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# The Application of Carbon Nanotube to Bone Cement

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## 1. Introduction

Bone cement is used as a grouting agent between the prosthesis and the bone as well as a method to anchor prosthesis in orthopedic implants such as total hip replacement. Basically, bone cement consists of two portions: (1) powder portion including pre-polymerized methylmethacrylate (PMMA) and initiator (benzoyl peroxide) and (2) liquid portion including methylmethacrylate (MMA) monomer and promoter (N, N-dimethyl-p-toluidine). When two portions are mixed, the initiation is activated by promoters that make the free radicals (initiators). The free radicals react with monomers for polymerization (Park & Lakes, 1992). Some disadvantages of PMMA bone cement are found such as significant poor mechanical properties which may cause failure of the cement. For instance, PMMA bone cement is considerably weaker than bone (Saha & Pal, 1984) and the tensile stresses of PMMA bone cement are comparatively low (Saha & Pal, 1986). Vallo et al. used cross-linked PMMA beads to prepare cements by replacing 30% of the PMMA powder and showed an increase in the flexural strength value of 22.4%. The cross-linked beads resulted in more effective reinforcing filler than plain PMMA beads (Vallo et al., 2004). Basgorenay et al. modified acrylic bone cement by addition of hydroxyapatite and ammonium nitrate. A linear relation was observed in compression strength (from 98 to 111 MPa) and in tensile strength (from 27 to 21 MPa) upon HA addition, and in the compression strength (from 103 to 85 MPa) and in the tensile strength (from 22 to 17 MPa) with NA addition (Basgorenay et al., 2006). Kwon et al. prepared bone cements incorporated with montmorillonite (MMT) to improve their mechanical properties. The measured compressive strength of the bone cement with 1 wt % MMT was  $113.6 \pm 3.9$  MPa, which is higher than that of the bone cement without MMT ( $110.1 \pm 2.0$  MPa). The measured tensile strength of the control bone cement with 1 wt % MMT was  $27.2 \pm 4.4$  MPa, which is higher than that of the bone cement without MMT ( $22.3 \pm 3.8$  MPa) (Kwon et al., 2007).

Carbon nanotube is known for a larger aspect ratio and higher modulus (Iijima, 1991). Kearns and Shambaugh found that the tensile strength of polypropylene fibers reinforced with carbon nanotube could increase 40% (Kearns & Shambaugh, 2002). There are several studies related to the preparation and characterization of carbon nanotube/poly(methyl methacrylate) composites. For example, Jin 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 (Jin et al., 2001). Stephan et al. prepared poly(methyl methacrylate)-singlewalled carbon nanotube composites by solution mixing (Stephan et al., 2000). Cooper et al. used a polymer extrusion technique to prepare carbon nanotube mixed in a poly(methyl methacrylate) matrix and found that the impact strength was significantly improved by even small amounts of single-wall nanotube (Cooper et al., 2002). Jia et al. prepared poly(methyl methacrylate)/carbon nanotube composites by an in-situ process. Their studies show that carbon nanotube could participate in the polymerization of PMMA initiated by AIBN and form a strong combining interface between the carbon nanotube and the PMMA matrix (Jia et al., 1999).

The purpose of this study is to enhance the mechanical properties of bone cement with carbon nanotube. In this study, the various systems of bone cement reinforced with carbon nanotube were fabricated. The mechanical properties of bone cement were characterized using tensile as well as compressive analysis and dynamic mechanical analysis (DMA). The results show that introduction of carbon nanotube is able to enhance the mechanical properties of bone cement.

2. Materials and Methods

Multiwall carbon nanotube was able to purify by nitric acid solution. The 0.5 g of multiwall carbon nanotube and 100 ml of 3 M of nitric acid solution were mixed in round-bottom flask by ultrasonication for 30 minutes, followed by reflux at 120°C for 12 hours. Then the mixture was cooled down to room temperature. The nitric acid solution of the mixture was taken out and the multiwall carbon nanotube was washed by distilled water until pH 7 of the filtrate. The multiwall carbon nanotube was dried in oven at 120°C for 12 hours.

2.1 Preparation of PMMA/carbon nanotube powder

Multiwall carbon nanotube (CNT) (40 ~ 60 nm in diameter, 0.5 ~ 40 mm in length) was purchased from Desunnano Co., Ltd and used as received without further treatment in this study. MMA monomer was supplied from Kanto Chemical Co., Inc. The composition of PMMA/CNT composites manufactured by in-situ process is listed in Table 1. Benzoyl peroxide (BPO) was used as initiator. The procedure for fabrication of PMMA/carbon nanotube composites was first dissolution of BPO in MMA monomer by stirring at room temperature. After well mixture of BPO and MMA monomer, carbon nanotube was added into the mixture followed by sonication and polymerized at 50°C. When the mixture became viscous, it was poured into mold for further reaction by the process of baking as following steps: (1) 60°C for 2 hours, (2) 80°C for 2 hours, and (3) 100°C for 3 hours. PMMA/CNT powder was prepared from PMMA/CNT composites ground by grinder.

MMA (g)	CNT (g)	BPO (g)	Note
100	0.1	2	(100/0.1)
100	0.2	2	(100/0.2)
100	0.27	2	(100/0.27)
100	0.43	2	(100/0.43)
100	0.59	2	(100/0.59)
100	0.75	2	(100/0.75)

Table 1. The composition of PMMA/CNT composites manufactured by in-situ process

2.2 Preparation of bone cement reinforced with carbon nanotube

The commercial cement, OSTEObOND, was used as well in this study. The OSTEObOND was purchased from Zimmer (Warsaw, Indiana, USA). Several systems of bone cement reinforced with carbon nanotube were prepared. The composition of liquid portion of the bone cement was the same in each system. The compositions of the bone cement in each system are shown in Table 2. The specimens of bone cement were prepared by mixing at the ratio of 1/2 at the liquid portion to the powder portion and left to solidify in a designed shape.

	Powder portion (g)		Commercial Liquid portion (ml)
	Commercial powder	PMMA/CNT powder (pmma/cnt)*	
System 1	20	0	10
System 2	17	3 (100/0.1)	10
System 3	17	3 (100/0.2)	10
System 4	17	3 (100/0.27)	10
System 5	17	3 (100/0.43)	10
System 6	17	3 (100/0.59)	10
System 7	17	3 (100/0.75)	10

\*(pmma/cnt) indicates the ratio of PMMA/CNT by weight in pre-polymeric composites.

Table 2. The composition of the bone cement in each system

2.3 Analysis

The tensile and compressive strength of bone cement was characterized using INSTRON 5582. The specimens for tensile analysis are referred to the work of Harper and Bonfield (Harper & Bonfield, 2000). The specimens have the dimensions: 75 mm in length, 5 mm in width, approximately 3.5 mm in thickness, with a gauge length of 25 mm. The crosshead speed employed was 5 mm/min. The compressive analysis of bone cement corresponded to ASTM F451. The crosshead speed was 25 mm/min. The diameter and length of the specimens were 6.0 mm and 12.5 mm, respectively.

The dynamic mechanical properties of bone cements were measured using dynamic mechanical analysis (DMA 2980, TA Instruments), with the clamp of single cantilever. The dimensions of the rectangular specimens for DMA were 35mm×11mm×2.7mm. The measuring temperatures ranged from 25 to 150°C at 3°C/min, and the frequencies swept at 1 Hz, 3 Hz, 5 Hz, and 10 Hz. The glass transition temperature of a sample was labelled using the tan δ peak, which occurs at the highest temperature.

The surface of the gold-coated test specimens was observed using Scanning Electron Microscope (SEM) (JEOL, JSM-6700F) at an accelerating voltage of 10 kV.

Thermogravimetric analysis (TGA) experiment was performed with Thermogravimetric analyzer (TGA-2050, TA Instruments Inc) under air flow at a heating rate of 10°C/min. The

temperature of the curing acrylic bone cement was measured using a thermocouple. The measuring probe was situated in the bone cement.

3. Results and discussion

Table 3 shows the tensile and compressive strength of the bone cements tested in this study. System 1 is a commercial product which has tensile strength and compressive strength of 40.49 MPa and 105.33 MPa, respectively. Harper and Bonfield report that the tensile strength of Osteobond bone cement is  $38.2 \pm 2.65$  MPa (Harper & Bonfield, 2000). Compressive strength of bone cement usually varies from 44 to 103 MPa (Saha & Pal, 1984). Systems 2 to 7 are the bone cements containing carbon nanotube. Both tensile and compressive strength of System 2 are about 18% and 23%, respectively higher than that of System 1. It indicates that the introduction of PMMA/CNT pre-polymeric composites is able to enhance mechanical properties of bone cement. Compared with Kwon’s study of MMT modified bone cement showed in introduction section, the compressive strength of carbon nanotube modified bone cement exhibited significant increase (23%) than that of MMT modified bone cement (2.7 % increasing in compressive strength). Figure 1 shows the stress-strain curves of System 1 and System 2 tested in tensile strength. It indicates that the toughness of System 2 is better than that of System 1. Therefore, CNT modified bone cement should be able to block crack propagation.

	Tensile strength (MPa)	SD	Compressive strength (MPa)	SD
System 1	40.49	1.79	105.33	21.92
System 2	48.03	1.55	130	4.16
System 3	48.36	1	130.16	3.83
System 4	48.01	3.09	127.25	2.44
System 5	45.55	1.65	130.02	7.41
System 6	45.86	4.23	129.06	3.37
System 7	46.58	4.65	127.83	3.54

Table 3. The tensile and compressive strength of the bone cements tested in this study

Figure 2 illustrates the storage moduli of the bone cement systems as a function of temperature at the frequency of 3 Hz. A storage modulus in DMA can be seen as the stiffness of material. At low temperatures, the storage moduli of the all samples do not show significant difference. Since only strength of the powder portion of bone cement was increased, the liquid portion of bone cement was remained the same as commercial product. However, when the temperature increases to more than 100 °C, System 1 exhibits higher storage modulus than the others. Figure 3 is the tan  $\delta$  values of the cement systems as a function of temperature at the frequency of 3 Hz. The glass transition temperature of a sample was labeled using the tan  $\delta$  peak. Figure 4 is the glass transition temperatures of the

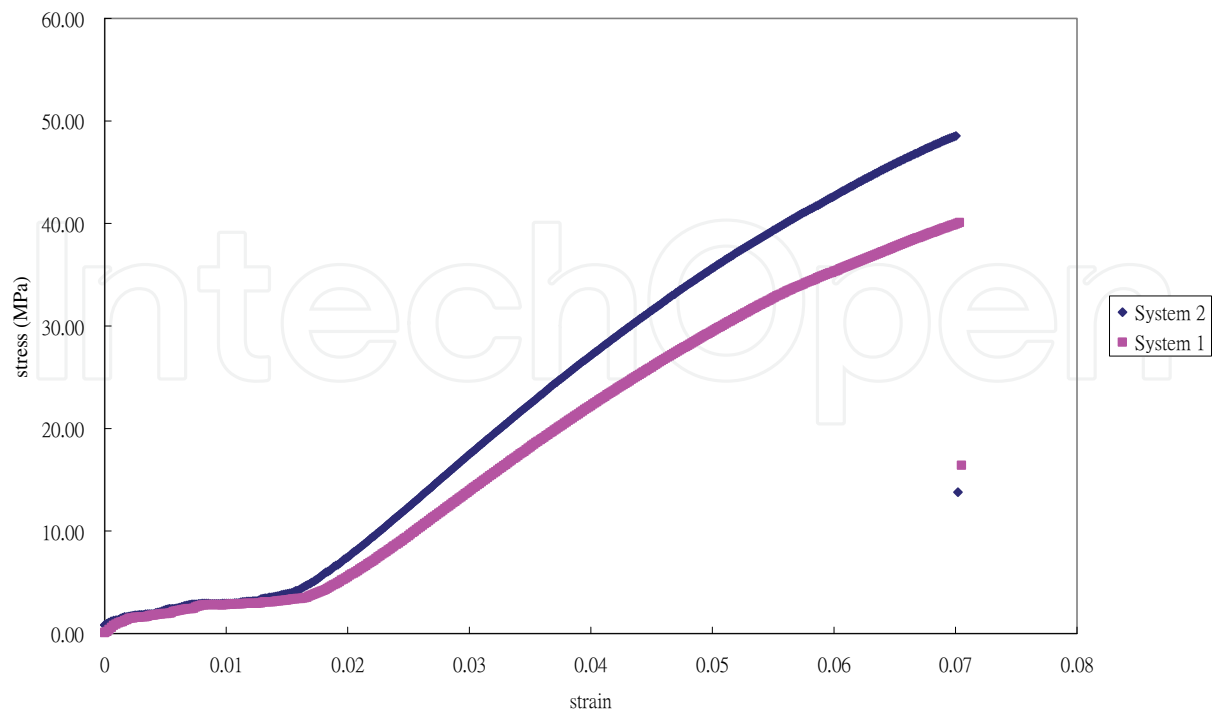


Fig. 1. The stress-strain curves of System 1 and System 2 tested in tensile strength

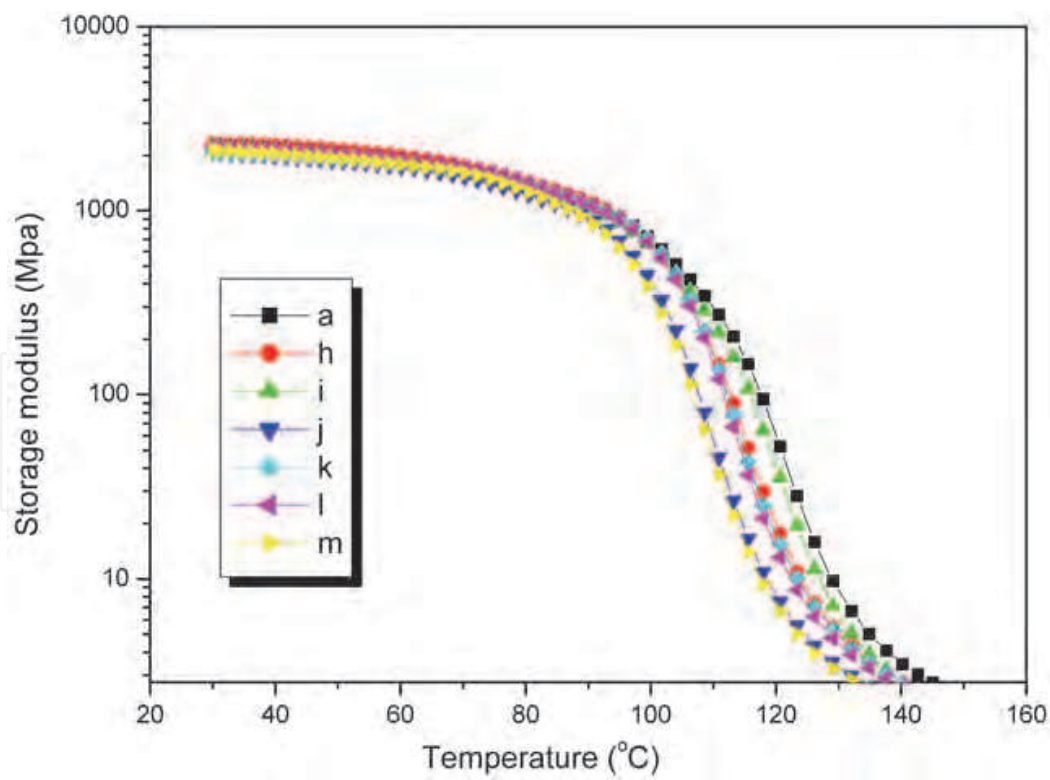


Fig. 2. The storage moduli of the bone cement systems as a function of temperature at the frequency of 3 Hz (a: System1, h: System 2, i: System 3, j: System 4, k: System 5, l: System 6, m: System 7)



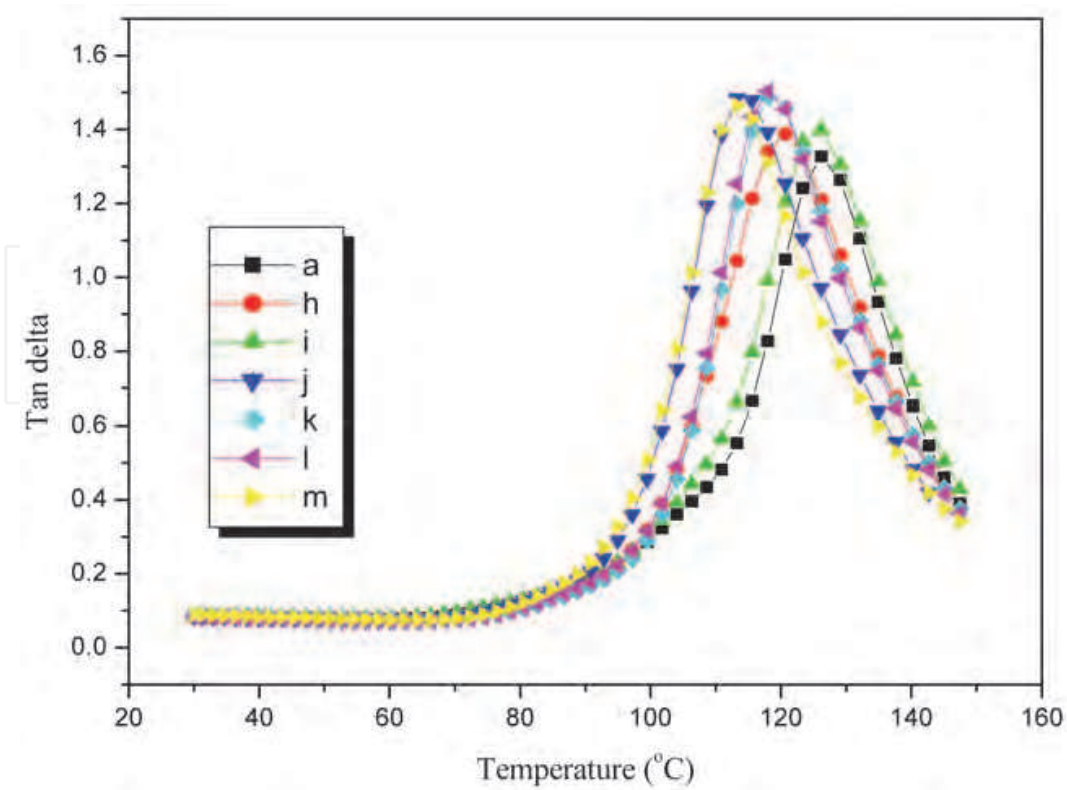


Fig. 3. The  $\tan \delta$  values of the cement systems as a function of temperature at the frequency of 3 Hz. (a: System1, h: System 2, i: System 3, j: System 4, k: System 5, l: System 6, m: System 7)

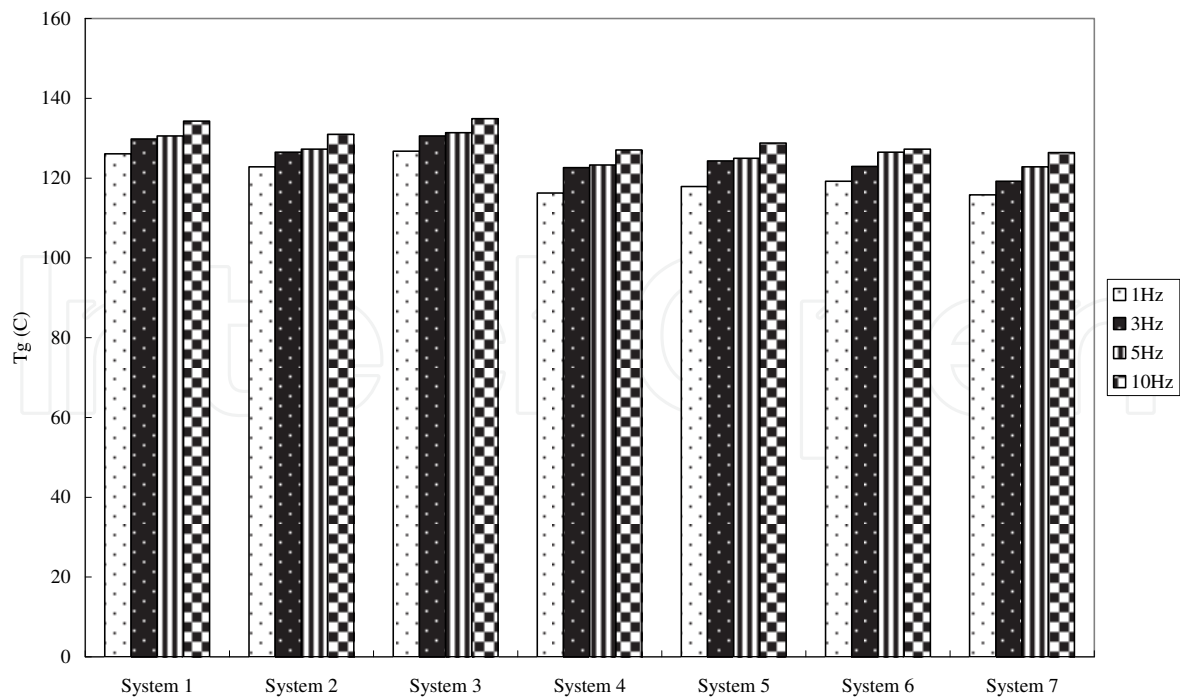


Fig. 4. The glass transition temperatures of the bone cements measured using DMA at the frequencies of 1 Hz, 3 Hz, 5 Hz, and 10 Hz

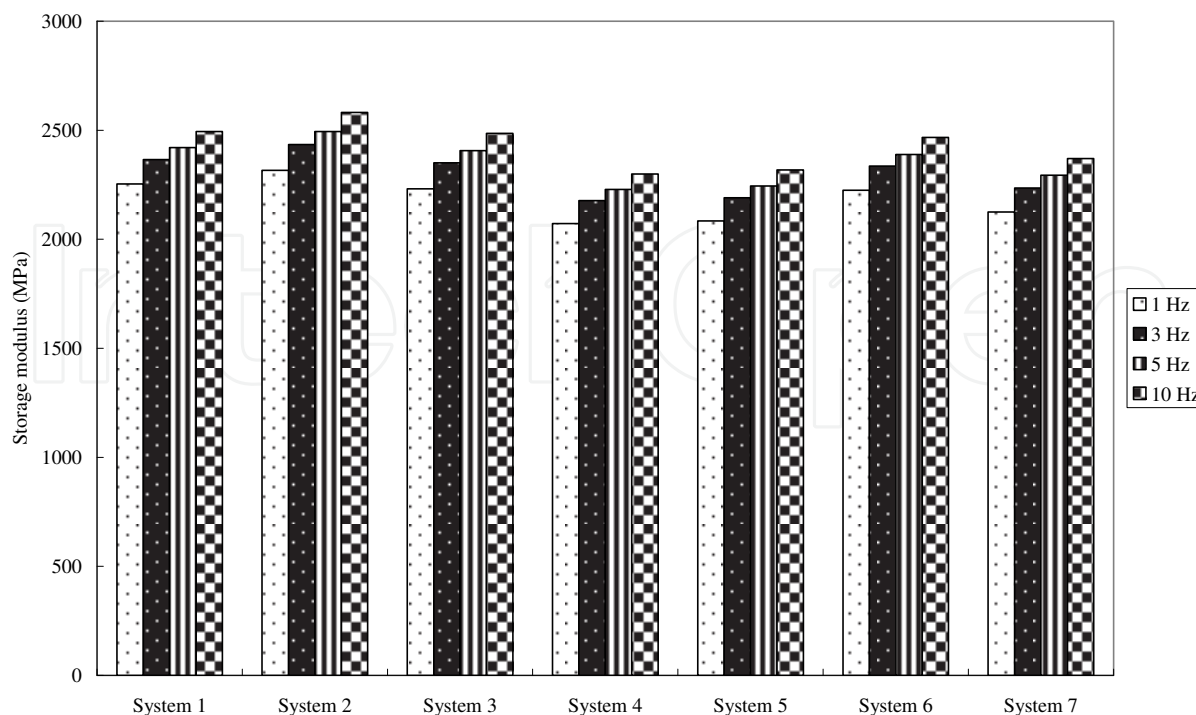


Fig. 5. The storage moduli of the bone cements measured using DMA at the frequencies of 1 Hz, 3 Hz, 5 Hz, and 10 Hz

bone cements measured using DMA at the frequencies of 1 Hz, 3 Hz, 5 Hz, and 10 Hz. System 1 (commercial product) has the highest T<sub>g</sub> among the bone cement. The lower T<sub>g</sub> of the modified bone cement may be due to carbon nanotube acted as plasticizer. The dynamic mechanical properties of viscoelastic materials, such as polymeric composites, are time dependent. When sweep frequency increases, the glass transition temperatures of the bone cements exhibit higher. Figure 4 is the storage moduli of the bone cements measured using DMA at the frequencies of 1 Hz, 3 Hz, 5 Hz, and 10 Hz. The storage modulus of bone cement also increases, when sweep frequency increases. Figure 6 is the surface of the CNT modified bone cement observed using SEM. It is obvious that carbon nanotube existed in bone cement. Usui et al. uses CNTs to promote bone regeneration (Usui et al., 2008). Therefore, it is expected for CNT modified bone cement in promoting bone regeneration.

Figure 7 is the SEM image of the multiwall carbon nanotube without purification. Figure 8 is the SEM image of the multiwall carbon nanotube after purification. The multiwall carbon nanotubes after purification still retained fibrous structure without damage. Figure 9 and Figure 10 are TGA curves of the multiwall carbon nanotube samples without purification and after purification, respectively. It is obvious that the multiwall carbon nanotube without purification contained impurities about 13%. After purification, the impurities in multiwall carbon nanotube were dramatically down to about 2%. The decomposition temperature of the multiwall carbon nanotube without purification was about 623°C. After purification, the decomposition temperature of the multiwall carbon nanotube sample was increased to about 670°C. It was due to the decrease of the content of the non-nanotube carbon in multiwall carbon nanotube after purification.



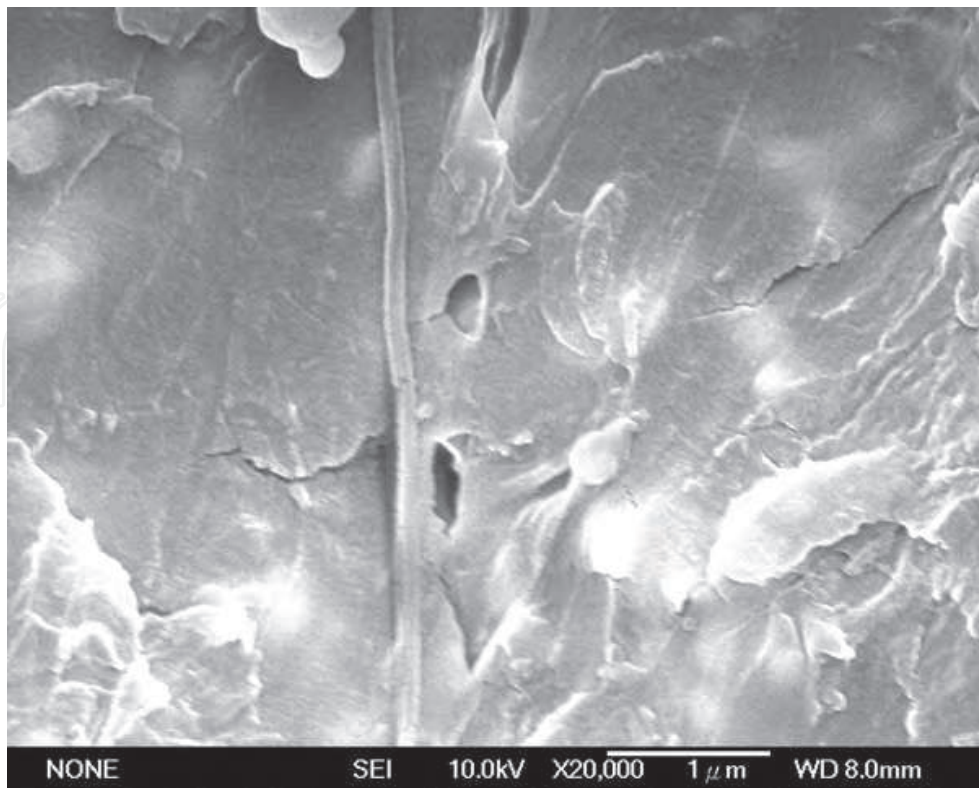


Fig. 6. The surface of the CNT modified bone cement observed using SEM

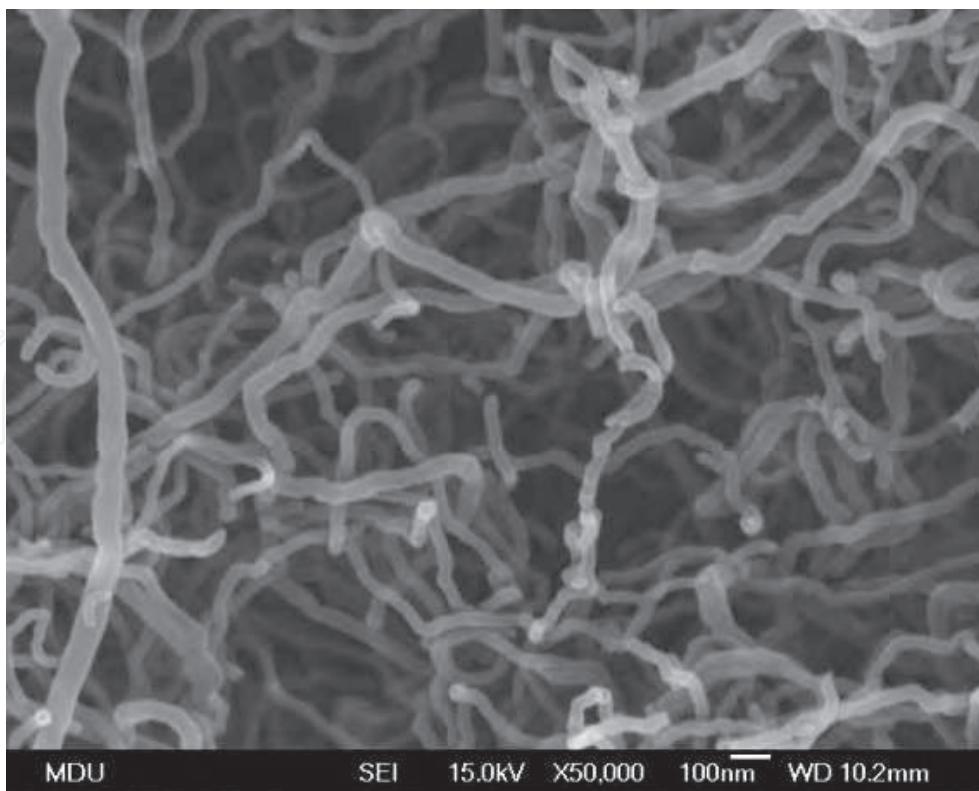


Fig. 7. The SEM image of the multiwall carbon nanotube without purification

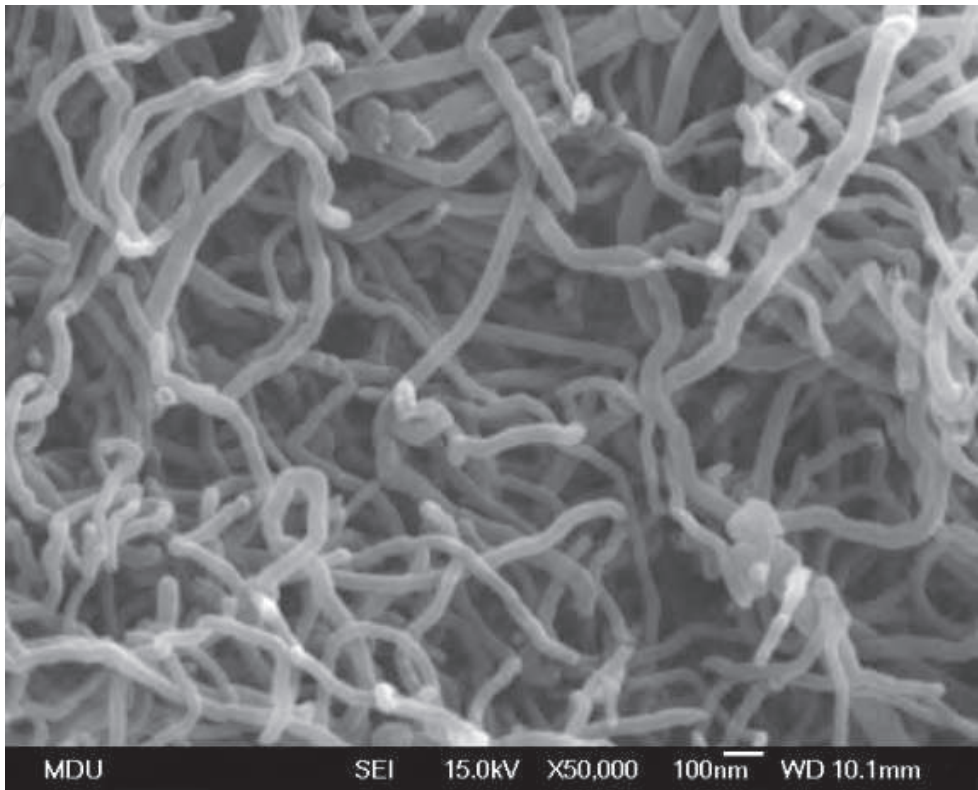


Fig. 8. The SEM image of the multiwall carbon nanotube after purification

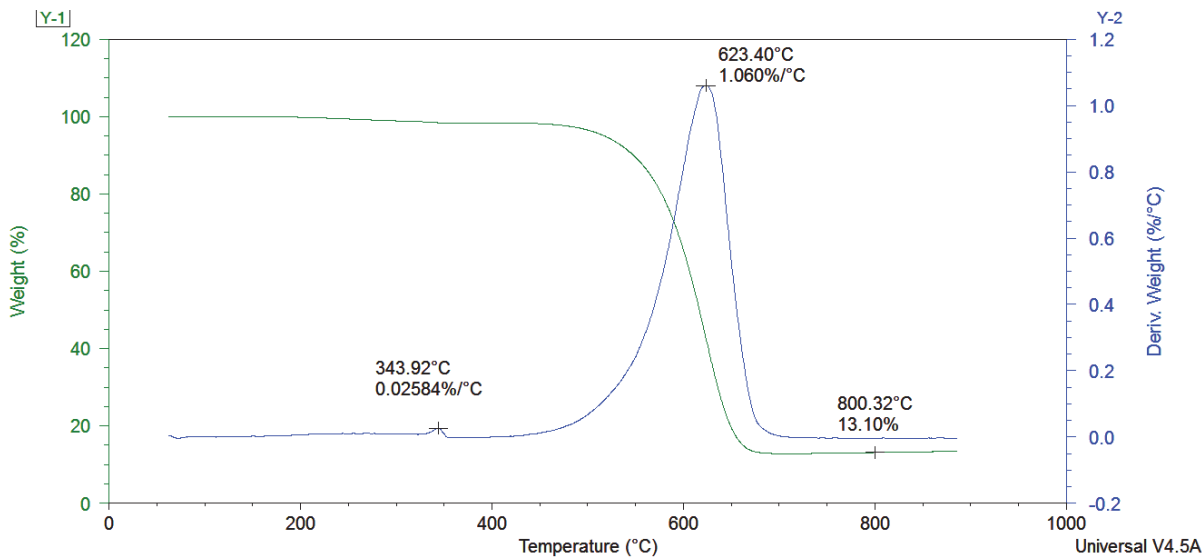


Fig. 9. The TGA curve of the multiwall carbon nanotube sample without purification

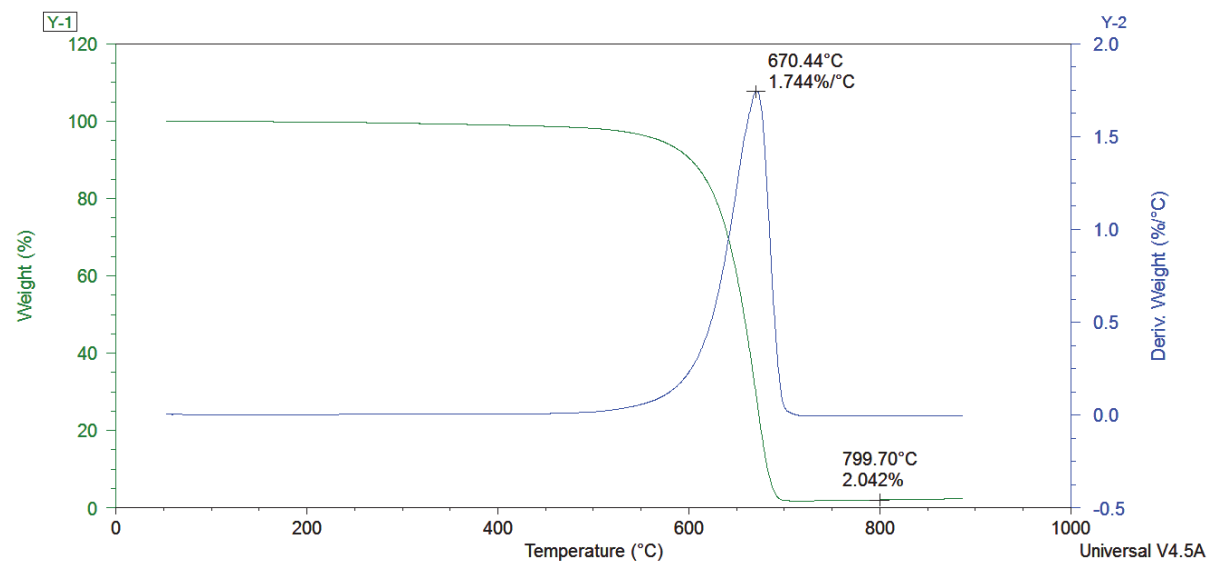


Fig. 10. The TGA curve of the multiwall carbon nanotube sample after purification

Figure 11 is the temperature profile of the curing acrylic bone cement modified by multiwall carbon nanotube. The maximum curing temperature of the acrylic bone cement modified by multiwall carbon nanotube was about 60°C. Figure 12 is the temperature profile of the curing acrylic bone cement without modification of multiwall carbon nanotube. Since the multiwall carbon nanotube was first to be prepared as PMMA/carbon nanotube powder, the PMMA/carbon nanotube powder as a pre-polymerized composite was not reacted further during the curing of the bone cement. Therefore, the curing temperature of the acrylic bone cement modified by multiwall carbon nanotube should be similar to that of the acrylic bone cement without modification of multiwall carbon nanotube.

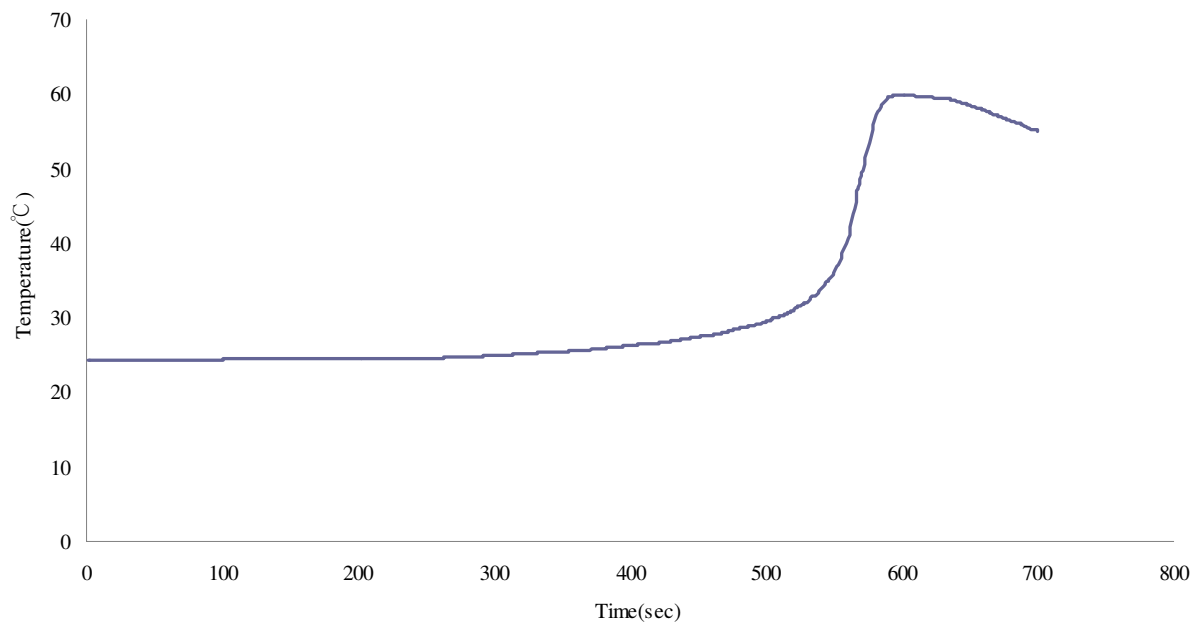


Fig. 11. The temperature profile of the curing acrylic bone cement modified by multiwall carbon nanotube

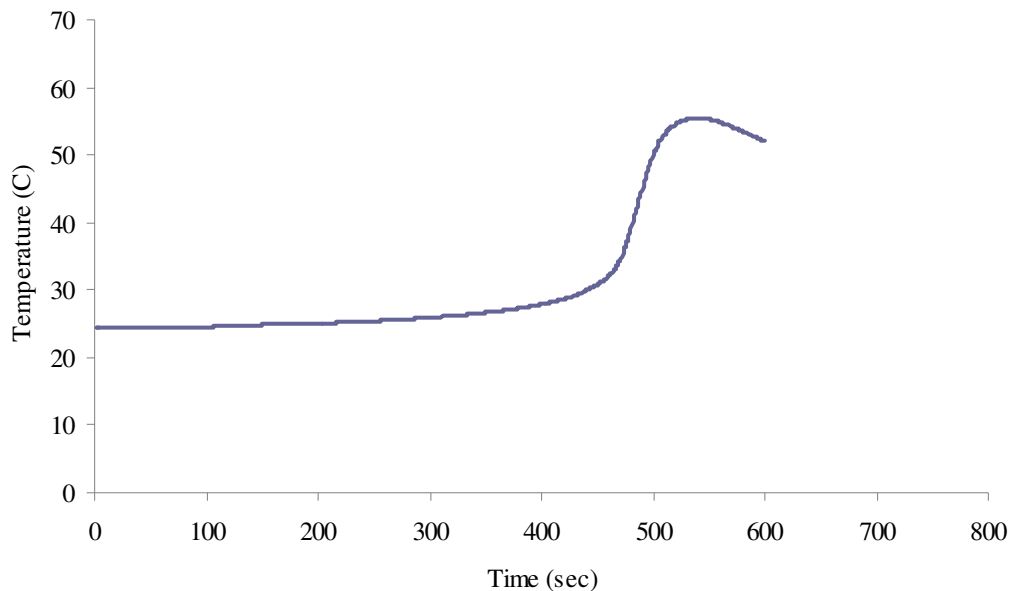


Fig. 12. The temperature profile of the curing acrylic bone cement without modification of multiwall carbon nanotube

### 3. Conclusion

In this study, we have prepared a new type of bone cement reinforced with carbon nanotube. In order to achieve better dispersion of carbon nanotube in bone cement, we first fabricated PMMA/CNT composites and then ground them as powder form to be introduced into bone cement. This kind of modified bone cement exhibits excellent material properties such as tensile and compressive strength. The results show potential usage in clinical applications.

### 4. Acknowledgment

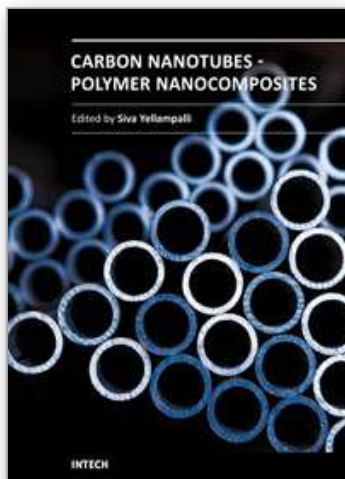
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## **Carbon Nanotubes - Polymer Nanocomposites**

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Polymer nanocomposites are a class of material with a great deal of promise for potential applications in various industries ranging from construction to aerospace. The main difference between polymeric nanocomposites and conventional composites is the filler that is being used for reinforcement. In the nanocomposites the reinforcement is on the order of nanometer that leads to a very different final macroscopic property. Due to this unique feature polymeric nanocomposites have been studied exclusively in the last decade using various nanofillers such as minerals, sheets or fibers. This book focuses on the preparation and property analysis of polymer nanocomposites with CNTs (fibers) as nano fillers. The book has been divided into three sections. The first section deals with fabrication and property analysis of new carbon nanotube structures. The second section deals with preparation and characterization of polymer composites with CNTs followed by the various applications of polymers with CNTs in the third section.

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