

Toughening Effect of Comonomer on Acrylic Denture Base Resin Prepared via Suspension Copolymerization

Junping Zheng, Lei Wang, Yumei Hu, Kangde Yao

Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

Received 28 January 2011; accepted 27 April 2011

DOI 10.1002/app.34757

Published online 24 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this article, three copolymers used as denture base resins were prepared via suspension copolymerization using butyl acrylate (BA), butyl methacrylate (BMA), or methyl acrylate (MA) with methyl methacrylate (MMA), respectively. The homopolymers and copolymers were characterized by ^{13}C nuclear magnetic resonance (^{13}C NMR). The influence of the three comonomers on the mechanical property was investigated in details and the fracture surfaces of copolymer specimens were examined using scanning electron microscopy (SEM). Meanwhile, the T_g values of three copolymers were examined by differential scanning calorimetry (DSC). The results indicate that, poly(methyl methacrylate) (PMMA) copolymers with

BA, BMA, or MA have been successfully prepared via suspension copolymerization. The presence of BA, BMA, or MA could improve the mechanical property especially the impact strength, the toughness of the materials was remarkably improved. The toughening effect of BMA monomer is most significant. When the content of BA is 2 wt %, the flexural strength improves by 51% and the impact strength improves by 81.3%. The T_g values of three copolymers all decrease. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2406–2413, 2012

Key words: PMMA; suspension copolymerization; mechanical property; denture base resin

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is the resin of choice for fabrication of denture bases in clinical dentistry. Denture base materials require high strength including tensile strength, flexural strength, and impact strength to resist the effect of complex forces in the oral cavity. On the other hand, it is requested that materials exhibit small deformation under forces. At present, PMMA has been widely applied to various prosthetic replacement operations. For comfortable long lasting wear, the desired denture base materials should possess a desired balance of stiffness and toughness. The stiffness of the commercial denture base materials seems satisfactory. However, the toughness of PMMA cannot sufficiently satisfy the requirements of prosthetic replacement. Even though PMMA denture base materials have optimal choice of clinical experience and indication, the arrangement of false teeth, and the most reasonable operation process, there are still

some problems on mechanical strength, especially the low impact strength, which frequently causes the breakage of denture base materials.^{1–3}

In the past few decades, various attempts have been taken to improve the mechanical property of acrylic denture base resin.^{3–11} Two main methods have been adopted with the purpose of making the mechanical property better. One is the chemical modification of acrylic resin through the incorporation of rubber, which has been successful in terms of improving the impact strength. However, the incorporation of rubber has not been entirely successful in that it can contribute to the reduced stiffness, enhanced creep, and water sorption.^{8,9} The other is the reinforcement of acrylic resin by introducing reinforcements into the PMMA matrix, which is a commonly used method. The reinforcing effect of metallic reinforcement is not reliable despite of a long history. At present, fiber and nanoparticle have become the most commonly used reinforcements of the denture base. For instance, Köroglu et al. compared the transverse strength, modulus of elasticity, and impact strength values of unreinforced heat-polymerized and microwave-polymerized denture base resin with those of denture base resin reinforced with continuous unidirectional E-glass, woven E-glass and UHMWPE fibers.¹⁰ Lee et al. synthesized the PMMA/SiO₂-CaO nanocomposite. This nanocomposite could potentially be applied as a

Correspondence to: J. Zheng (jppzheng@tju.edu.cn).

Contract grant sponsor: Program for New Century Excellent Talents in University, People's Republic of China.

filler material of PMMA bone cement and dental composite resin because of its good apatite-forming ability and improved fracture toughness.¹¹ Some properties especially tensile strength of PMMA matrix could be significantly enhanced via these approaches. However, it is unsatisfactory in improving the toughness of matrix, in other words, the flexural strength and impact strength have not been significantly improved.

Copolymerization approach is considered as an attractive method for preparing the ductile materials. In recent years, copolymerization approach has also been aware of a potential candidate as a method for improving the toughness of PMMA denture base resin. Only PMMA-based materials by suspension polymerization can be widely applied in dentures¹² and surgical bone cements.¹³ However, to the best of our knowledge, few studies were reported on the suspension copolymerization of methyl methacrylate (MMA). Davy et al. synthesized novel iodinated methacrylate copolymers via suspension copolymerization to obtain X-ray opaque denture base resins.¹⁴ A heat-resistant copolymer using N-cyclohexylmaleimide (CHMI) and styrene (St) with MMA has been synthesized by a solution copolymerization method and a suspension copolymerization method.¹⁵ A methacrylate copolymer based on isobornyl methacrylate (IBMA) and MMA prepared in an aqueous suspension via free-radical polymerization has been reported, and the heat resistance was improved.¹⁶ Obviously, there was no report about improving the mechanical property of denture base resin, although prepared by a suspension copolymerization method.

To improve the mechanical property especially the toughness of acrylic denture base resin, in this article, three copolymers were prepared via suspension copolymerization using butyl acrylate (BA), butyl methacrylate (BMA), or methyl acrylate (MA) with MMA, respectively. Three comonomers mentioned above rather than other comonomers were chosen for two reasons. First, double bonds are contained in acrylic or methyl acrylic monomers so that polymerization and cross-linking are available. Second, both BA and BMA have flexible side groups, while there is less obstacle for the movement of MA compared with MMA. The aim of this article is to improve the toughness of PMMA matrix without damaging other properties, especially the tensile strength.

EXPERIMENTAL

Materials

MMA, BA, BMA, and MA were purchased from Da-Mao Institute of Chemical Agents (Tianjin, China) and purified by the standard treatment with 5 wt % aqueous NaOH followed by deionized water. MMA,

BA, and MA were distilled at a normal pressure. These four monomers then were stored at low temperature before use. Benzoyl peroxide (BPO, analytical grade, Beijing Chemical Factory, Beijing, China) was used as an initiator. Hydroxyethyl cellulose (HEC, analytical grade, Heda Co., Shandong, China) was used as a dispersant. Sodium dodecyl benzene sulfonate (SDBS, analytical grade, Tianjin Tianzhi Fine Chemical Co., Tianjin, China) was used as a surfactant. Other reagents were all of analytical grade. Deionized water was used throughout.

Suspension copolymerization of three copolymers

Three copolymers were prepared respectively by suspension copolymerization in three-necked, round-bottomed flask equipped with a reflux condenser, a nitrogen gas inlet and a stirrer. Mixtures (60 mL) of varying proportions of MMA and each comonomer (the content of BA, BMA, or MA varied from 0 wt % to 5 wt %) were added to the three-necked flask respectively and followed by adding deionized water (180 mL) containing 1.8 g HEC and 0.072 g SDBS. The achieved mixtures were stirred at 300 rpm under a nitrogen atmosphere for 30 min to obtain homogeneous suspension systems. Then, the suspension copolymerization reactors were heated to 75°C. After BPO (0.6 g) was employed to the system, the reaction was performed for 6 h under stirring at 700 rpm. The products were repeatedly washed with deionized water, followed by filtered and then dried in a vacuum oven overnight at 65°C to obtain powder of three copolymers, which named as P(MMA-co-BA), P(MMA-co-BMA), and P(MMA-co-MA), respectively.

Preparation of specimens of mechanical property

Obtained copolymer powders and dental base resin (liquid) supplied by Shanghai Dental Material Co. (Shanghai, China) were mixed with the mass ratio of 1.5:1 and introduced into the resin dough. The dough were put into the mold and pressed under a pressure of 4 MPa in a pressing apparatus. The mold was placed in water and heated to 70°C, and this temperature was maintained for 90 min. The temperature of the water was then increased to 100°C and kept for 60 min. The specimens were removed from the mold after cooling to room temperature and the polished specimens were divided into two groups. A group of specimens were used for further mechanical tests. The other group of specimens were immersed in the artificial saliva at 37°C for 7 days before carrying out the mechanical tests.

The standard of specimens which was in accordance with the standard of making specimens for denture bases was specified as follows: the standard of bending specimens was 64 mm × 10 mm × 3.3

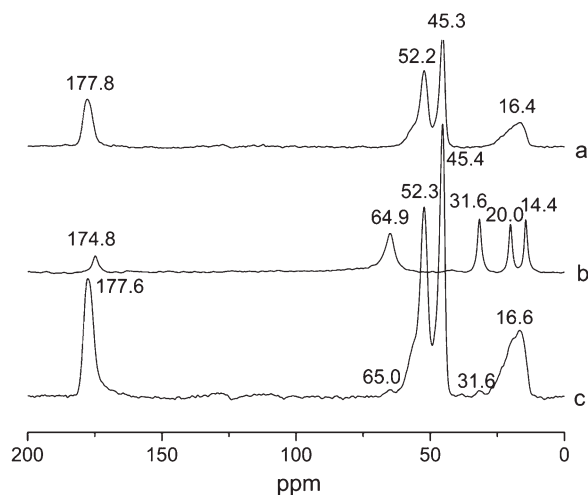


Figure 1 Solid-state ^{13}C NMR spectra of (a) PMMA, (b) PBA, and (c) P(MMA-co-BA) (the content of BA is 2 wt %).

mm, the standard of tensile specimens was 50 mm \times 7 mm \times 2 mm, the standard of impact specimens was 80 mm \times 10 mm \times 4 mm (thickness of notch: 2 mm) and the standard of specimens for hardness tests was 50 mm \times 50 mm \times 6 mm.

Mechanical tests

The three-point bending tests of the specimens were performed at room temperature by using a Testometric Universal Tester M350-20kN at a crosshead speed of 5 mm/min. The span between loading points was 50 mm. At least five specimens were tested for each samples and mean values are reported.

The tensile tests of the specimens were carried out at room temperature by using a Testometric Universal Tester M350-20kN at a crosshead speed of 2 mm/min. At least five specimens were tested for each samples and mean values are reported.

The impact tests of the specimens were carried out at room temperature by using a Charpy Impact Tester XJJ-50. The span between loading points was 50 mm. At least five specimens were tested for each samples and mean values are reported.

The Rockwell hardness of the samples were measured at room temperature by using a Rockwell Apparatus XHRD-150. Three points selected randomly were tested for each samples and mean values are reported.

Characterization

The solid-state ^{13}C NMR spectra were obtained on Varian Infinity plus 300 WB spectrometer operating at 300 MHz. The chemical shifts were expressed with respect to the signal of tetramethylsilane.

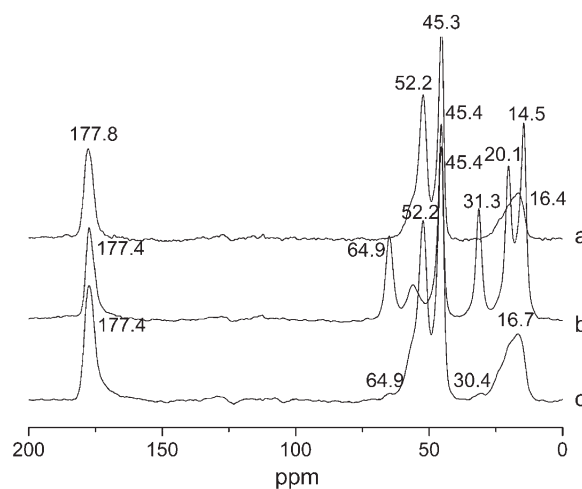


Figure 2 Solid-state ^{13}C NMR spectra of (a) PMMA, (b) PBMA, and (c) P(MMA-co-BMA) (the content of BMA is 2 wt %).

Examination of the fracture surfaces was performed on a Philips XL-30 scanning electron microscope (SEM). The fracture ends of the tensile specimens were sputter coated with a thin layer of gold before examination.

Differential scanning calorimetry (DSC) was carried out with a Perkin Elmer Pyris Diamond DSC instrument range from 25 to 200°C at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Synthesis of three copolymers

To confirm the success of suspension copolymerization, ^{13}C NMR was used. The solid-state ^{13}C NMR spectra of the homopolymers and copolymers (the content of comonomer is 2 wt %) are shown from Figures 1-3.

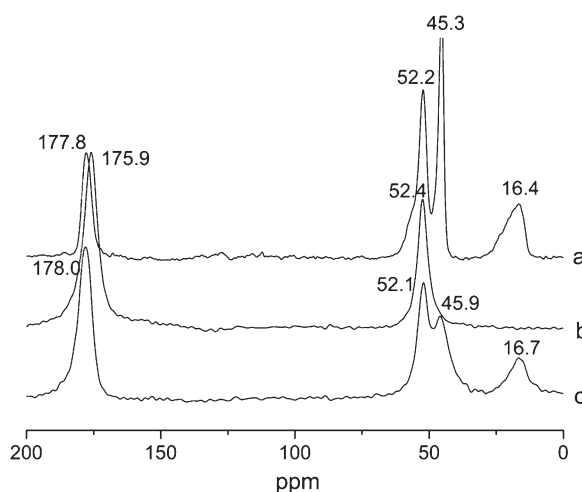


Figure 3 Solid-state ^{13}C NMR spectra of (a) PMMA, (b) PMA, and (c) P(MMA-co-MA) (the content of MA is 2 wt %).

TABLE I
Mechanical Property of Pure PMMA And P(MMA-co-BA)

Mechanical property	BA content (wt %)					
	0	1	2	3	4	5
Flexural strength (MPa)	130.7 ± 1.2	159.3 ± 1.6	190.1 ± 1.3	192.2 ± 2.3	196.5 ± 1.5	176.1 ± 2.6
Flexural modulus (GPa)	8.15 ± 0.08	9.31 ± 0.04	9.97 ± 0.12	9.19 ± 0.06	8.75 ± 0.07	8.72 ± 0.05
Flexural strain at break (%)	2.23 ± 0.06	2.49 ± 0.02	2.71 ± 0.07	2.95 ± 0.04	3.02 ± 0.06	2.65 ± 0.05
Tensile strength (MPa)	46.5 ± 1.3	47.2 ± 0.9	47.5 ± 2.1	59.1 ± 2.5	53.4 ± 1.5	47.2 ± 1.8
Young's modulus (GPa)	4.69 ± 0.02	5.05 ± 0.05	5.68 ± 0.03	5.75 ± 0.01	5.44 ± 0.02	5.12 ± 0.04
Elongation at break (%)	5.83 ± 0.12	5.84 ± 0.24	5.99 ± 0.09	8.72 ± 0.08	7.49 ± 0.20	7.00 ± 0.11
Impact strength (KJ/m ²)	6.4 ± 0.9	8.1 ± 0.6	8.9 ± 1.2	9.6 ± 1.3	10.7 ± 0.5	9.0 ± 1.0

The ¹³C NMR spectra of all polymers show the appearance of signal at 174–178 ppm corresponds to the carbon atom of —C=O. In the ¹³C NMR spectra of three copolymers, there are mainly three strong resonance humps: around 52 ppm (the carbon atom in —O—CH₃), around 45 ppm (the quaternary carbon atom) and around 16 ppm (the carbon atom in —CH₃), which correspond to the structure of PMMA.

In the ¹³C NMR spectra of P(MMA-co-BA) and P(MMA-co-BMA), there are also two weak resonance humps: around 65 ppm (the carbon atom in —O—CH₂—) and around 31 ppm (the carbon atom in —CH₂—CH₂—), which correspond to the structure of PBA and PBMA, respectively. The content of BA or BMA is so slight that the resonance humps corresponding to BA or BMA in the ¹³C NMR spectra of copolymers are not obvious. In Figure 3, the signal at 52.2 ppm is weaker than that at 45.3 ppm in the ¹³C NMR spectrum of PMMA, however, the signal at 52.1 ppm is stronger than that at 45.9 ppm in the ¹³C NMR spectrum of P(MMA-co-MA), which is due to the contribution of MA (there is a strong signal at 52.4 ppm in the ¹³C NMR spectrum of PMA). So it can be concluded that all of three copolymers have been successfully prepared via suspension copolymerization.

Mechanical property

The mechanical property of PMMA and three copolymers with different content of comonomers are shown from Tables I–III. It is obvious that the

tensile properties, flexural properties, and impact properties of three copolymers all firstly increase and then decrease with the increase of comonomer content.

Table I shows that the tensile strength of P(MMA-co-BA) achieves the maximum of 59.1 MPa which increases by 27.1% compared with pure PMMA when the content of BA is 3 wt %. Meanwhile, Both the Young's modulus and elongation at break also achieve the maximum. The flexural strength and impact strength reach their peaks simultaneously, which improves by 50.3% and 67.2%, respectively compared with pure PMMA when the content of BA is 4 wt %. At the same time, the flexural strain at break also reaches its peak. Table II shows that the tensile strength, flexural strength, and impact strength of P(MMA-co-BMA) reach their peaks simultaneously when the content of BMA is 2 wt %. Compared with pure PMMA, the tensile strength slightly improves by 4.1%, the flexural strength achieves 197.4 MPa which improves by 51% and the impact strength achieves 11.6 KJ/m² which improves by 81.3% when the content of BMA is 2 wt %. Meanwhile, the flexural strain at break also reaches its peak. The toughening effect of BMA monomer is particularly significant. Table III shows that the tensile strength of P(MMA-co-MA) achieves the maximum of 53.8 MPa which increases by 15.7% compared with pure PMMA when the content of MA is 3 wt %. Meanwhile, Both the Young's modulus and elongation at break also achieve the

TABLE II
Mechanical Property of Pure PMMA And P(MMA-co-BMA)

Mechanical property	BMA content (wt %)					
	0	1	2	3	4	5
Flexural strength (MPa)	130.7 ± 1.2	178.9 ± 2.2	197.4 ± 2.3	184.6 ± 3.2	173.3 ± 2.6	154.4 ± 3.5
Flexural modulus (GPa)	8.15 ± 0.08	10.4 ± 0.24	7.36 ± 0.30	8.35 ± 0.15	9.51 ± 0.26	9.36 ± 0.22
Flexural strain at break (%)	2.23 ± 0.06	3.90 ± 0.11	4.65 ± 0.09	4.60 ± 0.14	3.75 ± 0.16	3.44 ± 0.06
Tensile strength (MPa)	46.5 ± 1.3	46.3 ± 0.8	48.4 ± 1.2	46.7 ± 1.0	45.4 ± 0.3	42.2 ± 0.6
Young's modulus (GPa)	4.69 ± 0.02	6.46 ± 0.15	5.12 ± 0.20	4.52 ± 0.23	5.08 ± 0.16	5.47 ± 0.24
Elongation at break (%)	5.83 ± 0.12	5.97 ± 0.16	6.76 ± 0.20	6.92 ± 0.22	5.49 ± 0.08	4.79 ± 0.11
Impact strength (KJ/m ²)	6.4 ± 0.9	7.6 ± 0.4	11.6 ± 1.0	10.2 ± 0.8	9.8 ± 0.2	8.6 ± 0.6

TABLE III
Mechanical Property of Pure PMMA And P(MMA-co-MA)

Mechanical property	MA content (wt %)					
	0	1	2	3	4	5
Flexural strength (MPa)	130.7 ± 1.2	146.4 ± 1.8	148.5 ± 2.0	150.2 ± 2.6	186.9 ± 3.1	162.2 ± 0.7
Flexural modulus (GPa)	8.15 ± 0.08	5.84 ± 0.16	5.88 ± 0.23	6.31 ± 0.30	6.47 ± 0.19	6.14 ± 0.34
Flexural strain at break (%)	2.23 ± 0.06	3.36 ± 0.03	3.48 ± 0.32	4.55 ± 0.21	4.78 ± 0.18	4.50 ± 0.09
Tensile strength (MPa)	46.5 ± 1.3	47.0 ± 0.2	48.0 ± 0.5	53.8 ± 0.8	47.5 ± 1.5	34.8 ± 0.7
Young's modulus (GPa)	4.69 ± 0.02	5.42 ± 0.30	5.67 ± 0.12	6.01 ± 0.08	5.88 ± 0.05	4.93 ± 0.19
Elongation at break (%)	5.83 ± 0.12	5.83 ± 0.15	6.09 ± 0.04	7.09 ± 0.09	5.55 ± 0.16	4.37 ± 0.02
Impact strength (KJ/m ²)	6.4 ± 0.9	7.9 ± 0.6	9.1 ± 0.8	9.6 ± 0.9	11.1 ± 1.2	10.9 ± 0.4

maximum. The flexural strength and impact strength reach their peaks simultaneously which improves by 43% and 73.4%, respectively compared with pure PMMA when the content of MA is 4 wt %. At the same time, the flexural strain at break also reaches its peak.

The possible reasons for P(MMA-co-BA) and P(MMA-co-BMA) can be explained similarly as follows: (1) The weak-polarity groups with a longer side-chain are introduced into the PMMA molecules because of the presence of BA or BMA chain segments, which decreases the interaction force between PMMA molecules so that the molecular chains become more flexible. This implies that the flexural strength is increased and the toughness of PMMA matrix can be improved. However, the content of residual BA or BMA monomers in the copolymers becomes larger when the content of BA or BMA is relatively excessive (BA content > 4 wt % or BMA content > 2 wt %). The presence of comonomers in the copolymers will lead to the decrease of the flexural strength. (2) The free volume can become larger with the introduction of BA or BMA chain segments, which makes it easier for the molecular chains to change their conformations when subjected to impact so that much more impact energy can be absorbed. This implies that the impact strength is increased. However, the presence of BA or BMA monomers in the copolymer will also lead to the decrease of the impact strength when the content of BA is more than 4 wt % or that of BMA is more than 2 wt %. (3) Similarly, it is easy for the molecular chains to change their conformations under a stretching condition for the reason that the presence of BA or BMA chain segments makes the molecular chains become more flexible. The tensile strength can be slightly improved. However, the presence of comonomers in the copolymers will equally lead to the decrease of the tensile strength when the content of BA is more than 3 wt % or that of BMA is more than 2 wt %.

The possible reasons for P(MMA-co-MA) can be explained as follows: (1) As a matter of fact, there is

not a long side-chain in MA chain segments to make the molecular chains become more flexible, but the molecular chains can actually become more flexible considering that PMA is a kind of elastomer, hence the flexural strength is also increased and the toughness of PMMA matrix can be improved as well. However, the presence of MA monomers in the copolymer will lead to the decrease of the flexural strength when the content of MA is relatively excessive (MA content > 4 wt %). (2) Compared with MMA chain segment, there is one less methyl side group in MA chain segment, which contributes to the enhancement of the abilities for chain segments to move, and furthermore, makes it easier for the molecular chains to change their conformations when subjected to impact so that much more impact energy can be absorbed. This implies that the impact strength is increased. However, the presence of MA monomers in the copolymer will also lead to the decrease of the impact strength when the content of MA is more than 4 wt %. (3) For the same reason, it is easy for the molecular chains to change their conformations under a stretching condition. The tensile strength can be slightly improved. However, the presence of MA monomers in the copolymer will lead to the decrease of the tensile strength significantly when the content of MA is >3 wt %.

SEM photographs of the fracture surfaces of pure PMMA and PMMA copolymers with 2 wt % BA, BMA, or MA are shown in Figure 4. Apparently, the fracture surfaces of three copolymers seem coarse compared with that of pure PMMA. It illustrates that the presence of BA, BMA, or MA can improve the toughness of PMMA matrix remarkably, which is similar to some previous work to toughen the PMMA through copolymerization by methods other than suspension. For instance, the functional acrylic latexes based on the terpolymer of BA-MMA-glycidyl methacrylate (GMA) were prepared with different amounts of GMA via semi-batch emulsion polymerization, and for the uncured latex films, the flexibility was improved using higher GMA in the feed.¹⁷ The 2,3,4,5,6-Pentafluoro and 4-trifluoromethyl 2,3,5,6-

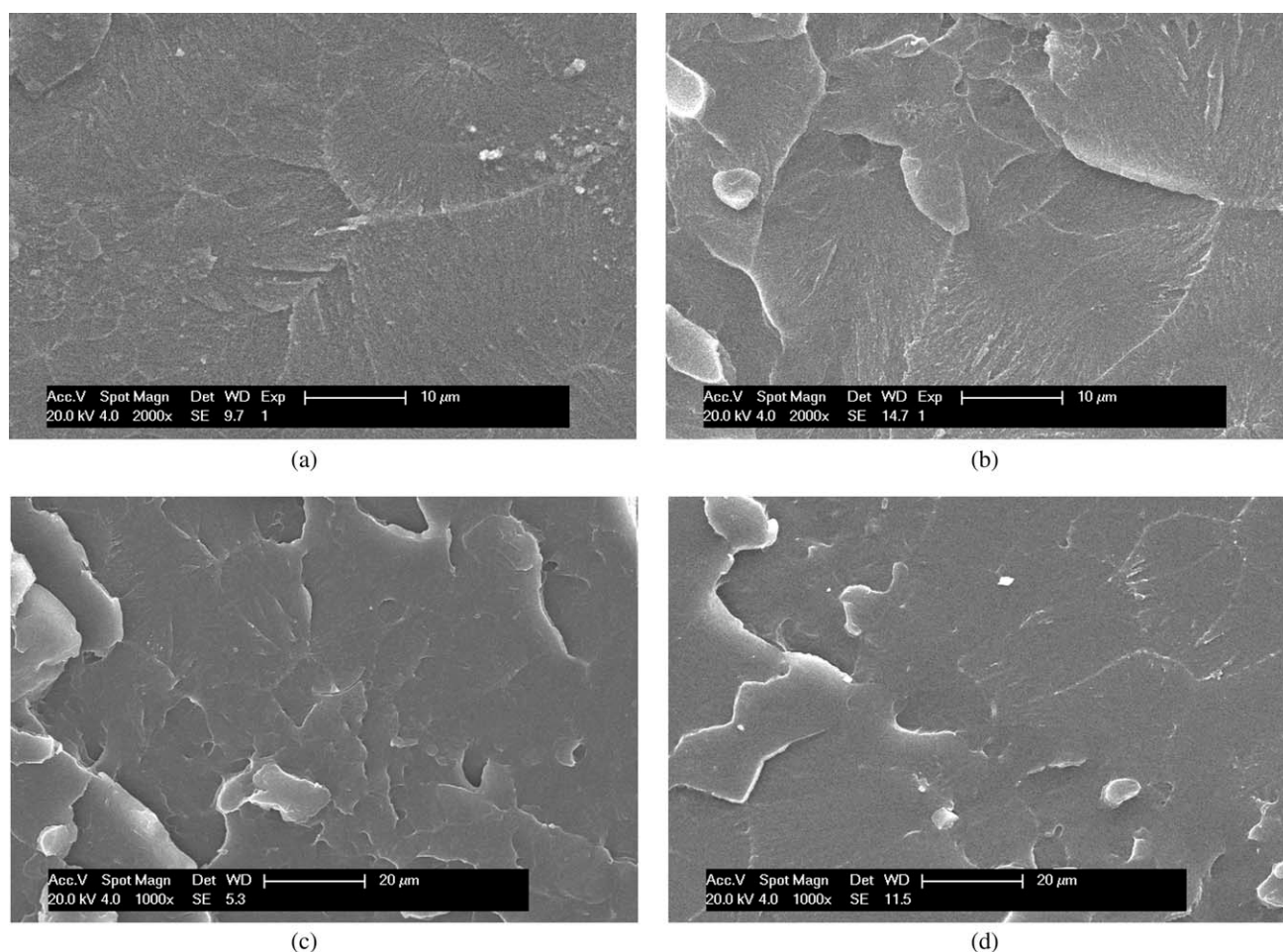


Figure 4 SEM photographs of the fracture surfaces of (a) pure PMMA, (b) P(MMA-co-BA), (c) P(MMA-co-BMA), and (d) P(MMA-co-MA) (the content of three comonomers is 2 wt %).

tetrafluoro styrenes were readily copolymerized with MMA by a free-radical initiator, and the copolymer films obtained were transparent and flexible.¹⁸

The effect of the comonomers on the hardness of PMMA matrix is shown in Figure 5. It can be observed that the hardness of three copolymers all tends to decrease with the increase of the comonomer content. Compared with pure PMMA, the hardness of P(MMA-co-BA), P(MMA-co-BMA) and P(MMA-co-MA) slightly decreases by 3.7%, 2%, and 2.3%, respectively when the content of comonomers is 5 wt %. It suggests that the introduction of the comonomers has little effect on hardness of PMMA matrix.

It is necessary to investigate the influence of the saliva environment on the mechanical property of copolymers since it is unavoidable for the acrylic denture base resins to contact with saliva. The tensile strength and flexural strength of pure PMMA and three copolymers examined after immersing 7 days under the artificial saliva environment are shown in Figure 6. First, both the tensile strength and flexural strength of pure PMMA and three

copolymers all slightly decrease under the artificial saliva environment. Furthermore, the decreased degree of three copolymers is slighter than that of

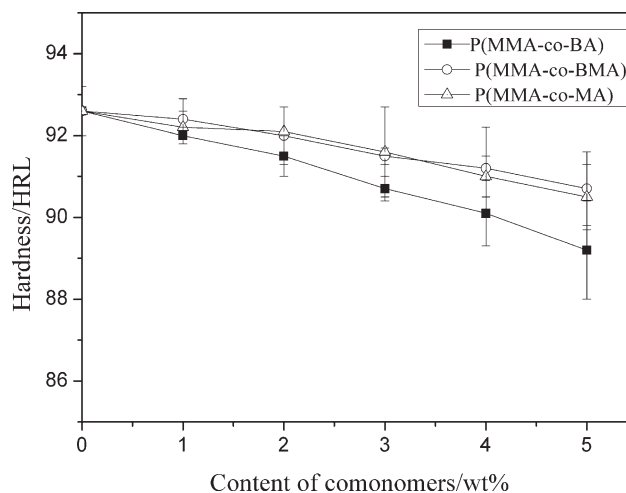


Figure 5 The effect of the comonomers on the hardness of PMMA matrix.

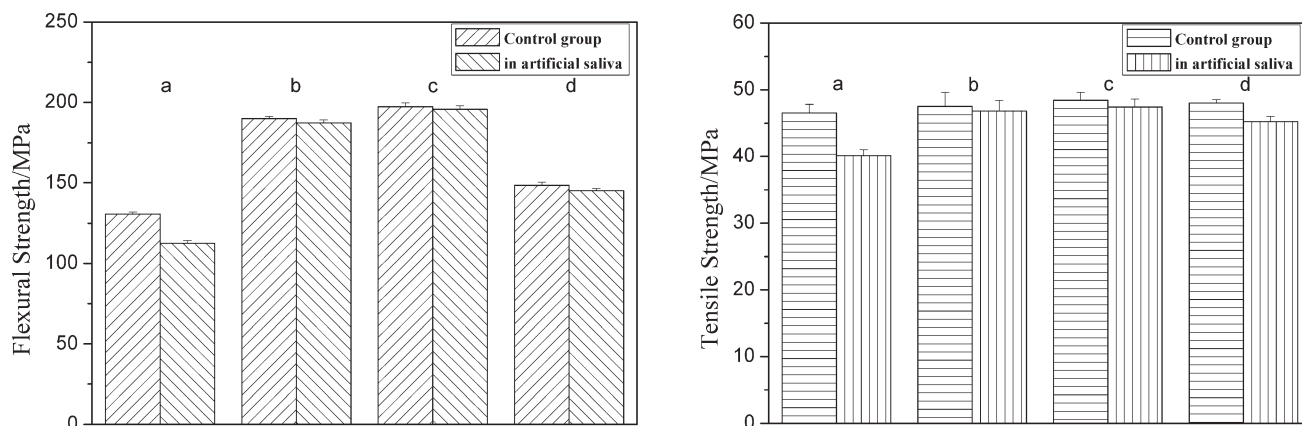


Figure 6 (i) Flexural strength: The influence of the artificial saliva environment on the flexural strength of (a) pure PMMA, (b) P(MMA-co-BA), (c) P(MMA-co-BMA), and (d) P(MMA-co-MA) (the content of three comonomers is 2 wt %); (ii) Tensile strength: The influence of the artificial saliva environment on the tensile strength of (a) pure PMMA, (b) P(MMA-co-BA), (c) P(MMA-co-BMA), and (d) P(MMA-co-MA) (the content of three comonomers is 2 wt %).

pure PMMA in terms of the tensile strength and flexural strength. The tensile strength of pure PMMA decreases by 13.8% under the artificial saliva environment while that of three copolymers decrease by 1.5%, 2.1%, and 5.8%, respectively. The flexural strength of pure PMMA decreases by 13.9% under the artificial saliva environment while that of three copolymers decrease by 1.4%, 0.8%, and 2.2%, respectively. It is obvious that this result is very valuable and significant for the denture base materials.

T_g values of three copolymers

DSC curves of P(MMA-co-BA) with different BA contents are shown in Figure 7, and the results are

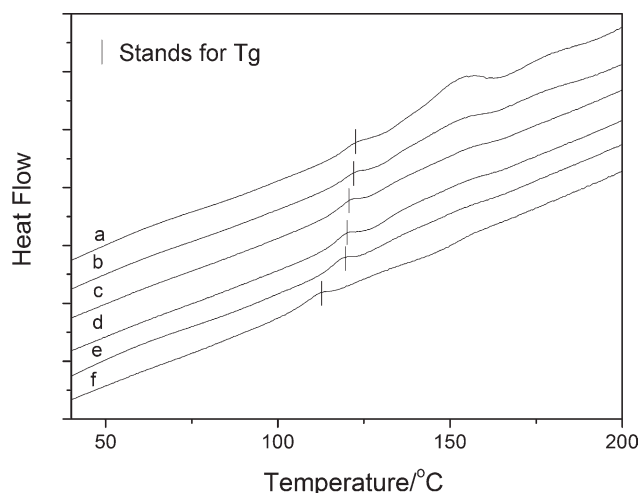


Figure 7 DSC curves of P(MMA-co-BA) with different BA contents (a) 0 wt %, (b) 1 wt %, (c) 2 wt %, (d) 3 wt %, (e) 4 wt %, and (f) 5 wt %.

listed in Table IV. The endothermic peak near 115°C is related to the glass transition of pure PMMA, while the P(MMA-co-BA) with different BA contents exhibit reduced T_g values, and the T_g value slightly reduces with the increase of BA content. When the BA content achieves 5 wt %, the T_g value of P(MMA-co-BA) reduces by nearly 10°C compared with that of pure PMMA. An explanation is that the weak-polarity groups with a longer side-chain are introduced into the PMMA molecules because of the presence of BA chain segments, which leads to a decrease of the T_g by improving chain flexibility.

The T_g values of two other copolymers were examined as well, and DSC results of them are consistent with that of P(MMA-co-BA). The T_g values of both P(MMA-co-BMA) and P(MMA-co-MA) all slightly reduce with the increase of BMA or MA content. The explanation for P(MMA-co-BMA) is that the weak-polarity groups with a longer side-chain are introduced into the PMMA molecules because of the presence of BMA chain segments, which leads to a decrease of the T_g by improving chain flexibility, and the explanation for P(MMA-co-MA) is that compared with MMA chain segment, there is one less methyl side-group in MA chain segments, which leads to a decrease of the T_g by improving chain flexibility.

TABLE IV
DSC Results of P(MMA-co-BA) with Different BA Contents

BA content (wt %)	0	1	2	3	4	5
T_g (°C)	115.0	114.3	113.1	112.0	111.4	105.6

CONCLUSIONS

The solid-state ^{13}C NMR spectra results indicated that PMMA copolymers with BA, BMA, or MA were successfully prepared via suspension copolymerization. The results of mechanical tests showed that: (1) with the increase of BA, BMA, or MA content, the tensile, flexural, and impact properties were all improved in some degree and tended to increase followed by decrease. The tensile strength was slightly improved, and the flexural and impact strength were dramatically improved, especially the impact strength, which was confirmed by SEM results of the fracture surfaces. The improved degree of P(MMA-co-BMA) in terms of the flexural strength and impact strength was greatest, in other words, the toughening effect of BMA monomer is most significant. (2) The hardness of three copolymers all tended to decrease with the increase of the comonomer content. However, it could be concluded that the introduction of the comonomers has little effect on hardness of PMMA matrix. (3) The artificial saliva environment had a certain effect on the mechanical strength of pure PMMA and three copolymers, however, the mechanical strength of copolymers was more stable than that of pure PMMA under the artificial saliva environment. Above all, the decreased mechanical strength still sufficiently meets the requirements of the denture base materials. The reduced T_g values of three copolymers were all attributed to the improved chain flexibility. This fur-

ther confirmed that the toughness of PMMA matrix was improved.

References

1. Zappini, G.; Kammann, A.; Wachtera, W. *J Prosthet Dent* 2003, 90, 578.
2. Machado, C.; Sanchez, E.; Azer, S. S.; Uribe, J. M. *J Dent* 2007, 35, 930.
3. Jancar, J.; Hynstova, K.; Pavelka, V. *Compos Sci Technol* 2009, 69, 457.
4. Jagger, D. C.; Harrison, A.; Jandt, K. D. *J Oral Rehabil* 1999, 26, 185.
5. Vallittu, P. K. *J Prosthodont* 1996, 5, 270.
6. Park, S. E.; Chao, M.; Raj, P. A. *Int J Dent* 2009, 2009, 841431.
7. Franklin, P.; Wood, D. J.; Bubb, N. L. *Dent Mater* 2005, 21, 365.
8. Cho, K.; Yang, J.; Park, C. E. *Polymer* 1998, 39, 3073.
9. Lalonde, L.; Plummer, C. J. G.; Manson, J. A. E.; Gérard, P. *Eng Fract Mech* 2006, 73, 2413.
10. Köroglu, A.; Özdemir, T.; Usanmaz, A. *J Appl Polym Sci* 2009, 113, 716.
11. Lee, K. H.; Rhee, S. H. *Biomaterials* 2009, 30, 3444.
12. Acosta-Torres, L. S.; Barceló-Santana, F. H.; Álvarez-Gayosso, C. A.; Reyes-Gasga, J. *J Appl Polym Sci* 2008, 109, 3953.
13. Kim, S. S.; Park, T. S.; Shin, B. C.; Kim, Y. B. *J Appl Polym Sci* 2005, 97, 2340.
14. Davy, K. W. M.; Anseau, M. R.; Berry, C. *J Dent* 1997, 25, 499.
15. Dong, S. S.; Wei, Y. Z.; Zhang, Z. Q. *J Appl Polym Sci* 1999, 72, 1335.
16. Park, S. I.; Lee, S. I.; Hong, S. J.; Cho, K. Y. *Macromol Res* 2007, 15, 418.
17. Bakhshi, H.; Zohuriaan-Mehr, M. J.; Bouhendi, H.; Kabiri, K. *J Mater Sci* 2011, 46, 2771.
18. Lou, L.; Koike, Y.; Okamoto, Y. *J Polym Sci Part A: Polym Chem* 2010, 48, 4938.