

Studies of the Mechanical and Thermal Properties of Cross-linked Poly(methylmethacrylate-acrylic acid-allylmethacrylate)-Modified Bone Cement

Yu-Hsun Nien, Jason Chen

Department of Polymer Materials, Kun Shan University, Yung-Kang City, Tainan Hsien 71003, Taiwan

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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. One of the disadvantages of using polymethylmethacrylate (PMMA) as bone cement is shrinkage of the cement during polymerization. Shrinkage of the cement during polymerization may lose the good load transfer through the interface between the bone and bone cement, and is a source of prosthetic loosening. A crosslinked poly(methylmethacrylate-acrylic acid-allylmethacrylate) was applied to bone cement, because it was found that this copolymer exhibits the ability to absorb body fluids and swell in a controlled manner to compensate shrinkage of the cement during polymerization. In this study, the crosslinked poly(methylmethacrylate-acrylic acid-allylmethacrylate) modified bone cement

was prepared and characterized using tensile analysis and dynamic mechanical analysis. The results show that the modified bone cement is able to enhance the mechanical properties of bone cement. From dynamic mechanical analysis, the transition temperature and the $\tan \delta$ value of the cement may be affected by prepolymerized crosslinked poly(methylmethacrylate-acrylic acid-allylmethacrylate) powder. From the observation of the fracture surfaces of the cements, the modified bone cement may improve fracture toughness. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3727–3732, 2006

Key words: bone cement; PMMA; swell; dynamic mechanical analysis

INTRODUCTION

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: (1) powder portion, including prepolymerized 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.¹ There are several disadvantages of using poly(methylmethacrylate) (PMMA) as bone cement, such as shrinkage of the cement during polymerization^{2–5} and apparent brittleness of PMMA bone cements, because of their low fracture toughness values.⁶ Shrinkage of the cement during polymerization may lose 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 crosslinked poly(methylmethacrylate-acrylic acid-allylmethacrylate) (poly(MMA-AA-AMA)), 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 crosslinked poly(MMA-AA-AMA) copolymer is able to induce bone ingrowths in the interface of bone and this copolymer.¹⁴ By introducing crosslinked poly(MMA-AA-AMA) 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 The purpose of this study is to enhance the mechanical properties of bone cement, using crosslinked poly(MMA-AA-AMA)-modified bone cement. In this study, the various systems of crosslinked poly(MMA-AA-AMA) modified bone cement 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). The results show that the modified bone cement is able to enhance the mechanical properties of bone cement. From DMA,

Correspondence to: Y.-H. Nien (nien@mail.ksu.edu.tw).

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TABLE I
The content of the Commercial Cement Used in This Study

Powder portion	Liquid portion
Poly[(methyl methacrylate)- <i>co</i> -styrene] 87.5% W/W	Methyl Methacrylate 99.25% V/V
Barium Sulfate 10% W/W	<i>N,N</i> -Dimethyl- <i>p</i> -toluidine 0.75% V/V
Benzoyl Peroxide 1.00–2.50% W/W	Hydroquinone 75 ± 10 ppm

the transition temperature and the $\tan \delta$ value of the cement may decrease, when prepolymerized crosslinked poly(MMA-AA-AMA) powder is added into cement. From the observation of the fracture surfaces of cements, the modified bone cement may improve fracture toughness.

EXPERIMENTAL

Materials

Initiator 2,2'-azobisisobutyronitrile (AIBN) was purchased from Showa Chemical Co. Methyl methacrylate (MMA), acrylic acid (AA), and allylmethacrylate (AMA) monomers were purchased from Kanto Chemical Co. (Japan), Alfa Aesar (Ward Hill, MA), and Acros Organics (Morris Plains, NJ), respectively. The commercial cement used in this study is OSTEO-BOND® purchased from Zimmer (Warsaw, IN).

Method

Preparation of prepolymerized crosslinked poly(MMA-AA-AMA) powder

The preparation of prepolymerized crosslinked poly(MMA-AA-AMA) powder is based on our previous study.¹⁵ Polymerization was carried out in bulk using a free-radical polymerization with the initiator AIBN. Varying ratios of MMA/AA monomers were mixed thoroughly with desired amounts of the

crosslinker, allylmethacrylate (AMA), and the initiator. The amount of the initiator used was fixed, in all cases, to 0.4 g/100 mL of the total mixture. The compositions of MMA, AA, and AMA monomers at volume ratios of 80/20/10 and 70/30/10 (MMA/AA/AMA) were polymerized. The component was mixed and then allowed to stand for several hours before polymerization to ensure complete degassing. Polymerization was conducted in tightly sealed glass test tubes and placed upright in a temperature controlled water bath. The course of the polymerization was chosen so as to prevent the formation of gas bubbles. The temperature was gradually raised (3°C/h) over several days to 65°C and kept at that temperature for 2 days. The glass tubes were removed from the bath, allowed to cool, and the polymer samples retrieved after breaking the seal. After this primary polymerization stage was completed, the samples were postcured to complete the crosslinking reaction and to ensure that no free monomers still remained. This was accomplished by placing them in a temperature-controlled oven where the temperature was raised slowly (1°C/min) to 150°C. The samples were left at 150°C for a period of at least 5 h, followed by overnight cooling. Then, the crosslinked poly(MMA-AA-AMA) in bulk form was ground into powder by Scienceware Micro-Mill grinder.

Preparation of crosslinked poly(MMA-AA-AMA)-modified bone cement

The commercial cement used in this study is OSTEO-BOND®. The content of the commercial cement is listed in Table I, which is provided by the supplier. Several systems of crosslinked poly(MMA-AA-AMA)-modified bone cement were prepared. The composition of liquid portion of the bone cement was the same in each system. The compositions of powder portion of the bone cement in each system are shown in Table II. The specimens of bone cement were prepared by mixing two portions at the ratio of 1/2 (liquid portion to powder portion) to solidify in designed shape for

TABLE II
The Compositions (By Weight) of Powder Portion and Liquid Portion of the Bone Cement Used in Each System

	Powder portion		Liquid portion
	Commercial product (g)	P(MMA-AA) powder (MMA/AA/AMA: 80/20/10) (g)	P(MMA-AA) powder (MMA/AA/AMA: 70/30/10) (g)
System 1	20	0	10
System 2	19	1	10
System 3	17	3	10
System 4	19	0	10
System 5	17	0	10

TABLE III
The Mechanical Properties of the Bone Cement Systems Used in This Study

	Yield strength (MPa)	SD	Strength (MPa)	SD	Young's modulus (MPa)	SD	Extension rate (%)	SD
System 1	16.9	4.9	31.3	9.0	393.7	23.03	7.3	0.9
System 2	22.6	5.6	39.3	3.0	412.4	22.23	8.8	0.4
System 3	19.7	2.3	36.2	4.7	402.7	27.70	8.3	0.9
System 4	18.2	1.2	33.1	4.2	378.5	34.19	8.1	0.7
System 5	14.5	3.5	26.6	6.1	322.7	24.94	7.5	1.9

further characterization. The procedures of mixing bone cement were based on the instruction provided by the supplier. For instance, 10 g of liquid portion was mixed with 20 g powder portion in an inert mixing bowl at room temperature, and stirred with an inert spatula until the powder was completely saturated with the liquid. Then, the mixture was poured into Teflon mold for solidification.

Analysis

The mechanical properties of bone cements were characterized using tensile analysis (Gotech TS-2000-M). The specimen for tensile analysis has the following dimensions: 75 mm in length, 5 mm in width, ~3.5 mm in thickness, with a gauge length of 25 mm, which are referred from the work of Harper and Bonfield.¹⁶ The crosshead speed employed was 5 mm/min. The dynamic mechanical properties of cements were measured by dynamic mechanical analysis (DMA 2980, TA Instruments), with the clamp of single cantilever. The dimensions of the rectangular specimens for DMA are 35 × 11 × 2.7 mm³. The measuring temperatures ranged from 25 to 150°C at 3°C/min, and the frequencies swept at 1, 3, 5, and 10 Hz. The Tg of a sample was labeled using the tan δ peak, which occurs at the highest temperature. The fracture surfaces of

bone cements after tensile analysis were observed by scanning electron microscopy (JEOL JSM-6700F).

RESULTS AND DISCUSSION

Table III shows the mechanical properties of the bone cements tested in this study. System 2 shows the highest yield strength among the cement systems. The introduction of prepolymerized crosslinked poly(MMA-AA-AMA) powder, which has the volume ratio of 80/20/10 (MMA/AA/AMA), leads the increase of yielding strength of bone cement. It may be caused by the crosslinked poly(MMA-AA-AMA) powder. However, the prepolymerized crosslinked poly(MMA-AA-AMA) powder, which has the volume ratio of 70/30/10 (MMA/AA/AMA), does not improve the yielding strength of bone cement. It implies that the overbalance of AA may reduce the yielding strength. The trend of the strengths of the cements with various systems is similar to that of the yield strengths of the cement systems. For the results of Young's modulus of cement systems, the higher the component of AA, the lower is the Young's modulus of the cement. The extension rates of the modified cements exhibit higher than that of commercial product. Compared to the above results of mechanical properties, the prepolymerized crosslinked poly(MMA-AA-AMA) powder that has the volume ratio of 80/

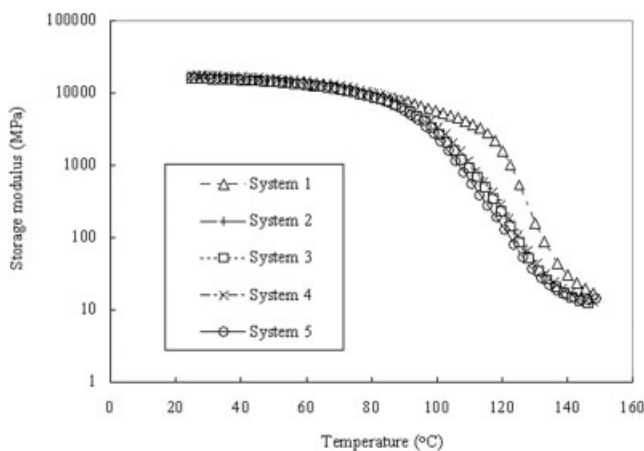


Figure 1 The storage moduli of the five bone cement systems as a function of temperature at the frequency of 1 Hz.

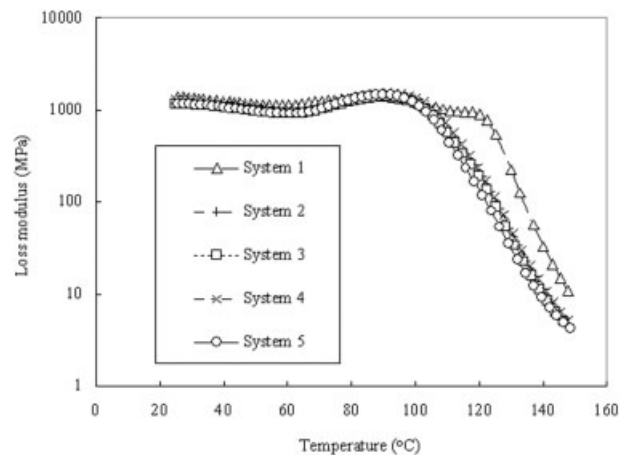


Figure 2 The loss moduli of the cement systems as a function of temperature at the frequency of 1 Hz.

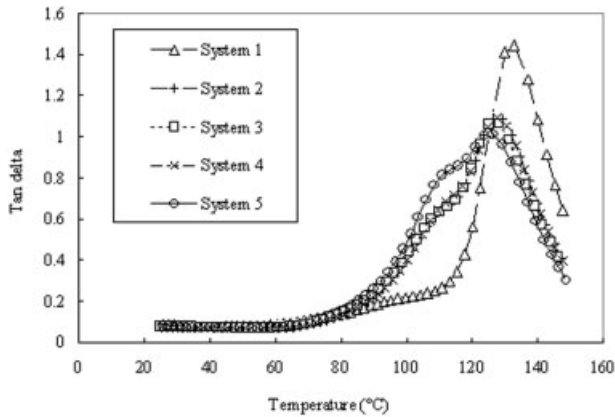


Figure 3 The $\tan \delta$ values of the cement systems as a function of temperature at the frequency of 1 Hz.

20/10 (MMA/AA/AMA) is a better candidate than that of 70/30/10 (MMA/AA/AMA), as an additive in bone cement to improve mechanical properties.

Figure 1 illustrates the storage moduli of the five bone cement systems as a function of temperature at the frequency of 1 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. However, when the temperature increases (100–125°C), System 1 exhibits higher storage modulus than the others. The loss moduli of the cement systems as a function of temperature at the frequency of 1 Hz are illustrated in Figure 2. Loss modulus in DMA is an indication of energy dissipation. It is related to molecular motions within the polymer, which can absorb and dissipate impact energy. In this study, the glass transition temperatures of the samples were determined by $\tan \delta$ peak, which occurs at the highest temperature, as shown in Figure 3. The introduction of prepolymerized crosslinked poly(MMA-AA-AMA) powder results in the variation of T_g slightly. When prepolymerized crosslinked poly(MMA-AA-AMA) powder was added, the $\tan \delta$ value decreases. The crosslinked poly(MMA-AA-

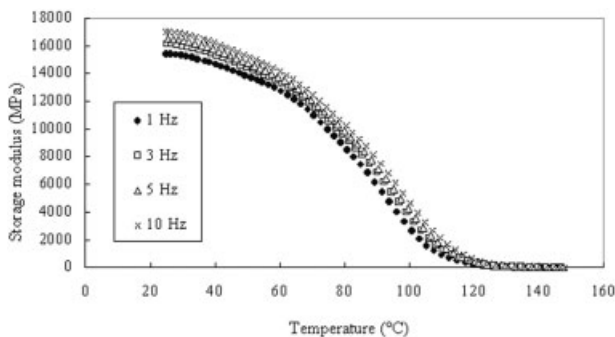


Figure 4 The storage moduli of System 3 at various frequencies as a function of temperature.

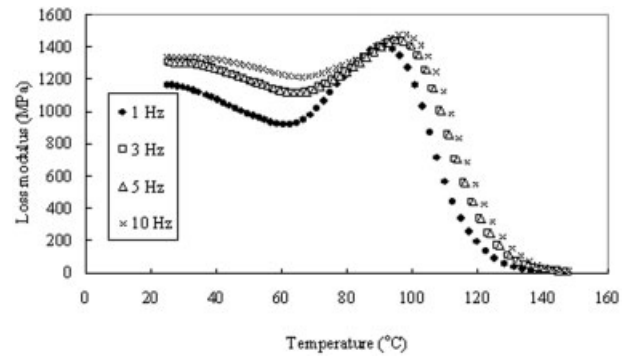


Figure 5 The loss moduli of System 3 at various frequencies as a function of temperature.

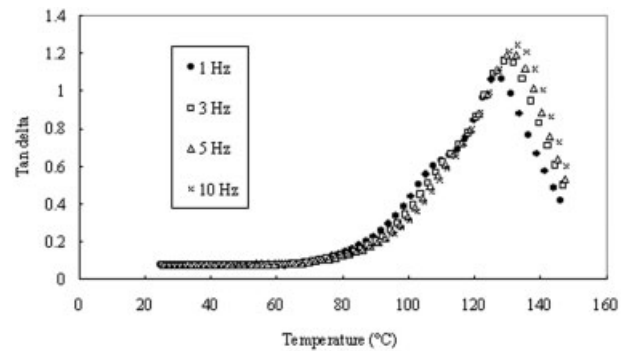


Figure 6 The $\tan \delta$ values of System 3 at various frequencies as a function of temperature.

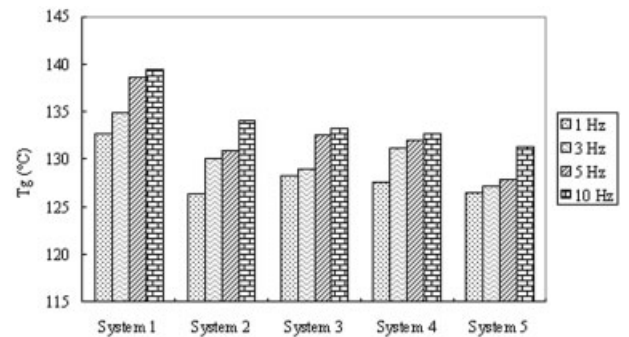


Figure 7 The glass transition temperatures of the cements at various frequencies.

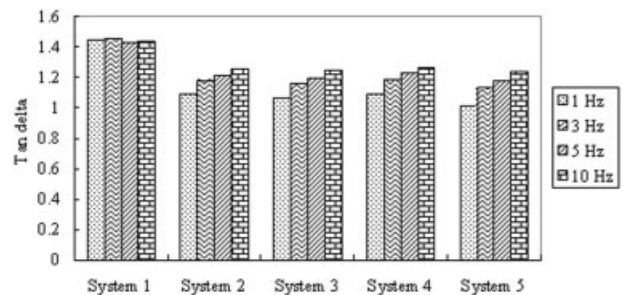
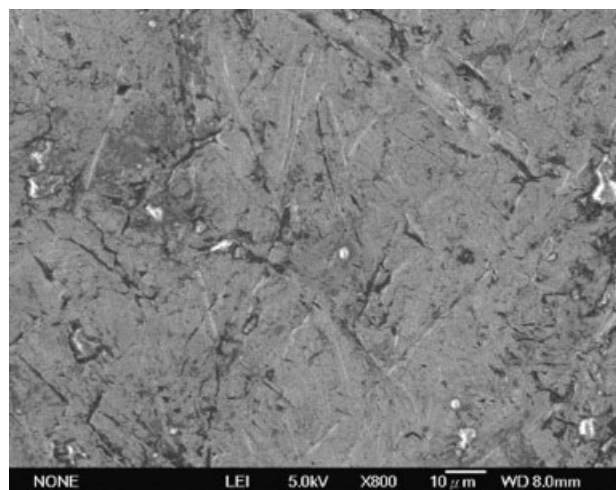
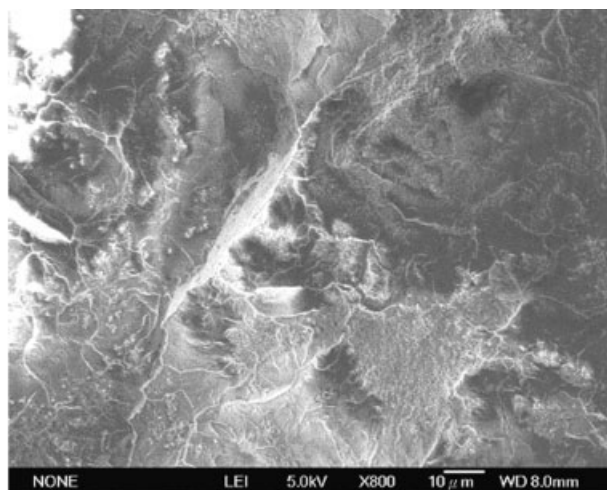


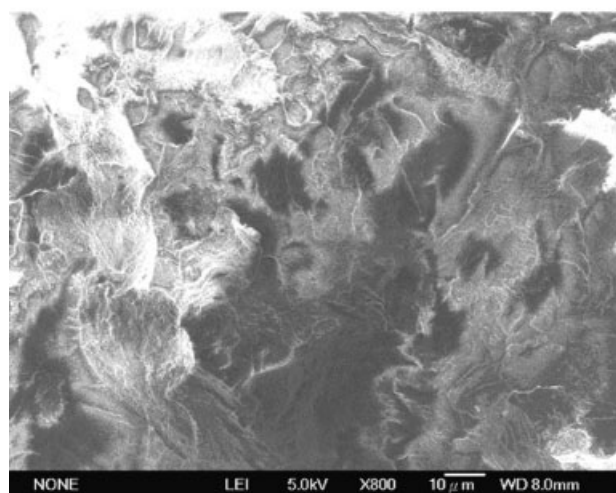
Figure 8 The $\tan \delta$ values of the cements at various frequencies.



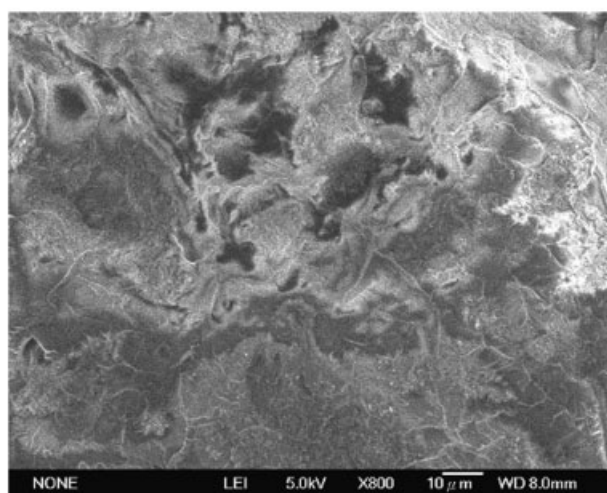
(a)



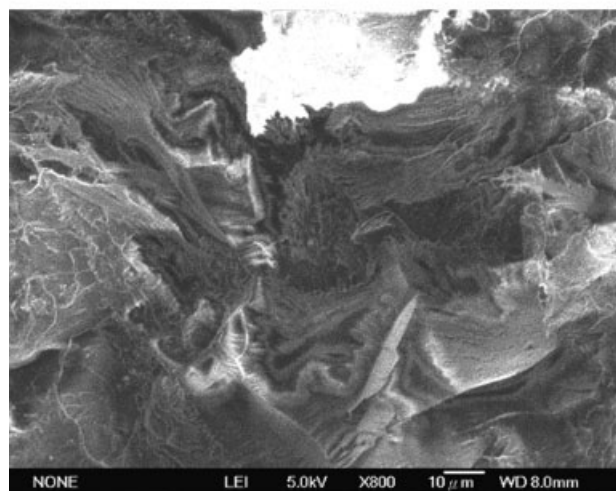
(b)



(c)



(d)



(e)

Figure 9 The fracture surface of System 1 (a); System 2 (b); System 3 (c); System 4 (d); System 5 (e).

AMA) may contribute to this result. Note that the commercial powder was made of poly[(methyl methacrylate)-costyrene]. The styrene in the copolymer is a rigid component, which presents higher T_g. Lower T_g of the modified cements may be caused by the modified cements containing fewer poly[(methyl methacrylate)-costyrene].

The dynamic mechanical properties of viscoelastic materials, such as polymeric composites, are time dependent. Figure 4 shows the storage modulus of System 3 at various frequencies as a function of temperature. When sweep frequency increases, the storage modulus of the cement exhibits higher. Figure 5 demonstrates the loss modulus of System 3 at various frequencies as a function of temperature. The damping peak of the cement shifts to higher temperature while the frequency becomes higher. In Figure 6, which is the tan δ value of System 3 at various frequencies as a function of temperature, the tan δ peak of the cement shifts to higher temperature at higher frequency. In addition, the tan δ value occurred at higher temperature also increases at higher frequency. The glass transition temperatures and the tan δ values of the cements at various frequencies are summarized in Figures 7 and 8, respectively.

Figure 9(a–e) are the fracture surfaces of the System 1 to System 5, respectively, after breaking in tensile analysis observed by SEM. The fracture surface of the commercial bone cement presents a flat surface, which indicates brittleness. On the contrary, the modified bone cements have rougher fracture surfaces than those of commercial one. It implies that the modified bone cements exhibit higher fracture toughness than those of commercial one.

CONCLUSIONS

Crosslinked poly(MMA-AA-AMA)-modified bone cement has been prepared and characterized in this study. The proper introduction of prepolymerized

crosslinked poly(MMA-AA-AMA) powder, which has the volume ratio of 80/20/10 (MMA/AA/AMA), is able to increase mechanical properties of bone cement, such as yield strength, strength, Young's modulus, and extension rate. From DMA, the transition temperature and the tan δ value of the cement may decrease, when prepolymerized crosslinked poly(MMA-AA-AMA) powder is added to cement. Both T_g and tan δ value of cement increase while sweep frequency increases. The analysis of fracture surfaces of cements demonstrates that the modified bone cements may improve fracture toughness. The results show potential usage in clinical applications.

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