

Mechanical Behavior of Dual-Rubber-Modified SAN

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Synopsis

The use of either an SBS block copolymer or an emulsion-made methyl-methacrylate-grafted rubber alone failed to give any significant increase in the toughness of brittle poly(styrene-co-acrylonitrile) (SAN), even at concentrations up to 50%. However, a combination of the two rubber modifiers produced a strong synergistic toughening. All specimens were prepared by injection molding; however, annealing to relax orientation did not significantly alter this synergistic effect. The use of mechanical dilatometry showed that post-yield deformation of blends containing both modifiers involved some crazing just after yielding but subsequent deformation was mostly due to shear yielding. Addition of SBS alone to SAN resulted in a mixed crazing/shear yielding mode of post-yield deformation with the relative proportions of the two mechanisms being constant up to failure. In contrast, the small emulsion graft particles alone gave rise to a predominant shear yielding deformation. A qualitative mechanism for the synergism is discussed.

INTRODUCTION

For rubber toughened brittle polymers, the average size of the rubber particles and their size distribution have a major effect on properties of the blend.¹⁻⁴ In high impact polystyrene, a dual particle size distribution is effective for enhanced toughness.² In styrene copolymers, the usefulness of a rubber phase with a bimodal particle size distribution has been known for some time.^{4,5} However, the cases where the two particle populations are different both in size and kind have received very little attention except in the patent literature.⁵⁻⁹

In a previous article,¹⁰ we described a synergistic toughening effect which occurred when two distinctly different rubber modifiers were added to a styrene/acrylonitrile (SAN) copolymer. One modifier, a methacrylated butadiene-styrene emulsion-made graft polymer (MBS) has a particle diameter of 0.18 μm . Its outer shell, essentially poly(methyl methacrylate) or PMMA, is miscible with the SAN matrix and, thus, was presumed to provide good adhesion to the matrix. The other modifier, a styrene-butadiene-styrene or SBS triblock copolymer, was found to exist as irregularly shaped particles in the SAN matrix with dimensions between 1 and 5 μm . Neither polystyrene nor polybutadiene are miscible with SAN, and, thus, these particles were presumed to adhere less well to the SAN matrix than the MBS particles.

The MBS provided some toughening of SAN, while the SBS modifier did not improve the impact properties at all, as expected. However, a large

increase in the impact properties was found when the two modifiers were used together.

We suggested a possible mechanism for this synergistic effect based on a dual mode of energy absorption. This mechanism envisions that the large and poorly adhering SBS domains initiate crazes, while the small and better adhering MBS particles are responsible for the formation of shear bands that act to impede craze growth and are involved in the craze termination process.

This article reports additional work designed to determine whether the proposed energy absorption mechanisms are responsible for the synergistic toughening observed in these materials. By measuring the volume dilatation during a stress-strain experiment, one can learn about the post-yield mechanisms of deformation.¹¹ The slope of the volume vs. longitudinal strain curve, $(1/V_0)(dV/d\epsilon)$, distinguishes between dilatational processes such as crazing (slope = 1) and shear yielding (slope = 0).¹ An intermediate value indicates that both mechanisms are involved (i.e., slope = 0.3 means 70% shear yielding and 30% crazing). Of course, if other dilatational processes are involved (e.g., delamination or hole formation), specific percentages for each of the two main processes may not be assigned with any degree of certainty. In such a case, the shear yielding contribution is higher than indicated by the slope, and the crazing share is less. Nevertheless, stress dilatometry measurements still provide useful preliminary information about the toughening mechanisms of new polymeric materials. This study of the synergistic toughening of SAN with dual rubber systems suggests new directions for the toughening of brittle polymers.

MATERIALS AND EXPERIMENTAL PROCEDURES

The matrix polymer used here is a commercial product of Dow Chemical Co. designated as Tyril 1000. It is a styrene/acrylonitrile copolymer with an acrylonitrile content of 25% by weight having $\bar{M}_w = 336,000$ and $\bar{M}_n = 160,000$. The impact modifiers used are also commercial products. Kraton 1101, an SBS block copolymer, is a product of Shell Chemical Co. and has a rubber content of 69–71% by weight. Acryloid KM-680, a methacrylated butadiene-styrene or MBS graft copolymer, is a product of Rohm and Haas Co. The MBS contains about 80% rubber by weight and consists of uniform spheres of 0.18 μm in diameter. Further details about these materials are given elsewhere.¹⁰

The materials were mixed in the appropriate ratios using a one inch Killion extruder ($L/D = 30$) outfitted with a high shear mixing screw having a compression ratio of 3:1. Each batch of materials was extruded twice to ensure uniform mixing. The extrudate was pelletized and dried at least 12 h at 75°C, and then injection-molded into tensile and Izod impact bars using an Arburg 305 molding machine. Some of the bars were then annealed for 48 h at 130°C to reduce orientation that occurred during the injection molding process. Annealing was carried out in a fixture to avoid specimen distortion.

Notched Izod impact strengths were measured according to ASTM D256-56 using both a pendulum type tester and a Dynatup 730 instrumented drop tower. The tensile bars were tested with a stress dilatometer using a crosshead speed of 0.2 in./min. Further details of the stress dilatometer are described elsewhere.¹¹

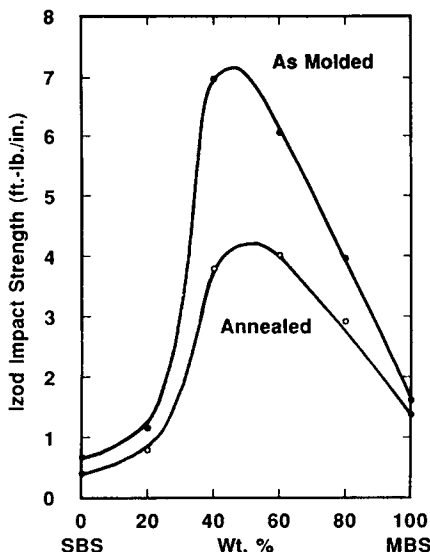


Fig. 1. Izod impact strength of injection molded SAN blends with SBS and MBS. Total modifier content is 50%. Annealing was carried out at 130°C for 48 h.

RESULTS AND DISCUSSION

In our previous article¹⁰ we showed that impressive increases in notched Izod impact strength of an SAN copolymer could be achieved through the simultaneous addition of two specific dissimilar rubber modifiers. This synergistic effect is clearly seen in Figure 1, where at 50% level of total modifier a maximum toughness is reached at certain proportions of the two. Neither MBS nor SBS, up to 50% concentration, is an effective impact modifier for SAN when used alone. The lack of toughening of SAN at this concentration by MBS must stem from the small size ($0.18 \mu\text{m}$) of these particles since the methyl methacrylate graft layer of MBS provides adhesion between the rubber and the matrix phases. SBS is not an effective modifier since it may not provide necessary levels of adhesion with the SAN matrix.

While the levels of impact strength reported in Figure 1 are impressive, it is important to note that 50% by weight of modifier is a high loading. However, the total rubber content in these blends is less than 40% by weight since the MBS is about 80% rubber and the SBS contains approximately 70% polybutadiene segments with the remainder being rigid phase. Even so, most commercial ABS products contain less rubber than this. Typically, for mass-made products the rubber content is 8–20% while emulsion processes may produce products having 20–30% rubber.

Orientation developed during injection molding may be a factor in the results reported previously (see Fig. 1). Therefore, Izod test bars were annealed to render them more isotropic and then tested. These results which are also shown in Figure 1 demonstrate that orientation is not the sole cause of this synergism. As expected, the annealed bars had lower impact strengths in all cases, but the synergistic effect beyond that when either modifier is used alone remains.

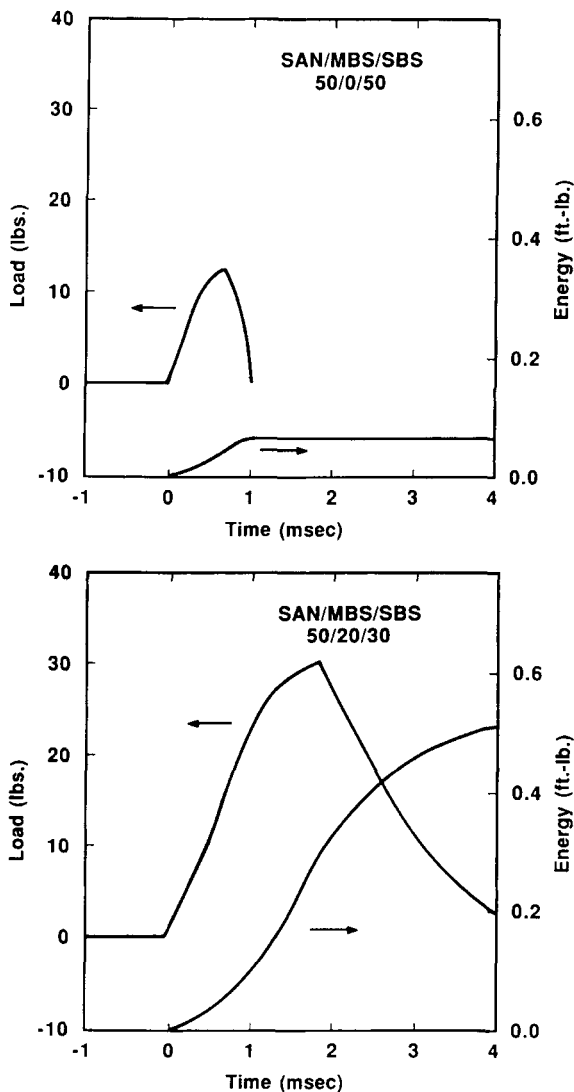


Fig. 2. High speed (9 ft/s) load-time and energy-time traces of SAN blends with SBS and MBS. Notched Izod specimens were used in an instrumented drop tower.

Figure 2 shows Izod impact results for three blends using the Dynatup instrumented impact tester. Besides the obvious difference in energy to break, the time span or strain to failure of each test differs. The times for the samples of 50/50 SAN/SBS and 50/50 SAN/MBS to break are relatively short compared to that for the sample containing both MBS and SBS. The 50/20/30 SAN/MBS/SBS sample corresponds roughly to the peak of the curve seen in Figure 1. The short failure time for the two-component blends is indicative of their brittle nature. Figure 3 gives a plot of the total energy to break obtained by the instrumented impact test. As can be seen, the shape of these curves is similar to those in Figure 1.

As an aid to understand the reasons for this behavior, stress and volume dilatation were measured simultaneously during elongational straining using

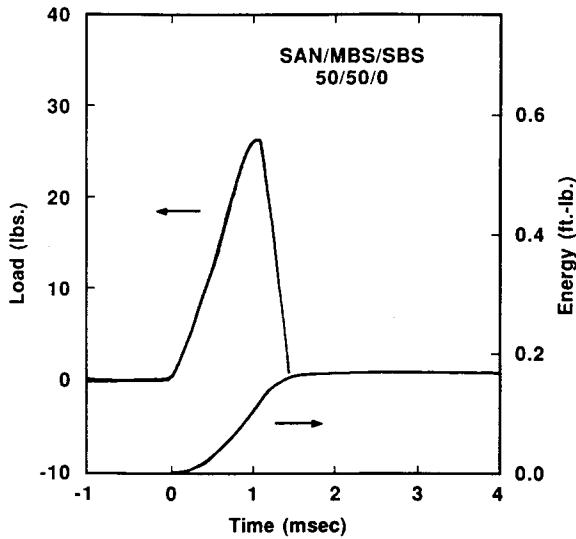


Fig. 2. (Continued from the previous page.)

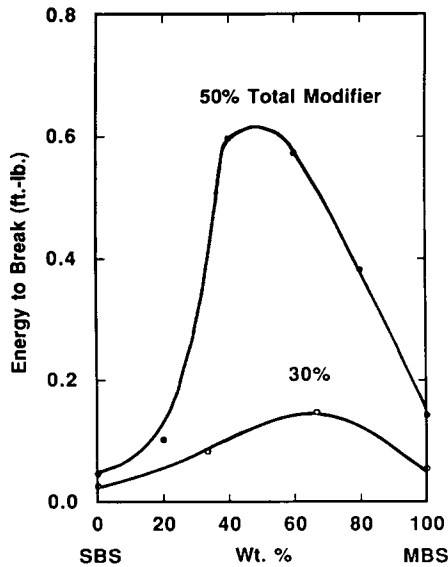


Fig. 3. Energy to break of notched Izod specimens of SAN blends with SBS and MBS. An instrumented drop tower was used for the tests.

an Instron to which the stress dilatometer mentioned earlier was attached. Figure 4 shows results for three typical runs. In the post-yield region, there is a constant rate of volume dilatation for SAN containing rubber only from SBS which suggests that crazing contributes significantly to the mechanism of deformation and continues up to the point of failure. In the post-yield region of SAN containing rubber from only MBS, there is little change in volume dilatation which indicates shearing as the dominant mode of deformation. When both types of modifier are present, there is a significant change in volume dilatation just after the yield but beyond about 20% elongational strain there is essentially no further dilatation. This suggests that crazing contributes to

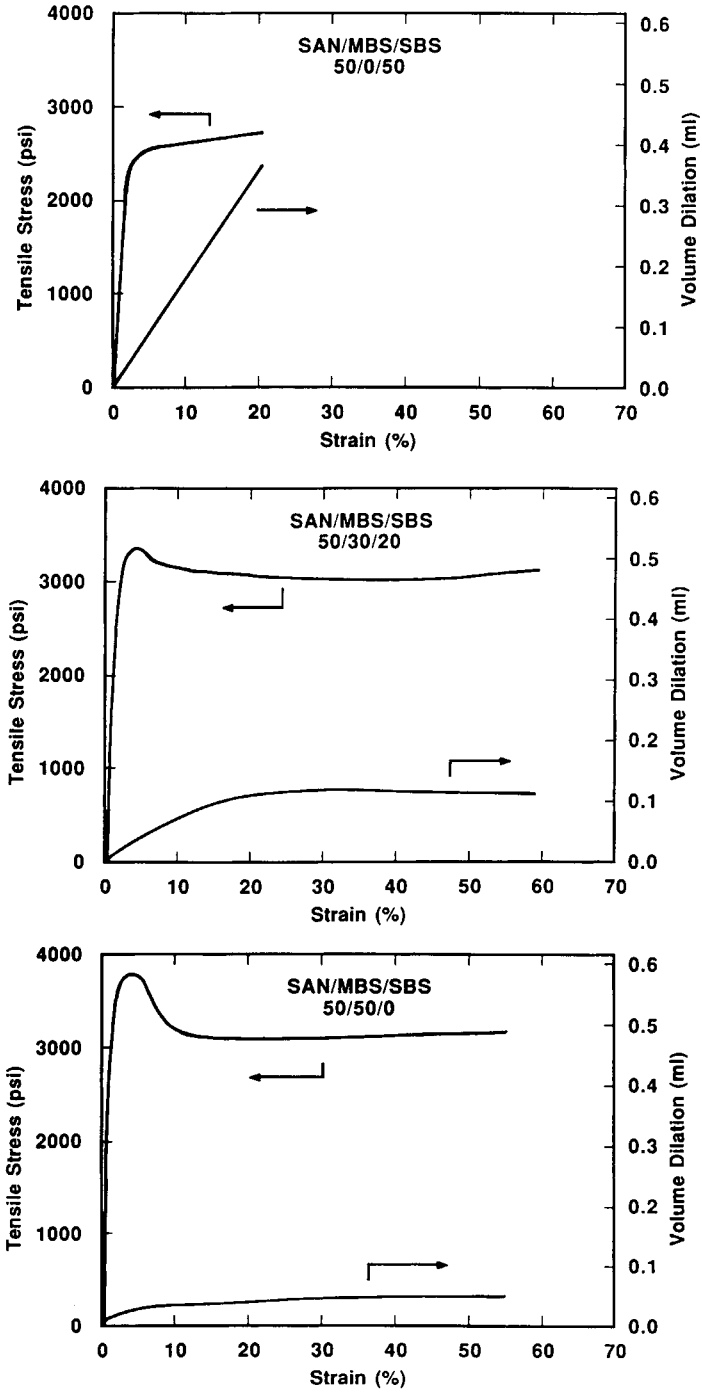


Fig. 4. Stress-strain and volume dilatation-strain curves of SAN blends with SBS and MBS.

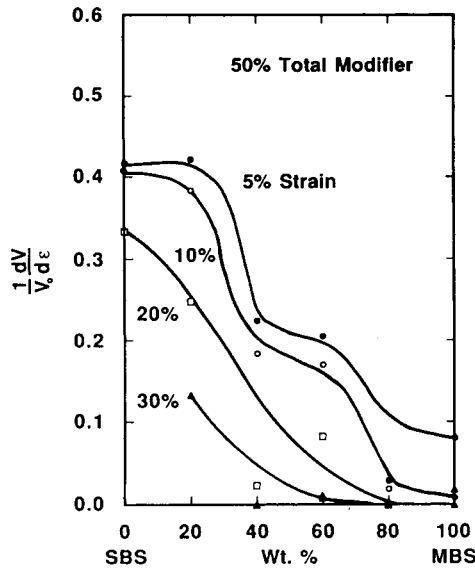


Fig. 5. Slope of the volume dilatation-strain curves at various strain levels of SAN blends with SBS and MBS.

the deformation mechanism during the early post-yield region but this gives way to a shearing mode at higher straining.

More detailed examination of the post-yield deformation behavior is shown in Figures 5 and 6 by plotting the slopes of the volume dilatation curves against the proportion of the two types of modifiers (at a total modifier content of 50%) and the elongational strain. Each line in Figure 6 corresponds

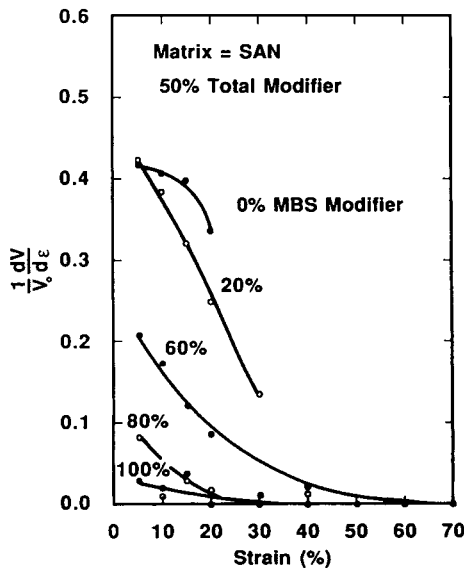


Fig. 6. Slope of the volume dilatation-strain curves of SAN blends with SBS and MBS. At 50% total modifier content, the individual curves represent the various MBS levels.

to a fixed level of elongational strain with 5% being the lowest level at which all compositions were in the post-yield region. The lines drawn are simply to aid viewing of the data and not to imply statistical significance of the shapes shown. Each line in Figure 6 corresponds to a fixed proportion of the two types of modifiers, and these results are simply a cross-plot of those shown in Figure 5. While crazing is a significant mode of deformation when SBS is the sole modifier, these quantitative results indicate that this mode contributes no more than about 40% to the deformation mechanism with shearing presumably accounting for the remainder. The reason for such a low apparent level of crazing may be related to a high concentration of SBS and molecular orientation due to injection molding. As MBS modifier replaces the SBS, the contribution of shearing increases. The shear contribution also increases the larger the total elongational strain. The proportion of the two modifier types strongly influences the nature of the deformation process and affects the ultimate level of toughness that can be achieved. It seems reasonable to speculate that the crazes formed when there is a high proportion of SBS present readily become cracks that lead to early failure. On the other hand, a high proportion of MBS fails to initiate significant crazing and the resulting energy absorption prior to failure is minimal. An appropriate combination of the two apparently leads to a delicate balance of the two processes and the optimum ductility observed.

SUMMARY AND CONCLUSION

It has been shown that a brittle SAN copolymer is not significantly toughened by up to 50% of relatively large (1–5 μm) rubber particles created by blending with an SBS block copolymer or by addition of small (0.18 μm) emulsion-made rubber particles having a PMMA graft layer. However, a combination of the two types of particles leads to very significant or synergistic toughening at high total rubber content. The current volume dilatation results for injection-molded specimens show that at low strain rates that SBS leads to crazing as a significant and continuous mode of deformation up to failure which is accompanied by significant shear yielding, while MBS leads to shearing as the only mechanism of deformation from yield to failure. The relative contribution of the crazing and shearing modes can be continuously altered by appropriate combinations of SBS and MBS type rubber particles. We believe the synergism in toughening that results from incorporation of both SBS and MBS stems from a delicate balance of these two modes of post-yield deformation. The presence of SBS initiates crazes early in the yield process while the presence of MBS promotes shear banding that helps prevent these crazes from becoming cracks. Evidently the shear process alone is not as effective for energy absorption as is crazing which does not lead to cracks. Of course, because of the effects of strain rate on the deformation mechanism of polymers like SAN,¹² the relative proportions of crazing and shear yielding under impact conditions may differ quantitatively from those assigned here by low strain rate volume dilatation measurements. However, the qualitative picture at high strain rates should remain much the same as that described above.

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