

行政院國家科學委員會專題研究計畫 成果報告

研究以碳奈米纖維強化 Cross-Linked  
Poly(methylmethacrylate-acrylic acid)改質型骨泥的機  
械性質

計畫類別：個別型計畫

計畫編號：NSC92-2626-E-168-001-

執行期間：92年08月01日至93年07月31日

執行單位：崑山科技大學應用纖維造形系

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報告類型：精簡報告

處理方式：本計畫涉及專利或其他智慧財產權，2年後可公開查詢

中 華 民 國 93 年 10 月 15 日



行政院國家科學委員會專題研究計畫成果報告  
研究以碳奈米纖維強化 Cross-linked  
Poly(methylmethacrylate-acrylic acid)改質型骨泥的機械性質  
[Study of the Mechanical Behavior of Cross-linked  
Poly(methylmethacrylate-acrylic acid)-modified Bone Cement  
Reinforced with Carbon Nanofiber]

計畫編號：NSC 92-2626-E-168-001

執行期限：92年8月1日至93年7月31日

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### 一、中文摘要

在骨骼整形手術中，骨泥是用來當作人工取代體與骨骼間的填充物以分散施力，並且用來固定人工取代體。以 PMMA 當作骨泥材料有些缺點，如骨泥在聚合時會收縮且 PMMA 材質過脆，因其碎裂韌性差。骨泥收縮會導至骨泥與骨骼間施力轉移能力變差。施力轉移能力變差是人工取代體鬆動的一個原因。PMMA 的機械性質差將造成骨泥使用不成功。本研究顯示碳奈米纖維可強化的交聯 P(MMA-AA)改質型骨泥進而增強骨泥的機械性能。

**關鍵詞：**骨泥、PMMA、膨脹、碳奈米纖維

### Abstract

Bone cement is used as load-distributing filler between the prosthesis and the bone as well as a method to anchor prosthesis in orthopedic implants. There are several disadvantages of using PMMA as bone cement such as shrinkage of the cement during polymerization and apparent brittleness of PMMA bone cements because of their low fracture toughness values. Shrinkage of the cement during polymerization may loss the good load transfer through the interface between the bone and bone cement and is a source of prosthetic loosening. The poor mechanical properties of PMMA may lead to failure of the cement. In this study, the results show that the

mechanical properties of cross-linked P(MMA-AA) modified bone cement reinforced with carbon nanofiber are able to improved compared with commercial bone cement.

**Keywords:** bone cement, PMMA, swell, carbon nanofiber

### 二、緣由與目的

Bone cement is used as load-distributing filler 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 typically: (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 monomers for polymerization [1]. There are several disadvantages of using poly(methylmethacrylate) (PMMA) as bone cement such as shrinkage of the cement during polymerization [2, 3, 4, 5] and apparent brittleness of PMMA bone cements because of their low fracture toughness values [6]. Shrinkage of the cement during polymerization may loss the good load transfer through the interface between the

bone and bone cement and is a source of prosthetic loosening. The poor mechanical properties of PMMA may lead to failure of the cement [7, 8].

From our previous studies of cross-linked poly(methylmethacrylate-acrylic acid) (P(MMA-AA)), it is found that this copolymer exhibits the ability to absorb body fluids and swell in a controlled manner [9-13]. Gualtieri et al. have reported that cross-linked P(MMA-AA) copolymer is able to induce bone ingrowths in the interface of bone and this copolymer [14]. By introducing cross-linked P(MMA-AA) copolymer into bone cement, the fixation strength in the interface of bone and cement can be improved by the controllable swelling of the modified bone cement to compensate the shrinkage of the cement during polymerization [15]. Kathy et al. compared osteoblast proliferation on larger-diameter carbon fibers (i.e., dimensions larger than 100 nm) with carbon nanofibers (i.e., dimensions 100 nm or less) and found that the latter enhance the functions of osteoblasts [16]. Carbon nanotubes are known for a larger aspect ratio and higher modulus [17]. Lozano and Barrera mixed carbon nanofibers with polypropylene to enhance thermal stability and storage modulus of the nanofiber composites [18]. Kearns and Shambaugh found that the fiber tensile strength of polypropylene fibers reinforced with carbon nanotubes could increase 40% [19]. 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 nanotubes are well dispersed in the polymer matrix and the storage modulus of the composites is significantly increased [20]. Stephan et al prepared poly(methyl methacrylate)-singlewalled carbon nanotube composites by solution mixing [21]. Cooper et al. used a polymer extrusion technique to prepare carbon nanotubes mixed in a poly(methyl methacrylate) matrix and found that the impact strength was significantly

improved by even small amounts of single-wall nanotubes [22]. Jia et al prepared poly(methyl methacrylate)/carbon nanotube composites by an in situ process. Their studies show that carbon nanotubes can participate in the polymerization of PMMA initiated by AIBN and form a strong combining interface between the carbon nanotubes and the PMMA matrix [23]. Haggemueller et al. also found that reinforced poly(methyl methacrylate) with Single-wall carbon nanotubes increase tensile strength and modulus by 54% and 94%, respectively, when 8 wt% of nanotubes was used [24].

The purpose of this study is to enhance the mechanical properties of bone cement using cross-linked P(MMA-AA) modified bone cement reinforced with carbon nanofibers. In this study, the various systems of cross-linked P(MMA-AA) modified bone cement reinforced with carbon nanofiber were fabricated. The mechanical properties of bone cement were characterized using tensile analysis and dynamic mechanical analysis (DMA). The fracture surfaces of bone cement after tensile analysis were observed by scanning electron microscopy (SEM). In addition, differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) were conducted to characterize the thermal properties of bone cement. The results show that addition of carbon-nanofibers is able to enhance the mechanical properties of bone cement. The glass transition temperatures of bone cement increase while carbon nanofiber was introduced into bone cement. From the observation of fracture surfaces, the modified bone cements exhibit higher toughness than commercial one.

### 三、研究方法

#### **Preparation of pre-polymerized cross-linked P(MMA-AA) powder**

The preparation of pre-polymerized cross-linked P(MMA-AA) powder is based on our previous study [15]. Polymerization will be carried out in bulk using a free radical polymerization with the initiator AIBN (2,2'-azobisisobutyronitrile) (Showa

Chemical Co., Ltd.). Varying ratios of methylmethacrylate (MMA) / acrylic acid (AA) monomers will be mixed thoroughly with desired amounts of the cross-linker and the initiator. The amount of the initiator used will be fixed, in all cases, to 0.4g/100 ml of the total mixture. The composition of MMA, AA and allylmethacrylate (AMA) monomers at volume ratio of 80/20/10 (MMA/AA/AMA) and 70/30/10 will be applied to this copolymer. The component will be mixed and then allowed to sit for several hours before polymerization to ensure complete degassing. Polymerization will be conducted in glass test tubes, which will be tightly sealed and placed upright in a temperature controlled water bath. The course of the polymerization is chosen so as to prevent the formation of gas bubbles. The temperature will be gradually raised (3°C/hr) over several days to 65°C and kept at that temperature for two days. The glass tubes will be removed from the bath, allowed to cool and the polymer samples retrieve after breaking the tubes. After this primary polymerization stage is completed, the samples will be post-cured to complete the cross-linking reaction and to insure that no free monomers still remained. This will be accomplished by placing them in a temperature-controlled oven where the temperature is raised slowly (1°C/min) to 150°C. The samples will be left at 150°C for a period of at least five hours followed by overnight cooling. Then, the cross-linked P(MMA-AA) in bulk form will be ground into powder by Scienceware Micro-Mill grinder purchased from Fisher Scientific, Fair Lawn, NJ.

#### **Preparation of PMMA/carbon nanofiber composites powder**

Carbon nanofibers (CN) (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/CN composites manufactured by the in situ processes is listed in Table 1. Benzoyl peroxide (BPO) was used as initiator. The procedure for fabrication of PMMA/carbon

nanofiber composites was first dissolution of BPO in MMA monomer by stirring at room temperature. After well mixture of BPO and MMA monomer, carbon nanofiber 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/CN composites powder was prepared from PMMA/CN composites ground by Scienceware Micro-Mill grinder.

#### **Preparation of cross-linked P(MMA-AA) modified bone cement reinforced with carbon nanofibers**

There are several systems of cross-linked P(MMA-AA) modified bone cement reinforced with carbon nanofibers will be prepared. The composition of liquid portion of the bone cement will be the same in each system. That is methyl methacrylate monomer 95wt% and ethylene glycol dimethacrylate 5wt% (as in commercial cement). The compositions of powder portion of the bone cement in each system are shown in Table 2 except initiator benzoyl peroxide. The weight percentage of benzoyl peroxide in powder portion of bone cement will be 0.2% (as in commercial cement) in each system.

The specimens of bone cement will be prepared by mixing the ratio of liquid portion to powder portion at ½ to solidify in designed shape for further characterization.

#### **Characterization of bone cements**

The mechanical properties of bone cements were characterized using tensile analysis (Gotech TS-2000-M) and dynamic mechanical properties of cements were measured by dynamic mechanical analysis (DMA 2980, TA Instruments). The fracture surfaces of bone cements after tensile analysis were observed by scanning electron microscopy (JEOL JSM-6700F). In addition, differential scanning calorimetry (Perkin Elmer Pyris Diamond DSC) and thermogravimetric analyzer (Perkin Elmer

TGA 7 Thermogravimetric Analyzer) were conducted to characterize the thermal properties of bone cements.

#### 四、結果與討論

The tensile analyses of bone cements are listed in Table 3 and 4. System 3 exhibits the highest yield strength, strength, toughness, young's modulus, and extension rate among all of the samples. It indicates that the additions of PMMA/CN composites and pre-polymerized cross-linked P(MMA-AA) powder with right composition are able to enhance mechanical properties of bone cement. Table 5 shows the glass transition temperatures of bone cements measured using DSC. All of the modified bone cements have higher Tg than commercial one. Table 6 is the list of thermal stabilities of bone cements tested by TGA. System 4 demonstrates the highest thermal stability compared to the others. Table 7 and 8 are the Tg and  $\tan \delta$  of the bone cements observed by DMA at different frequency, respectively. In DMA, the Tg of a sample was labeled using the tan delta peak, which occurs at the highest temperature. The Tg observed by DSC is different from that observed by DMA. The glass transition temperatures of all samples measured at higher frequency is similar while the Tg of commercial one measured at lower frequency is slightly higher than the others. However, all of the samples show that the glass transition temperatures of the samples shift to higher temperatures while frequency increases. It indicates that the glass transition involves molecular relaxations, which is related to time and temperature. Therefore, when the testing frequency increases, the molecular relaxations can only occur at higher temperatures. In Table 8, the  $\tan \delta$  slightly decreases with the increase of additions such as PMMA/CN composites powder and pre-polymerized cross-linked P(MMA-AA) powder. Figure 1 to Figure 3 are the fracture surfaces of the System 1, Sample 4 and Sample 2, respectively, after breaking in tensile analysis observed by scanning electron microscopy. The fracture surface of the commercial bone

cement presents a flat surface, which indicates brittle. On the contrary, the modified bone cements have rougher fracture surfaces than commercial one. It implies that the modified bone cements exhibit higher fracture toughness than commercial one.

#### 五、計畫成果自評

In this project, we have manufactured a new type of bone cement. This kind of modified bone cement exhibits excellent material properties such as yield strength, strength, toughness, young's modulus, and extension rate. The results show potential usage in clinical applications. We have applied for Taiwan patent.

Table 1. The composition of PMMA/CN composites used in this study

MMA (g)	CN (g)	CN (wt %)	BPO (g)
50	0.1	0.2	1

Table 2. The compositions (by weight) of powder portion and liquid portion of the bone cement used in each system

	Powder portion				Liquid portion
	P(MMA) (Commercial product)	P(MMA-AA) powder (MMA/AA/AMA: 80/20/10)	P(MMA-AA) powder (MMA/AA/AMA: 70/30/10)	PMMA/CN composites powder	MMA (Commercial product)
System 1	20	0	0	0	10
System 2	17	2	0	1	10
System 3	17	1	0	2	10
System 4	17	0	2	1	10
System 5	17	0	1	2	10

Table 3. The tensile analyses of bone cements

	0.2% yield (MPa)	yield strength (MPa)	strength (MPa)
System 1	10.4	16.9	31.3
System 5	9.9	15.6	30.7
System 4	10.6	17.4	33.7
System 3	15.0	25.1	41.7
System 2	9.3	16.7	28.5

Table 4. The tensile analyses of bone cements (continuous)

	toughness	young modulus (MPa)	extension rate (%)
System 1	165.4	393.7	7.3
System 5	163.1	368.7	7.3
System 4	185.4	370.0	8.3
System 3	238.1	448.8	8.7
System 2	149.2	356.9	7.0

Table 5. The glass transition temperatures of bone cements measured using DSC

	T <sub>g</sub> (°C)
System 1	93.4
System 2	127.3
System 3	128.4
System 4	117.8
System 5	135.7

Table 6. The list of thermal stabilities of bone cements tested by TGA

	The temperature for 50% weight loss	The temperature for 20% weight loss
System 1	372	332
System 5	371	331
System 4	380	337
System 3	370	325
System 2	368	324

Table 7. The T<sub>g</sub> of the bone cements observed by DMA at different frequency

	1 Hz	3 Hz	5 Hz	10 Hz
System 5	128.3	132.0	132.8	136.2
System 4	128.9	132.5	133.3	136.7
System 3	129.5	133.3	134.2	137.8
System 2	128.3	132.1	132.9	136.2
System 1	133.1	136.9	137.9	138.9

Table 8. The tan δ of the bone cements observed by DMA at different frequency

	1 Hz	3 Hz	5 Hz	10 Hz
System 5	1.2	1.3	1.3	1.3
System 4	1.2	1.2	1.3	1.3
System 3	1.3	1.3	1.3	1.3
System 2	1.2	1.3	1.3	1.3
System 1	1.4	1.5	1.5	1.4

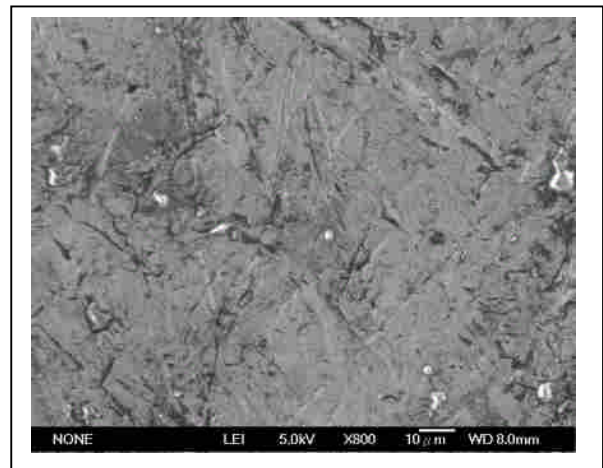


Figure 1. The fracture surface of the System 1 after breaking in tensile analysis

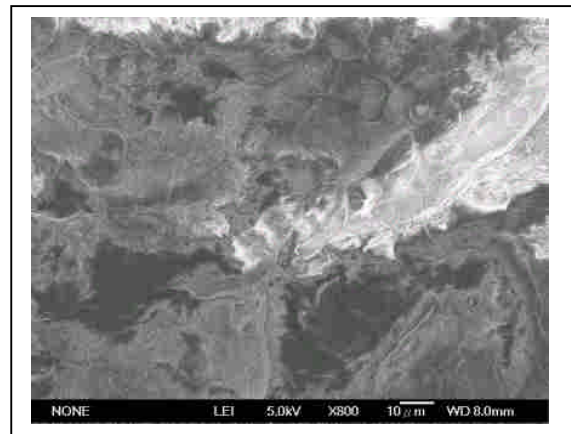


Figure 2. The fracture surface of the System 4 after breaking in tensile analysis

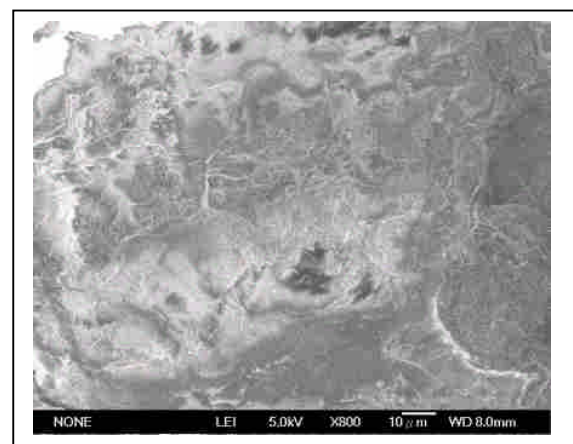


Figure 3. The fracture surface of System 2 after breaking in tensile analysis

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