

## Detecting the Thermal Properties of Bone Cement by Temperature Sensor

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**Abstract:** Polymethylmethacrylate-based (PMMA) bone cements containing functionalized carbon nanotubes (CNTs) were prepared, and the thermal properties of the resultant nanocomposite cements were characterized in accordance with the international standard for acrylic resin cements. The aim of this study was to determine the peak temperatures during the polymerization reaction in PMMA bone cement by thermocouple (temperature sensor). The CNTs were uniformly dispersed in the cement matrix. The setting time of the cement increased and the maximum temperature during exothermic polymerization reaction was effectively reduced by the incorporation of functionalized CNTs. This reduction decreased thermal necrosis of the respective nanocomposite cements, which probably could reduce the hyperthermia experienced in vivo.

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**Keywords:** PMMA, Thermal properties, Thermocouple, CNTs.

### 1. Introduction

Polymethylmethacrylate-based (PMMA) bone cements have been extensively used in orthopaedic surgery for 40 years [1, 2], such as hip implants (femoral and acetabular parts), knee implants [3], etc. The polymerization of PMMA bone cement is a highly exothermic chemical reaction. As a consequence of mixing the polymer powder and liquid monomer constituents, the dough viscosity and temperature of the cement increases [4]. The level of polymerization heat generated is about 57 kJ per mole of methyl methacrylate [5]. Though the highest temperature measured during the polymerization reaction is only exhibited for a short period (1–2 s), it has been reported that these peak temperature could give rise to thermal necrosis, which is the key factor for aseptic loosening of an implant fixed with PMMA bone cement [6].

There are a lot of studies [7-10] for reducing the heat generated during the polymerization reaction of

PMMA bone cement. Many of these studies have incorporated various additives into the polymer matrix with the aim of decreasing the peak temperature, such as, polyethylene fibres, glass fibres, long macroscopic carbon fibres, and titanium fibres [11]. Due to the poor fibre-polymer matrix bonding, increased viscosity, poor additive dispersion and distribution, the use of these additives have been less than successful [8].

Carbon nanotubes (CNTs) are promising materials for many potential applications due to their remarkable structure, mechanical, electrical, and thermal properties. Nowadays, the incorporation of CNTs into polymeric matrices is a vast area of study and research [12].

Xie [13] reported a significant improvement ( $\approx 125\%$ ) in the thermal conductivity of an epoxy based polymer when SWCNTs (1 wt%) were added. Choi [14] also observed an increase ( $\approx 300\%$ ) in the thermal conductivity of an epoxy polymer when SWCNTs (3 wt%) were added. It has also been

reported that alignment and optimum dispersion of CNTs is important in the context of improving the thermal properties of a nanocomposite [13]. The CNTs must create a well dispersed, overlapping network facilitating the transport of heat energy.

However, the hydrophobic and inert nature of the surface of pristine CNTs is unfavorable for these applications. Therefore, it is necessary to improve the dispersibility of CNTs in a variety of solvents and polymer matrices by modifying the surface, either chemically or physically. For PMMA bone cement composites applications, CNTs functionalization is needed to improve dispersion as well as to promote interfacial bonding. Wet chemical oxidation is recognized as an efficient way for CNTs functionalization, promoting dispersion and surface activation at the same time [15]. Oxygen-containing functional groups (OH, C=O, and COOH) are anchored on the surface of CNTs by strongly oxidizing media such as ozone, oxygen plasma, or, most frequently, nitric acid. However, one of the main drawbacks of acid oxidation methods is the occurrence of CNTs fragmentation and defect generation in the graphitic network [16]. Therefore, we try to find a compromised method between the functionalization parameters (acid concentration, treatment time) and CNTs damage, and it seems reasonable to assume that there exist sufficiently mild experimental conditions that can lead to successful functionalization without significant CNTs damage.

In this study, CNTs/PMMA bone cement nanocomposites were synthesized using surface functionalized CNTs (f-CNTs). We used a temperature sensor to determine the peak temperatures during the PMMA cement polymerization reaction with the international standard for acrylic resin cements [17].

## 2. Materials and Methods

### 2.1. Materials

CNTs (with 20–40 nm in outer diameter and > 95 % purity) were purchased from Shenzhen Nanotech Port Co., Ltd, which were synthesized via chemical vapor deposition. The pristine CNTs will be referred as p-CNTs, and the functionalized CNTs will be referred as f-CNTs. The concentrated nitric acid (65–68 wt.%) were obtained from Jinan Le Qi Chemical Reagent Co. Ltd. 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). The PMMA bone cement is created by mixing the solid (powder) components with the liquid in accordance with ISO 5833 [17], usually in the ratio 2 g powder /1 ml liquid.

### 2.2. Functionalization of the CNTs

For functionalization, 0.5 gram of p-CNTs were added to 100 mL concentrated HNO<sub>3</sub> in a round bottom flask, equipped with reflux condenser, magnetic stirrer (400 rpm) and a thermometer which was fixed in the preheated oil bath. Then the mixtures were refluxed at preconcerted temperatures of 80 °C, 120°C and 160°C with refluxing time 2 h, respectively. Subsequently, the HNO<sub>3</sub> were distilled at ambient environment. This procedure could lighten the post-treatment. Following, the samples were filtered using a 0.1 µm size polytetrafluoroethylene membranes and were washed by deionized water until the pH value was about 7, and were dried at 200 °C for 12 h.

### 2.3. Characterization of the CNTs

The presence of functional groups on the carbon nanotubes was assessed visually by means of the time required to sediment in a polar solvent. For this experiment, 5 mg of CNTs were sonicated (ultrasonic bath) in 15 ml water for 10 min. Then, the CNTs solution was removed from the bath and the time required for the CNTs to sediment was monitored.

FT-IR spectra were obtained on KBr discs containing a very small amount of the functionalized CNTs. The FT-IR analysis was conducted with a Nicolet-Protege 460 in the spectral range from 4000 to 600 cm<sup>-1</sup>.

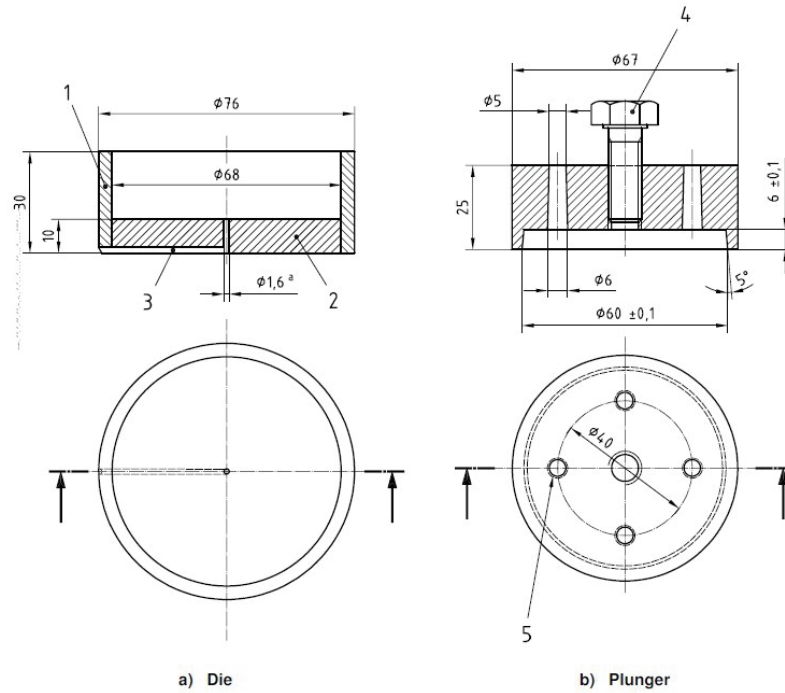
Properties of p-CNTs and f-CNTs samples were characterized by Scanning electron microscope (JEOL SEM JSM 6460 LV Japan, 2003), which was used for analysis of the CNTs morphology.

### 2.4. Apparatus and Procedure to Fabricate the CNTs/PMMA Bone Cement

The exothermic reaction occurs when the powder and liquid components are mixed, and the peak temperature attained by the bulk is recorded. The setting time is defined as the time taken to reach a temperature midway between ambient and maximum. Four units of cement are tested.

#### 2.4.1. Apparatus

The dimensions of mould and plunger are shown in Fig. 1. The mould was made of polytetrafluoroethylene, poly, polyoxymethylene, or high density polyethylene, equipped with a thermocouple of wire diameter approximately 0.5 mm, positioned with its junction (3±0.5) mm above the internal surface of the mould base. The thermocouple and converting device has the ability to convert the thermocouple output signal into temperature readings and making a continuous record of temperature [17].



**Fig. 1.** Mould for determination of maximum temperature and setting time.

**Key**

- 1 outer ring;
- 2 bottom;
- 3 channel for thermocouple;
- 4 optional polymer screw of any suitable size to aid removal of test specimen;
- 5 four tapered holes for extrusion of excess material;

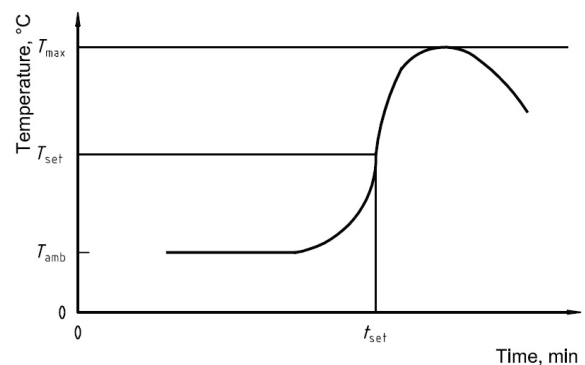
## 2.4.2. Experimental Procedure

- 1) Record the ambient temperature from the thermocouple in the mould;
- 2) Mix all the components of a single unit of cement following the manufacturer's instructions;
- 3) Start the timing device as soon as the powder and liquid come into contact;
- 4) Fill the mould with approximately of cement immediately after the mixing is completed. Seat the plunger in the mould and clamp the plunger with clamp to ensure a constant volume. A reinforcing polymer plate may be used along the bottom of the die to prevent warping of the die during polymerization and expansion of the cement. Trim off any cement expelled from the mould;
- 5) Continue the temperature measurement until shortly after the temperature begins to fall.

## 2.4.3. Calculation and Expression

For each unit of cement, plot the recorded temperatures against time, and record the highest temperature attained to the nearest 1 °C as the maximum temperature for the sample. An example of a plot is shown in Fig. 2. Calculate the average value for the four determinations. Round the result to the

nearest 1 °C and record this as the maximum temperature.



**Fig. 2.** Typical curve for determination of maximum temperature and setting time.

For each unit of cement, determine from the plot made in last step. The setting time,  $t_{set}$ , measured from the beginning of mixing until the temperature of the polymerizing mass reaches the setting temperature  $t_{set}$  defined as equation (1) (as given in ISO 5833 - 2002.) [17]:

$$t_{set} = \frac{1}{2}(T_{max} + T_{amb}) \quad (1)$$

where

$T_{amb}$  is the recorded ambient temperature;

$T_{max}$  is the highest temperature attained.

Record the value of  $t_{set}$  to the nearest 5 s. Calculate the average value of  $t_{set}$  for the four determinations. Round the result to the nearest 15 s, and express this as the setting time.

### 3. Results and Discussions

#### 3.1 Infrared Spectroscopy of CNTs

FT-IR was conducted on pristine and functionalized CNTs and their corresponding spectra are shown in Fig. 3. For the p-CNTs, the IR spectrum shows important absorption bands at  $3436\text{ cm}^{-1}$  (assigned to OH stretching),  $2921$  and  $2960\text{ cm}^{-1}$  (attributed to asymmetric and symmetric  $\text{CH}_2$  stretching),  $1631\text{ cm}^{-1}$  (corresponding to conjugated  $\text{C}=\text{C}$  stretching), and  $1097\text{ cm}^{-1}$  (assigned to  $\text{C}-\text{O}$  stretch in alcohols). The presence of these functional groups on the untreated CNTs implies that they were introduced during the proprietary production and/or purification (manufacturing) processes. Fig. 3 also shows that after the oxidation treatments, the same infrared absorptions remained although there were changes in intensity and, in some cases, new peaks arose. After oxidation, the f-CNTs exhibited the bands with the addition of a major intensity band at  $1714\text{--}1726\text{ cm}^{-1}$ , which can be assigned to stretching vibrations of carbonyl groups ( $\text{C}=\text{O}$ ) present in carboxylic acids ( $\text{RCOOH}$ ). The high intensity of this band indicates that the oxidation process was completed under these oxidation.

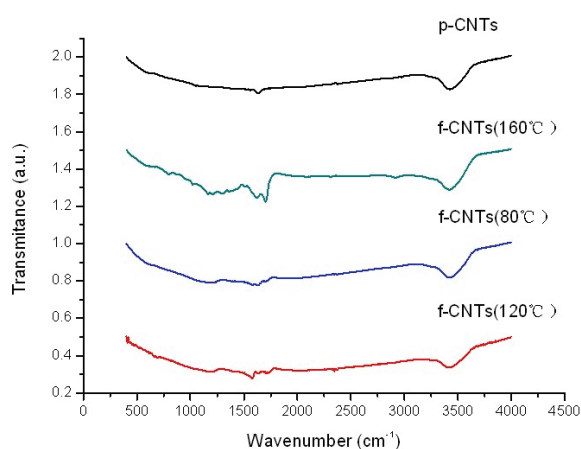


Fig. 3. FT-IR spectra of pristine p-CNTs and oxidized f-CNTs.

In addition, the broad shoulder band in the  $2800\text{--}3500\text{ cm}^{-1}$  region is attributed not only to the presence of hydroxyl and carboxylic groups but also to the traces of water in the KBr discs that was used for the analysis, which is inaccessible to be fully removed.

#### 3.2. SEM of CNTs

The morphology of pristine CNTs as well as those treated with  $\text{HNO}_3$  were investigated by scanning electron microscopy, as shown in Fig. 4. Fig. 4 shows the best reflux temperature is  $120\text{ }^\circ\text{C}$ .

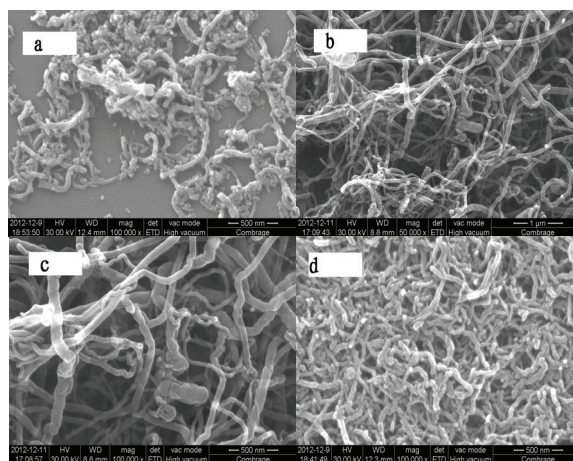


Fig. 4. SEM images of p-CNTs and oxidized CNTs at various oxidation temperatures and time: (a) p-CNTs, (b) 2 h  $80\text{ }^\circ\text{C}$ , (c) 2 h  $120\text{ }^\circ\text{C}$ , (d) 2 h  $160\text{ }^\circ\text{C}$ .

#### 3.3. Thermal Properties of CNTs/PMMA Bone Cement

Adding  $0.2\text{ wt}\%$  CNTs to cement led to a significant reduction in the extent of the polymerization reaction (Table 1). For each specimen determined, the results were evaluated for statistical significance using an one-way analysis of variance with  $p < 0.05$  denoting significance. Post hoc tests were conducted using the Student-Newman-Keuls and Duncan methods (SAS 8.02; SAS Institute, USA). Mixing the pristine CNTs into the liquid monomer using magnetic agitation produced the greatest reduction ( $p\text{-value} < 0.001$ ) in the degree of polymerization, with the  $T_{max}$  value reduced by  $\approx 17\%$  and the  $t_{set}$  value increased by  $\approx 61\%$  when compared to the control specimen. Observing the thermal properties for the functionalized CNTs/PMMA cements, it can be noted that adding the CNTs at various oxidation temperatures ( $80\text{ }^\circ\text{C}$ ,  $120\text{ }^\circ\text{C}$ ,  $160\text{ }^\circ\text{C}$ ) to the liquid monomer followed by magnetic stirring significantly ( $p\text{-value} < 0.001$ ) reduced the  $T_{max}$  ( $\approx 33\%$ ,  $\approx 48\%$ ,  $\approx 39\%$ ) and

increased the  $t_{set}$  ( $\approx 92\%$ ,  $\approx 129\%$ ,  $\approx 110\%$ ) when compared with the control specimen respectively.

Obviously, the f-CNTs which were oxidized at  $120\text{ }^{\circ}\text{C}$ , had the best effectiveness to reduce the high temperature and to extend the setting time. This is a significant finding because thermal properties failure of the bone cement mantle remains a major problem in joint replacement surgery.

**Table 1.** Summary of data from thermal studies (Mean $\pm$ SD) of control, pristine CNTs, functionalized CNTs load bone cement.

CNTs Type	Oxidizing temperat. ( $^{\circ}\text{C}$ )	Thermal Properties	
		$T_{\max}$ ( $^{\circ}\text{C}$ )	$t_{set}$ (s)
Control specimen (no CNTs)	\	92.6 $\pm$ 2.5 <sup>a</sup>	651.2 $\pm$ 2.6 <sup>a</sup>
p-CNTs	\	76.6 $\pm$ 2.3 <sup>b</sup>	1062.3 $\pm$ 2.3 <sup>b</sup>
f-CNTs	80	62.8 $\pm$ 2.1 <sup>c</sup>	1265.2 $\pm$ 5.3 <sup>c</sup>
f-CNTs	120	48.8 $\pm$ 2.1 <sup>c</sup>	1488.2 $\pm$ 3.9 <sup>c</sup>
f-CNTs	160	56.8 $\pm$ 2.1 <sup>c</sup>	1367.2 $\pm$ 4.5 <sup>c</sup>

<sup>a</sup>denotes  $p$ -values  $< 0.001$ , indicating a statistically significant difference between control cement and other cements tested.

<sup>b</sup>denotes  $p$ -values  $< 0.001$ , indicating a statistically significant difference between magnetic stirring (p-CNTs) and other cements tested.

<sup>c</sup>denotes  $p$ -value  $< 0.001$ , indicating a statistically significant difference between magnetic stirring (f-CNTs) and other cements tested.

## 4. Conclusions

The oxidized CNTs were successfully performed by means of a  $\text{HNO}_3$  hydrothermal functionalization method. The result showed the best reflux temperature is  $120\text{ }^{\circ}\text{C}$  and the optimal reflux time is 2 hours. Incorporating 0.2 wt% oxidized CNTs to PMMA bone cement could improve the thermal properties of the resultant nanocomposite. The peak temperature was determined by a thermocouple (temperature sensor). The level of heat produced within the exothermic polymerization reaction of the PMMA bone cement was significantly reduced when functionalized CNTs were added. This reduction in exotherm could reduce the hyperthermia experienced in vivo.

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