

# Preparation and Characterization of Crosslinked Poly(methylmethacrylate-acrylic acid sodium salt)-Modified Bone Cement

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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. In this study, crosslinked poly(methylmethacrylate-acrylic acid sodium salt), denoted as poly(MMA-AAS-AMA), was applied to bone cement. Allylmethacrylate (AMA) was used as a cross-linking agent. It was demonstrated by FTIR that the wavenumbers of the asymmetrical and symmetrical stretching vibrations for carboxylate anion of poly(MMA-AAS-AMA) were 1586 and 1407  $\text{cm}^{-1}$ , respectively. The poly(MMA-AAS-AMA)-modified bone cement was prepared and characterized using tensile and compressive test. An excess of poly(MMA-AAS-AMA) in bone cement caused poor

mechanical properties of the modified bone cement, because poly(MMA-AAS-AMA) absorbed water. In dynamic mechanical analysis, the excessive content of poly(MMA-AAS-AMA) lowered the stiffness of the modified bone cement, because of water existed in poly(MMA-AAS-AMA). The glass transition temperature of the bone cement shifted to higher temperature at higher frequency because of viscoelasticity. Based on swelling measurement, the modified bone cement was able to swell in controlled manner, and the swelling rate of the modified bone cement was improved. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2839–2846, 2010

**Key words:** bone cement; polymethylmethacrylate; swelling

## 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, commercial bone cement consists of two portions typically: (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.<sup>1</sup>

The bone cement fixation creates two interfaces: (1) bone/cement and (2) cement/implant. In the current application of the bone cement used for anchoring femoral prostheses, it was reported that 10% of the problems was related to the cement/implant interface and 11% to the bone/cement interface.<sup>1</sup> In

addition, one of the disadvantages of using PMMA as bone cement is shrinkage of the bone cement during polymerization of MMA.<sup>2</sup> Shrinkage of bone cement during polymerization may cause loss of load transfer through the interface between the bone and bone cement and is a source of prosthetic loosening.<sup>3</sup> The typical shrinkage of the conventional acrylate-based bone cements is about 1–2%. Loosening is the failure of implantation. The other disadvantage is the poor bonding to bone or prosthesis leading to prosthetic loosening.<sup>4,5</sup>

In our previous studies, crosslinked poly(methyl methacrylate-acrylic acid-allyl methacrylate), denoted as poly(MMA-AA-AMA), was able to absorb body fluid and swell in controlled manner. The swelling of the copolymer was constrained by the surrounding bone, and consequently, an interfacial pressure was developed at the bone-polymer interface. This interfacial pressure, in turn, increased the frictional resistance and improved significantly the fixation strength of the implants.<sup>6–11</sup> Thus, crosslinked poly(MMA-AA-AMA)-modified bone cement could compensate the shrinkage of bone cement during polymerization. However, the absorbable rate of poly(MMA-AA-AMA) was slow. To address this weakness, we used crosslinked poly(methylmethacrylate-acrylic acid sodium salt) [poly(MMA-AAS-AMA)]-modified bone cement, which consisted of

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**TABLE I**  
**The Content of the Commercial Cement**

Powder portion	Liquid portion
Poly[(methylmethacrylate)- <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 conventional acrylate-based bone cement modified in powder portion by introducing a certain amount of crosslinked poly(MMA-AAS-AMA) in powder portion. Allylmethacrylate (AMA) was used as a crosslinking agent.

In this article, we first polymerized poly(MMA-AA-AMA) as described in our previous article.<sup>12</sup> Then, the poly(MMA-AA-AMA) was converted into poly(MMA-AAS-AMA) by dipping in sodium hydroxide solution followed by washing and drying. The poly(MMA-AAS-AMA) was ground into powder form and introduced into bone cement.

The purpose of this study was to prepare crosslinked poly(MMA-AAS-AMA)-modified bone cement and characterize them using Fourier transform infrared spectroscopy, thermogravimetric analyzer, and dynamic mechanical analysis (DMA). In addition, swelling behavior of bone cement was studied, and the tensile and compressive strength of the modified bone cement were also measured.

## EXPERIMENTAL

### Preparation of prepolymerized crosslinked poly(MMA-AAS-AMA) powder

Polymerization was carried out in bulk using a free radical polymerization with the initiator 2,2-azobisisobutyronitrile (Showa Chemical). The monomers of methylmethacrylate (MMA)/acrylic acid (AA)/AMA were mixed at the volume ratios of 80 mL/20 mL/10 mL and 70 mL/30 mL/10 mL separately with the initiator at the amount of 0.4 g/100 mL of the total mixture. MMA, AA, and AMA were purchased from Kanto Chemical (Japan), Alfa Aesar (USA), and Acros Organics (USA), respectively. Polymerization was conducted in glass test tubes, which were tightly sealed and placed upright in a temperature-controlled water bath. The temperature was gradually raised (3°C/h) over several days to 65°C and kept at that temperature for 2 days. Then, the glass tubes were removed from the bath, allowed to cool, and the polymer samples were retrieved after breaking the tubes. After this primary polymerization stage was completed, the samples were postcured to complete the crosslinking reaction and to insure that there were no left free monomers. This was accomplished by placing them in a temperature-controlled

oven, where the temperature was raised slowly (1°C/min) up 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 dipped into 1M of sodium hydroxide solution for several days until full saturation followed by washing with distilled water to fabricate crosslinked poly(MMA-AAS-AMA). The crosslinked poly(MMA-AAS-AMA) was dried and washed alternatively for several times. Finally, the dried crosslinked poly(MMA-AAS-AMA) was ground into fine powder and sieved on a 140 mesh screen.

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

The commercial bone cement (Osteobond bone cement purchased from Zimmer) was used as well in this study. The content of the commercial bone cement provided by the supplier is listed in Table I. Several systems of the crosslinked poly(MMA-AAS-AMA)-modified bone cement were prepared. The specimens of bone cement were prepared by mixing 10 mL of the liquid portion and 20 g of the powder portion and left to solidify in a designed shape. The composition in the liquid portion for all the bone cement systems was the same, and 10 mL of the liquid portion from the commercial product was used in each bone cement system. The various compositions in the powder portion of the bone cement for each system are shown in Table II. The denotation of the commercial system was Osteobond bone cement, which contained 20 g of commercial powder in powder portion. System 80–19-S was the crosslinked poly(MMA-AAS-AMA)-modified bone cement, which contained in powder portion 19 g of commercial powder and 1 g of crosslinked poly(MMA-AAS-AMA) at a volume ratio of 80/20/10 (MMA/AAS/AMA). System 70–19-S was the crosslinked poly(MMA-AAS-AMA)-modified bone cement,

**TABLE II**  
**The Various Compositions in the Powder Portion of the Bone Cement for Each System: Commercial Bone Cement and Crosslinked Poly(MMA-AAS-AMA)-Modified Bone Cement**

System	Commercial product	Powder (g)		Liquid (mL) Commercial product
		80/20/10	70/30/10	
Commercial	20	0	0	10
80–19-S	19	1	0	10
70–19-S	19	0	1	10
80–17-S	17	3	0	10
70–17-S	17	0	3	10

**TABLE III**  
**The Various Compositions in the Powder Portion**  
**of the Bone Cement for Each System: Crosslinked**  
**Poly(MMA-AA-AMA)-Modified Bone Cement**

System	Commercial product	Powder (g)		Liquid (mL) Commercial product
		80/20/10	70/30/10	
80-19	19	1	0	10
70-19	19	0	1	10
80-17	17	3	0	10
70-17	17	0	3	10

which contained in powder portion 19 g of commercial powder and 1 g of crosslinked poly(MMA-AAS-AMA) at a volume ratio of 70/30/10 (MMA/AAS/AMA). System 80-17-S contained in powder portion 17 g of commercial powder and 3 g of crosslinked poly(MMA-AAS-AMA) at a volume ratio of 80/20/10 (MMA/AAS/AMA). System 70-17-S contained in powder portion 17 g of commercial powder and 3 g of crosslinked poly(MMA-AAS-AMA) at a volume ratio of 70/30/10 (MMA/AAS/AMA).

To compare with the swelling rates of the crosslinked poly(MMA-AAS-AMA)-modified bone cements, the crosslinked poly(MMA-AA-AMA)-modified bone cements were also prepared as shown in Table III. The denotations of the crosslinked poly(MMA-AA-AMA)-modified bone cement systems are similar to those in Table II, but the volume ratio of the crosslinked poly(MMA-AA-AMA)-modified bone cement systems is based on MMA/AA/AMA.

### Analysis

The chemical characterization of the sample was performed by Fourier transform infrared spectroscopy (Perkin Elmer, Spectrum one). Thermogravimetric analysis (TGA) experiment was performed with Thermogravimetric Analyzer (PerkinElmer, PYRIS 1 TGA) under air flow at a heating rate of 20°C/min. The dynamic mechanical properties of the 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 35 × 11 × 2.7 mm<sup>3</sup>. The measuring temperatures ranged from 25 to 150°C at 3°C/min, and the frequencies swept at 1, 3, 5, and 10 Hz. For sinusoidal oscillations,  $\tan \delta = E''/E'$ , where  $E''$  is loss modulus and  $E'$  is elastic modulus.<sup>13</sup> From the variation of  $\tan \delta$  with temperature, there was a peak corresponding to  $\alpha$ -transition. The  $\alpha$ -transition corresponded to the glass transition of bone cement.<sup>14</sup>

### Swelling measurement

Swelling measurements (described here as percentage weight changes) were carried out on the commercial bone cement and the modified bone cement containing MMA/AAS/AMA or MMA/AA/AMA at various ratios. Five specimens of each system were fully immersed in saline solution (0.9% NaCl solution obtained from Otsuka Taiwan) and kept at 37°C for 1200 h. The specimens had the dimensions: 6.0 mm in diameter and 12.5 mm in length. At various time intervals the swollen specimens were weighed, after being surface dried, and the percentage swell at any given time (% weight gain, %W) was calculated as follows:

$$\%W = [(W_t - W_0)/W_0] \times 100,$$

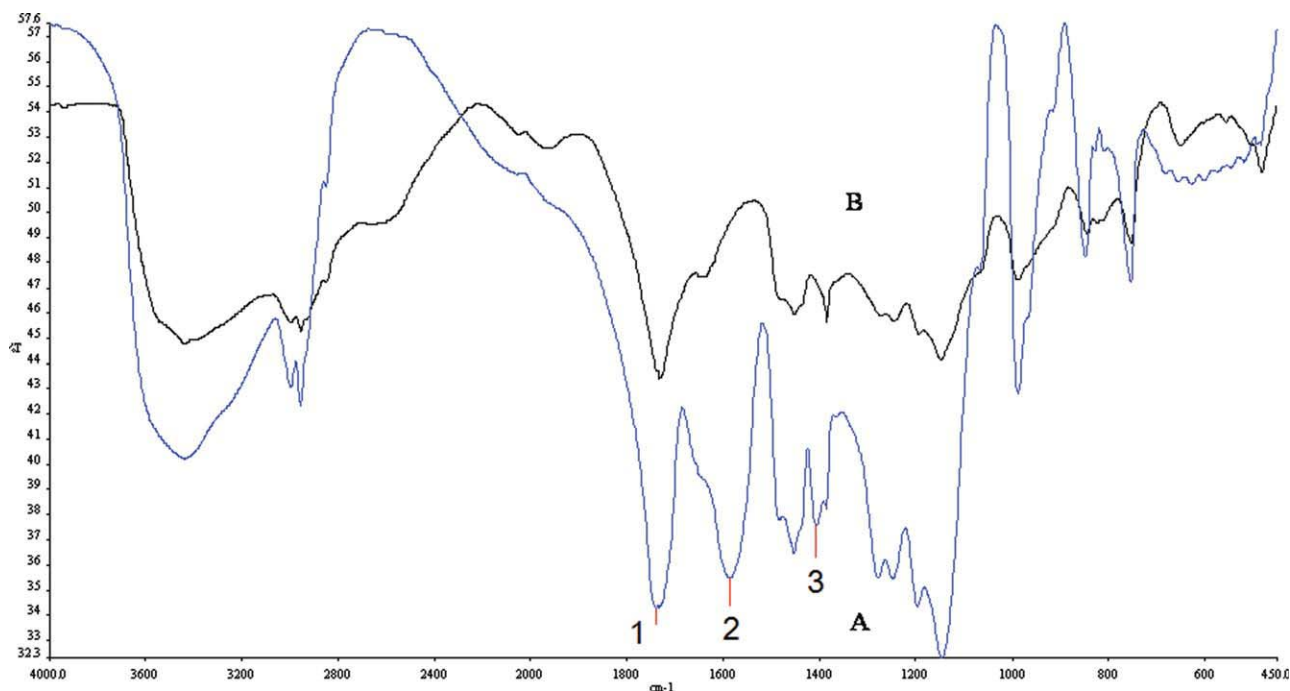
where  $W_t$  is the weight of the specimen at time  $t$  and  $W_0$  is the weight of the specimen in the dry state at time zero.

### Tensile test and compressive test

Before testing, all the specimens were fully immersed in saline solution (0.9% NaCl solution obtained from Otsuka Taiwan) and kept at 37°C for 1200 h. The tensile strength and the compressive strength of bone cement were measured using INSTRON 5582. The compressive analyses of the bone cements were according to ASTM F 451. The diameter and length of a specimen for compressive analysis of bone cement were 6.0 and 12.5 mm, respectively. The crosshead speed for compressive test was 25 mm/min. The tensile analyses of the bone cements were according to the work of Harper and Bonfield.<sup>15</sup> The crosshead speed for tensile test was 5 mm/min. The dimensions of a specimen for tensile analysis were 75 mm in length, 5 mm in width, and ~ 3.5 mm in thickness, with a gauge length of 25 mm.

## RESULTS AND DISCUSSION

Figure 1 is the FTIR spectra of prepolymerized crosslinked poly(MMA-AAS-AMA) and crosslinked poly(MMA-AA-AMA) powder. The absorption peaks of carbonyl stretching in carboxylic acid and ester are 1710-1780 cm<sup>-1</sup> and 1750-1735 cm<sup>-1</sup>, respectively. The absorption peak of carbonyl group in both crosslinked poly(MMA-AAS-AMA) and crosslinked poly(MMA-AA-AMA) powder was about 1738 cm<sup>-1</sup> (Peak 1 in Fig. 1). The wavenumbers of the asymmetrical and symmetrical stretching vibrations attributed to the carboxylate anion are around 1570-1550 cm<sup>-1</sup> (strong) and around 1420-1400 cm<sup>-1</sup> (weak).<sup>16,17</sup> Rufino and Monteiro show that the wavenumber of asymmetric stretching vibration for

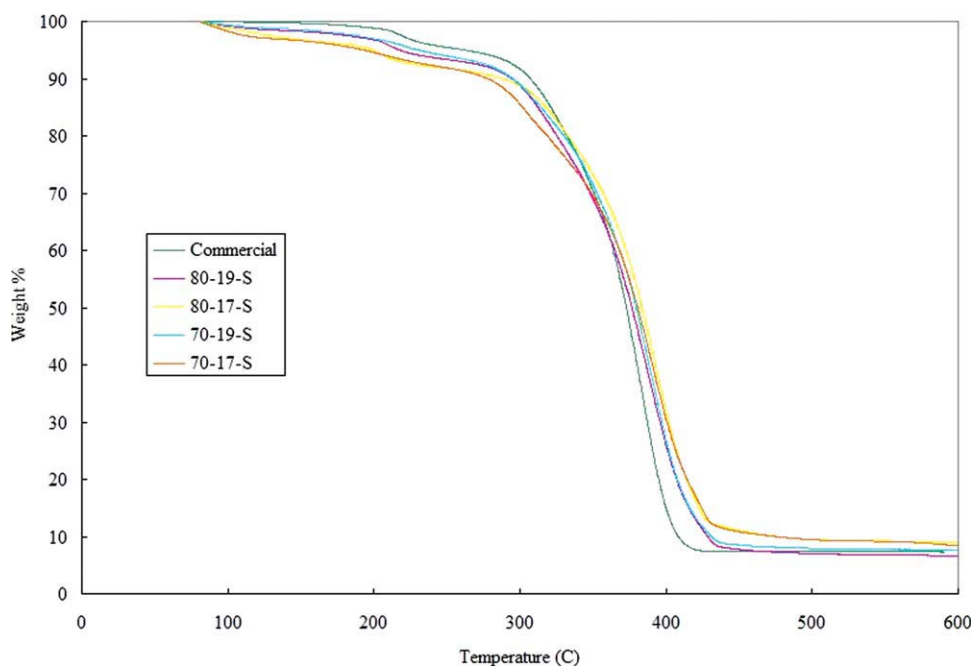


**Figure 1** The FTIR spectra of (A) crosslinked poly(MMA-AAS-AMA) and (B) crosslinked poly(MMA-AA-AMA). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

sodium salts of poly(methacrylic acid) is  $1566\text{ cm}^{-1}$ .<sup>18</sup> Hadzija and Spoljar determined the infrared spectroscopy of  $\text{COO}^-$  antisymmetric stretch vibration at  $1580\text{ cm}^{-1}$ .<sup>19</sup> In this study, the wavenumbers of the asymmetrical and symmetrical stretching vibrations for carboxylate anion of crosslinked poly(MMA-AAS-AMA) were  $1586$  and  $1407\text{ cm}^{-1}$  (Peaks

2 and 3 in Fig. 1), respectively. The crosslinked poly(MMA-AA-AMA) did not show these peaks, because of no carboxylate ion existed in the cross-linked poly(MMA-AA-AMA).

Figure 2 represents the mass loss of the bone cements observed by TGA. The measured thermal degradation temperatures ( $T_d$  at 90 and 50%) of the



**Figure 2** The mass loss of the bone cements observed by TGA. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

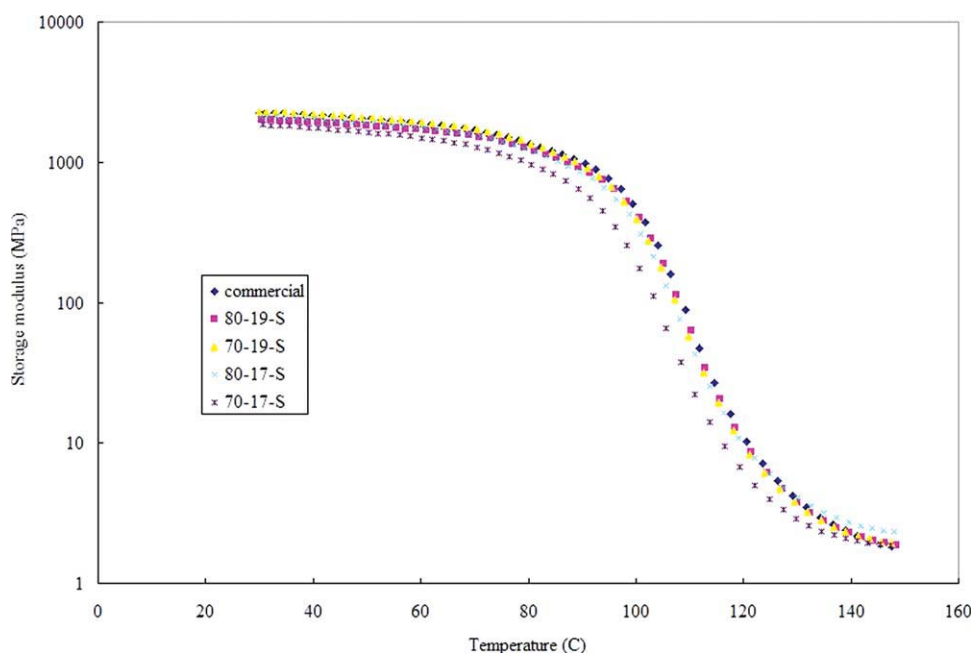
**TABLE IV**  
The Measured Thermal Degradation Temperatures ( $T_d$  at 90 and 50%) of the Bone Cements

System	$T_d$ 90% (°C)	$T_d$ 50% (°C)
Commercial	305	372
80-19-S	291	376
70-19-S	292	379
80-17-S	280	383
70-17-S	272	380

bone cements are summarized in Table IV. For all the crosslinked poly(MMA-AAS-AMA)-modified bone cements, the  $T_d$  at 90% was lower than that of the commercial bone cement. The more content of crosslinked poly(MMA-AAS-AMA) powder in the modified bone cement exhibited lower  $T_d$  at 90%, because the crosslinked poly(MMA-AAS-AMA) might still contain a small amount of H<sub>2</sub>O resulted from the conversion from crosslinked poly(MMA-AA-AMA) to crosslinked poly(MMA-AAS-AMA). However, the  $T_d$  at 50% of the commercial bone cement was lower than that of all the crosslinked poly(MMA-AAS-AMA)-modified bone cement. The more content of crosslinked poly(MMA-AAS-AMA) in the modified bone cement resulted in the higher  $T_d$  at 50%. It suggested that crosslinked poly(MMA-AAS-AMA) plays a role in thermal stability, because crosslinked poly(MMA-AAS-AMA) possessed network structure to resist thermal degradation.

Figure 3 shows the storage moduli of the five systems at 1 Hz across temperature range. It was found

that the storage moduli of all the specimens did not display significant difference at lower temperature. System 70-17-S illustrated a decrease of the modulus value across the entire temperature range. It implied that the excessive content of crosslinked poly(MMA-AAS-AMA) could lower the stiffness of the modified bone cement. It might result from the small molecular such as H<sub>2</sub>O existed in crosslinked poly(MMA-AAS-AMA) due to the conversion from crosslinked poly(MMA-AA-AMA) to crosslinked poly(MMA-AAS-AMA). It could be confirmed by TGA in Figure 2. System 70-17-S had the largest weight loss at around 100°C compared with the other bone cement systems. The large weight loss of the modified bone cement at around 100°C resulted from the vaporization of H<sub>2</sub>O. The role of H<sub>2</sub>O was similar to plasticizer, which could lower the stiffness of the bone cement. Table V is the glass transition temperatures of the five systems determined by DMA according to the method of Yang et al.'s work.<sup>14</sup> The effect of the crosslinked poly(MMA-AAS-AMA) on the glass transition temperature of the bone cement was not obvious in this study. Figure 4 is the storage moduli of System 80-19-S at various frequencies across temperature range. When sweep frequency increased, the storage modulus of the bone cement exhibited higher. The glass transition temperature of the bone cement also shifted to higher temperature at higher frequency. It was due to time dependence for the viscoelasticity of the bone cement. The viscoelastic bone cement exhibited both elastic and energy dissipation behavior. The  $T_g$  involved segmental motion



**Figure 3** The storage moduli of the five systems at 1 Hz across temperature range. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE V**  
**The Glass Transition Temperatures of the Five Systems**  
**Determined by Tan  $\delta$  Peak**

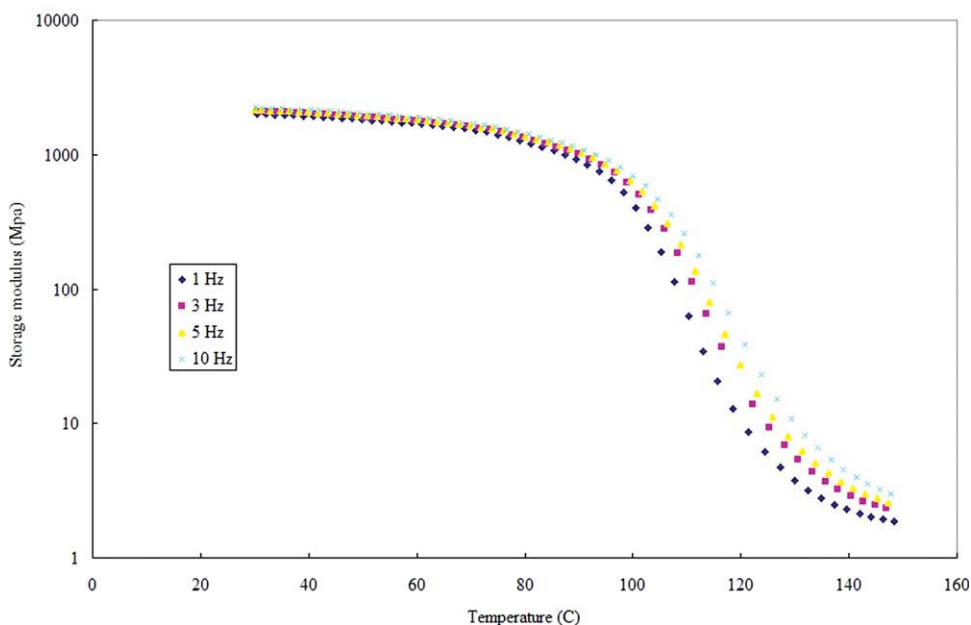
System	1 Hz	3 Hz	5 Hz	10 Hz
Commercial	114.6	121.2	122.1	125.7
80-19-S	115.6	119.2	123	123.8
70-19-S	115.4	119	119.7	123.4
80-17-S	113.6	117	120.6	123.3
70-17-S	111	117.2	118	121.5

in polymer. As the frequency increases, the relaxation associated with the  $T_g$  could only occurred at higher temperatures.

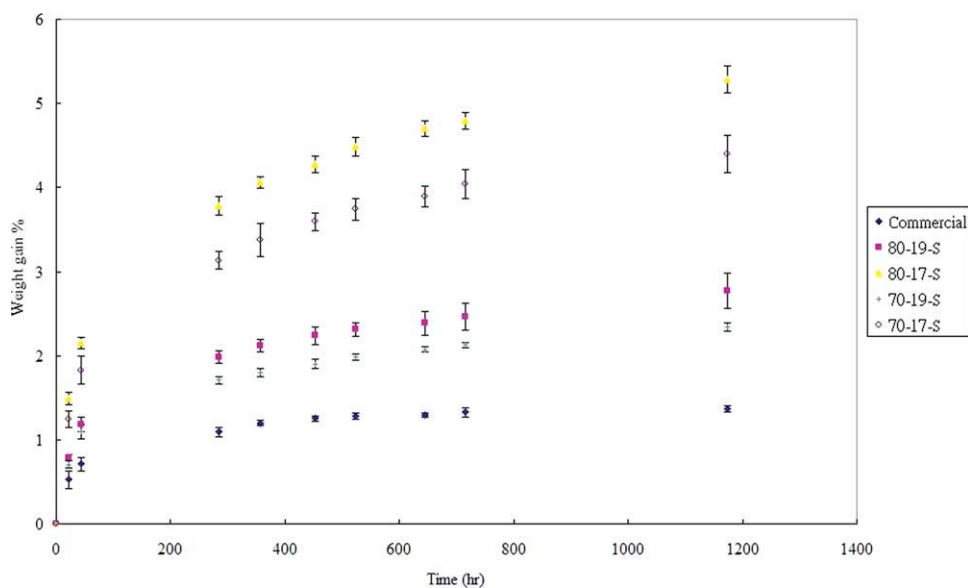
Figure 5 is the swelling measurements of the crosslinked poly(MMA-AAS-AMA)-modified bone cement systems in saline solution at 37°C for 1200 h. The more crosslinked poly(MMA-AAS-AMA) powder in the modified bone cement resulted in a higher weight gain. The absorption of water was mainly contributed by the portion of acrylic acid sodium salt (AAS). Figure 6 is the swelling measurements of the crosslinked poly(MMA-AA-AMA)-modified bone cement systems in saline solution at 37°C for 1200 h. The weight gain percentages and swelling rates of the crosslinked poly(MMA-AAS-AMA)-modified bone cement systems were much higher than those of the crosslinked poly(MMA-AA-AMA)-modified bone cement systems. It was due to the contribution of AAS in the modified bone cement. AAS was considered to possess anionic and cationic charges leading to better ability to absorb water than

AA. Once the outer shell of bone cement swelled, water penetrated easily the inner core of the modified bone cement. Thus, the swelling rate of the modified bone cement was also improved. In Figure 5, System 70-17-S had less weight gain than System 80-17-S. The reason was that System 70-17-S in the beginning contained more H<sub>2</sub>O than System 80-17-S did. This could be confirmed again by TGA in Figure 2, where System 70-17-S had larger weight loss than System 80-17-S at around 100°C. System 70-19-S also showed less weight gain than System 80-19-S. In Figure 6, System 70-17 had higher weight gain than System 80-17 and System 70-19 had higher weight gain than System 80-19. It was caused by the more component of AA in the crosslinked poly-(MMA-AA-AMA)-modified bone cement systems. The carboxylic acid of AA is hydrophilic.

Table VI is the results of the tensile and compressive strength of the bone cement tested in this study. Harper and Bonfield reported that the tensile strength of the Osteobond bone cement was  $38.2 \pm 2.65$  MPa.<sup>15</sup> The tensile strength of the Osteobond bone cement we measured was  $40.2 \pm 4.9$  MPa. The compressive strength of bone cement usually varies from 44 to 103 MPa.<sup>20</sup> Our measurement in the compressive strength of the Osteobond bone cement was  $105.3 \pm 21.9$  MPa. The tensile and compressive strength of the commercial system, System 80-19-S and System 70-19-S, are comparable. System 80-17-S and System 70-17-S had lower tensile and compressive strength than the commercial bone cement. It was due to the absorption of water by more crosslinked poly(MMA-AAS-AMA) leading to the weakness of mechanical properties. Crosslinked



**Figure 4** The storage moduli of System 80-19-S at various frequencies across temperature range. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



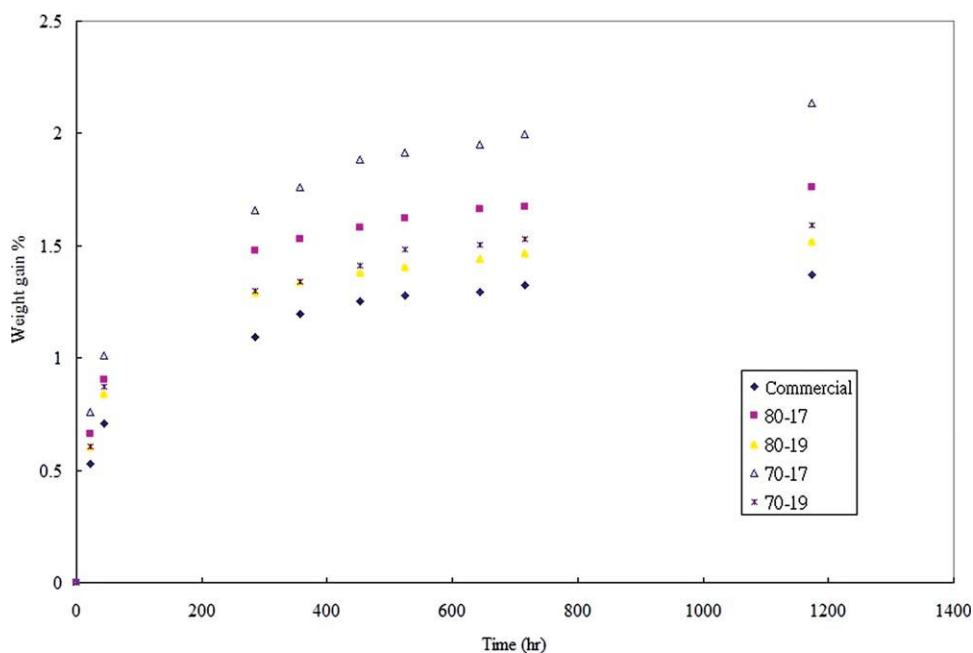
**Figure 5** The swelling measurements of the crosslinked poly(MMA-AAS-AMA)-modified bone cement systems in saline solution at 37°C for 1200 h. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

poly(MMA-AAS-AMA) is hydrophilic. Therefore, the proper content of crosslinked poly(MMA-AAS-AMA) in bone cement was able to swell. However, the excess of crosslinked poly(MMA-AAS-AMA) could lower the mechanical properties of the modified bone cement.

## CONCLUSIONS

Crosslinked poly(MMA-AAS-AMA)-modified bone cement has been prepared and characterized in this

study. It was demonstrated by FTIR that the wave-numbers of the asymmetrical and symmetrical stretching vibrations for carboxylate anion of cross-linked poly(MMA-AAS-AMA) were 1586 and 1407  $\text{cm}^{-1}$ , respectively. From TGA, it illustrated that introducing crosslinked poly(MMA-AAS-AMA) powder improved the thermal stability of bone cement. In DMA, the excessive content of poly(MMA-AAS-AMA) lowered the stiffness of the modified bone cement, because of water existed in



**Figure 6** The swelling measurements of the crosslinked poly(MMA-AA-AMA) bone cement systems in saline solution at 37°C for 1200 h. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE VI**  
**The Results of the Tensile and Compressive Strength of the Bone Cement Tested in This Study**

System	Tensile strength (MPa)	SD	Compressive strength (MPa)	SD
Commercial	40.2	4.9	105.3	21.9
80-19-S	36.6	1.4	100.4	4.7
70-19-S	33.2	7.6	104.7	10.8
80-17-S	24.4	0.7	81.6	3.8
70-17-S	23	13.4	78.8	10.2

poly(MMA-AAS-AMA). The glass transition temperature of the bone cement shifted to higher temperature at higher frequency because of viscoelasticity. For swelling measurement, the weight gain percentage and swelling rate of crosslinked poly(MMA-AAS-AMA)-modified bone cement systems were much higher than those of crosslinked poly(MMA-AA-AMA)-modified bone cement systems. The proper content of crosslinked poly(MMA-AAS-AMA) in bone cement was able to swell. The excess of crosslinked poly(MMA-AAS-AMA) could lower the mechanical properties of the modified bone cement.

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