An Efficient Functionalization Method for the Multiwalled Carbon Nanotubes and Their Applications in PMMA Bone Cement

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Received: 7 April 2013 /Accepted: 14 May 2013 /Published: 30 May 2013

Abstract: In this work, an efficient procedure for the functionalization of multiwalled carbon nanotube (MWCNTs) based on nitric acid oxidation was presented. The morphologies of MWCNTs oxidized under various conditions were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The FTIR provided clear evidence for the presence of carboxylic groups (–COOH) attached to the surface of MWCNTs resulting from the acid treatment. The unfunctionalised MWCNTs (p-MWCNTs) and carboxyl functionalized MWCNTs (f-MWCNTs) were successfully applied into the Polymethyl methacrylate (PMMA) bone cement. The resultant mechanical experiment indicated that the f-MWCNTs were a promising additive to improve the compressive strength and bend strength of the PMMA bone cement. The morphology and degree of dispersion of the MWCNTs in the PMMA matrix at different scales were analyzed by SEM. Improvements in mechanical properties were attributed to the MWCNTs arresting or retarding crack propagation through the cement by providing a bridging effect into the crack, normal to the direction of crack growth. Copyright © 2013 IFSA.

Keywords: MWCNTs, PMMA, Bone cement, Mechanical properties.

1. Introduction

Since their discovery in 1991 by Iijima [1], carbon nanotubes have attracted considerable interest because of their unique physical, chemical, electronic, and mechanical properties [2]. In order to acquire the optimal performance of MWCNTs in various applications, high-purity carbon MWCNTs are indispensable. Pristine MWCNTs are generally produced along with amorphous carbon, metal particles and carbon nanoparticle clusters, particularly with a highly hydrophobic surface which seriously hindered their further applications. To date, the removal of impurities and chemical surface modification of carbon materials often processed in the strong oxidant (e.g. HNO₃, HCl or mixtures of H₂SO₄/HNO₃) [3, 4], in which a large amount of acid or a long time of refluxing were used, let alone afterwards wash and separation with high-speed centrifugation. Herein, we report an efficient and simple procedure for the functionalization of MWCNTs based on nitric acid oxidation to overcome the mentioned drawbacks existed in traditional methods.
In the past few decades, the polymethylmethacrylate (PMMA) bone cement is extensively used for primary cemented arthroplasty and orthopaedic surgery [5-7]. Approximately 50 % of all orthopedic implants utilize PMMA-based bone cement to achieve implant fixation [8], such as total hip and total knee replacements (femoral and acetabular parts), etc, where it plays a vital load-bearing function, generating a layer between the artificial polymeric components and the surrounding bone. It is well documented that PMMA bone cement is sensitive to fatigue-related cracking and impact-induced failure [9]. Active or overweight patients with implants fixed with PMMA bone cement are at the risk of cement mantle failure, which occurs in 5 % of all total joint replacement patients by 10 years postoperatively [10]. Failure rates of 67 % have been recorded after 16 years in patients less than 45 years old.

There is a lot of literature reporting methods for improving the mechanical properties of PMMA bone cement. These studies have incorporated various additives into the polymer matrix with the aim of improving mechanical properties. The use of these additives has been less effect due to the poor fibre–polymer matrix bonding, dispersion and distribution. The incorporation of MWCNTs into polymers has been used to improve mechanical properties and to retain the structural capabilities of the polymer matrix. Jin [15] et al. studied multi-walled carbon nanotube/poly(methyl methacrylate) composites fabricated by melting blending and found that the nanotube was well dispersed in the polymer matrix and the storage modulus of the composites was significantly increased. Marrs [10] investigated the influence of MWCNTs in PMMA-based bone cements. They reported moderate improvements (13 % – 24 %) in the static properties when 2 wt% MWCNTs were incorporated into the methyl methacrylate–styrene cement. Marrs also reported significant improvements (>300 %) in the dynamic properties when MWCNTs (2 wt%) were added to the same bone cement. However, these studies used non-clinically relevant methods to ensure optimal dispersion of the MWCNTs into the bone cement. The uniform distribution of MWCNTs within the polymer matrix is critical for maximizing the interfacial bond between the MWCNTs and polymer matrix and therefore achieving optimal improvements in mechanical properties.

In this work, we presented an efficient procedure for the functionalization of MWCNTs based on nitric acid oxidation. PMMA/MWCNTs bone cement nanocomposites with a weight loading of 0.6 % were prepared using 2 different methods of MWCNTs incorporation. The mechanical properties of the resultant nanocomposite cements were characterized in accordance with the international standard for acrylic resin cements. The morphology and degree of dispersion of the MWCNTs in the PMMA matrix at different scales were analyzed using scanning electron microscopy.

2. The Functionalization of MWCNTs

2.1. Experiment Materials and Instruments

The MWCNTs synthesized by Chemical Vapor Deposition (CVD) with a length of 5-15 μm (purity > 95 %, outer diameter 40-60 nm) were purchased from Shenzhen Nanotech Port Co., Ltd. The pristine MWCNTs will be referred as p-MWCNTs, and the functionalized MWCNTs will be referred as f-MWCNTs. The concentrated HNO3 (65–68 wt.%) were purchased from Jinan Le Qi Chemical Reagent Co. Ltd.

The MWCNTs was studied by the following instruments: magnetic stirring apparatus with a temperature controller and a propeller-type agitation system (51450-xx); Thermal gravimetric analyzer (SDT Q600 V8.3); Fourier transform infrared spectroscopy (Nicolet Magna-IR Spectrometer 550, the spectra were run on KBr pellets containing 1 wt.% of MWCNTs sample which were dried in air at 200 °C for 24 h); scanning electron microscopy (SEM, JEOL JSM-7600F); Universal material testing machine (LR10Kplus).

2.2. Purification of MWCNTs

Removal of amorphous carbon, metal catalyst and surface functionalization of MWCNTs were achieved in one-step as follow: MWCNTs (1 g) and 100 ml concentrated HNO3 (65–68 wt.%) were poured into a three-necked flask (250 ml). The MWCNTs were refluxed at the temperatures of 120 °C, 160 °C, 200 °C for several hours, respectively. And then, transfer the solution into a wide mouth dish to evaporate the acid and solution, rather than traditional high-speed centrifugation because the used acid is a highly volatile; therefore it is unnecessary to centrifugation. Finally, black piece of powders were obtained and immersing them in de-ionized water for several times to remove dissolved impurities.

2.3 MWCNTs Characterization

2.3.1. Thermal Stability of MWCNTs

The TGA profiles measured in flowing air for p-MWCNTs and f-MWCNTs are shown in Fig. 1, where the samples were heated at a heating rate of 10 °C/min. The figure shows the metal impurities in the f-MWCNTs have been completely removed at 700 °C, however, the residues of p-MWCNTs accounts for about 4 %.

2.3.2. Fourier Transform Infrared Spectroscopy

FTIR spectra were obtained at room temperature in the transmittance mode. The samples were ground
with KBr and pressed into pellets. The FTIR spectra for the p-MWCNTs and f-MWCNTs are shown in Fig. 2.

![Fig. 1. TG analysis of p-MWCNTs and f-MWCNTs.](image1)

In the spectrum of p-MWCNTs, the main feature observed at 1580 cm\(^{-1}\) is characteristic of the stretching of C=C bonds, related to the expected nanotube phonon modes. The structure at 3440 cm\(^{-1}\) can be assigned to vibrational modes of the –OH groups, indicating the presence of functional groups even in the raw material. In the spectrum of the acid treated material, all those bands are enhanced, including a feature at about 1210 cm\(^{-1}\) that was not well defined in the spectrum of the raw material. The strong absorption band appearing at 1717 cm\(^{-1}\) is related to the carboxylic group (–COOH) vibrations. These results show that the acid treatment is responsible for an increase in the functionalization of the nanotubes.

### 2.3.3. The SEM of MWCNTs

Fig. 3 shows the SEM images of the p-MWCNTs (Fig. 3 a) and f-MWCNTs (Fig. 3 b–e) oxidized at various temperatures viz 120 °C, 160 °C and 200 °C for 4 hours. Initially, the raw MWCNTs have a very broad length distribution bearing very high average length as shown in Fig. 3a. MWCNTs oxidized at 120 °C have a larger diameter distribution, starting from 100 to 1000 nm in length (Fig. 3b). However, comparatively thin and short was observed for the oxidation conditions at 160 °C (Fig. 3c) with increasing oxidation temperature. This result indicated that MWCNTs were damaged during oxidation and became shorter. For the oxidation at the temperatures of 200 °C by the oxidation time of 4 hours (Fig. 3d) and 6 hours (Fig. 3e), the length distributions are nearly identical and no significant changes were observed.

![Fig. 2. FTIR spectra of p-MWCNTs and f-MWCNTs.](image2)

![Fig. 3. SEM images of p-MWCNTs and f-MWCNTs.](image3)

The effects of refluxing temperature during oxidation of MWNTs on properties of nanotubes were investigated. In this research, the changes in length of MWNTs was systematically monitored for various oxidation temperatures and refluxing time. The average length of MWNTs decreased dramatically with increase in the temperature of oxidation. The purification process applied in this work results in a high quality MWCNTs material. The controlled surface modification of MWCNTs was successfully performed by means of a HNO3
hydrothermal functionalization method and the present study allows to draw the following conclusions:

(1) A controlled functionalization using the described HNO₃ hydrothermal method can be achieved by setting with precision the temperature. Fig. 3 shows the best reflux temperature is 200 °C.

(2) The observed dependency in temperature suggests that activation energy is controlling the functionalization process.

(3) The length of MWNTs decreased dramatically when the refluxing time and temperature were increased. The optimal reflux time is 4 hours.

3. Experiment of the PMMA / MWCNTs Bone Cement

3.1. Materials and Preparation of the Bone Cement

The bone cement used was Radiopaque bone cement containing gentamicin (Biomet Orthopaedics Switzerland GmbH), which comprised of PMMA powder (40.8 g) and methyl methacrylate (MMA) liquid monomer (20 mL) (Table 1).

| Table 1. Composition of PMMA bone cement. |
|----------------|----------------|----------------|
| Constituent     | Mass (g)       | Volume (ml)    |
| Polymethyl methacrylate (PMMA) | 33.6           |                |
| Benzoyl Peroxide (BPO)      | 0.3            |                |
| Zirconium dioxide          | 6.1            |                |
| Gentamicin sulphate         | 0.8            |                |
| Methyl Methacrylate (MMA)   | 19.73          |                |
| N,N-dimethyl-p-toluidine (DmpT) | 0.27         |                |

The PMMA bone cement is created by mixing the solid (powder) components with the liquid, usually in the ratio 2 g powder/1 ml liquid. Basically, PMMA bone cement contains two portions: the powder portion including PMMA and initiator (e.g. benzoyl peroxide, BPO); the liquid portion including methylmethacrylate (MMA) monomer and promoter (e.g. N,N-dimethyl-p-toluidine, DmpT). When the two portions are mixed, the initiation is activated by promoters that make the free radicals (initiators). The free radicals react with monomers for polymerization [16].

MWCNTs (0.6 wt%) were incorporated into the precursors prior to mixing the PMMA powder and MMA monomer. The different MWCNTs were incorporated into the bone cement using one of the following methods: (i) magnetically stirring the MWCNTs in the MMA component for 24 h at room temperature; (ii) dispersing the MWCNTs in the MMA monomer using an ultrasonic disintegrator.

Subsequently, the bone cements were mixed under ambient conditions according to the manufacturer’s instructions. Once mixed the bone cement was injected into the appropriate mould.

Specimens for mechanical testing were prepared by injecting the bone cement into a PTFE mould, which were cured for 24 h. Subsequently, the rough specimen edges were removed by sanding with 1200 μm grit silicon carbide abrasive. Specimens for measuring compressive properties were in the form of cylinders of 12 mm length and 6 mm diameter. The specimens for quantifying the bend properties were in the from of rectangular bars of 75 mm in length, 10 mm in width and 3.3 mm in thickness.

3.2. Mechanical Properties

The mechanical properties of each bone cement mix were determined in accordance with ISO 5833. All tests were conducted using the Lloyds materials testing machine operating at a crosshead speed of 5.0 mm/min. Each compressive specimen was tested to failure. The bend strength for each specimen was determined using a four point bend test arrangement. The load and deflection at mid-span were recorded to failure for each specimen. The mechanical properties are summarized in Table 2 for the control cement and the PMMA/MWCNTs bone cements incorporating functionalised and unfunctionalised MWCNTs.

| Table 2. The data from mechanical studies (Mean±SD) of control, unfunctionalised, carboxy1 functionalised MWCNTs loaded cements. |
|----------------|----------------|----------------|---------------|---------------|
| Cement type    | MWCNTs type    | Mechanical property |
|                |                | Compressive     | Bend          |
|                |                | Strength (MPa)  | Strength (MPa) |
| Control        |                | 74.6±2.5*       | 51.2±2.6*     |
| Magnetic stirring | Unfunctionalised | 76.6±2.3*       | 53.2±2.3*     |
| Ultrasonic disintegration | Unfunctionalised | 80.6±2.1*       | 54.1±2.4*     |
| Magnetic stirring | Functionalised | 88.8±2.1*       | 68.2±2.3*     |
| Ultrasonic disintegration | Functionalised | 92.9±2.2*       | 74.1±2.2*     |

*denotes $p$-values < 0.01, indicating a statistically significant difference between control cement and other cements tested.

*denotes $p$-values < 0.01, indicating a statistically significant difference between magnetic stirring (p-MWCNTs) and other cements tested.

*denotes $p$-value < 0.01, indicating a statistically significant difference between ultrasonic disintegration (p-MWCNTs) and other cements tested.

*denotes $p$-value < 0.01, indicating a statistically significant difference between ultrasonic disintegration (f-MWCNTs) and other cements tested.

*denotes $p$-value < 0.01, indicating a statistically significant difference between magnetic stirring (f-MWCNTs) and other cements tested.
The addition of p-MWCNTs into the cements using magnetic stirring did not have a wholly positive effect on the mechanical properties of the resultant cement. Improvements in the compressive strength (≈2.6%; p-value < 0.01) and bend strength (≈1.8%) were observed compared with the control. Incorporating the p-MWCNTs into the monomer using sonication improved the compressive strength (≈8%; p-value < 0.01) and bend strength (≈5.8%). On the contrary, the incorporation of f-MWCNTs into the bone cements presented obvious reinforcement of the mechanical properties of the PMMA/MWCNTs bone cement. By the magnetic stirring, the compressive strength (≈19%; p-value < 0.01) and bend strength (≈33%) were observed compared with the control, and by ultrasonic disintegration, the improvements in compressive strength (≈24.5%) and bend strength (≈45%; p-value < 0.01) were noted compared with the control cement.

As shown in Fig. 4 and Table 2, we observed that surface modification of the MWCNTs with carboxyl groups could significantly improve the compressive and bend properties of the PMMA/MWCNTs bone cement, especially by the ultrasonic disintegration.

![Magnetic (p-MWCNTs)](image1.png) ![Ultrasonic (p-MWCNTs)](image2.png) ![Magnetic (f-MWCNTs)](image3.png) ![Ultrasonic (f-MWCNTs)](image4.png)

**Fig. 4.** The fracture surface of the PMMA/ MWCNTs bone cement.

The results of this study demonstrated that adding MWCNTs (0.6 wt%) to the polymer powder or liquid monomer components, prior to cement mixing with a proprietary mixing system, improved the mechanical properties of the resultant cement, provided the appropriate method for incorporating the MWCNTs was used. This is a significant finding because mechanical failure of the bone cement mantle remains a major problem in joint replacement surgery.

4. Conclusions

The surface modification of MWCNTs was successfully performed by means of a HNO₃ hydrothermal functionalization method. The result showed the best reflux temperature is 200 °C and the optimal reflux time is 4 hours. Incorporating 0.6 wt% f-MWCNTs to PMMA bone cement enhanced the compressive strength and bend strength of the resultant nanocomposite, provided the appropriate method for incorporating the MWCNTs was used. This is a significant finding because mechanical failure of the bone cement mantle remains a major problem in joint replacement surgery. The extent of the effect depended on the type of MWCNTs, method of introduction used and the properties being quantified. Improvements in mechanical properties were attributed to the MWCNTs being well dispersed within the PMMA cement, thereby arresting/retarding crack propagation through the cement.

Acknowledgments

The authors would like to thank all editors for their help with the paper proofreading. This study was carried out with financial support from the National Natural Science Foundation of China (50779032), Postdoctoral Foundation of China (20090451330) and Shandong Province Natural Science Foundation Project (ZR2010EM024).

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Sensors & Transducers, Vol. 21, Special Issue, May 2013, pp. 36-41


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