Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Copolymerization of Multi-Methacrylate Derivatives of Styrene-Allyl Alcohol Copolymer with Styrene and Methyl Methacrylate Monomers

Bill. M. Culbertson[a]; Yuhua Tong[a]; Qichun Wan[a]
[a] The Ohio State University, Columbus, OH, USA

To cite this Article Culbertson, Bill. M. , Tong, Yuhua and Wan, Qichun(1997) 'Copolymerization of Multi-Methacrylate Derivatives of Styrene-Allyl Alcohol Copolymer with Styrene and Methyl Methacrylate Monomers', Journal of Macromolecular Science, Part A, 34: 7, 1249 — 1260

To link to this Article: DOI: 10.1080/10601329708009383

URL: http://dx.doi.org/10.1080/10601329708009383

J.M.S.—PURE APPL. CHEM., A34(7), pp. 1249-1260 (1997)

NOTES

COPOLYMERIZATION OF MULTI-METHACRYLATE DERIVATIVES OF STYRENE-ALLYL ALCOHOL COPOLYMER WITH STYRENE AND METHYL METHACRYLATE MONOMERS

BILL. M. CULBERTSON, YUHUA TONG, QICHUN WAN

The Ohio State University
Postle Hall
305 W. 12th Ave.
Columbus, OH 43210-1241
USA

Key Words: Styrene-allyl alcohol copolymer; Styrene; Methyl methacrylate; Thermal polymerization; Glass transition temperature; Transesterification reaction; Differential Scanning Calorimetry; Compressive strength

ABSTRACT

Multi-methacrylate derivatives of styrene-allyl alcohol copolymer (SAA) were obtained by esterification reaction with methyl methacrylate (MSAA). Thermal polymerizations of MSAA with styrene and methyl methacrylate (MMA) were investigated by differential scanning calorimetry. The content of MSAA and the methacrylate groups pendant on SAA strongly affected the polymerization behavior. The results of thermal analysis and extraction studies suggested that the cured PS-MSAA mixtures were stable, crosslinked networks, and the polymerized MAA-MSAA formulations exhibited semi-IPNs structure. The PS-MSAA semi-IPNs showed potential for improving the toughness modification of polystyrene.

INTRODUCTION

Development of new matrix resins, for dental composites, is a well established area of study in our laboratory [1-3]. Recently, part of our research work has dealt with the functionalized, very low molecular weight styrene-allyl alcohol copolymer (SAA). SAA has a high percentage of primary hydroxyls (-CH_2OH) and aromatic rings, facilitating the synthesis of SAA derivatives. For example, using suitable catalysst, SAA is easily esterified with methyl methacrylate (MMA). SAA based multi-methacrylates (MSAA) were shown to be useful in formulating dental restoratives or composites with improved mechanical properties [4].

Polystyrene (PS) has been produced for a wide variety of uses. But, the brittleness and low T_g for PS renders it useless for many applications, without toughness modification. Many successful ways have been documented for toughening PS via the inclusion of compliant rubber particles [5-8]. The modification of PS with MSAA, to improve properties, has received little attention. One of the components in SAA is styrene, which helps to insure the compatibility of PS and MSAA. Secondly, both styrene and MSAA have free-radical polymerizable C=C double bonds. Thirdly, SAA has a low ($<70°C$) glass transition temperature T_g. All of these factors suggest the potential for using MSAA to modify the toughness of PS through copolymerization. This paper reports some preliminary results on the copolymerization of styrene with MSAA.

Methyl methacrylate (MMA) has the same functional C=C double bond as MSAA. Thus, with free-radical initiators, it is possible to obtain crosslinked plastics based on MSAA modification of PMMA. Therefore, the copolymerization of MMA and MSAA will also be briefly discussed in this paper.

EXPERIMENTAL SECTION

Materials

Styrene-allyl alcohol copolymer (SAA), methyl methacrylate (MMA), sodium methoxide, phenothiazine and styrene were received from Aldrich. These chemicals were used without further purification. Free radical initiator benzoyl peroxide (BPO), from Polysciences Inc., was used after recrystallization from chloroform/methyl alcohol solution.

The SAA, obtained as solid, white flakes, has hydroxl number 210±20 (milliequiv./grams) and molecular weight (GPC) 1, 600±300 (no. avg.) or 3, 000±600 (wt. avg.). In the SAA molecular chain, the ratio of styrene to allyl alcohol units is 2:1

Preparation of MSAA

A 1000 ml, three-necked, round bottom flask was fitted with a Dean-Stark trap, thermometer, mechanical stirrer and condenser. SAA (66.5 g) was dissolved in 500 ml of tetrahydrofuran and combined with MMA (100 g, 1.0 mol). Using sodium methoxide (1.8 g) as a catalyst and phenothiazine (0.5 g) as an inhibitor, the reaction was run at 68°C, until no more methyl alcohol could be detected in the trap. Evaporating most of the solvent, the remaining mixture was poured into 1500 ml of distilled water, with vigorous stirring. The solid was collected by vacuum filtration, followed by drying the white precipitate for 10 h. in a freeze-dryer. The product was further dried in a vacuum oven at 40 °C for 5 h., giving MSAA (71.5 g) as a white powder, having a polymer melt temperature (PMT) onset at 67 °C. In contrast, SAA PMT onset is 72.18 °C.

The FT-IR spectrum of MSAA showed a very weak peak at 3400cm^{-1}, assigned to the -OH group, and two additional peaks at 1718cm^{-1} (-COO-) and 1637cm^{-1} (C=C), assigned to the methacrylate group in MSAA. Assigning the absorption peak at 1601 cm^{-1} to the phenyl group as an internal standard, the reaction degree P% of the hydroxl group substituted by the methacrylate group could be estimated by comparing the area of the peak at 3400 cm^{-1} to that of the peak at 1601 cm^{-1}. The result from the above experiment was for P = 88%. Using the same procedure, MSAA with P = 56% and P = 35% were also prepared.

Copolymerization of Styrene and MMA with MSAA

The bulk copolymerization of styrene with MSAA was performed as follows. In a sealed tube, MSAA and initiator (BPO) were dissolved in styrene. Under nitrogen, the tube was sealed and immediately put into a pre-heated oven at 100°C for 3 hours. Postcuring was achieved at 140°C for 1.5 h. After cooling to room temperature, a transparent bar was obtained. The copolymerization procedure of MMA and MSAA was the same as that described for the styrene system.

Instrumental Analysis

Thermal copolymerization and the determination of glass transition temperature (T_g) were carried out on the TA Instruments 910 Differential Scanning Calorimeter (DSC). The scanning rates, for copolymerization and T_g determinations, were 10°C/min. All samples were run under nitrogen atmosphere. Data were treated by the TA Thermal Analysis 2100 program.

Mechanical Properties

The samples for mechanical properties testing were directly cut from the bulk polymerization bars. Instron mechanical testing equipment was used, with the head moving speed set at 0.5mm/min for the compressive strength (CS) determinations.

RESULTS AND DISCUSSION

Polymerization of Styrene and MSAA Mixtures

MSAA oligomers, in the experimental range studied, were completely soluble in styrene. Thus, free radical polymerization of the MSAA-styrene mixtures, initiated by BPO, can occur for either the styrene or the methacrylate pendant group on MSAA. Further, the copolymerization of these two different C=C double bonds may also occur. For the samples containing different concentrations of the MSAA with P = 88%, the thermal polymerization traces from DSC are shown in Figure 1. Compared with the homopolymerization of pure styrene, the starting temperature and peak temperature of

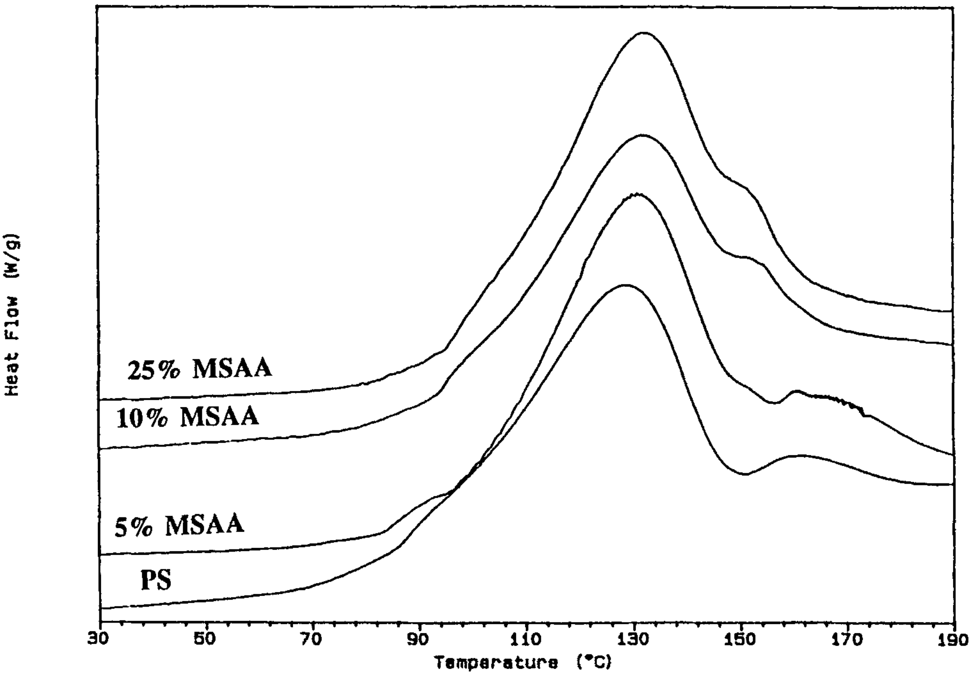

Figure 1. Thermal Polymerization Curves of Styrene/MSAA Mixtures with Different Content of MSAA (P=88%)

polymerization became higher with increasing MSAA(88%) in the mixtures, with no significant changes of the peak temperatures. Besides the main pre-polymerization peaks, a small post-polymerization peak could be observed in each trace. The peak temperature tends to move to a lower temperature with an increase of MSAA(88%) in the mixture. The post-polymerization peaks could possibly be attributed to the polymerization between macromolecular chains [9], which strongly depends on the movement and flexibility of the methacrylate functionalized MSAA chains. Generally, the MSAA molecular chain is more flexible than that of PS. As the MSAA content in the formulation is increased, lower post-polymerization temperatures are observed for the plastics.

The effect of the degree of hydroxl group converted to methacrylate group (P%) in MSAA on the polymerization is shown in Figure 2. With the same concentration of MSAA in the mixtures, the polymerization exothermic peak (ΔH) temperature increases

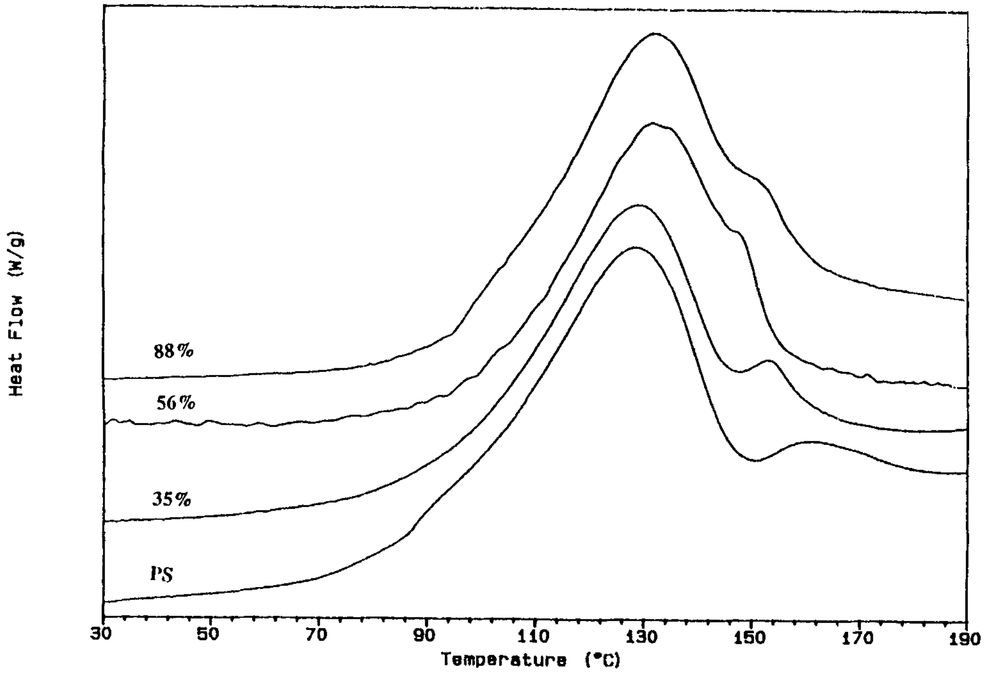

Figure 2. **Thermal Polymerization Curves of Styrene/MSAA Mixtures with Different P%**

with increasing P%. The post-polymerization peak temperature decreased with P%, but at P=88%, it moved slightly to a higher temperature. Although the MSAA chain is relatively flexible and could reduce the viscosity of the mixture during polymerization, more methacrylate groups pendant on the MSAA will increase the crosslink density, possibly retarding the post-polymerization.

Structure of PS-MSAA Copolymers

The copolymerization of styrene and MSAA mixtures should result in the formation of highly crosslinked polymer networks. For the samples containing 25% MSAA, the curves of the DSC measurements for these networks are shown in Figure 3. The sample with P=35% showed two glass transition temperatures (T_g) at 68.81°C and 84.57°C. According to the literature [10], the T_g of SAA is 69°C. This sample after polymerization appeared pale yellow, suggesting that phase separation occurred during polymerization.

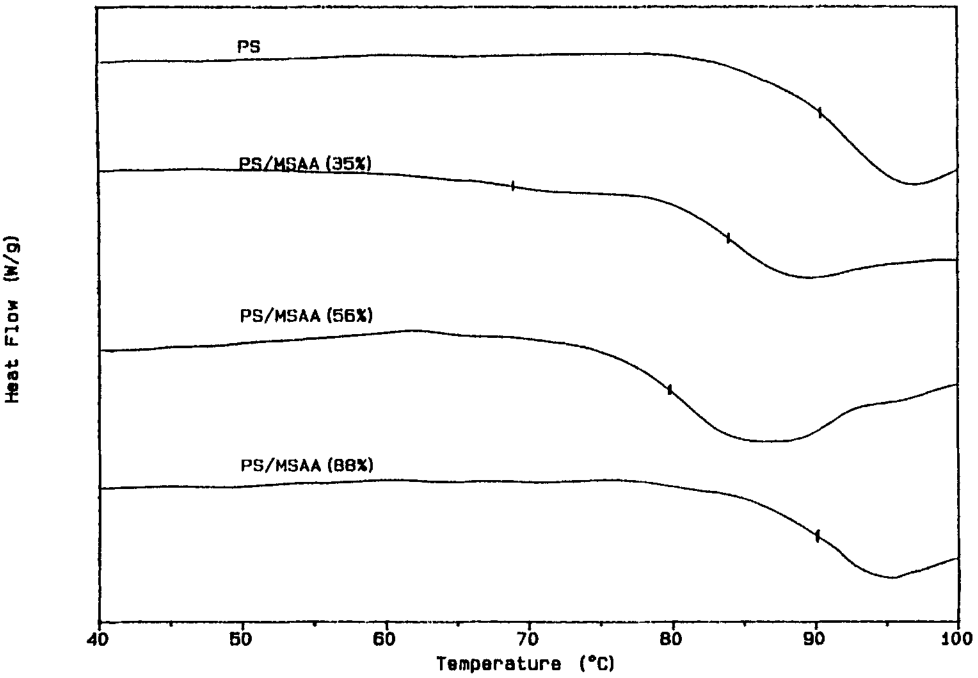

Figure 3. Glass Transition Temperatures of Cured PS/MSAA Mixtures

Only a single T_g could be observed for the cured styrene-MSAA mixture with higher P%. Samples with P=56% and P=88% were transparent, light brownish yellow plastics. These results indicated that more methacrylate groups pendant on the MSAA oligomer lead to a higher crosslink density in the plastic, which is favorable for the formation of homogeneous networks.

The effect of methacrylate groups pendant on the MSAA oligomer, on the structure of the crosslinked networks, was explored by extraction studies on the materials produced, using acetone and a Soxhlet extractor. After continuously extracting for 72 hours, the cured mixtures gave results in Table 1. After extraction, the T_g of all samples increased significantly, with the exception of the P=35% mixture, where the T_g stayed almost the same. Since the extractable fraction slightly increase as the P% decreases, the results provide evidence that there are covalent crosslinking between PS and MSAA in the network. In another words, there are stable crosslink networks in the cured materials.

Table 1. The Extraction and DSC Measurement Results of Cured PS-MSAA Mixtures[a]

Sample (P%)	Tg (°C)[b]	Tg (°C)[c]	weight loss (%)	remarks[d]
PS	92.71	—	100	colorless, TP
P=35%	68.81, 84.57	67.95, 94.77	3.95	PY, OP
P=56%	80.94	102.45	2.80	BY, TP
P=88%	90.92	113.76	1.08	BY, TP

a: all samples contained 25% MSAA; b: before extraction; c: after extraction;
d: BY = light brownish yellow, PY = pale yellow, OP = opaque, TP = transparent

The T_g of the extracted fraction from the styrene-MSAA copolymer and semi-interpenetrating polymer networks (Semi-IPN) MSAA/PS/Styrene copolymer is shown in Figure 4. The extracted fraction of MSAA/PS/Styrene IPNs had almost the same Tg (about 95°C) as that for pure PS. In contrast, the extracted fraction from the MSAA-styrene copolymer had a higher Tg at 100°C. Also, the weight loss after extraction for the MSAA-styrene copolymer mixtures are extremely small. These results indicate that little to no PS homopolymer exists in the MSAA-styrene copolymer.

Figure 5 shows the solvent (acetone) absorbing ability of these stable crosslink networks. This measurement was carried out at room temperature using acetone as solvent, with all samples having the same weight. To the samples containing 25% MSAA, the solvent absorbing abilities increased rapidly with decreasing P%. More methacrylate groups in the mixture resulted in a higher crosslinked density and tighter networks. Thus, the diffusion of solvent molecules in the networks became more difficult with increasing P%. For the sample with P = 35%, the acetone diffusion equilibrium could be observed before 15 hours. In contrast, the acetone diffusion rates were much slower for the other two samples with higher P%.

Mechanical Properties of PS-MSAA Crosslinked Networks

Compressive stress testing is commonly used to describe brittle materials. The compressive strength (CS) of all samples with different P% and different MSAA

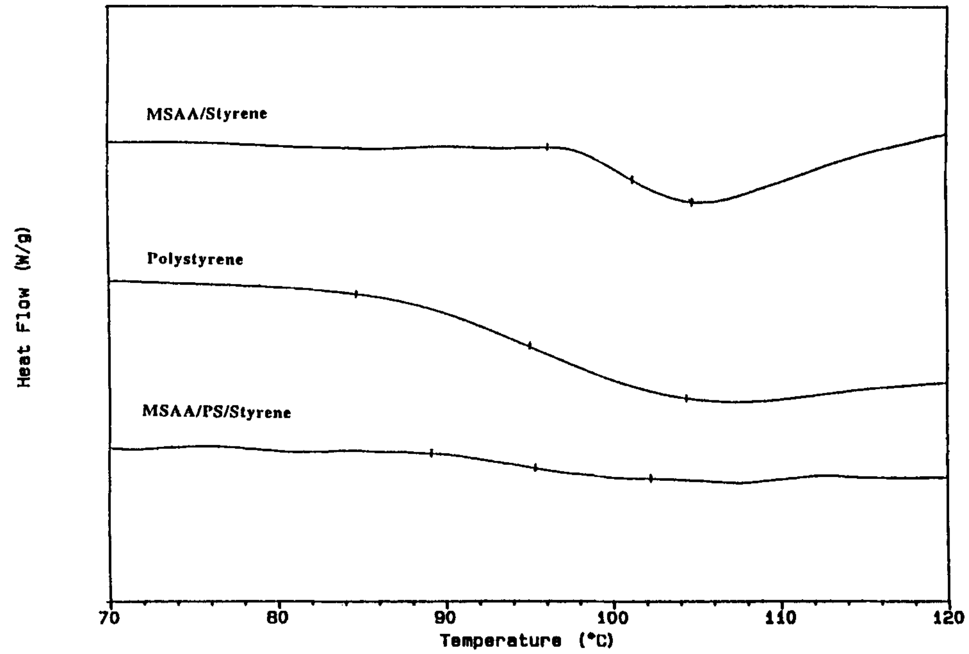

Figure 4. Glass Transition Temperatures of Cured MSAA/Styrene Mixtures and Semi-IPN MSAA/PS/Styrene

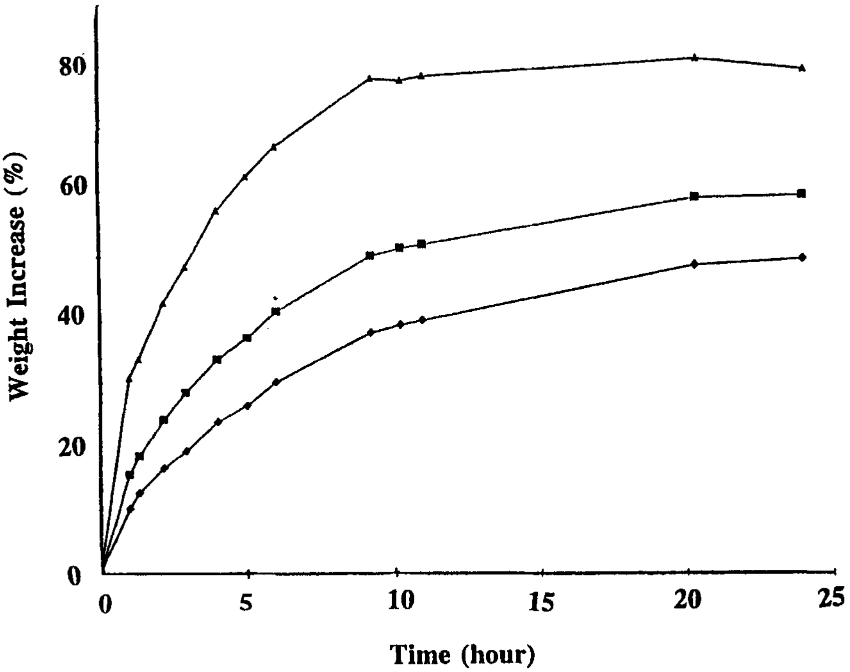

Figure 5. Acetone Diffusion Curves for Cured PS/MSAA Mixtures (◆ MSAA (P=88%) ■ MSAA (P=56%) ▲ MSAA (P=35%))

Table 2. The Compressive Strength Values of Cured PS-MSAA Mixtures

PS/MSAA[a] (P%)	100/0	75/25 (88)	75/25 (56)	75/25 (35)	90/10 (88)	90/10 (56)	90/10 (35)	95/5 (88)	95/5 (56)	95/5 (35)
CS, MPa	30.17	98.47	89.57	76.56	95.23	85.02	61.82	44.98	26.57	20.44

a: PS/MSAA: wt/wt

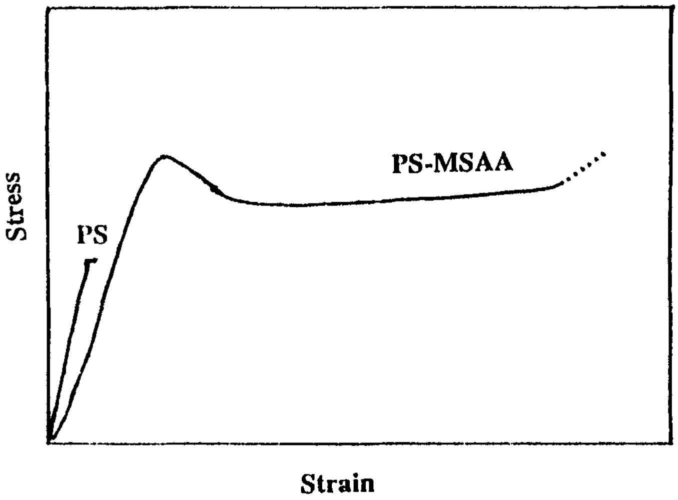

Figure 6. Stress-Strain Curves of PS and Cured PS-25%MSAA with P=88%

concentration are combined in Table 2. Increasing the content of MSAA in the mixtures or the methacrylate groups dependent on the SAA chains (P%), enhances the compressive strengths of the cured plastics. The CS value is highest for the sample with both higher MSAA concentration and higher value of P% . The stress-strain curves for PS and the sample containing 25% MSAA (P=88%) were shown in Figure 6. Pure PS is very brittle with low CS. In contrast, With the addition of MSAA, this sample showed a significantly enhanced CS value. Thus, the PS-MSAA semi-IPNs are of possible interest in the toughness modification of polystyrene.

Properties of MMA-MSAA Cured Mixtures

MSAA-methyl methacrylate mixtures, using BPO as a initiator, were thermally

Table 3. The Properties of Cured MMA-MSAA Mixtures

MMA/MSAA[a]	100/0	75/25	90/10	95/5	90/10	90/10
(P%)		(88)	(88)	(88)	(56)	(35)
T_g °C [b]	111.87	90.59	93.97	110.29	68.35, 105.62	67.67, 109.56
T_g °C [c]	—	—	80.13, 116.17	—	82.55, 118.69	75.44
Weight loss %	—	—	23	—	37	91

a: MMA/MSAA: wt/wt; b: before extraction; c: after extraction

polymerized to obtain MSAA modified PMMA plastics. All cured products were very brittle. The properties of these products are listed in Table 3. Within the experimental range studied, the polymerized formulations containing the MSAA oligomer with P=88% showed only one T_g, indicating homogeneous systems produced. Also, the T_g increased with a decreasing amount of the MSAA (P=88%) oligomer in the formulation. The cured mixtures containing 10% MSAA, with P=56 and 35% exhibited two T_g values. The lower T_g was close to that of SAA (T_g=69°C), and the higher T_g was close to that of pure PMMA (T_g =112°C). After extraction with acetone for 72 hours, all samples had significant weight loss. The weight loss increased vigorously with a decrease of methacrylate groups pendant on the SAA chains. For example, the sample containing 10% MSAA(P=35%) showed weight loss up to 91%, which is almost the same as the content of PMMA in the mixtures. Furthermore, the extracted residue from this sample showed a single T_g at 75.44°C, which is slightly higher than that of SAA. It has to be noted that the cured PMMA mixture containing 10% MSAA with P=88% showed two T_g values after extraction, instead of one T_g before extraction. The extracted fraction from these three samples had only one T_g at 112.36°C, which is extremely close to that of pure PMMA. All these results indicate that the cured mixtures of MSAA and MMA had semi-IPN structures, consisting of crosslinked MSAA-PMMA and thermoplastic PMMA.

CONCLUSIONS

1. The thermal polymerization behaviors of MSAA and styrene mixtures were

significantly affected by the content of MSAA and the number (P%) of methacrylate groups pendant on the SAA chains. High P% values was favorable for the copolymerization between MSAA and styrene.

2. The copolymerization of MSAA and styrene mixtures resulted in the formation of stable crosslinked polymer networks, no PS homopolymer could be detected in the cured formulation.

3. The semi-IPNs structures in the cured mixtures of MSAA and MMA were identified by DSC and extraction studies.

4. Compressive stress testing showed the potential for PS-MSAA semi-IPNs in the toughness modification of polystyrene.

REFERENCES

[1] B. M. Culbertson, W. A. Brantley, E. C. Kao and T. Grentzer, *J. Dent. Res., 69:207 (1990)*

[2] B. M. Culbertson, W. A. Brantley, J. Sang and T. Lo, *J. Dent. Res., 72:178 (1993)*

[3] B. M. Culbertson, A. Tiba, *J. Dent. Res., 73:127 (1994)*

[4] B. M. Culbertson, Yuhua Tong and Qicun Wan, *J. Dent. Res., 76:506 (1997)*

[5] L. H. Sperling, *Chemtech, 18:104-109 (1988)*

[6] C. B. Bucknall, *Toughened Plastics, Applied Science Publishers, London, 1977, Adv. Polym. Sci., 27:121 (1978)*

[7] D. Braun, M. Klein, G. P. Hellmann, *J. Appl. Polym. Sci., 60:981-990 (1996)*

[8] L. A. Cazzaniga, R. E. Cohen, *Polym. Eng. & Sci., 34 (12):1005 (1994)*

[9] Robert W. Lenz, *Organic Chemistry of Synthetic High Polymer, Interscience Publishers, (1967)*

[10] Aldrich Inc. *sample information.*