The Effects of Blending Small Amounts of Homopolystyrene on the Mechanical Properties of a Low Styrene Content Styrene-Butadiene-Styrene Block Copolymer

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Tensile, cyclic, and tear properties were compared for several styrene-butadiene-styrene (SBS) triblock copolymers, KRATON D2104, D1101 and D1102, and blends of D2104 with monodisperse polystyrene of various molecular weights. D2104 is expected to have a morphology of polystyrene spheres in a polybutadiene continuous matrix. The mechanical properties of D2104 were compared to the properties of SBS materials which have higher styrene contents and exhibit cylindrical or lamellar morphologies. Blending the D2104 with polystyrene (molecular weights ranging from 2000 to 51,000) to 24 and 28 wt % total styrene content showed that the tensile strength obtained for a blend was dependent on the molecular weight of the polystyrene added. Cycle testing of the D2104-polystyrene blends showed that with increasing polystyrene content the softening effect increases with increasing strain. This indicates that the degree of phase continuity of the polystyrene domains may be changing from a spherical morphology to a cylindrical morphology similar to that of pure SBS with 28 wt % styrene content. Tear test results for the blends were also observed to be similar to the results for pure SBS of the same total polystyrene content.

INTRODUCTION

Over the last two decades, many studies have been performed on the mechanical properties of styrene-butadiene-styrene (SBS) block copolymers (1–29). These studies have emphasized effects of styrene content (1–11), block molecular weight (5–15), and processing techniques (7, 9, 17–27). Within the last decade, a significant interest has developed in the mechanical properties of blends of SBS block copolymers with polystyrene (8, 27–34). These studies have investigated how high loadings of polystyrene can result in producing a material of increased tensile strength as compared to the unblended SBS block copolymer. Explanations have been developed concerning either the inclusion of polystyrene into the styrene-block domains or the development of separate polystyrene homopolymer domains in the sample.

With few exceptions (5–7), all of the studies done on SBS systems have concerned block copolymers with at least 25 wt % styrene content but less than

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50 wt % styrene content. This is significant because at this level of styrene content in the block copolymer the predominant styrene phase morphology involves cylindrical or lamellar domains (27, 29, 35, 36). In contrast, for SBS block copolymers with less than 25 wt % styrene content, a significant portion of the styrene phase morphology involves spherical domains (3, 37). As a result of this difference in morphology, SBS triblock copolymers with less than 25 wt % styrene content have mechanical properties which are isotropic and closer to that of a vulcanizate.

In the present study, mechanical and morphological properties of an SBS block copolymer with 20.8 ± 0.5 wt % styrene content are compared with mechanical and morphological properties of other SBS block copolymers with styrene contents ranging up to 48.2 wt %. Blends of nearly monodisperse polystyrene with the 20.8 wt % styrene content SBS block copolymer are made to 24 wt % and 28 wt % total styrene content. Comparisons of the mechanical properties of the blends are made with the unblended block copolymer as well as a block copolymer with a styrene content of 28 wt %.

Studies of the mechanical and morphological properties of blends of relatively small amounts of polystyrene with SBS block copolymers are particularly significant for several reasons. Previous blending studies have generally loaded much greater amounts of polystyrene into block copolymers (8, 27–34) than done in this study, thus ignoring the interesting effects achieved at low loadings of polystyrene. In addition monodisperse polystyrenes have seldom (27, 38) been employed previously in studies of blends, meaning that the effect of polystyrene molecular weight has not been effectively examined. Studies (39–45) concerning the phase behavior of blends of SB diblock copolymers and polystyrene as well as other recent studies (46–48) with triblock and star copolymers indicate that the inclusion or exclusion of polystyrene in the styrene-block domains depends greatly on the molecular weights of the two polymers and overall composition of the blend. These types of observations were also seen in some of the earlier SBS-polystyrene blend studies (8, 27, 28), but this effect has not been examined completely. Consequently, this study will contribute materially to an understanding of the effects of polystyrene molecular weight on the blend properties as well as the effects of possible modification of styrene phase morphology from spherical to cylindrical domains upon increasing styrene-content from 20.8 to 28 wt % in the blend.

EXPERIMENTAL

The styrene-butadiene-styrene copolymers used in this study were KRATON® D1101, D1102, D2104 and TR-41-1647, TR-41-1648, and TR-41-1649 all produced by Shell Chemical Company. The characterization for these materials is summarized in *Table 1*. While characterization data are currently available in the literature for D1101, D1102 and the TR series copolymers, none is available for the D2104 block copolymer. The composition of D2104 was determined by UV absorbance spectroscopy. Using the known compositions of D1101 and D1102 the composition of D2104 was found (49) to be 20.8 ± 0.5 wt % styrene as calculated from Beer's law. The molecular weight of D2104 was determined by GPC.

The polystyrene used for blending was obtained from Pressure Chemical. The samples were all nearly

monodisperse $(M_w/M_n < 1.06)$ and had molecular weights of 2000, 4000, 9000, 17,500, and 51,000. The blends were prepared from D2104 and homopolystyrene such that the total styrene content of the blend was either 24 or 28 wt %. Preparation was done by initially dissolving the appropriate amounts of polystyrene and D2104 in toluene for two days, agitating periodically. The solution was then precipitated in methanol. The excess solvent was decanted off and the remaining solvent was evaporated in a fume hood until nearly dry and then in a vacuum oven at room temperature for two to three days. The polymers and blends were compression molded at 150°C and 140 MPa into films ranging in thickness from 0.2 to 1.3 mm.

Tensile, cycle, and tear tests were performed on an Instron 1125 Testing Machine at room temperature. Tensile tests were performed using dogbone tensile specimens having a gage length of 19.05 mm and a width of 4.4 mm. The samples were stretched to failure at a constant strain rate of 125 mm/min. Strain-controlled cycle tests were also performed using dogbone shaped specimens. The samples were pulled to a specified strain and released at the same rate of 125 mm/min for as many as 100 cycles. For tear testing, samples were cut in a trousers pattern which is used to determine the tear propagation resistance of plastic film (50). The legs were clamped into the grips of the Instron, and then the samples were torn completely through at a constant rate of 125 mm/min.

RESULTS AND DISCUSSION

Tensile Tests

The results of the tensile tests for the triblock copolymers studied are shown in *Fig. 1* as engineer-

Table 1. Characterization of SBS Copolymers.

Polymer Sample	Styrene Content (Wt %)	Block Molecular Weight (× 10⁻³)	References
TR-41-1649	48.2	14–30–14	(7, 21, 27)
KRATON D1101	30.0	17.5–84–18.6	(7, 25, 30)
TR-41-1648	29.3	16–78–16	(7, 21, 27)
KRATON D1102	28.0	10–51–10	(18)
TR-41-1647	26.8	7–36–6	(7, 27)
KRATON D2104	20.8	*	(44)*

* $M_N = 74,100$ and $M_W = 100,000$ as determined by GPC by Mr. Wayne Willkomm of the Department of Chemical Engineering and Materials Science at the University of Minnesota.
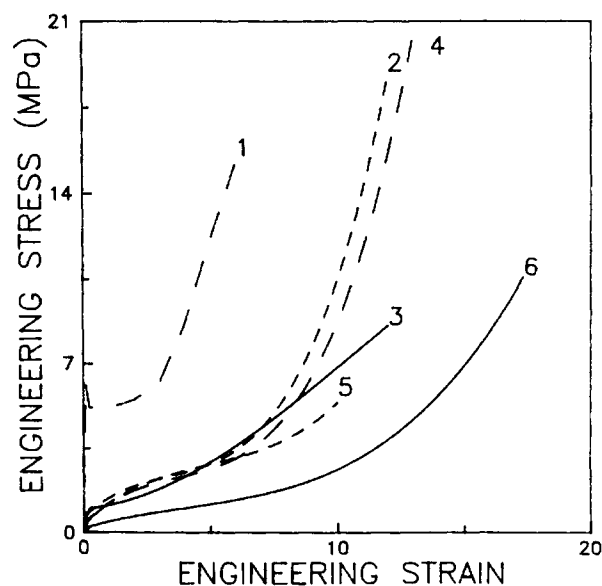

Fig. 1. Effect of composition of the tensile properties of SBS copolymers: (1) 48.2 wt % PS, (2) 30 wt % PS, (3) 29.3 wt % PS, (4) 28.0 wt % PS, (5) 26.8 wt % PS, (6) 20.8 wt % PS.

ing stress versus engineering strain. Besides showing results for D2104, D1101, and D1102, results are also given for the TR series SBS copolymers with styrene block contents ranging up to 48.2 wt %. The composition and molecular weights of these copolymers are given in *Table 1*. As observed by other researchers (4, 7, 12), changes in relative proportions of the polystyrene and the polybutadiene significantly influence the mechanical properties of SBS. These properties of the triblock copolymers depend on the nature of the hard glassy styrene domains which hold the elastic network together (7). Decreasing the styrene content in the block copolymers leads to a decrease in the material stress measured at a given strain and to an increase in the ultimate strain achieved.

The yield point and plastic flow which is observed for the copolymer containing 48.2 wt % polystyrene is due to the high degree of continuity in the styrene phases formed. After about 300–400% elongation the polystyrene microdomain structure is broken down and the polymer becomes rubbery and exhibits elastic extension as shown by the rise in the stress versus strain curve in *Fig. 1*. The D2104, containing only 20.8 wt % polystyrene, exhibits a very low modulus and high extensibility which is characteristic of a material having no degree of continuity in the polystyrene domains.

The copolymers with polystyrene compositions ranging from 26.8 to 30 wt % all have similar stress-strain curves up to an elongation of 500%. This indicates that the morphology of these materials is similar. Based on the composition and the initial modulus exhibits, these materials have a small degree of continuity in the polystyrene domains. Recent discussion by Diamant *et al.* (9), has suggested that the reason for an absence of definite yielding in these materials is due to a continually breaking up of the polystyrene phase, even during the initial stages of deformation. This would explain why the 26.8–30 wt % styrene copolymers exhibit a higher initial modulus than the 20.8 wt % styrene copolymer, even though a definite yield point is not observed for any of these materials.

Differences in the ultimate stress-strain properties (>500% elongation) of the materials in the 26.8 to 30 wt % styrene content range can be explained as a result of differences in the molecular weights. The large deformation response of SBS copolymers of similar composition has been observed to be significantly influenced by molecular weight differences (9, 14). TR-41-1647, having a low molecular weight, fails at lower ultimate stress and strain values and D1101, having a high molecular weight, fails at a higher stress and strain. The difference in ultimate stress and strain properties between D1102 and TR-41-1648 can be explained by the differences in the styrene block lengths for these copolymers. As the molecular weight decreases the amount of the mixed interfacial region relative to the pure styrene and pure butadiene domains increases (14); this in-

creased interfacial region leads to an increased extension of the material.

Tensile tests for all materials were also performed at a strain rate of 50 mm/min (not shown). These tests resulted in lower ultimate tensile strength and strain at failure for all the copolymers as expected (24).

The addition of monodisperse polystyrene to D2104 increased the material stress measured at all strains for both the 24 and the 28 wt % blends. These results are presented in *Figs. 2* and *3*. Some of the stress-strain measurements are also presented in *Tables 2* and *3*. The errors associated with the stress values were all within 10%. At low strains it is observed that the stress increases with increasing polystyrene molecular weight. At high strains, however, the maximum material stress observed is for the 9000 molec-
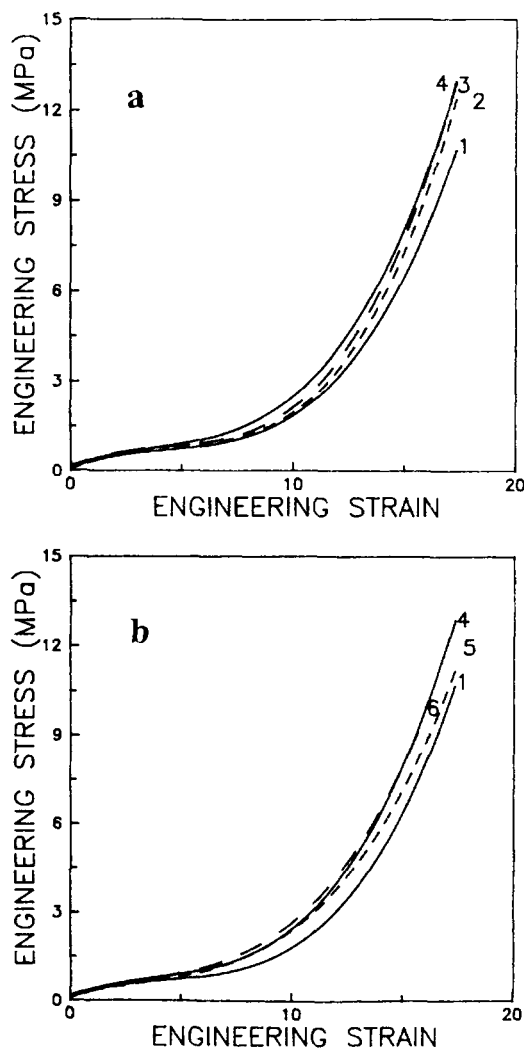

Fig. 2. Effect of homopolystyrene molecular weight on the tensile properties of a KRATON® D2104-polystyrene blend. Total styrene content for the blend is 24 wt %. Fig. 2a: (1) pure D2104, (2) D2104-2000 MW PS, (3) D2104-4000 MW PS, (4) D2104-9000 MW PS. Fig. 2b: (1) pure D2104, (4) D2104-9000 MW PS, (5) D2104-17,500 MW PS, (6) D2104-51,000 MW PS.
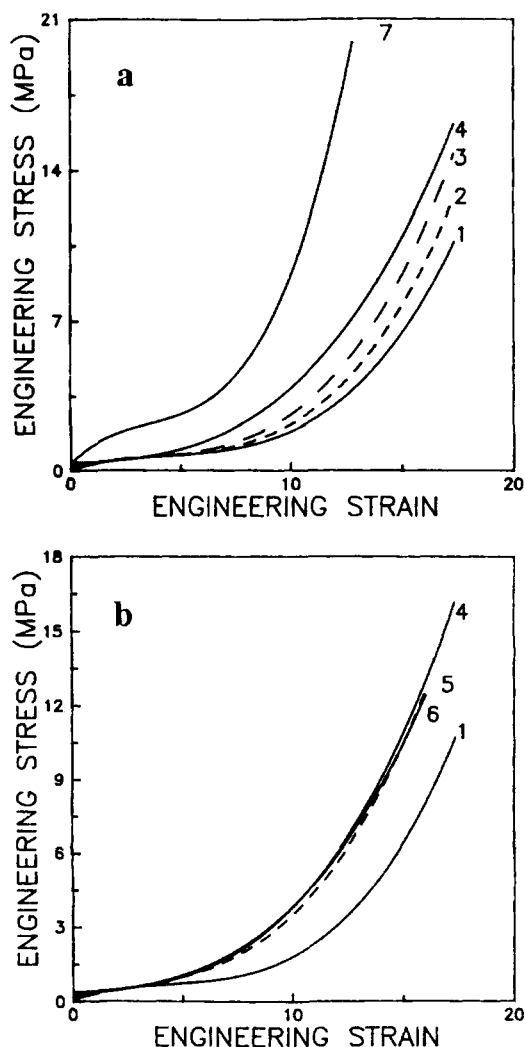
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Table 3. Tensile Properties for an SBS-PS Blend of 28 Wt % Polystyrene Content.

Polymer Sample	Stress Level (MPa)		
	Strain = 4	Strain = 12	Strain = 16
Pure D2104	0.7	3.0	8.6
2,000 MW PS	0.8	3.4	10.3
4,000 MW PS	0.8	4.0	12.3
9,000 MW PS	1.0	5.5	13.8
17,500 MW PS	0.9	5.7	12.3
51,000 MW PS	1.0	6.1	11.9

molecular weight polystyrene. For these blends the specimens consistantly failed early. From these observations it is clear that when the molecular weight of the polystyrene is 9000 or below the addition of the homopolymer enhances the strength of the material without reducing the extensibility. However, when the molecular weight is 17,500 or greater the improvement of the material strength is not as pronounced and the extensibility of the material is reduced. These results indicate that the dependence of homopolymer solubility into the domains of the corresponding block segments is very sensitive to the homopolymer molecular weight. The stress-strain behavior of D1102 is also presented in *Fig. 3*. For the same total styrene content the pure block copolymer exhibits higher stresses than the blend, as shown.

Many authors (39–48) have pointed out that the solubility of a homopolymer in the corresponding block microdomains decreases as the ratio of the homopolymer chain length to block sequence length is increased. Most of the studies (39–45) have used diblock copolymers. In these studies the maximum solubility was usually found to be large, up to 30% by weight depending on the homopolymer molecular weight (39). In work reported recently concerning triblock and star copolymers, the miscibility of the homopolymer was shown to decrease with increasing complexity of the copolymer (46). Because of the greater conformational restrictions in triblock copolymers the solubility of the homopolymer in corresponding domains is less than for diblock copolymers. This is supported by the results for the D2104-polystyrene blends. The variation in tensile properties observed with varying the homopolymer molecular weight indicate that even at very low loadings of the polystyrene (<10 wt % homopolymer) small differences in molecular weight can greatly affect the homopolymer solubility in the corresponding block domain.

If the molecular weight of the homopolymer is comparable to or less than that of the corresponding block in the block copolymer, then the homopolymer can be incorporated into the block domain. If the molecular weight is greater than the block molecular weight, a reduced amount of homopolymer can be solubilized (51) but at larger concentrations the homopolymer will form its own phase in the blend. This has been experimentally observed to some extent for studies of blends of D1101 with polystyrene (27–29).

Fig. 3. Effect of homopolystyrene molecular weight on the tensile properties of a KRATON® D2104-polystyrene blend. Total styrene content for the blend is 28 wt %. Fig. 3a: (1) pure D2104, (2) D2104-2000 MW PS, (3) D2104-4000 MW PS, (4) D2104-9000 MW PS, (7) pure D1102. Fig. 3b: (1) pure D2104, (4) D2104-9000 MW PS, (5) D2104-17,500 MW PS, (6) D2104-51,000 MW PS.

Table 2. Tensile Properties for an SBS-PS Blend of 24 Wt % Polystyrene Content.

Polymer Sample	Stress Level (MPa)		
	Strain = 4	Strain = 12	Strain = 16
Pure D2104	0.7	3.0	8.6
2,000 MW PS	0.8	3.1	9.6
4,000 MW PS	0.7	3.3	10.7
9,000 MW PS	0.8	3.8	10.5
17,500 MW PS	0.8	3.4	9.3
51,000 MW PS	0.8	4.1	9.4

ular weight polystyrene blends. This molecular weight is approximately equal to the styrene block length. It is also observed that the strain at failure for the blends is essentially unchanged except for the 28 wt % blends made from 17,500 and 51,000

In these studies, transmission electron microscopy was used in addition to measurements of the mechanical behavior to show that low molecular weight polystyrene was incorporated into the block domains while high molecular weight polystyrene formed its own phase. These blends (27–29) were made with homopolystyrene resulting in total styrene contents ranging from 42 to 86 wt %. Micrographs of the pure D1101 showed the morphology to be that of short polystyrene cylinders in the rubber matrix. After incorporation of a homopolymer of molecular weight lower than the corresponding block molecular weight, localized lamellar type structures were observed in the morphology. These observed changes were correlated to the stress-strain behavior of the materials. High molecular weight polystyrene blended with the D1101 was seen to form its own phase and leave the morphology of the SBS essentially unchanged. It would seem apparent from *Figs.* 2 and 3 that the same type of behavior holds true for blends with SBS exhibiting spherical morphology. Incorporation of the homopolystyrene into the D2104 block domains appears to render the domains more continuous when the molecular weight of the polystyrene is low as evidenced by the change in mechanical properties observed in this study. Only one of the polystyrene samples used in the blends with D1101 (27–29) was monodisperse. Using monodisperse polystyrene in the blends, as done here, allows for a much clearer understanding of how the molecular weight of the homopolymer determines the morphology of the blend.

Strain-controlled Cycle Tests

Strain-controlled cycle tests at a constant strain rate of 125 mm/min were performed to strains of 1, 2, and 5 for the D1101, D1102, and D2104. These triblock elastomers exhibit a stress-softening effect; the measured material stress level decreases as the specimen is cycled to a given strain (4, 8, 11, 17, 18). As the material is deformed, the continuity in the glassy domain morphology is broken up. This causes a residual stress in the sample which leads to a lowered stress measurement during subsequent extensions (17). As seen in *Fig. 4*, the drop in the measured stress level for D2104 with cycling stays relatively constant, 15 ± 3%, for the range of strains studied. This observation was expected based on the tensile test results. If D2104 has a predominantly spherical morphology as expected, the lack of continuity in the glassy phase would make it possible for the material to retain its morphology, and thus the material would not be expected to show a large degree of stress softening.

D1102 and D1101 on the other hand experience a much more significant stress softening effect as seen in *Figs. 5* and *6*, respectively. For D1102 the stress reduces 23% after 80 cycles to a strain of one; when the strain is increased to five the stress reduces by 43% after 80 cycles. After 80 cycles, D1101 has a reduction in stress of 14% for a strain of one and
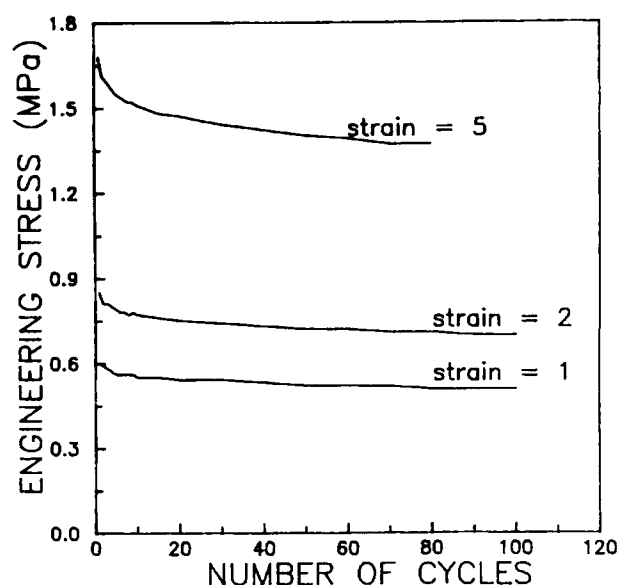

Fig. 4. Cyclic load curves for KRATON* D2104 cycled at various strains at a constant crosshead speed of 125 mm/min.
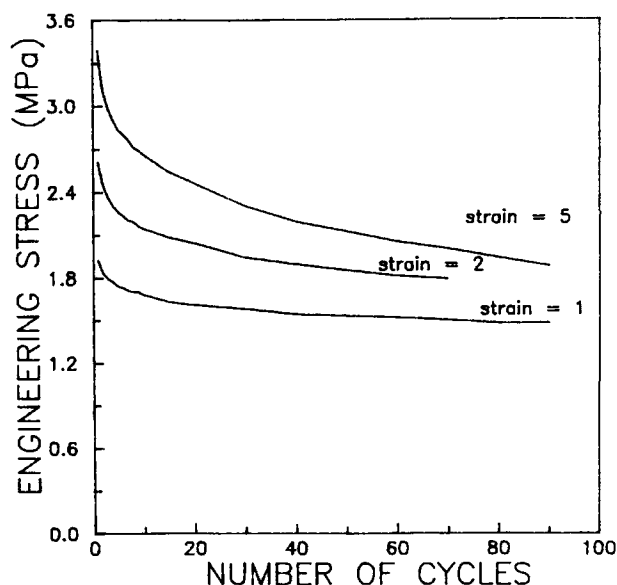

Fig. 5. Cyclic load curves for KRATON® D1102 cycled at various strains at a constant crosshead speed of 125 mm/min.

30% for a strain of five. The increase in stress softening observed as the strain is increased is due to a greater breakup of the styrene phases. Since these two copolymers have a higher styrene content, the styrene domains have a greater degree of continuity, and therefore the effect of elongation is to break up the continuous regions.

At this time it is unclear why the D1102 is exhibiting higher stresses and a larger stress softening effect than the D1101. Since the D1102 has a slightly lower styrene content, the opposite result was expected. It is also unclear why the D1102 data have a

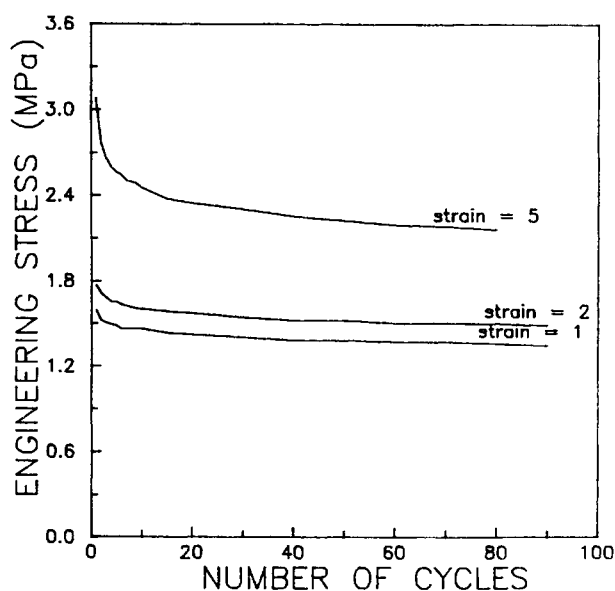L. S. Flosenzier, J. H. Rohlfing, A. M. Schwark, and J. M. Torkelson

Fig. 6. Cyclic load curves for KRATON® D1101 cycled at various strains at a constant crosshead speed of 125 mm/min.

much larger variability than either the D2104 or the D1101. All the results for the D1101, D2104, and the blends were repeatable to well within ±20% except for the D2104 cycling to a strain of 2 which was repeatable to within only ±50%. The D1102 results, however, did not have as good reproducibility. The variability was greater than ±20% for all the D1102 cycling results. The curves presented on Figs. 4 through 8 represent an average calculated from at least five individual runs at each strain. The significant variability in the data for D1102 could possibly be explained by the effect of processing conditions on the resultant morphology of the materials.

It has been observed by Canevarolo, et al. (52), that processing temperature and heat treatment can affect the final morphology of a 28 wt % polystyrene SBS copolymer. They observed that the material can only undergo internal stress relaxation for temperatures up to approximately 135°C, but that for temperatures above 145°C rearrangement of imperfections in the domain structure can result. In addition, Chung, et al. (53), observed that an SBS copolymer of about the same composition exhibits a multiphase structure below 140°C and a single phase structure above 150°C. The molding temperature under which these films were pressed was approximately 150°C. Since the compression molder which was used had limited temperature and pressure control, ±15°C and ±7 MPa, it is possible that some films were able to undergo a rearrangement of domain structure and thus develop a greater degree of continuity in the polystyrene domains while others were not. D1102 would be the most significantly affected because its composition is bordering the transition from a spherical to a cylindrical morphology and depending on the processing conditions the actual morphology of the material could be either predominantly spherical

or cylindrical. In addition, the morphology of the D2104 and the D1101 would be less likely to be affected by minor fluctuations in the molding temperature or pressure because their transition temperatures between internal relaxation and structure rearrangement would be different due to the differences in composition.

One interesting result is that close comparison of Figs. 5 and 6 reveals that even though D1102 exhibits higher stress levels than D1101 at the beginning of the tests, it falls to a lower stress level for
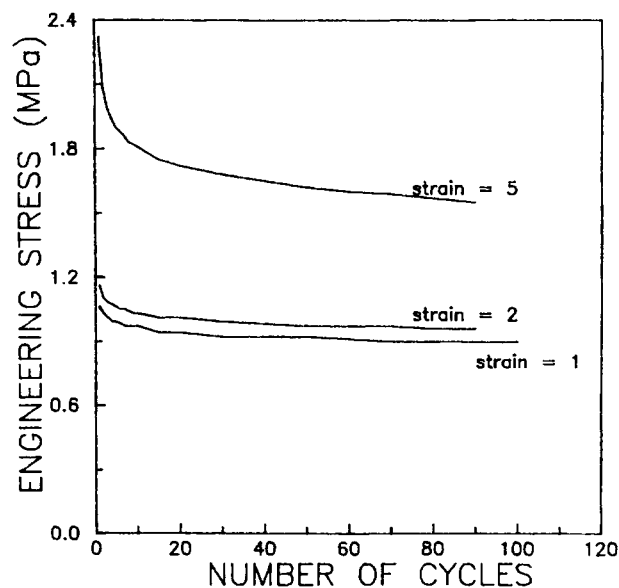

Fig. 7. Cyclic load curves for the 24 wt % total styrene content KRATON® D2104-polystyrene blend cycled at various strains at a constant crosshead speed of 125 mm/min.
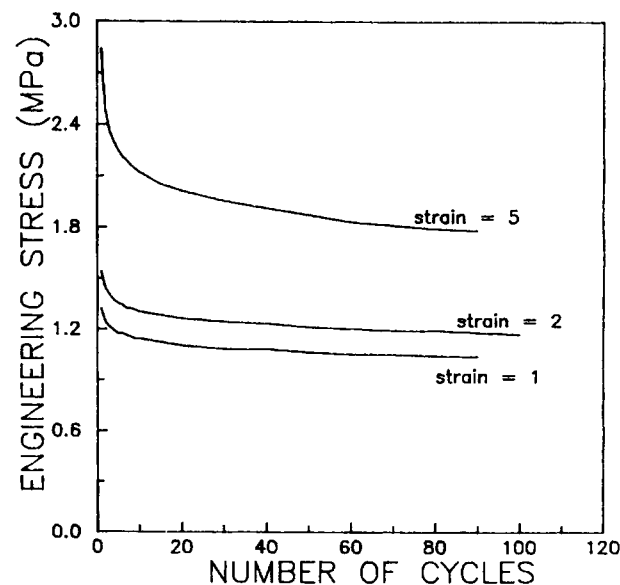

Fig. 8. Cyclic load curves for the 28 wt % total styrene content KRATON® D2104-polystyrene blend cycled at various strains at a constant crosshead speed of 125 mm/min.

cycles to a strain of 5. This suggests that the degree of breakup of the polystyrene phase is greater for the D1102 than for the D1101 after a large number of cycles. Once the continuity of the polystyrene phases has been broken down, the stress-strain curves are dependent on the volume fraction of the polystyrene (9). Since D1101 has a higher fraction of styrene, after a large number of cycles it should exhibit the higher stress level. This crossover is not observed at strains of 1 and 2 probably because the amount of deformation is not enough to completely break down the polystyrene microdomain structure.

For all samples the largest drop in stress occurs during the first cycle. This indicates that the greatest change in the morphology occurs during the first cycle. This has also been observed by other authors (8, 11, 17, 29).

Strain-controlled cycle tests were done for the D2104 blended with the 9000 molecular weight polystyrene. This blend was chosen so that the ratio of homopolymer molecular weight to corresponding block length would be unity. The results are given in *Fig. 7* for the 24 wt % blend and in *Fig. 8* for the 28 wt % blend. As had been observed earlier in the tensile tests the material stress increased with increasing total styrene content but was lower than the stress for the pure block copolymer of comparable styrene content. It is interesting to note that while the stress softening effect for the D2104 was not dependent on the strain to which the material was cycled, a much larger drop in stress is observed for the blends at the higher strains. The 24 wt % blend shows a 15% drop in stress after 80 cycles to a strain of one and a 32% stress decrease for cycles to a strain of five. After 80 cycles, the 28 wt % blend shows a 21% drop in stress for cycles to a strain of one and a 37% drop in stress for cycles at a strain of five. This enhanced stress softening is another indication that the degree of continuity in the rigid microphases of the blends is closer to that of the D1102 and D1101 than that of the D2104 and that the morphology of the blends has been altered from the spherical domains of the D2104 host copolymer to a cylindrical morphology or more likely a mix of spheres and short cylinders.

When a material undergoes irreversible deformation, the material will exhibit a 'permanent' deformation or set, increase in gage length, even after the load is released (10, 11). All specimens, both the pure copolymers and the blends, elongated during testing by approximately 10% (after cycles of strains of one) to 20% (after cycles of strains of five). There seemed to be no significant difference in the set observed for the different materials. In other studies (7, 8) it was seen that blends exhibited much larger sets than the pure copolymers. It must be remembered, however, that in these other studies higher homopolymer molecular weights and much higher homopolymer loadings were used and thus the morphological effects in this study are different. In all cases, annealing the specimen at room temperature for approximately 24–

48 hours returned the sample close to its original length. Even with the apparent recovery in length it would be expected that the specimens would still exhibit lower stresses due to an incomplete microstructural recovery than those originally measured based on the healing time which would be on the order of weeks or months at 25°C (10, 18).

Tear Tests

Figure 9 compares the tear strength measured for the three copolymers D2104, D1102, and D1101. The maximum tear strength was found to increase linearly with sample thickness for the copolymers in this study. As expected, D1101 has a higher tear strength than both the D1102 and the D2104 over most of the range of thicknesses studied. However, the dependence of tear strength for D1102 on sample thickness is different from the dependence observed for D1101 or D2104. The D1102 exhibits the highest tear strength for thin samples and the lowest tear strength for thick samples.

Experimentally, the materials appeared to tear by two different mechanisms. In general the D2104 tended to show large deformation and local stretching before any appreciable amount of tearing occurred. The D1101 tended to tear uniformly at a constant rate through the sample. D1102 exhibited both mechanisms but tore predominantly in the same manner as the D1101. These mechanisms are obviously associated with how the microstructure of the polymers affects the capacity for stress dissipation in the samples. It would also appear that the mechanism for fracture also affects the tear path. Samples that exhibited significant stretching tended to tear perpendicularly from the direction of the trouser cut, while the tear path associated with the other mechanism tore in the same general direction as the cut.
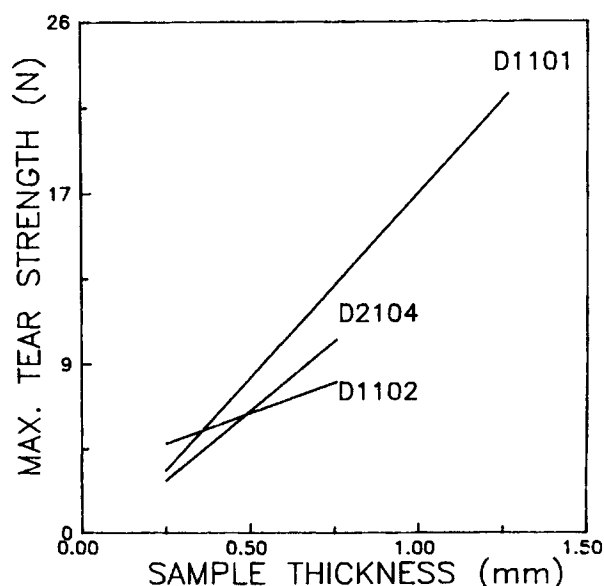

Fig. 9. *Measured tear strength as a function of sample thickness for unblended block copolymers.*

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In order to gain further insight into the differences in the tearing mechanisms of the materials, the scanning electron microscope (SEM) was used to examine the fracture surfaces. The samples were gold coated immediately after tearing and then viewed in the SEM within 24 hours. *Figure 10a* shows a jagged, layered fracture surface for D1101. These types of ledges, or chevron markings, are formed by intersecting tear paths. In elastomers they are attributed to the strength anisotropy which develops at high deformations (54). From this, it appears that catastrophic failure does not occur until a large number of cracks have developed. This may be the result of high stress dissipation of advancing cracks by the glassy polystyrene domains which are initially randomly oriented cylinders. This type of mechanism leads to noncontinuous tear paths and a layered fracture surface. *Figure 10b* exhibits long sinusoidal fibrils on an otherwise smooth fracture surface for D2104. Since the morphology is that of spherical polystyrene domains, the stress dissipating effect may not be as effective and therefore smoother, more continuous tear paths are observed. As shown in *Fig. 10c* the fracture surface for D1102 exhibits a combination of both a jagged layered surface similar to that observed for D1101 and the fibrils characteristic of the D2104.

These observations tend to agree generally with those observed by Kuriakose *et al.* (55). In SEM studies of tear failure Kuriakose, *et al.* (55), observed that the failure surface for a 14% styrene SIS block copolymer (I being Isoprene) had folds, lips, and fibrils characteristic of a high extent of deformation and continuous tear paths. For an SBS material with 48% styrene and containing 10 wt % silica the tear surface indicated laminar tearing between the hard and soft segments.

It is unclear why the D1102 copolymer follows a different dependence for the slope of the curve and why a crossover in tear strength appears for the different materials. It may be related in some way to the transition from one tearing mechanism to another which would be associated with a transition from a spherical morphology to a cylindrical morphology.

This same change in the dependence of tear strength with sample thickness is observed in the SBS-polystyrene blends as shown in *Fig. 11*. For the 24 wt % styrene blend the tear strength increases from that of the pure D2104, but the slope of the line is reduced. For the 28 wt % styrene blend the tear strength increases further and the slope becomes very close to that of the pure D1102. In addition, the tear strength for the blends are higher than that of the pure D1102. In order to be able to explain these observations adequately it will be necessary to examine further how the morphology of these materials is associated with the energy dissipation and tear mechanisms which are observed.

CONCLUDING REMARKS

In this study we have seen that the SBS copolymers with low styrene content exhibit lower strength than copolymers with higher styrene contents. This trend
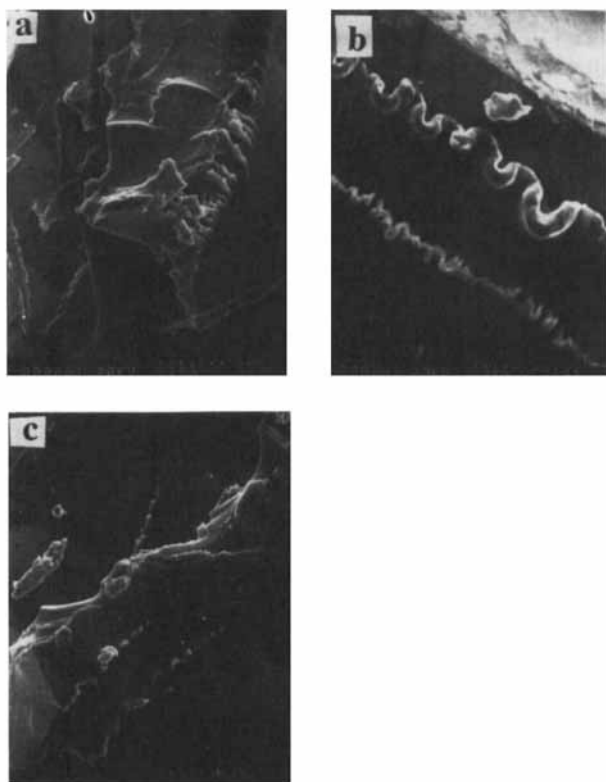

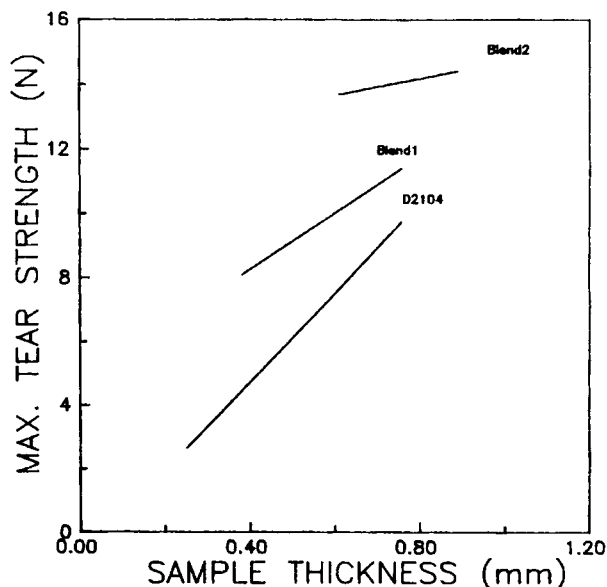Fig. 10. SEM micrographs of the fracture surface in torn samples of a: D1101, b: D2104, and c: D1102.

Fig. 11. Measured tear strength as a function of sample thickness for the KRATON® D2104-polystyrene blends; blend 1 is a 24 wt % PS content D2104-9000 MW PS blend, and blend 2 is a 28 wt % PS content D2104-9000 MW PS blend.

in the mechanical properties was expected since these properties are dependent on the degree of continuity which develops in the hard polystyrene domains. The degree of continuity in turn depends on the polystyrene content of the material. In addition we have seen that mechanical properties measured for blends of a pure block copolymer with monodisperse homopolystyrene are increased over the properties measured for the copolymer alone. The degree to which these properties are increased depends on the ratio of the homopolystyrene molecular weight to the styrene block length. The maximum increase is observed when this ratio is on the order of unity. These results indicate that molecular weight has a significant effect on the quality of the blending in the polystyrene domains, even at very low homopolymer loadings. It also appears from this study that increasing the polystyrene content of KRATON D2104 by blending with a homopolystyrene of the appropriate molecular weight may actually lead to a transition from a morphology of spheres to one of short cylinders without the appearance of a third phase. Future work will involve transmission electron microscopy to examine the morphology of the blends to confirm these results.

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