

Synergistic Effect of Dual Rubber System in Toughening Styrene Maleic Anhydride Copolymers

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ABSTRACT: Styrene maleic anhydride (SMA) copolymers were toughened by blending with two distinctly different rubber modifiers: styrene-butadiene-styrene (SBS) block copolymer and methacrylated butadiene-styrene emulsion-made graft copolymer (MBS). The modifiers were used both individually and in combination for the examination of their roles in toughening SMA. SMA was miscible with poly(methylmethacrylate) shell of MBS, whereas it was partially miscible with the polystyrene (PS) phase of SBS. When 40–50% of SBS was used in blends, the PS phase of SBS became immiscible with SMA. SBS did not improve the Izod impact

strength of SMA appreciably. A prominent synergistic toughening effect was experimentally observed when SBS and MBS were used in combination in brittle SMA. This effect may be attributed to the fact that the large SBS particles initiate crazes and small MBS particles with good adhesion to SMA matrix improve the ligament thickness, which may play a critical role in craze growth and termination. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2260–2267, 2003

Key words: blend; styrene maleic anhydride copolymer; toughening; impact resistant; craze

INTRODUCTION

Dispersing rubber particles throughout glassy polymer matrix has attracted much attention in finding new polymer blends with well-balanced performances in the last two decades.¹ Controlling and stabilizing rubber particle size are two key factors in toughening brittle polymers.² Either conducting the rubber-presented polymerization or blending with specially designed rubber particles with grafted shell can be used not only to achieve the well-controlled average rubber particle size but also to stabilize dispersed rubber phase in the matrix polymers.

Although styrene maleic anhydride (SMA) copolymers have high heat distortion temperatures because of incorporation of maleic anhydride in the copolymer chains, the brittleness limits their applications. As a result, the rubber-presented polymerization process developed in the 1970s,^{3,4} as well as blending with the grafted rubber particles, has been studied recently for impact modification of SMA copolymers.^{5–7} The factors involved in either chemical or physical process for the impact modification include the amount of rubber added, the size and morphology of the particles, and the degree of adhesion of rubber to the matrix. Moore et al.³ pointed out that the range of 0.1–10 μm in rubber particle size was required during the styrene maleic anhydride polymerization and the rubber particles of 0.3–1 μm were experimentally detected. By

using transmission electron microscope, Stretz et al.⁸ examined two rubber-toughened SMA samples from ARCO and observed the particles of 0.3–1.5 and 0.25–0.8 μm , respectively. Dharmarajan and Datta⁹ dispersed primary amine functionalized ethylene propylene elastomers (amine-EP) into SMA copolymers and found a very fine morphology where the amine-EP domains are approximately spherical with a diameter of 1–3 μm . Willis et al.¹⁰ used hydroxyamine as a coupling agent to make the formation of covalent linkages between bromobutyl rubber and SMA matrix and obtained rubber particle size in the range from 0.5 to 1 μm at 5% hydroxyamine concentration, which gained a fivefold reduction as compared with the particle size without hydroxyamine. As reviewed above, regardless of the type of rubber used, the rubber particle size in toughening SMA matrix falls into the same range as in toughening other styrenic polymers (i.e., 0.1–6 μm).^{9,11} This is the critical size range for rubber toughening brittle styrenic polymers.

It has been confirmed that the role of rubber particle size in toughening polymers is associated with the failure mode of the polymer matrix.¹² There are two main mechanisms of energy dissipation (i.e., failure modes) in polymer/rubber blends: matrix yielding and matrix crazing.¹³ Small particles effectively induce yielding, whereas large particles favorably initiate crazing. Wu¹³ divided polymers into two main categories: brittle and pseudoductile polymers. Although test conditions and specimen geometry may lead to either craze or yield in both categories, under normal circumstances brittle ones do tend to craze, whereas pseudoductile ones have a tendency toward

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yielding. According to the main chain compositions of polymers, Wellinghoff and Baer² also classified polymers into two main types: vinyl and main-chain aromatic polymers. The former has a tendency toward crazing; the latter has a tendency toward yielding. After measuring postyield volume change in tensile tests, Kim et al.⁵ claimed that the failure mechanism for rubber-modified SMA is primarily due to dilatational processes (most likely crazing) and no change in failure mode was observed as the content of maleic anhydride was varied. Dharmarajan and Datta⁹ also suggested that the failure mode for SMA matrix is crazing rather than shear yielding because of its entanglement density of 0.038 mmol/cm³ that is comparable to 0.056 mmol/cm³ for polystyrene (PS).

As mentioned above, the large size of rubber particles in effectively toughening brittle styrenic polymers is required because of their failure mode. Nevertheless, it was reported that a synergistic effect can occur when two or more different particle types or sizes are simultaneously blended with styrenic polymers.^{11,14,15} This effect has not been tested experimentally in previous studies on rubber-modified SMA.

In this article, by using a commercial methacrylated butadiene-styrene emulsion-made graft copolymer (MBS) and styrene-butadiene-styrene (SBS) triblock copolymer as impact modifiers in SMA matrix, the synergistic effect was examined.

EXPERIMENTAL

The SMA matrix polymer, BENMA 218, with maleic anhydride content of 18% by weight and $\bar{M}_w = 2 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 2.6$, was obtained from SINOPEC Shanghai Research Institute of Petrochemical Technology (SRIPT, Shanghai, China). YH792, an SBS copolymer used here as an impact modifier, was purchased from Hunan Yueyang Chemical Corp. (China) and has a rubber content of 60% by weight. The emulsion-made MBS, trademark M-511, with ~80% rubber by weight and consisting of uniform spheres 0.20 μm in diameter, was commercially available from Kaneka Singapore Co. (PTE), Ltd. Prior to use, SMA was dried at 80°C for at least 6 h, as well as SBS and MBS, which were dried under reduced pressure at 60°C for 2 h.

Blends of the impact modifiers and the SMA copolymer were prepared on a corotating 27-mm twin-screw extruder (L/D = 36, Leistritz AG Mic-27). The barrel temperatures were set from 190 to 250°C. The extrudate was pelletized and dried under reduced pressure at 90°C for 2 h and then injection molded into tensile, heat distortion temperature, and Izod testing bars by using an SZ-68/400 molding machine from Guangxi Liuzhou Plastics Mechanical Instrument Factory of China. Rectangular bars (30 \times 10 \times 1 mm³) for dynamic mechanical thermal analysis (DMTA) were prepared by compression molding.

The tensile bars were tested according to ASTM D638 by using a Lloyd LR50K testing machine with a computerized data acquisition system at a cross-head speed of 50 mm/min. Notched Izod impact strengths were measured according to ASTM D256 by using an impact tester from Hebei Chengde Testing Machine Factory (China, Model XJU-22). The glass transition temperatures of the blends were determined from the bending $\tan \delta$ versus temperature plots using DMTA II from Polymer Laboratories, and the measurements were carried out from -120 to 180°C at a frequency of 1 Hz and a heating rate of 4°C/min in the single-cantilever bending mode. The heat distortion temperatures of the blends were determined according to ASTM D648 by using a thermal property tester from Hebei Chengde Jinjian Testing Machine Factory (China, Model XRW-300 h_g). The morphologies of the virgin MBS modifier and blends were examined by scanning electron microscopy. A Japan Electron Co. (Model JSM-35C) electron microscope was used.

RESULTS AND DISCUSSION

Morphology

The scanning electron photographs shown in Figure 1(a) illustrate that the particles of the virgin MBS modifier significantly agglomerate. Nonetheless, the original emulsion particles can appear individually in the SMA matrix even at the high loading shown in Figure 1(b). It is seen in Figure 1(c) that the SBS copolymer emerges as the large and irregularly shaped particles in the matrix. Figure 1(d) further interprets that the MBS modifier can be well dispersed into the matrix and the large particles are still the SBS copolymer when these three components are blended together. It is obvious that the nature and size of the SBS particles are not affected by the MBS particles. Although it was reported in a previous study¹¹ that the SBS particles changed in size with a range from ~1 to ~5 μm , the variation of the size of these particles in this study is in a range of about 10–20 μm . This can be explained with the drop break-up mechanism for the formation of the SBS particles. In other words, the size of the SBS particles strongly depends on the mixing and rheological conditions. Thus, a bimodal distribution of particle sizes is observably formed.

SMA binary blends with MBS or SBS

Figure 2 clearly shows that there are two glass transition regions (T_{g1} and T_{g2}) in both MBS and SBS. The first transition (T_{g1}) at temperature < -60°C is undoubtedly attributed to the glass transition of polybutadiene (PB); the second one (T_{g2}) at temperature > 90°C is due to the glass transition of poly(methylmethacrylate) (PMMA) shell in the case of MBS and PS

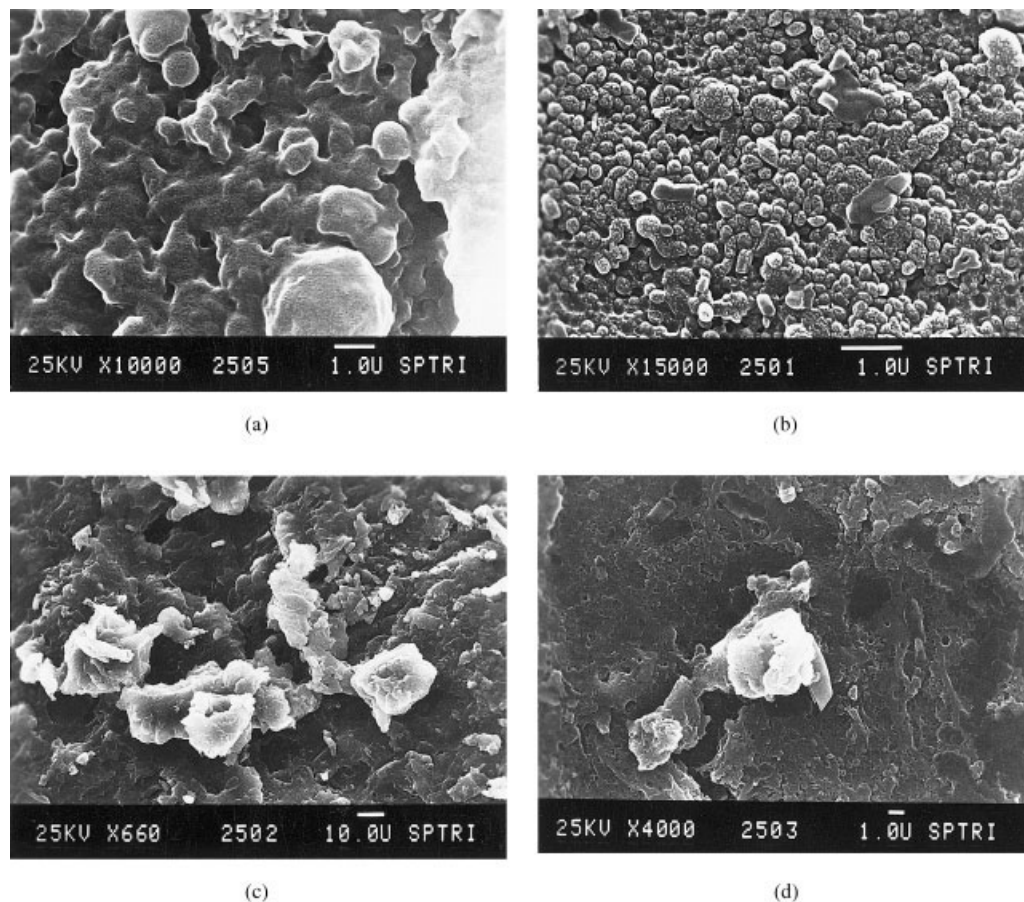


Figure 1 SEM photomicrographs for MBS, SMA/MBS, SMA/SBS, and SMA/MBS/SBS. (a) MBS Virgin particles; (b) SMA/MBS blend, ratio 50 : 50; (c) SMA/SBS blend, ratio 50 : 50; (d) SMA/MBS/SBS blend, ratio: 50/30/20.

phase of SBS. No apparent difference in T_{g1} between two modifiers in the lower temperature region was observed, which obviously implies that the PB rubbers incorporated in both of them are similar. On the other hand, the difference in T_{g2} is 11°C because of different hard phases for the two modifiers, as well as the fact that $\tan \delta$ peaks in higher temperature regions are broad, which can be interpreted in terms of composi-

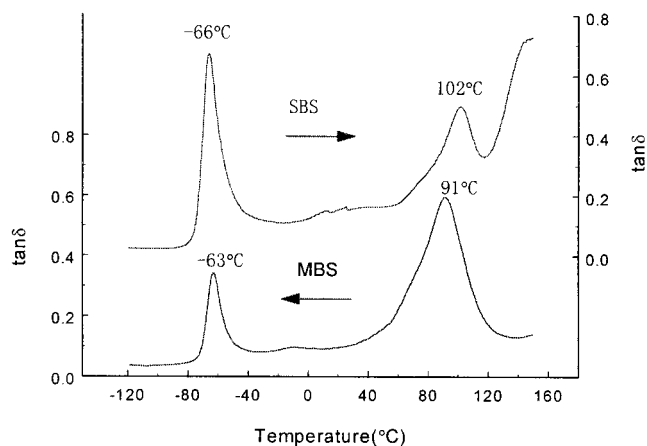


Figure 2 DMTA plots of MBS and SBS.

tion gradients within microdomains of block and core-shell copolymers.¹⁶

The DMTA results as shown in Figures 3 and 4 indicate that only two T_g 's were found at any composition ratio in the case of SMA/MBS blends, as well as

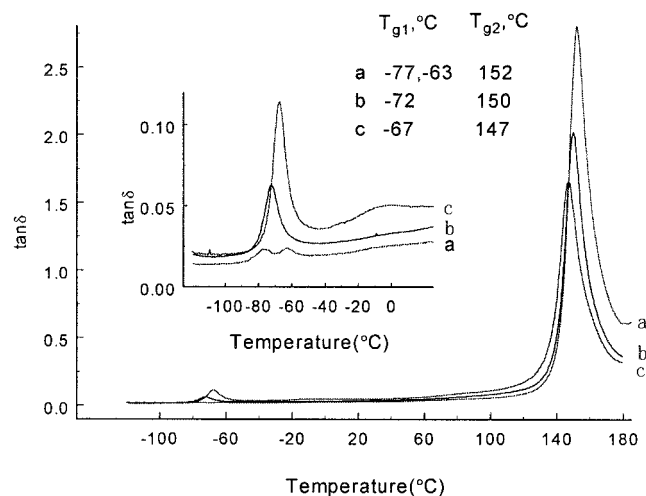


Figure 3 DMTA plots for SMA/MBS blends, SMA/MBS: (a) 90/10; (b) 70/30; (c) 50/50.

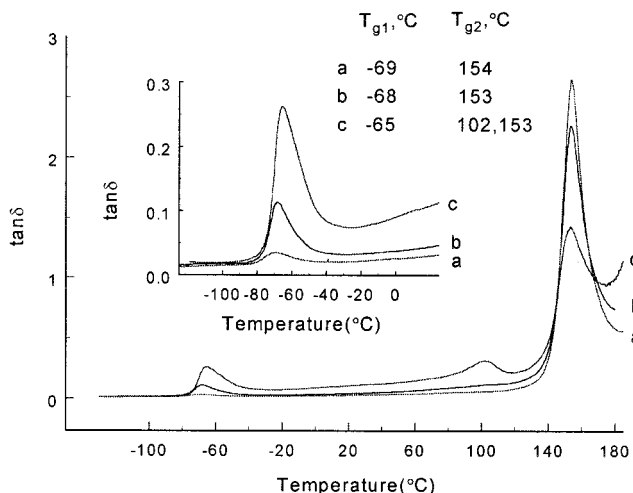


Figure 4 DMTA plots for SMA/SBS blends, SMA/SBS: (a) 90/10; (b) 70/30; (c) 50/50.

for most cases of the SMA/SBS blends except that three T_g 's were observed for 50% SBS in SMA matrix. Thus, SMA is immiscible with PB phase in MBS and SBS. SMA containing 18% MA is completely miscible with the PMMA shell of MBS as revealed in the earlier studies.¹⁶ SMA is partially miscible with PS phase of SBS because the glass transition in the case of 50% SBS in SMA reappeared at 102°C that was caused by the PS phase. In both cases, T_{g1} for the rubber phase decreases with the increase in SMA amount. This is consistent with previous studies¹⁶⁻¹⁸ and attributed to a negative pressure created by the difference in thermal expansion coefficients of the soft and hard phases. It is noteworthy that the drop in T_{g1} for SMA/MBS blends is larger than for SMA/SBS blends. This may also reflect a more favorable interaction between the PMMA shell of MBS and SMA as compared with that between the PS phase of SBS and SMA, or more likely reflects the difference in PB domain structure in MBS and SBS. It is interesting to point out that for 10% MBS in SMA matrix the T_{g1} splitting occurred as illustrated in the inset of Figure 3: one is located at -77°C and the other is located at -63°C that was observed in Figure 2 for pure MBS. This phenomenon was ascribed to a consequence of cavitation as described in the literature.¹⁹ The lower peak is caused by intact rubber particles, of which the density decreases because of large triaxial tensile stresses from differential thermal contraction and sequentially makes relaxation time decline and T_{g1} shift to a lower temperature. Besides, the upper peak is due to cavitated particles, of which the density is recovered to be the natural unstressed density and successively results in the decrease in free volume that finally makes the relaxation time increase and T_{g1} shift back to a higher temperature.

Figure 5 shows the stress-strain curves for the SMA/MBS and SMA/SBS blends. In the case of the

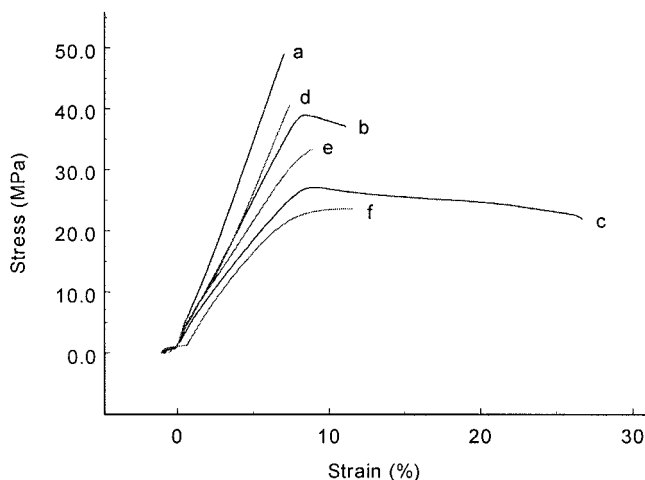


Figure 5 Stress-strain curves for SMA/MBS: (a) 90/10; (b) 70/30; (c) 50/50 and for SMA/SBS: (d) 90/10; (e) 70/30; (f) 50/50.

SMA/MBS blends, there is a well-defined yield stress which is greater than the ultimate stress at break except for 10% MBS in SMA. However, for the SMA/SBS blends, no well-defined yield stress occurred as reported for other SBS blends in a previous article,¹¹ which, to some extent, verifies again the poor compatibility or adhesion between PS phase of SBS and SMA than between the PMMA phase of MBS and SMA. It is also observable in Figure 5 that the increase in the amount of impact modifiers leads to the decrease in the ultimate stress at break or yield stress and the ultimate stresses at break for SMA/SBS blends are accordingly lower than those for SMA/MBS blends. As seen in Figure 6, MBS improves the Izod impact strength more effectively than SBS does. This is in accord with the results for styrene acrylonitrile copolymer (SAN)/MBS blends in a previous article.¹¹

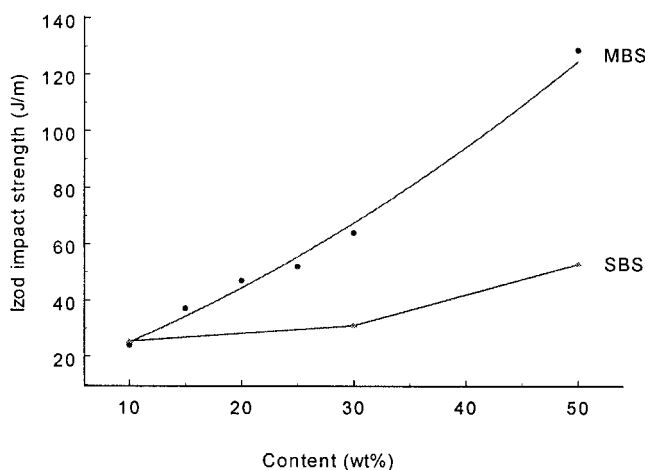


Figure 6 Plots of notched Izod impact strength as a function of contents of MBS and SBS, respectively.

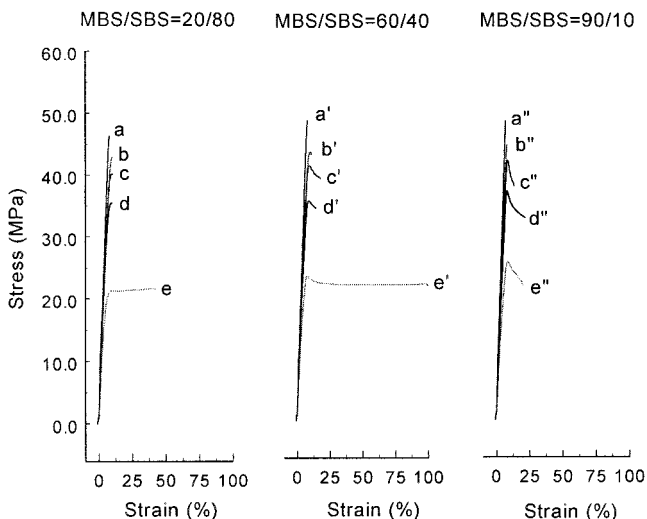


Figure 7 Stress-strain curves for SMA/(MBS + SBS) blends (a, a', a''): 90/10; (b, b', b''): 80/20; (c, c', c''): 75/25; (d, d', d''): 70/30; (e, e', e''): 50/50.

Again, it may be further illustrated that the adhesion of SMA to MBS is better than to SBS.

SMA ternary blends with combinations of MBS and SBS

It has been proposed that the synergistic toughening with a bimodal distribution of particle sizes is a new direction for toughening brittle polymers²⁰ and many earlier studies^{11,14,15} also showed that dual rubber systems with different particle size distributions do exhibit better performance in some polymer matrices (in particular, styrenic polymers, such as acrylonitrile-butadiene-styrene copolymer, PS, and SAN) than a single rubber does. Therefore, it is of particular interest to investigate the synergistic effect in toughening SMA matrix with combinations of MBS and SBS from the viewpoint of its usefulness in engineering thermo-plastic areas such as automotive applications.²¹

The stress-strain plots in Figure 7 exhibit the changes in tensile strength and elongation with the variation of combinations of MBS and SBS at different contents of total modifiers. The ultimate stress at break is inversely proportional to the content of total modifiers at fixed combinations and is almost independent of the ratio of MBS to SBS. In the cases of the ratio of 20% MBS to 80% SBS, most of the blends have no well-defined yield stresses and display their brittleness except the blend [Fig. 7(e)], which contains 50% total modifiers as well as has the prominent yield stress and large elongation at break as compared with Figure 5(f). In the cases of the ratio of 60% MBS and 40% SBS, the blend containing 10% total modifiers as indicated in Figure 7(a') demonstrates no yield stress and characteristic feature of brittleness; the rest of the blends show their characteristic features of yield

stress. Similarly, for the cases of the ratio of 90% MBS to 10% SBS, the blends, which contain 10 and 20% total modifiers as shown in Figures 7(a'') and 7(b''), respectively, have only exhibited their brittle deformation, while the remaining blends display their deformations with yield stresses. For the blends that have the yield stresses, it is found by comparison at fixed contents of total modifiers that the differences between the yield stress and ultimate stress at break become large as the ratio of MBS to SBS increases, and the largest elongation at break appears at 50% total modifiers and the ratio of 60% MBS to 40% SBS [Fig. 7(e')]. It seems to indicate that the ratio of MBS to SBS affects the deformation of the blends.

Figure 8 demonstrates that the Izod impact strength varies with the content of total modifiers and ratio of MBS to SBS. The occurrence of maximum Izod impact strength in varying the ratio of MBS to SBS clearly confirms that the synergistic effect with bimodal particle size distribution definitely exists in toughening SMA matrix. Evidently, the Izod impact strength for the blend with 50% total modifiers and the ratio of 60% MBS to 40% SBS [Fig. 8(e)] is dramatically higher than that with either of the two modifiers. In other cases, the maximum values of Izod impact strength are also considerably conspicuous, except Figure 8(a). These results further illustrate that the ratio of MBS to SBS significantly affects the toughness of the blends. In other words, the particle size distribution of the dual rubber system has to do with the toughening efficiency as expected in other styrenic polymers.^{11,14,15}

It is seen in Figures 9, 10, 11, and 12 that most of the results from DMTA measurements show two glass transitions as found in Figures 3 and 4, except for the case of Figure 9(a), in which the Izod impact strength in Figure 8(e) is still higher than that for the blends

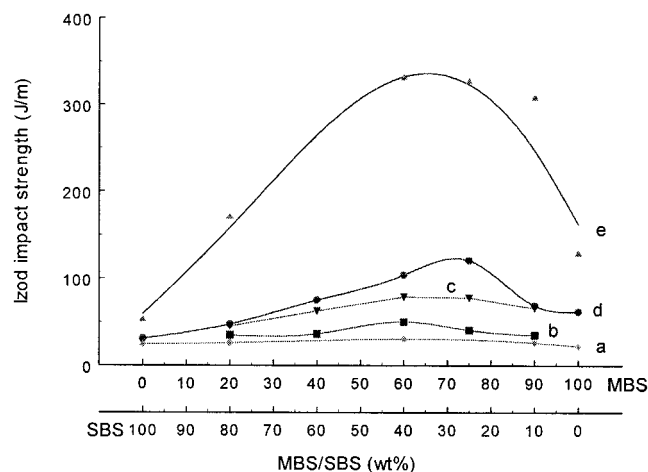


Figure 8 The plots of notched Izod impact strength for the SMA blends with combination of MBS and SBS as a function of ratio of MBS to SBS at various total modifiers contents: (a) 90/10; (b) 80/20; (c) 75/25; (d) 70/30; (e) 50/50.

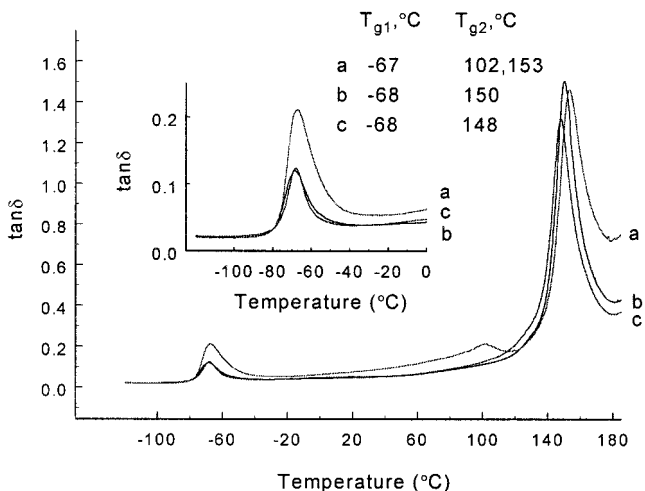


Figure 9 DMTA plots for SMA/MBS/SBS blends, MBS/SBS: (a) 20/80; (b) 60/40; (c) 90/10 at fixed amount of 50% total modifiers.

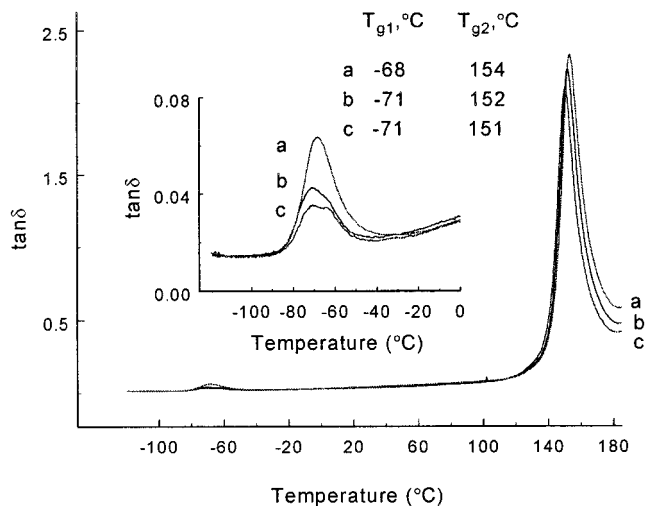


Figure 11 DMTA plots for SMA/MBS/SBS blends, MBS/SBS: (a) 20/80; (b) 60/40; (c) 90/10 at fixed amount of 20% total modifiers.

with either of the two modifiers. This manifests again that the hard phases of the impact modifiers are well miscible with SMA, although the compatibility of the two modifiers was not determined. With the decrease in the content of total modifiers, the T_{g2} peaks become narrower, whereas the T_{g1} peaks shift to lower temperature. The latter effect is in accordance with the observed results in Figures 3 and 4. In addition, the increase in the ratio of MBS to SBS leads to lowering T_{g1} as well.

It is reasonably expected that the addition of impact modifier to brittle polymer matrix usually impaired heat distortion temperatures (HDT) and some mechanical performances of the blends. In Figure 13, the plot of HDT for the blends as a function of total modifier content clearly shows the decrease in HDT

with increasing total modifier content. It is of interest to note that this effect is independent of the ratio of MBS to SBS (i.e., it is less likely related to the type of rubbers used in this study). Conformably, the flexural modulus decreases linearly with the increase in the content of total modifiers as presented in Figure 14. The ratio of MBS to SBS is also unlikely to be involved in deteriorating moduli of the blends.

The DMTA results from both the binary and the ternary blends, as indicated in Figures 4(c) and 9(a), reveal that the addition of SBS in an amount $\geq 40\%$ to the SMA matrix results in the appearance of glass transition temperature of the PS phase in SBS because of the partial miscibility or poor adhesion between the SBS and SMA and also imply that the addition of MBS

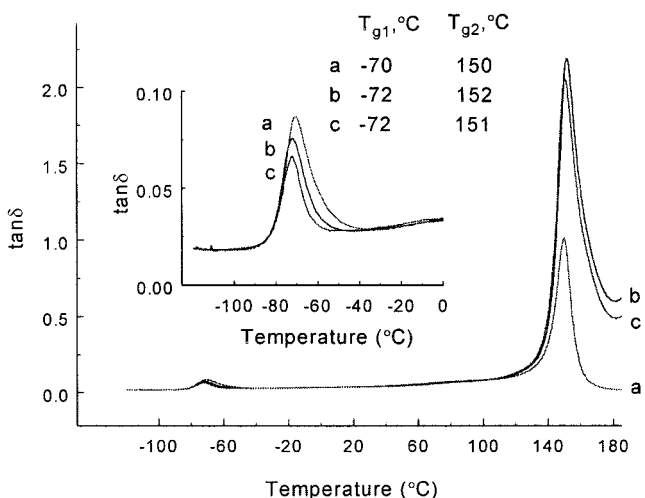


Figure 10 DMTA plots for SMA/MBS/SBS blends, MBS/SBS: (a) 20/80; (b) 60/40; (c) 90/10 at fixed amount of 30% total modifiers.

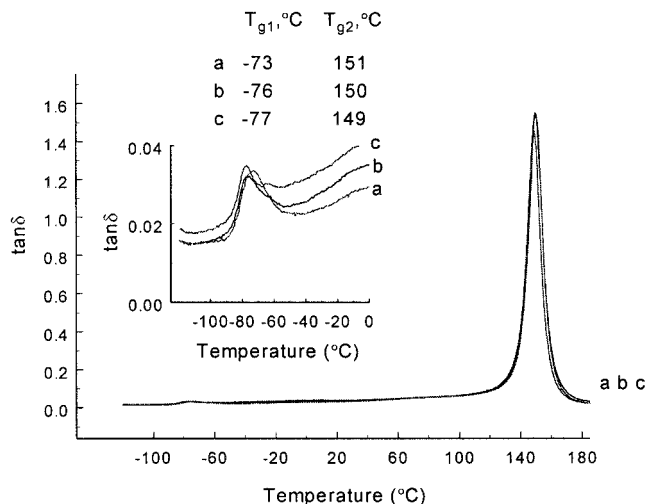


Figure 12 DMTA plots for SMA/MBS/SBS blends, MBS/SBS: (a) 20/80; (b) 60/40; (c) 90/10 at fixed amount of 10% total modifiers.

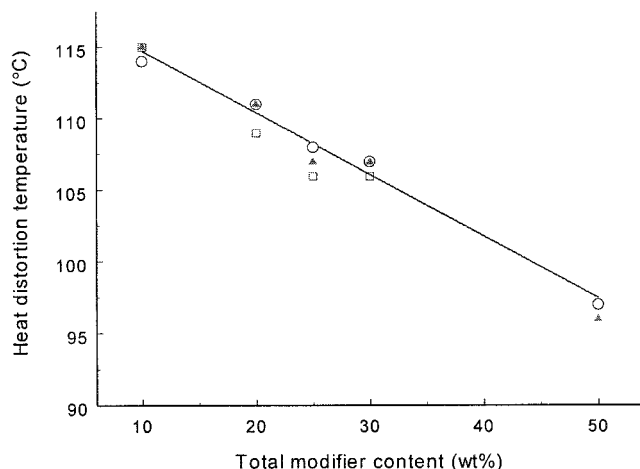


Figure 13 The plot of heat distortion temperature for SMA/MBS/SBS blends as a function of total modifier content, MBS/SBS: ○, 20/80; ▲, 60/40; □, 90/10.

was not able to improve their miscibility. The study by Chang and Hwu²² showed that PS and SMA are partially miscible because of their structural similarity. Lu et al.¹⁶ concluded that PS is not miscible with PMMA. Because the MBS used in this study is a core-shell impact modifier and NMR analysis showed that it did not contain styrene, the PMMA shell of the MBS is predictably immiscible with the PS phase of the SBS. The poor adhesion may account for inferior mechanical behaviors of SMA binary blends with the SBS modifier, although the particle size of the SBS is greater than that of the MBS and more likely to induce crazing. Although the PMMA shell of the MBS adheres well to SMA matrix, the addition of the MBS improves the Izod impact strength to a limited extent, even up to 50% MBS added, as shown in Figure 6. This may be interpreted in terms of small MBS particles that are more effective in initiating the yielding instead of the crazing¹³ and have less capability of controlling craze growth as well.

According to the generalized criterion for rubber toughening by Wu,²³ the conditions for toughening brittle matrices are

$$\tau < \tau_c \quad \text{and} \quad d > d_z$$

where τ is the matrix ligament thickness and τ_c is the critical matrix ligament thickness for the onset of brittle-tough transition; d is the diameter of the rubber particle and d_z is the minimum particle diameter for craze initiation. At a fixed amount of impact modifier, the matrix ligament is conversely proportional to particle size; however, large particles are more favorable for craze initiation. Hence, there is an optimum rubber particle size at which the toughness is the greatest. It is well known that the emulsion-made MBS particle size is usually less than $0.2 \mu\text{m}$ ^{11,24} and the dimension of

the agglomerated MBS particles is about $0.6 \mu\text{m}$ or less,²⁴ whereas the SBS particles have irregular shape with dimension of $1\text{--}5 \mu\text{m}$.^{11,20} As indicated in the Introduction, the most preferable size of rubber particle for toughening SMA matrix is $0.25\text{--}3 \mu\text{m}$. Obviously, the MBS used in this study cannot individually fulfill the above requirements. Although the dimension of the SBS particles appears more acceptable, the irregular morphology and poor adhesion limit their ability to terminate crazing and toughening efficiency. Therefore, neither the adhesion of impact modifier to matrix nor the particle size can be the sole factor that exclusively dominates the unexpected toughening effectiveness created by the use of combinations of MBS and SBS in this article.

By using two types of glass beads with poor and excellent adhesion, respectively, Dekkers and Heikens²⁵ studied the mechanism for the craze formation in PS. Their results showed that the craze formation or initiation is independent of the interfacial adhesion, which does affect crazing behavior; for instance, for poor adhesion beads the critical stress at which craze is induced is much lower than for excellent adhesion beads. With combinations of two kinds of MBS with 0.09 and $>0.3 \mu\text{m}$ diameters, Kishida et al.²⁴ was not able to further increase the notched Izod impact strength of the SMA/MBS blends as compared with that of the SMA blend with MBS particles of $>0.3 \mu\text{m}$ diameter alone. This is reasonably explained in terms of small particle size of MBS, which is not favorable to craze initiation. Hence, for the blends in which the MBS is partially replaced with the SBS at higher total modifiers contents as presented in Figure 8, the craze formation is importantly responsible for the dramatic increase in the Izod impact strength.

Usually, the crazing process includes craze initiation, growth, and termination. The efficient craze for-

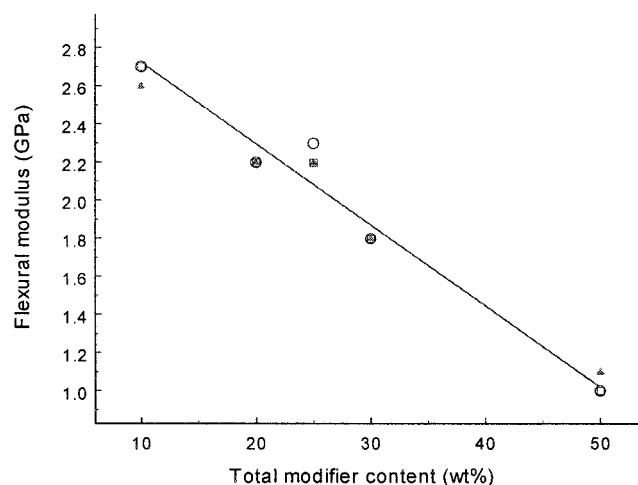


Figure 14 The plot of flexural modulus for SMA/MBS/SBS blends as a function of total modifier content, MBS/SBS: ○, 20/80; ▲, 60/40; □, 90/10.

mation is not able to completely account for the occurrence of the impressive toughness from combinations of MBS and SBS. After studying a synergism in toughening SAN with combinations of MBS and SBS, Fowler et al.²⁰ proposed a possible mechanism that predicts that the large SBS particles initiate crazes, whereas the small MBS particles responsibly induce the formation of shear bands that are effectively involved in terminating growing crazes. They further suggested that a high concentration of small particles at the craze tip interacts with the growing craze stress field to impede its further progress. They also mentioned the importance of minimum mean free path, which is conceptually similar to the matrix ligament thickness proposed by Wu.²³ Nevertheless, for the case of PS, no synergistic effect occurred in their study. On the contrary, the replacement of SBS with MBS caused rapidly decreasing notched Izod impact strength. They ascribed this to the small particle size and poor adhesion of MBS. Adding large rubber particles extracted from one kind of high impact-resistant polystyrene (HIPS) to the HIPS with small rubber particles, Hobbs¹⁴ found marginal synergistic effect in HIPS blends. It is still inferred that both the size and the adhesion of small particles play important roles in the occurrence of synergistic toughening effect. Moreover, Wu¹³ proposed that the pronounced synergistic effect in SAN seems to be due to an intricate combination of crazing and yielding. However, in this study, it is more persuadable that the addition of small MBS particles improves the SMA matrix ligament thickness because the crazing is more likely to be the dominating failure mode for SMA as introduced early. It is further speculated that the matrix ligament may play a critical role in craze growth and termination. This is why the adhesion of the small particles to matrix is important. It is concluded that with the combinations of the SBS and MBS, the occurrence of synergistic effect in toughening brittle SMA matrix can be elucidated in terms of the Wu's criterion for toughening brittle matrices.

CONCLUSION

The SBS and MBS modifiers were used both individually and in combination for the examination of their roles in toughening SMA. SMA is completely miscible with the PMMA shell of MBS while partially miscible with the PS phase of SBS. When 40–50% of SBS is used in blends, the PS phase of SBS became immiscible with SMA. The SBS did not improve the Izod impact strength of SMA appreciably. A prominent synergistic

toughening effect was experimentally observed when the SBS and MBS were used in combination in brittle SMA. The large SBS particles are propitious to craze formation, which seems to have no requirement for the strong adhesion of large particles to matrix. The small MBS particles are beneficial to the decrease in the matrix ligament thickness, which may be associated with craze growth and termination that to some extent require the strong adhesion of small particles to matrix. As predicted by Wu's criterion for toughening brittle matrices, the greatest toughness exists during balancing the two conditions ($\tau < \tau_c$ and $d > d_z$). It can be claimed consequently that the occurrence of both synergistic effect and the maximum toughness in this study may be attributed to the simultaneous fulfillment of the two above conditions, which were provided with two distinctly different rubber particles, respectively.

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