

Toughening of SMA Copolymers with an SAN-Grafted Rubber

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Synopsis

Styrene/maleic anhydride (SMA) copolymers were toughened by blending with a styrene/acrylonitrile (SAN) grafted rubber. The AN content of the SAN graft was fixed at 22.5% and the MA content of the SMA matrix was varied from 8 to 25%. The maximum impact strength was observed for blends based on SMA copolymers containing 14–17% MA (depending on the rubber content). These compositions are near the boundary of miscibility between the SMA matrix and SAN graft since miscibility of SMA and SAN occurs when the MA and AN contents are about the same in each copolymer. Dilatational processes were shown to be the major mechanism of deformation for these blends. Scanning electron microscopy was used to observe fracture surfaces as the miscibility between SMA and SAN or as the rubber content was changed. Toughening of miscible SMA/SAN matrices by this impact modifier was also examined. The results are discussed in terms of a variety of possible contributing factors including the coupling of the rubber to the matrix via miscibility of the latter with the SAN graft.

INTRODUCTION

It is often necessary to improve the toughness of glassy polymers by adding a dispersed rubber phase. The degree of improvement in toughness is influenced by numerous factors such as the amount of rubber added, the type of rubber, the degree of crosslinking, the level of adhesion of the rubber to the matrix, rubber particle size, etc.^{1–6} To obtain the needed adhesion between the matrix polymer and the rubber, emulsion rubber particles may be grafted with chains that are the same as or miscible with the matrix polymer.^{7–10} Many shell-core impact modifiers of this type are available. Block copolymers with hard blocks that can mix with the matrix are also used to achieve rubber particles that bond to the matrix phase.^{11–16}

The heat distortion temperature of styrenic polymers can be significantly improved by incorporation of maleic anhydride as a comonomer; however, such SMA copolymers are quite brittle and require impact modification^{17–19} to be most useful. The fact that styrene/acrylonitrile copolymers (SAN) can form miscible blends with SMA copolymers^{20–24} opens the possibility of using butadiene rubber grafted with SAN, like that used in ABS technology^{25,26} or for impact modification of poly(vinyl chloride),^{27,28} for toughening SMA materials. The relationship between AN and MA contents of these copolymers required for miscibility is illustrated in Figure 1.²⁴ As described elsewhere^{20–24} more fully, the optimum thermodynamic interaction appears to occur when the AN content of the SAN is nearly equal to the MA content of the SMA. If the mismatch in

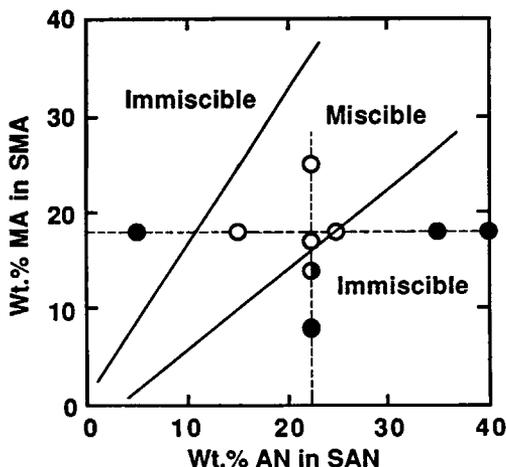


Fig. 1. Miscibility map for SMA/SAN blends. Points on the vertical line show the locations of the SMA matrix polymers and the SAN graft polymer used in these experiments. Points on the horizontal line show wt % AN in the graft polymer for blends with SMA 18.¹⁸

these compositions becomes too great, immiscibility results (see Fig. 1). This raises the question of how the composition of the SAN grafted to the rubber relative to that of the SMA matrix polymer affects mechanical behavior, especially toughness. This issue is the main focus of the work described here. In addition, the rubber toughening of miscible SAN/SMA blends has been examined. For both series of experiments, a single impact modifier having an estimated AN level of 22.5 wt % in the SAN graft (see the vertical dotted line in Fig. 1) was used. For the former series, the MA content of the SMA matrix was varied, while in the latter series the AN and MA levels of the matrix components were fixed at 25% by weight, but the ratio of SAN to SMA was varied. In addition to mechanical properties, fracture surfaces were examined by scanning electron microscopy and volume changes during post-yield deformation were measured. The results are discussed in the context of the central question of the matrix-graft interaction; however, other issues that complicate dealing with just that question are introduced.

Related information has been revealed in the patent literature,¹⁸ where a single SMA matrix was modified by a series of SAN-grafted butadiene rubber particles having different AN contents in the graft. Of course, the details of SAN and SMA copolymer miscibility as shown in Figure 1, were not known at the time that study was conducted so that it will be useful to reconsider these results in this context. The horizontal dotted line shown in Figure 1 defines the compositions of the copolymers used in the work by Stafford and Adams.¹⁸

EXPERIMENTAL

The SMA matrix polymers used in this study are described in Table I. An SAN-grafted emulsion-made rubber, Sumitomo BL-65, that contains equal amounts of rubber and SAN chains composed of 22.5% AN (SAN 22.5) was used as the source of rubber particles for toughening. About 40% of the total

TABLE I
Matrix Polymer SMA Used in This Study

	Molecular weight	Viscosity ^a	Source
SMA 8 ^b	$\bar{M}_n = 100,000$ $\bar{M}_w = 200,000$	8.65	Arco Chemical Co. (Dylark 232)
SMA 14	$\bar{M}_n = 90,000$ $\bar{M}_w = 180,000$	7.95	Arco Chemical Co. (Dylark 332)
SMA 17	Not available	5.65	Monsanto Co.
SMA 25 ^c	Not available	4.73	Monsanto Co.

^a Viscosity of a 10 wt % solution in methyl ethyl ketone at 25°C.

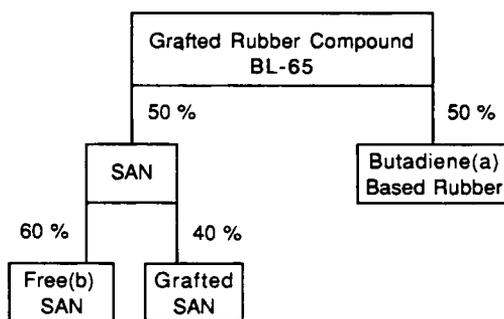
^b SMA denotes styrene/maleic anhydride copolymer and the numbers following the copolymer abbreviation indicate the weight percent of maleic anhydride.

^c Contains 25 wt % maleic anhydride and a small amount of a third monomer in addition to styrene.

SAN is bound to the rubber while the remainder is unbound or free SAN. Further information about the SAN grafted rubber is given in Figure 2 while the particle morphology is shown in Figure 3.

Blends of the grafted rubber and the SMA copolymers were prepared by melt mixing in a 1-in. Killion extruder ($L/D = 30$) using a high shear mixing screw with a compression ratio of 3 to 1. The SMA and the rubber were dried for at least 12 h at 90 and 70°C, respectively, before extrusion. Each blend was extruded twice to ensure uniform mixing, and the extruded pellets were dried again before compression-molding.

Standard specimens were obtained from $\frac{1}{8}$ -in. thick plaques for testing stress-strain and impact properties. Tensile properties were measured on an Instron 1137 tester with a computerized data acquisition system at a crosshead speed of 0.2 in./min and notched Izod impact strengths were obtained according to



(a) Butadiene accounts for 46 % of total mass of BL-65

(b) Free SAN contains 22.5 wt % AN and has $\bar{M}_n = 44,000$
and $\bar{M}_w = 167,000$

Fig. 2. Composition of BL-65-SAN-grafted butadiene emulsion-made rubber. Molecular weights determined by GPC using polystyrene as a standard.

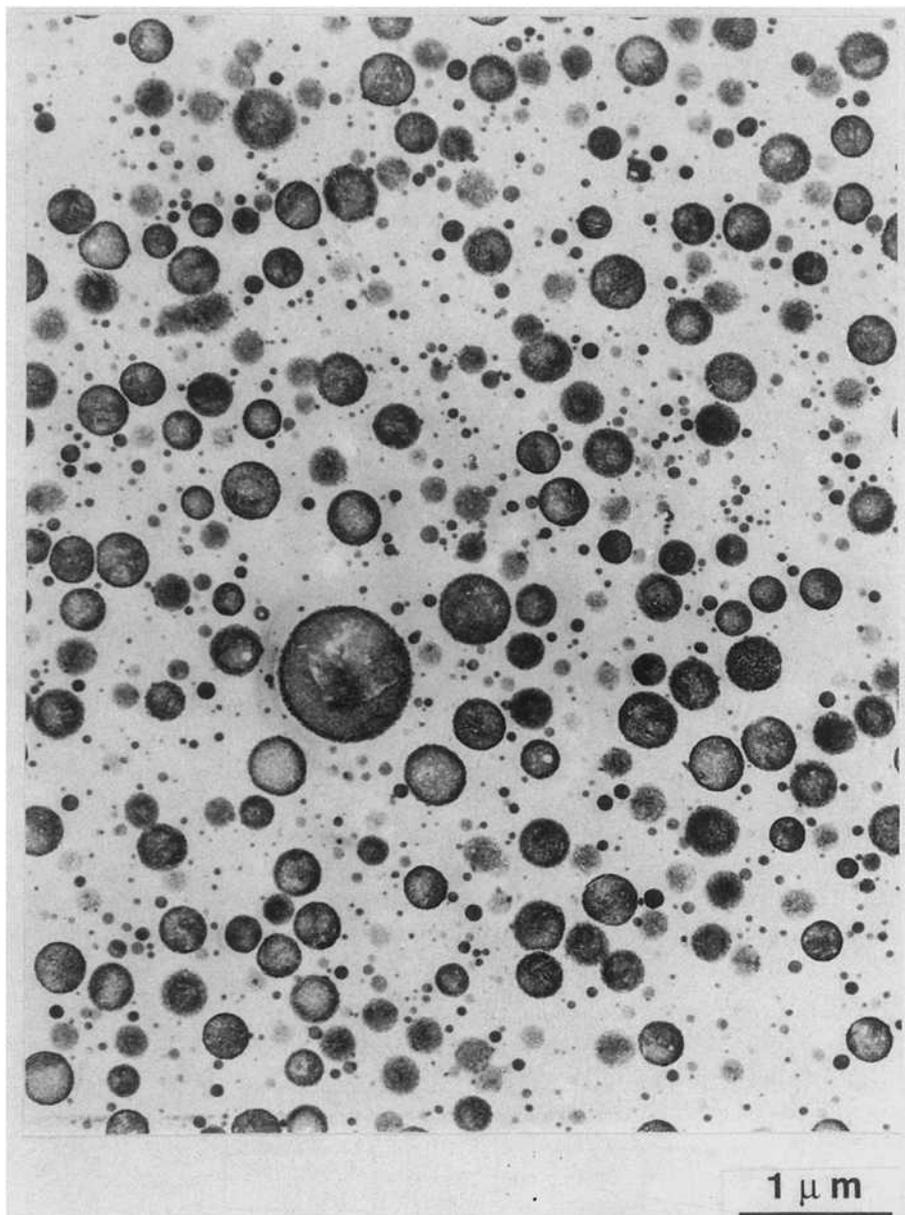


Fig. 3. Transmission electron photomicrograph of SAN-grafted rubber compound BL-65.

ASTM D256-56 using a pendulum type tester. At least five sample bars were tested on each instrument. Mechanical dilatometry measurements were made using a specially modified Instron machine with a water-filled chamber for measuring the volume change during extension. The details of this technique have been described elsewhere.^{29,30} Scanning electron photomicrographs of the fracture surfaces were obtained using a JEOL JSM-35C scanning electron microscope for samples fractured at room temperature and for ones prestrained in an Instron and fractured at liquid nitrogen temperature.

BINARY BLENDS

Tensile and Impact Properties

Figure 4 shows tensile properties of binary blends of SMA and the SAN-grafted rubber compound BL-65 plotted vs. maleic anhydride content of the SMA matrix for various levels of rubber. The percent rubber shown refers to the rubber content of the blend free of the grafted and ungrafted SAN. As expected, increasing the rubber content results in reductions in the modulus and strength and an increase in elongation at break. For the cases shown, strength and modulus increase with the maleic anhydride content of the SMA used. However, no curve is shown for the strength of the rubber-free SMA copolymers since these materials were quite brittle and reproducibility was poor. It appears that the strength of compression-molded SMA samples actually decreases with increasing MA content; however, poor reproducibility of strength measurements for these materials preclude quantification of this point.

As expected, Figure 5(a) shows that the notched Izod strength increases as the SAN-grafted rubber compound is added to each SMA copolymer matrix. Figure 5(b) shows impact strength plotted vs. the maleic anhydride content of the SMA matrix copolymers for various rubber contents. Impact strength [Fig. 5(b)] follows the same general trends as the elongation at break [Fig. 4(c)]. Both measures of ductility show that toughness initially increases with MA level reaching a maximum value at about 17% by weight MA and then appears to decrease with further incorporation of MA into the copolymer matrix. We believe that the initial increase in toughness is related to changes in miscibility of the SAN component of the BL-65 compound with the matrix SMA as the MA content of the latter is increased.

As seen in Figure 1, SMA 8 is not miscible with an SAN containing 22.5% by weight of AN. As a result of this, the grafted SAN will not mix completely with this SMA, which could result in inadequate mechanical coupling of the rubber phase with this matrix. Furthermore, the free SAN of the BL-65 compound may form a separate dispersed phase within this SMA matrix. Both factors preclude effective toughening. On the other hand, SMA 14 is right on the border of miscibility (see Fig. 1) with SAN 22.5; hence, the two issues mentioned above for SMA 8 are less serious concerns. SMA 14 is clearly miscible with SAN 22.5 according to Figure 1 so that the free SAN can mix homogeneously with the SMA matrix and the mechanical bond between the matrix and the rubber ought to be adequate since the grafted SAN should also mix well with the matrix. These aspects of SAN/SMA blend phase behavior provide a rational basis for the increased toughness of the blend as the MA content of the SMA increases. However, according to Figure 1, SMA 25 is clearly within the miscibility window for SAN 22.5; yet blends based on this material are much less tough than those based on either SMA 14 or SMA 17. We speculate that this may be because the inherent ductility of SMA copolymers seems to decrease with increased MA content as suggested earlier. This may stem in part from the trend among the SMA copolymers in Table I of reduced molecular weight as MA content increases. In other words, two factors seem to be in operation. First, miscibility of SAN 22.5 increases with MA content of the SMA copolymers considered and this works in favor of improved toughness. Second,

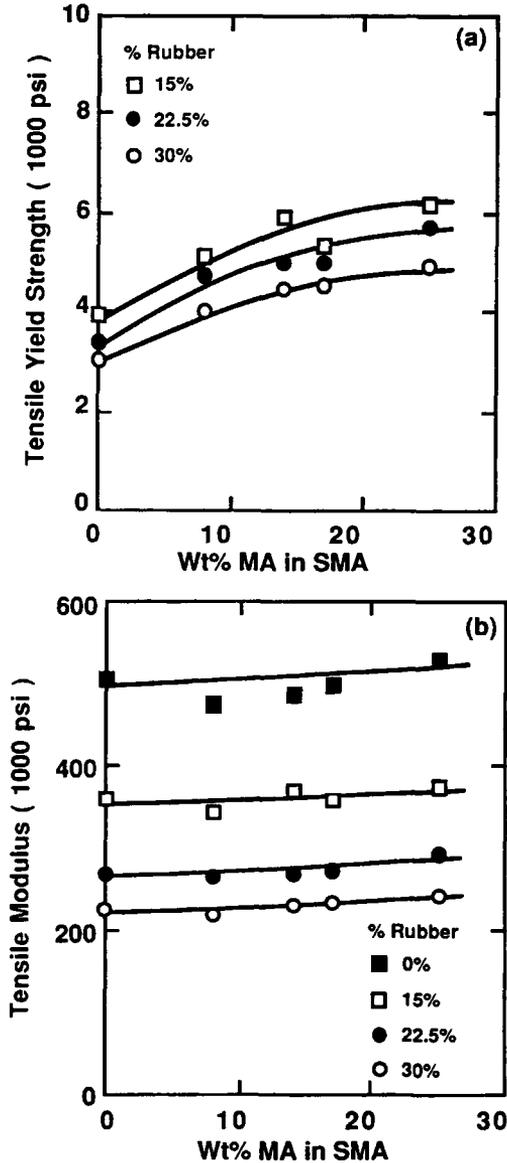


Fig. 4. Tensile properties of rubber toughened SMA blends as a function of wt % MA in matrix SMA at rubber contents of 0, 15, 22.5, and 30%: (a) tensile yield strength; (b) tensile modulus; (c) strain at break.

we propose that the intrinsic ductility of the matrix, however, decreases within this progression, and the two factors taken together result in a maximum in toughness vs. MA content. It is important to point out that definitive evidence for this proposal has not been presented, although it seems consistent with all the facts available and with trends we have found in other systems.³¹

Rubber particle size could be another factor in the interesting trends shown in Figures 4(c) and 5(b). It is generally believed that there is an optimum rubber particle size for efficient toughening of each matrix. In these experiments,

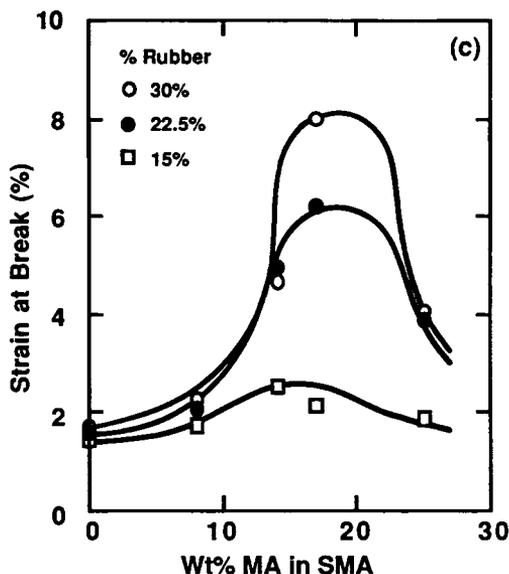


Fig. 4. (Continued from the previous page.)

the ultimate rubber particle size, or particle size distribution, has been held constant as the SMA matrix was varied. The optimum particle size needed for each SMA might vary in such a way to contribute to the trends seen. That is, these particles could be of a size that is considerably more efficient for SMA 14 and SMA 17 than for SMA 25. In addition, there could be varying levels of agglomeration of the rubber particles in each SMA so that the “effective” size varies in a way that contributes to the observed response. Clearly, these are simply speculative points that ought to be considered, and further investigation will be required to understand fully the results shown in Figures 4(c) and 5(b).

The results reported by Stafford and Adams¹⁸ are easier to interpret in terms of graft-matrix interactions since they varied the composition of the SAN graft and held fixed the compositions of the SMA matrix (see horizontal line in Figure 1). In their work, they used the same rubber seed latex for forming the SAN grafted modifier. Figure 6 shows their notched Izod values plotted vs. the AN content of the SAN graft for an SMA matrix containing 18% by weight of maleic anhydride (8 cP, 10% solution viscosity). The rubber content for each composition was held fixed at 18% by weight. Clearly, there is a maximum in toughness versus AN content of the graft. The compositions where the SAN graft is miscible with the SMA 18 (see Fig. 1) have the greatest toughness. These results clearly demonstrate, in the absence of the other complicating issues involved in Figure 5(b), that toughness is greatest when the interaction (or miscibility) of graft and matrix is maximized.

Deformation Behavior

Post-yield volume changes were measured during tensile testing in a mechanical liquid displacement stress dilatometer to assess the relative contribution of shear or dilatational deformation mechanisms for various blend com-

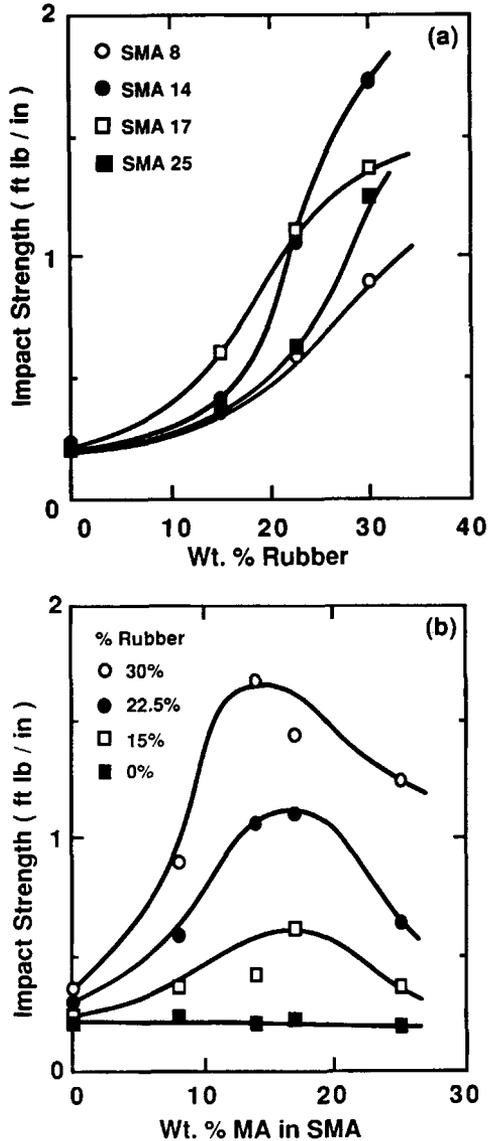


Fig. 5. Notched Izod impact strength of rubber toughened SMA blends as a function of (a) wt % rubber for various SMA copolymers and (b) wt % MA in SMA at different rubber contents.

positions.³²⁻³⁶ Table II shows the results for the blends containing 22.5 and 30% rubber in terms of the slope of the volume-strain curve ($1/V_0 dV/d\epsilon$). This quantity is the dilatational fraction of the deformation mechanism involved. No lateral contraction of the specimen (slope = 1) represents a deformation entirely due to dilatational processes, most often caused by crazing such as found in high impact polystyrene.³⁷⁻⁴⁰ Hole formation or interfacial delamination during straining may also cause dilatation. When there is no dilatation or volume change at all (slope = 0), shear yielding is the sole mechanism of deformation. Intermediate values of the slope of volume-strain curve indicates

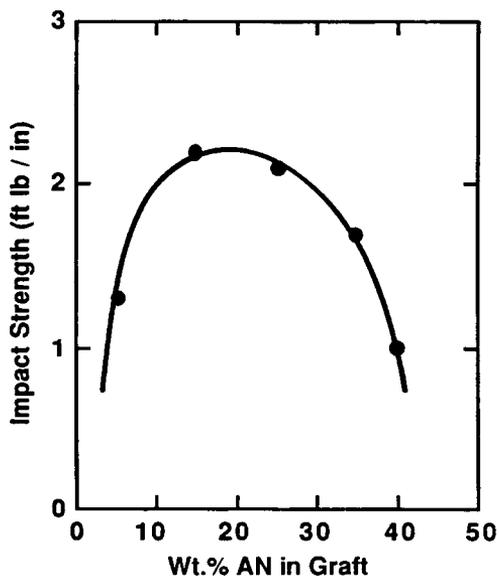


Fig. 6. Notched Izod impact strength of rubber-modified SMA 18 (8 cP). Total rubber content = 18% by weight; AN level in the graft was varied (18).

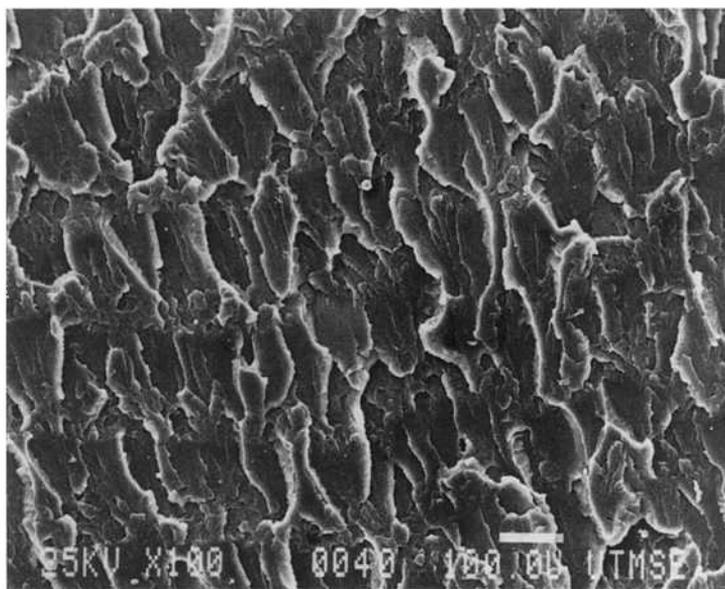
that at least two mechanisms contribute to the deformation in a combined manner. The deformation in the present case for blends containing 22.5 or 30% rubber is primarily due to dilatational processes (most likely crazing) since the values are all above 0.8 as shown in Table II. Comparing the deformation mode for these blends with the results of the impact strength in Figure 5(b), no change in deformation mode was observed as MA content varied. However, blends containing the higher rubber content show a slightly smaller dilatational contribution.

Scanning Electron Microscopy

Fracture surfaces of rubber toughened SMA copolymers were examined by scanning electron microscopy. Blends containing the lowest amount of rubber (15%) were found to have similar fracture surfaces, typical of semibrittle polymers, where only a hint of craze-whitening may be observed with the naked eye. Figure 7 shows a low magnification photomicrograph of such a fracture surface for an SMA 14 blend. It is characterized by a field of "fracture domains" of about 100 μm in their long dimension. These fracture domains cover the

TABLE II
Slope of Volume-Strain Curve of Rubber-Toughened SMA Blends

Matrix polymer	22.5% rubber	30% rubber
SMA 14	0.96	0.86
SMA 17	0.96	0.93
SMA 25	0.99	0.90



100 μm

Fig. 7. SEM photomicrograph of fracture surface for SMA 14 matrix with 15% rubber. Fractured at room temperature in an Izod tester.

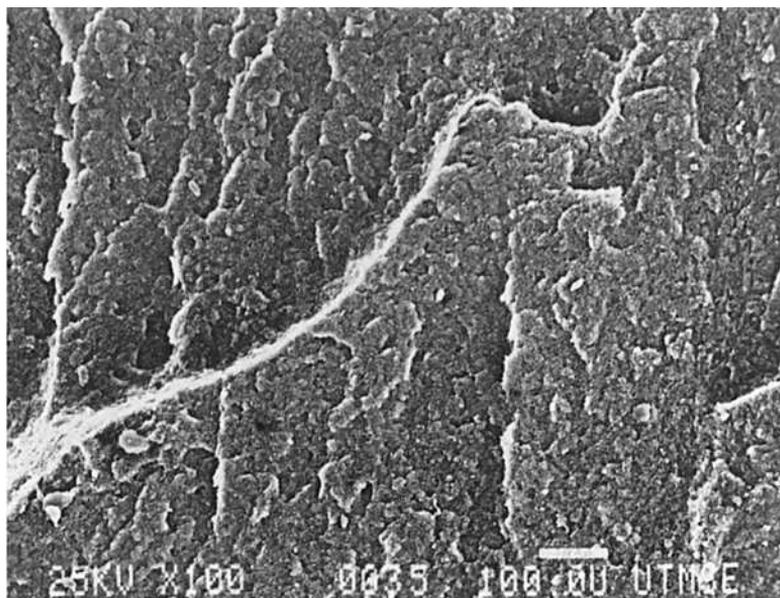
surface quite uniformly and are found to be present in all SMA blends containing 15% rubber. At 30% rubber content, the blends showed to the naked eye a somewhat more whitened fracture surface and the size of the fracture domains was considerably reduced as seen in Figure 8 for SMA 8 and SMA 14 blends. At higher magnification, the fracture surface of blends containing 30% rubber show some features typical of other rubber-toughened polymers. Particularly, the toughest blend with SMA 14 [Fig. 9(a)] shows some plastic flow on the fracture surface which is typical of high impact blends. However, the fracture surface of the blend with SMA 25 does not exhibit these features [Fig. 9(b)]. This may be due to the relatively low molecular weight of this matrix.

Figure 10 shows a fracture surface of an SMA 14 blend containing 30% rubber created at liquid nitrogen temperature for a specimen that had been prestrained (whitened) at room temperature. A similar experiment with a high impact polystyrene showed craze residues and some phase separation between the matrix and rubber particles.³⁰ In the present case, however, there are some indications of rubber particle dislocations, but there is no hint of craze residues.

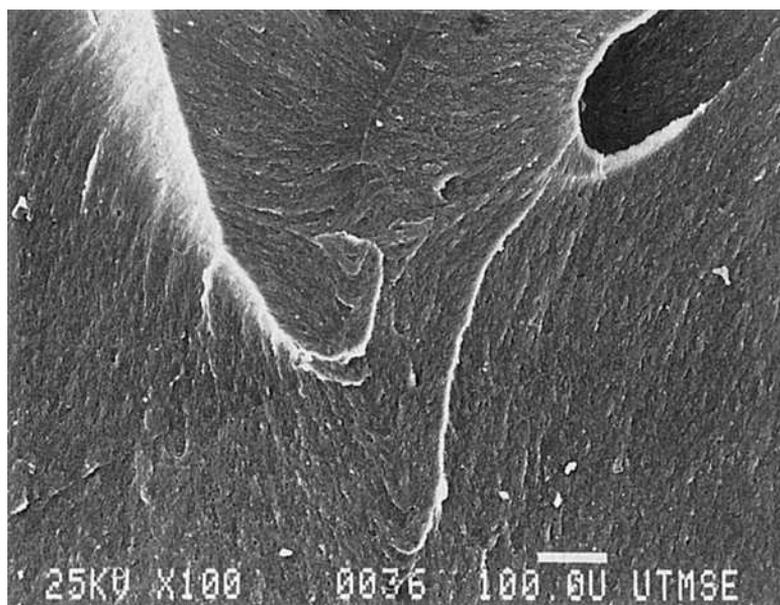
It may be concluded that the rubber-modified SMA blends show characteristic features of fracture surfaces associated with semibrittle blends. More evidence of flow and the appearance of 3-dimensional features would be expected of tougher blends.

TERNARY BLENDS

Because of the miscibility relationship shown in Figure 1, blends of SMA 25 and an SAN containing 25% by weight acrylonitrile have a single, composition



(a)



(b)

100 μ m

Fig. 8. SEM photomicrographs of fracture surfaces for (a) SMA 8 matrix with 30% rubber and (b) SMA 14 matrix with 30% rubber. Fractured at room temperature in an Izod tester.

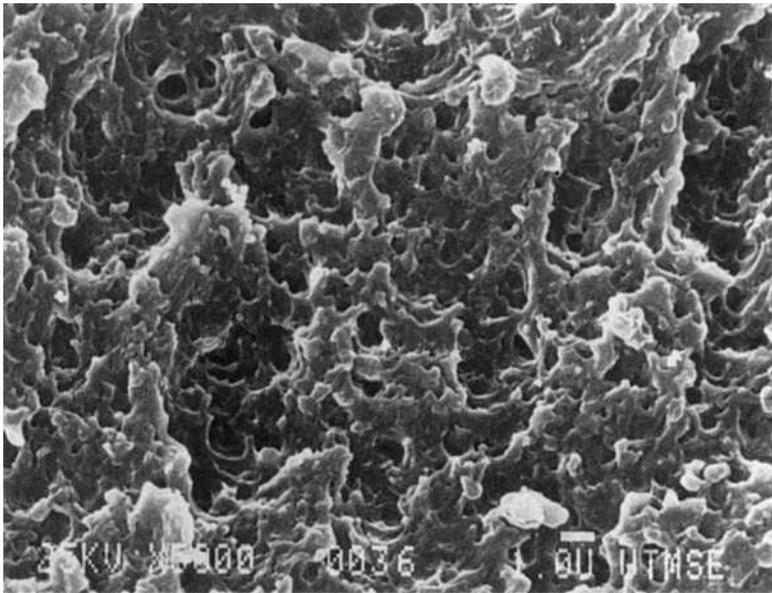
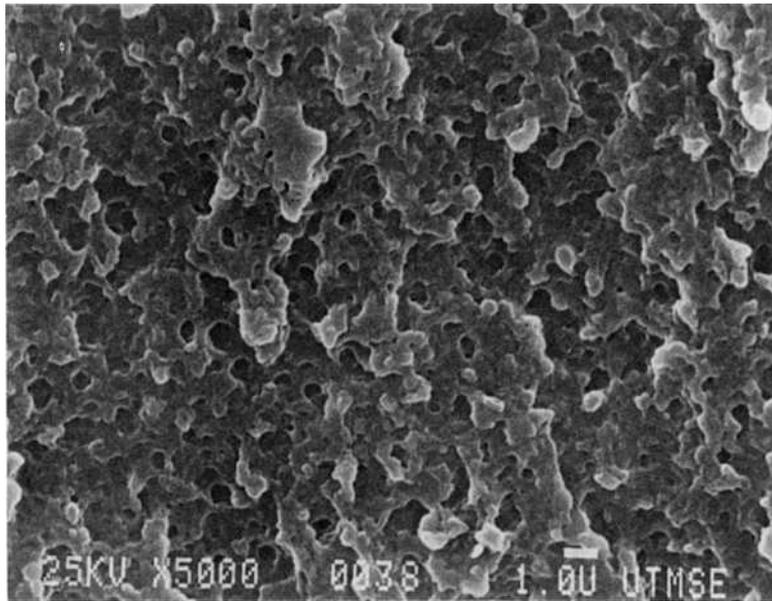
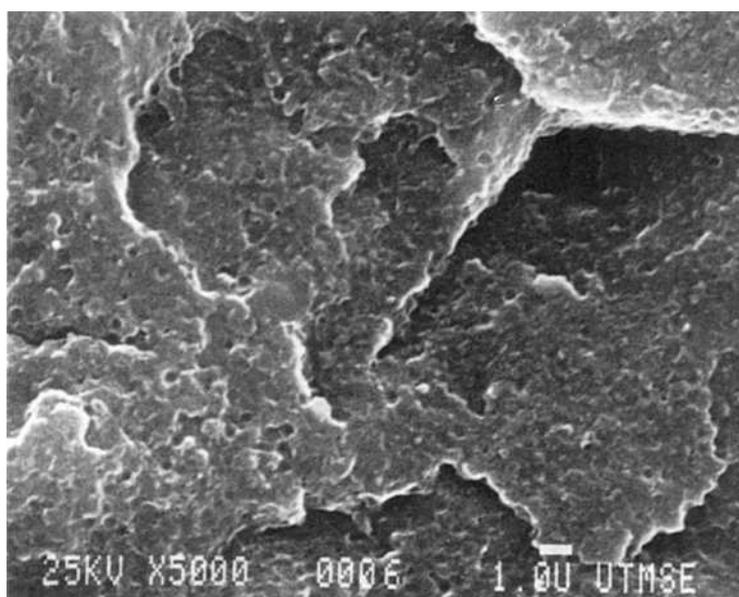
**(a)****(b)****2 μm**

Fig. 9. High magnification SEM photomicrographs of fracture surfaces of (a) SMA 14 with 30% rubber and (b) SMA 25 with 30% rubber fractured at room temperature.



2 μ m

Fig. 10. SEM photomicrographs of a fracture surface of SMA 14 matrix with 30% rubber prestrained and then fractured at liquid nitrogen temperature.

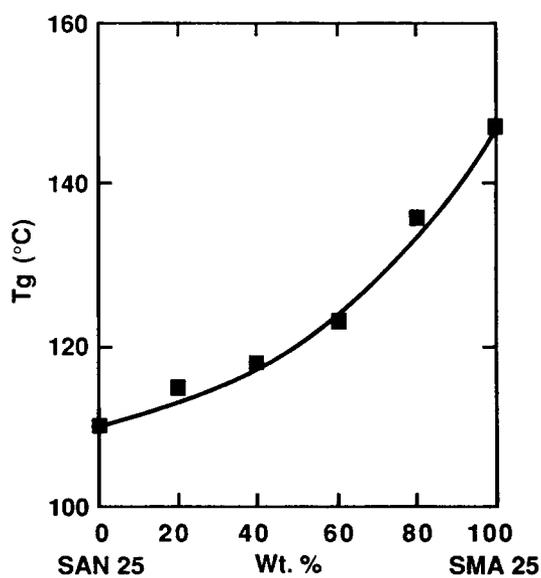


Fig. 11. Glass transition behavior of blends of SMA 25 and SAN 25 as a function of wt % SMA 25.

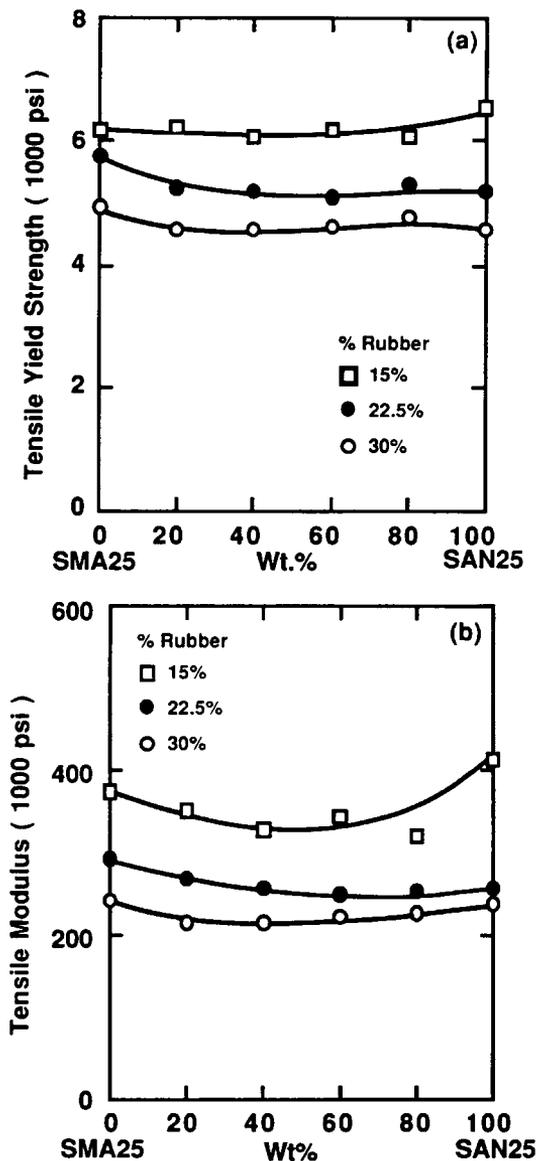


Fig. 12. Tensile and Izod impact properties of rubber-toughened SMA 25/SAN 25 blends at rubber contents of 15, 22.5, and 30%: (a) tensile yield strength; (b) tensile modulus; (c) strain at break; (d) notched Izod impact strength.

dependent glass transition as shown in Figure 11. By adding the BL-65 compound to SAN 25, an ABS type material is generated that is considerably tougher than the rubber-modified SMA compositions discussed earlier. By adding the BL-65 compound to miscible SMA25/SAN 25 blends, an interesting trade-off between thermal resistance, i.e., T_g , and toughness can be established. Figure 12 shows tensile properties of such materials at varying rubber levels. Binary blends of SMA 25 and SAN 25 were rather brittle, and reproducibility was poor. As expected, strength and modulus decrease with addition of rubber, but

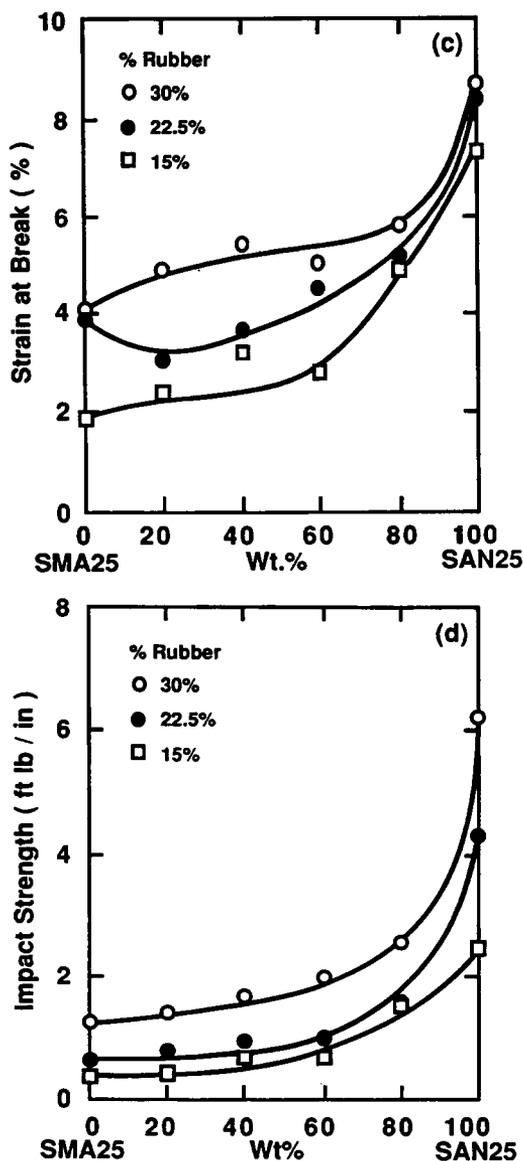


Fig. 12. (Continued from the previous page.)

these properties do not vary greatly with the proportion of SAN 25 or SMA 25 in the matrix. On the other hand, strain at break goes up as rubber is added and as the fraction of SAN 25 in the matrix increases. The latter observations generally parallel the notched Izod impact values shown in Figure 12(d). Unfortunately, toughness does not follow an additive relation, for fixed rubber levels, between that of SAN 25 and SMA 25 matrices. However, this behavior is consistent, through perhaps more extreme, with that observed in other systems.^{41,42} Of course, optimization of processing protocols and the rubber modifier could be expected to lead to materials having higher performance levels.

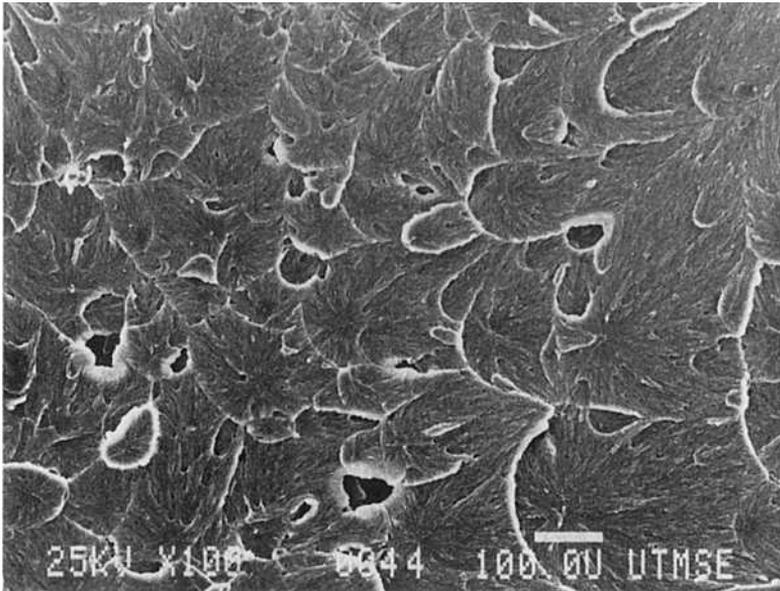
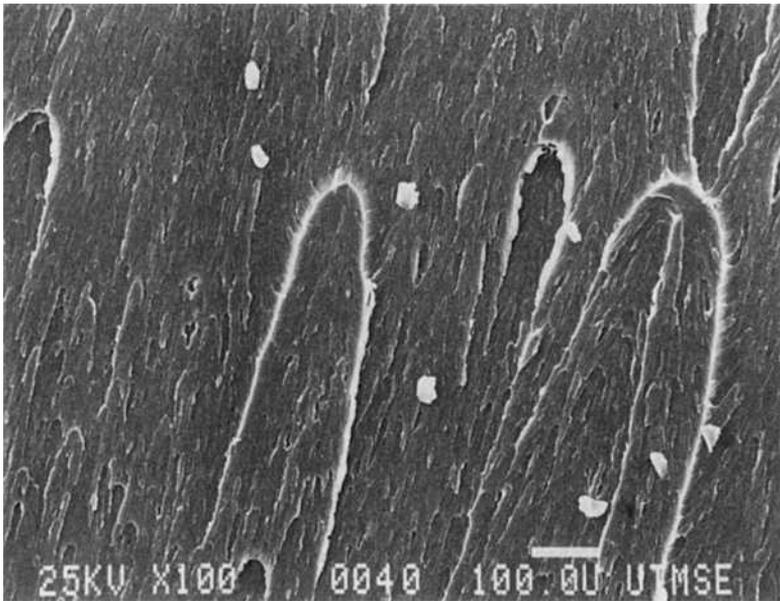
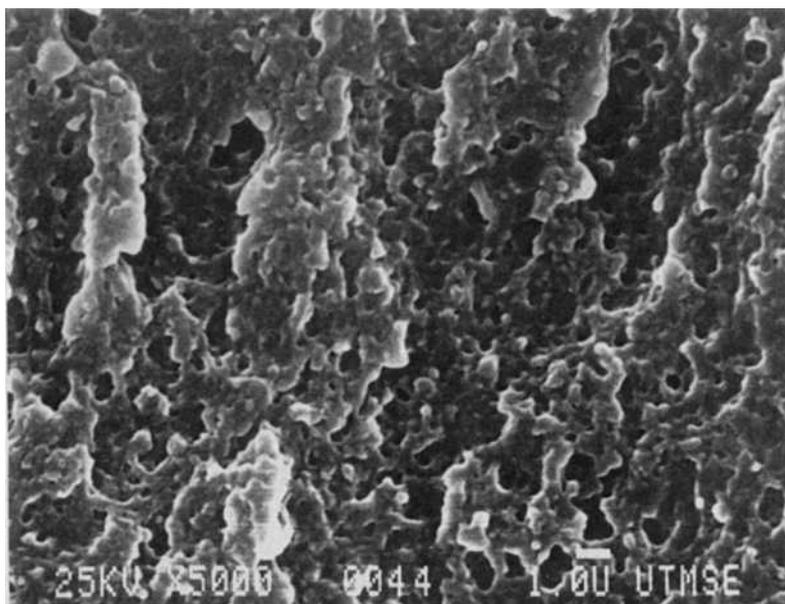
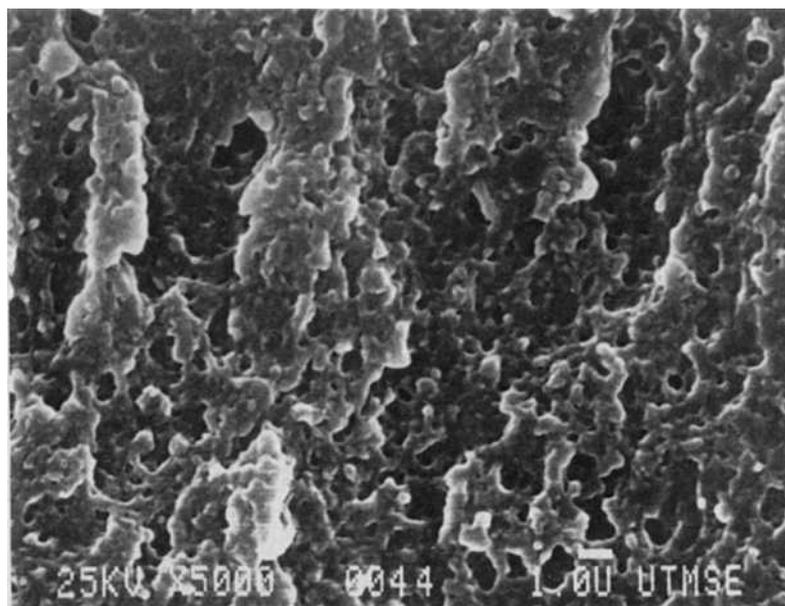
**(a)****(b)****100 μ m**

Fig. 13. SEM photomicrographs of fracture surfaces of ternary blends with the following weight compositions: (a) SMA 25/SAN 25/SAN 22.5 grafted rubber compound (24/16/60); (b) SMA 25/SAN 25/SAN 22.5 grafted rubber compound (8/32/60).



(a)



(b)

2 μ m

Fig. 14. High magnification SEM photomicrographs of ternary blends in Figure 13: (a) SMA 25/SAN 25/SAN 22.5 grafted rubber compound (24/16/60); (b) SMA 25/SAN 25/SAN 22.5 grafted rubber compound (8/32/60).

Figure 13 shows fracture surfaces of ternary blends at low magnification. Blends with higher SAN portions [Fig. 13(b)] have fewer crack initiation sites than those with less SAN 25 [Fig. 13(a)]. At higher magnification, blends with more SAN 25 [Fig. 14(b)] show some plastic flow while those with less SAN 25 [Fig. 14(a)] do not. Apparent indication of some plastic flow in Figure 13(b) is similar to that observed in Figure 9(a), which is characteristic of toughened blends. These photomicrographs are quite consistent with the increase in toughness observed on adding SAN 25 to these blends.

CONCLUSIONS

Addition of SAN (22.5%) grafted emulsion rubber particles to a series of styrene/maleic anhydride copolymers results in maximum toughness when the matrix polymer contains 14–17% MA. The increase in toughness with MA content up to this level appears to be related to increased miscibility of the SAN with the SMA matrix. This provides a better mechanical coupling of the rubber to the matrix via the grafted SAN chains and eliminates any immiscible phase created by ungrafted or free SAN chains. The SMA matrix containing 25% MA is miscible with SAN 22.5, but this matrix appears to be inherently less ductile apparently because of its low molecular weight and/or high MA content and cannot be toughened as effectively.

As shown here and elsewhere,¹⁸ SMA copolymers are toughened only moderately by the incorporation of grafted rubber particles even when the grafted chains are miscible with the matrix. Notched Izod impact values of only about 2 ft lb/in. are achieved even at high rubber loadings. Similar studies with a series of SAN matrices have shown that their impact strengths can be readily increased up to 10 ft lb/in.³¹

In addition to SMA copolymers, it is of interest to note that a number of other amorphous glassy polymers show a similar incapability of being highly toughened by rubber modification. Even at high rubber concentration, their ductility is increased only by a small amount. Such polymers include PMMA, poly(vinyl toluene), and many styrene copolymers designed to have a high heat deformation temperature. Comonomers such as α -methylstyrene, acrylic acid, acenaphthalene, and para *t*-butyl styrene serve as examples.^{43–45} A considerable effort has been expended to develop tough styrenic polymers with heat deformation temperatures significantly above 100°C. Only limited success has been possible.⁴⁶ The reasons for the lack of ability of these polymers to be significantly toughened may be varied and complex, but having further insight into these causes would perhaps permit design of improved polymer blends. Some of the factors include: inability to develop a high concentration of crazes, craze initiation stress near the fracture stress, variation in ability to shear yield, too high an entanglement molecular weight giving rise to relatively weak craze structure,⁴⁷ inability to exhibit plastic flow in certain multiphase environments, absence of optimum particle size or particle size distribution, etc.

References

1. C. B. Bucknall, *Toughened Plastics*, Applied Science, London, 1977.
2. S. Y. Hobbs, *Polym. Eng. Sci.*, **26**, 74 (1986).
3. A. M. Donald and E. J. Kramer, *J. Appl. Polym. Sci.*, **27**, 3729 (1982).
4. M. E. Fowler, H. Keskkula, and D. R. Paul, *Polymer*, **28**, 1703 (1987).
5. B. Z. Jang, *Polym. Eng. Sci.*, **25**, 643 (1985).
6. S. Wu, *Polymer*, **26**, 1855 (1985).
7. J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.*, **24**, 525 (1984).
8. M. Rink, T. Ricco, W. Lubert, and A. Pavan, *J. Appl. Polym. Sci.*, **22**, 429 (1978).
9. W. M. Barentsen and D. Heikens, *Polymer*, **14**, 579 (1973).
10. D. Heikens, N. Hoen, W. Barentsen, P. Piet, and H. Ladan, *J. Polym. Sci. Polym. Symp.*, **62**, 309 (1978).
11. P. S. Tucker, J. W. Barlow, and D. R. Paul, *Macromolecules*, **21**, 1687 (1988).
12. R. Fayt, P. Hadjiandreou and Ph. Teyssie, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 337 (1985).
13. T. D. Traugott, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **28**, 2947 (1983).
14. A. K. Gupta and S. N. Purwar, *J. Appl. Polym. Sci.*, **31**, 535 (1986).
15. S. D. Sjoerdsma, J. Dalmolen, A. C. A. M. Bleijenberg, and D. Heikens, *Polymer*, **21**, 1469 (1980).
16. G. Riess and Y. Jolevet, *Adv. Chem. Ser.*, **142**, 243 (1975).
17. M. Narayana, H. Keskkula, and J. E. Mason (to The Dow Chemical Co.), U.S. Pat. 3,641,212 (1972).
18. O. L. Stafford and J. J. Adams (to The Dow Chemical Co.), U.S. Pat. 3,642,949 (1972).
19. Br. Pat. 1,315,219 (1973) (to BASF).
20. W. J. Hall, R. L. Kruse, R. A. Mendelson, and Q. A. Tremantozze, *Am. Chem. Soc. Symp. Ser.*, **229**, 49 (1983).
21. D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
22. J. Kressler, H. W. Kammer, G. Schmidt-Naake, and K. Herzog, *Polymer*, **29**, 686 (1988).
23. Y. Aoki, *Macromolecules*, **21**, 1277 (1988).
24. J. H. Kim, J. W. Barlow, and D. R. Paul, *J. Polym. Sci. Polym. Phys. Ed.*, **27**, 223 (1989).
25. M. R. Grancio, *Polym. Eng. Sci.*, **12**, 213 (1972).
26. J. N. Sultan and F. J. McGarry, *Polym. Eng. Sci.*, **13**, 29 (1973).
27. H. Breuer, F. Haaf, and J. Stabenow, *J. Macromol. Sci. Phys.*, **B14**(3), 387 (1977).
28. H. Keskkula and A. A. Pettis (to The Dow Chemical Co.) U.S. Pat. 3,626,033 (1971).
29. M. Schwarz, Ph.D. dissertation, University of Texas at Austin, 1988.
30. M. C. Schwarz, H. Keskkula, and D. R. Paul, *J. Appl. Polym. Sci.*, **35**, 653 (1988).
31. H. Kim, H. Keskkula, and D. R. Paul, to appear.
32. W. J. Coumans, D. Heikens, and S. D. Sjoerdsma, *Polymer*, **21**, 103 (1980).
33. W. J. Coumans and D. Heikens, *Polymer*, **21**, 957 (1980).
34. F. Ramsteiner and W. Heckmann, *Polym. Commun.*, **25**, 178 (1984).
35. L. C. Cessna, *Polym. Eng. Sci.*, **14**, 696 (1974).
36. C. B. Bucknall and D. Clayton, *J. Mater. Sci.*, **7**, 202 (1972).
37. H. Keskkula, M. Schwarz, and D. R. Paul, *Polymer*, **27**, 211 (1986).
38. C. B. Bucknall, P. Davis, and I. K. Partridge, *J. Mater. Sci.*, **21**, 307 (1986).
39. M. E. J. Dekkers and D. Heikens, *J. Appl. Polym. Sci.*, **28**, 3809 (1983).
40. A. M. Donald and E. J. Kramer, *J. Mater. Sci.*, **17**, 2351 (1982).
41. E. A. Joseph, M. D. Lorenz, J. W. Barlow, and D. R. Paul, *Polymer*, **23**, 112 (1982).
42. R. P. Kambour, in *Polymer Blends and Mixtures*, D. J. Walsh, J. S. Higgins, and A. Macconnachie, Eds., NATO ASI Series E: No. 289, Martinus Nijhoff, Dordrecht, 1985, p. 331.
43. E. M. Hagerman, *J. Appl. Polym. Sci.*, **13**, 1873 (1969).
44. Br. Pat. 820,154 (1959) (to Monsanto Co.).
45. H. Keskkula, unpublished data.
46. R. A. Mendelson, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 1975 (1985).
47. E. J. Kramer, *Polym. Eng. Sci.*, **24**, 761 (1984).

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