental results show that above a concentration of 0.1% a noticeable decrease of the Young modulus is clearly identified (Fig. 8b). This discrepancy may be due to the fact that the modeling did not take into account two physical phenomena, which, in view of the experiments, are important, namely: 1) the interaction between nanotubes and 2) the character of the interface between the MWCNTs and the matrix. Increasing the MWCNTs concentration up to a certain level promotes a mutual interaction between a crossed pair or a coarse mesh of nanotubes (Fig. 9).

Consequently, the set of nanotubes can act as a deformation lock, either in extensional or shear mode, giving rise to improved mechanical properties. An identical behavior was noticed by analyzing the effect of the MWCNT concentration on a PMMA matrix.\cite{33} It should be mentioned that the SEM images clearly show that after a concentration of 0.1% MWCNTs, a drop of homogeneity in the nanotubes–matrix contact occurs, giving rise to the formation of voids and internal cavities with the eventual reduction in the mechanical performance of the composite. In fact, most likely, these defects act as nucleation sites for internal crack tips and mutual link-up modes, with a fast degradation of the structure integrity and eventual breakdown. Fatigue tests were performed in artificial bones to confirm this analysis (Fig. 10). In the tests, after one million cycles, the nanocomposite of composition 0.1% MWCNT–PMMA/HA does not present any signal of crack propagation and delamination (Fig. 10a and b). But when we performed the same type of fatigue tests for PMMA-only nanocomposites, we can clearly observe delami-

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**Table 1.** Average values of hardness (H) and elastic modulus (E) for different concentrations of MWCNTs in the PMMA/HA composites.

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<tr>
<th>MWCNT Content [%]</th>
<th>0.00</th>
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<th>0.1</th>
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<td>H [GPa]</td>
<td>0.288</td>
<td>0.510</td>
<td>3.460</td>
<td>1.321</td>
<td>0.624</td>
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<tr>
<td>E [GPa]</td>
<td>5.949</td>
<td>14.022</td>
<td>69.528</td>
<td>28.08</td>
<td>10.56</td>
</tr>
</tbody>
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**Figure 7.** Typical load–displacement curves of indentations made at a peak indentation load of 10 mN on PMMA/HA nanocomposites with various amounts of MWCNT reinforcement.

**Figure 8.** Hardness (a) and elastic modulus values (b) as a function of indentation depth.
nation and cracks in Figure 10c and d, respectively.

3. Conclusion

Herein, we demonstrate a freeze-granulation technique to synthesis a novel nanocomposite of carbon-nanotube-reinforced PMMA/HA for next-generation biomedical applications. By using this method, it is possible to increase material homogeneity and also optimize the amount of MWCNTs in the PMMA/HA matrix. High-magnification SEM images (see Fig. 3) show that a concentration of 0.1% MWCNTs performs the best reinforcement for the PMMA/HA nanocomposites. The hardness and elastic modulus of MWCNT-reinforced PMMA/HA nanocomposites increase with increasing concentration of nanotubes up to around 0.1 wt%. Beyond this limit, further addition of MWCNTs to the PMMA/HA matrix yields a considerable decrease of these mechanical properties. This can be explained in terms of the nanotube-matrix contact homogeneity: a further increase of the amount of nanotubes may lead to the formation of voids and internal cavities, which can negatively impact the mechanical performance of the composite.

4. Experimental

Aqueous Dispersion of Functionalized Carbon Nanotubes: Commercially available (purity >95%, Nanocyl-3150) multiwalled carbon nanotubes with lengths of 1–5 μm and diameters of 5–10 nm were suspended in a 3:1 mixture of concentrated H2SO4 (18.4 M)/HNO3(16 M) and sonicated in a water bath for 24 h. The resulting suspension was then diluted with water, and the MWCNTs were
collected on a 100 nm pore membrane filter and washed with deionized water. The resultant functionalized MWCNTs (MWCNT–COOH) were investigated by Fourier transform IR (Nicolet AVATAR-360 FT-IR spectrophotometer) and visible micro-Raman (Jobyn Ivon T64000, λ = 514.5 nm) spectroscopies. IR spectra of COOH-functionalized MWCNTs showed the carbonyl stretching at 1729 cm⁻¹ but in Raman spectra this signal was inactive. In Raman spectra a band centered at 1300 cm⁻¹ was attributed to sp³-hybridized carbon in the hexagonal framework of the nanotube walls. This disorder mode band was enhanced as functional groups were attached to the side walls of the nanotubes [34–38] (see Supporting Information S1 and S2). Acid–base titrations [39, 40] were performed to determine the concentration of COOH in acid-treated MWCNTs. The result indicated that around 3% carbon atoms were functionalized with COOH groups.

To obtain a homogeneous dispersion of MWCNT–COOH in water, an aqueous dispersant NanoSperse AQ (http://www.nano-lab.com/dispersant-suspensions.html)—a surfactant consisting mainly of poly(oxy-1,2-ethanediyl), tetramethyl-5-decyne-4,7-diol, and butoxyethanol—was used. The typical procedure involves mixing of 100 mg of MWCNT–COOH in 100 mL of distilled water with 4 mL of dispersant, and then keeping the mixture in a ultrasonication bath for one hour. The final product has a black color and no settling of MWCNTs is evident (Fig. 11).

Freeze-Granulation Technique to Produce the Nanocomposite of PMMA and HA with Dispersed MWCNTs: The well-dispersed MWCNT aqueous mixture was obtained for four different weight percentages of MWCNTs, namely, 0.01, 0.1, 0.5, and 1%. Each solution was mixed with a composite of commercially available PMMA (high-viscosity, bone-cement purity >99%, Johnson and Johnson Co.) and HA (particle size 2–3 μm with purity >98%, Agoramat-Advanced Materials) in 1:2 ratio by weight percentage. The homogenous mixture of HA powders and PMMA were prepared by ball milling. There was no effect on HA powder size distribution during ball milling, thus, restricting agglomeration of HA powder during mixing of PMMA with HA.

The freeze-granulation technique (Power Pro Freeze-granulator L5-2, Sweden) was performed with the objective of drying the nanocomposite of MWCNT-reinforced PMMA/HA powder to preserve the material homogeneity and enhance the dispersion of the nanoparticles in the composite matrix. Figure 12 shows the schematic diagram for the step-by-step freeze-granulation procedure, which yielded the synthesis of MWCNT-reinforced PMMA/HA nanocomposite. Granules with no cavities can be formed, and, without migration of small particles, a high degree of granule homogeneity can be achieved, while mild drying avoided oxidation of the powder. Also, lower granule density and the aid of evenly distributed low concentration MWCNTs will give softer granules with a wide granule size distribution. The freeze-dried nanoparticles were then collected and finally dried in vacuum for 3 days. In order to dry any remaining liquid the nanocomposite was kept for 24 h in the oven at 40°C.

Surface Characterization: Field-emission scanning electron microscopy (Hitachi S-800, and SU-70, 30 kV) was performed to study the...
dispersion and distribution of the MWCNTs in PMMA-modified HA matrix. The phase composition and purity of the samples were investigated by using a Philips Xpert-MPDA rhodochrosite with Co Kα radiation at 45 kV and 40 mA. Room-temperature micro-Raman studies were also performed to study the integration of MWCNTs within the PMMA/HA nanocomposite material.

**Mechanical Properties:** Nanoindentation tests were performed using the MTS Nano Indenter XP with a Berkovich diamond tip. [24–26] The hardness and elastic modulus of the PMMA/HA nanocomposites with different MWCNT percentages were measured as a function of indentation depth using a continuous stiffness measurement (CSM) method. The typical nanoindentation test consists of seven subsequent steps: approaching the nanocomposite surface; determining the contact point; loading to peak load; holding the tip for 10 s at the peak load; unloading 90% of peak load; holding the tip for 100 s at 10% of the peak load for thermal-drift correction; and finally, unloading completely. The hardness and elastic modulus were obtained from the curves using the Oliver–Pharr method. [26]

Received: August 5, 2007
Revised: November 2, 2007
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