

Effects of Mixing Ratio and Monomer Composition on Morphology and Mechanical Properties of SMI/SAN Blends

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ABSTRACT: This article was concerned with the morphology and mechanical properties of blends of poly(styrene-*co*-*N*-phenylmaleimide) (SMI) and poly(styrene-*co*-acrylonitrile) (SAN) as functions of the mixing ratio of the blends and the acrylonitrile content in SAN. Differential scanning calorimetry (DSC) and field-emission scanning transmission electron microscopy (FE-STEM) were used for the morphology characterization, and tensile strength and K_I (stress intensity factor in mode I), for the mechanical property comparison. The miscibility of the polymers was clearly distinguished using the number of glass transitions shown in the DSC thermograms. FE-STEM supports the DSC results, assisting in understanding the blend morphology for the immiscible blends in terms of the shape and size of the dispersed phase. The mechanical properties suggest that the miscible blends are superior to the immiscible counterparts and illustrate how the acrylonitrile content in SAN and the molecular weights of SMI and SAN affect the toughness of the miscible blends. We conclude from the study that the miscibility between SMI and SAN is an important factor for toughness enhancement of the blends. As a miscible blend, the mechanical properties improve with increase of the acrylonitrile content in SAN and the molecular weight of SMI and SAN. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 513–523, 1998

Key words: miscibility; polymer; blends; SMI; SAN

INTRODUCTION

The imide-based copolymers have gained much interest in industry for their high-temperature resistance. One of the imide-based copolymers, poly(sty-

rene-*co*-*N*-phenylmaleimide) (SMI) (Fig. 1), developed in late 1980s,¹ shows a glass transition temperature of nearly 200°C. Such a high T_g , plus low production costs,² provides a huge potential for SMI in various applications. Pure SMI, however, cannot be extruded or injection-molded, due to its brittleness. Therefore, other polymers are added to enhance its processibility. Poly(styrene-*co*-acrylonitrile) (SAN) is known for its miscibility with SMI³ and is used to blend with SMI to improve the processibility and toughness.^{4,5} With one component that has a high thermal resistance, and another, good toughness, the SMI/SAN blends provide flexibility in tailoring the thermal and mechanical prop-

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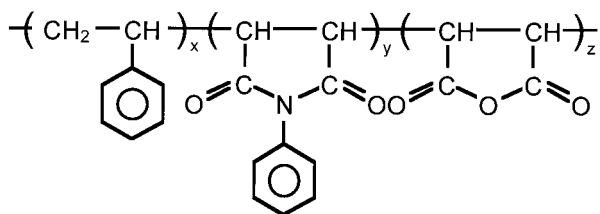


Figure 1 Chemical structure of SMI, a random copolymer of styrene, *N*-phenylmaleimide, and maleic anhydride. For SMI55, the weight ratio of the monomers is 45 : 53 : 2, and for SMI42, 58 : 40 : 2.

erties through a variation in the mixing ratio of the constituent polymers. Although this is a low-cost alternative for new material development, the advantage can be appreciated only if the blends' thermal resistance and mechanical properties are fully understood.

In this article, an experimental study on the thermal resistance and mechanical toughness of SMI/SAN blends is presented. Parameters used in the study are the mixing ratio and the acrylonitrile content in SAN. The study is part of a project on poly(acrylonitrile-butadiene-styrene) (ABS) that uses SMI to improve the thermal resistance. Previous mechanical testing² has shown that the improvement of the thermal resistance was accompanied with a decrease in the toughness. Therefore, a project was established to search for methods that enhance the mechanical toughness of the SMI-added ABS. The focus of this article was on the toughness and miscibility between the constituents in the matrix, that is, SMI and SAN.

EXPERIMENTAL

Materials

The SMI/SAN blends were provided by Denka Co. (Chiba, Japan). Two SMIs (SMI42 and SMI55) and six SANs (with different acrylonitrile content in the range of 22–40 wt %) were used to make totally 10 SMI/SAN blends. Information on the monomer composition for each polymer is given in Table I. The molecular weight (weight-average molecular weight) was measured using gel permeation chromatography (GPC), and the acrylonitrile content, by element analysis. In the rest of the text, names given in the table will be used to refer to the polymers. It should be noted that the SMI contains 2 wt % of maleic anhydride. The blends were prepared using a twin-screw extruder, then injection-molded to form dumbbell specimens.

Morphology Characterization

The blend miscibility was characterized using a differential scanning calorimeter (DSC220, Seiko Instruments Inc.) and a field emission scanning electron microscope (FE-SEM, Hitachi S4100). The former was used for T_g measurement, and the latter, for visualization of the blend morphology. A single T_g is expected for miscible blends, while two T_g 's, for the constituents of immiscible blends.

The Hitachi S4100 FE-SEM is equipped with a detector that is placed underneath the sample stage, therefore allowing the machine to be operated in a transmission mode, like a scanning transmission electron microscope (FE-STEM). For this work, the accelerating voltage of the FE-STEM was set at 15 keV, an emission current of 6 μ A, and working distance of 5 mm. Specimens of less than 30-nm thick were sliced from the as-extruded pellet using an ultramicrotome (Reichert Ultracut S, Leica) equipped with a Diatome diamond knife. The high flux of electrons from the field-emission electron gun is capable of providing contrast between phases with a small difference in density. It was reported⁶ that a threshold of 0.02 g/cm³ in the density difference is sufficient to give a contrast between phases in the FE-STEM micrographs. This is essential for the study of the SMI/SAN blends, as no staining agent is known to be able to stain one of the constituents. The constituent polymers for the study have densities of 1.07, 1.15, and 1.18 for SAN, SMI42, and SMI55, respectively,² which are sufficiently different to provide a contrast between SMI- and SAN-dominated phases.

In the DSC study, specimens were first heated to 280°C, 10°C below the recommended injection-molding temperature. After 5 min at that temperature, the specimens were cooled to 30°C and then reheated to 280°C. Heating and cooling rates were always kept at 20 K/min.

The T_g from the first heating cycle showed a scattering of $\pm 1.5^\circ\text{C}$ among specimens from the same blend, possibly due to variation in the residual strains introduced in the compounding process, while the T_g from the second heating cycle showed a scattering within $\pm 0.2^\circ\text{C}$. Therefore, only the T_g from the second heating cycle was used for the miscibility evaluation. In addition to the T_g , the glass transition was also characterized using onset temperatures of the glass transition (T_L) and the highest temperature of the glass transition (T_H). Figure 2 depicts how these temperatures were defined on a DSC thermogram. It should be noted that in some

Table I Information on the Constituent Polymers Used in the Study

Polymer Name	Monomers (wt %)			Molecular Weight (M_w)	M_w/M_n
SMI55	St (45.0)	PMI (53.0)	MAH (2.0)	167,000	2.0
SMI42	St (58.0)	PMI (40.0)	MAH (2.0)	128,000	2.0
SAN40	St (59.0)	AN (41.0)		69,000	1.9
SAN33	St (66.3)	AN (33.7)		103,000	2.0
SAN28	St (72.2)	AN (28.8)		185,000	2.0
SAN26	St (74.1)	AN (25.9)		126,000	2.0
SAN24	St (76.3)	AN (23.7)		194,000	2.0
SAN22	St (77.5)	AN (22.5)		123,000	2.0

In the column of "Monomers (wt %)," St represents styrene; PMI, *N*-phenylmaleimide; MAH, maleic anhydride; and AN, acrylonitrile.

literature the T_L in Figure 2 was taken as the glass transition temperature.

Mechanical Testing

Two mechanical tests, the simple tensile test and the single-edge-notched tensile (SENT) test, were used to evaluate the mechanical properties of the blends. The tests were conducted using a Shimadzu universal testing machine (Model DDS-5000) operated at a crosshead speed of 5 mm/min and 1 mm/min for the tensile tests and SENT tests, respectively.

The injection-molded specimens have a gauge section of 75 mm in length, 12.8 mm in width, and 3 mm in thickness. The notch for the SENT specimens were introduced in the middle of the gauge section. The notch is approximately 0.4 mm

wide and 4.5 mm long along the specimen width dimension. Before the SENT tests, a fresh crack tip was introduced using a new razor blade.

The SENT test results were used to calculate K_I (stress intensity factor in mode I), following the recommendation described in ASTM E399-90. On the experimental curve of force versus displacement, a force P_Q was determined from intersection of the curve with a straight line plotted from origin with 5% offset of the slope. When P_Q was on the left of the maximum force, P_Q was used in the following two equations for the K_I calculation. Otherwise, the maximum force was used to replace P_Q for the K_I calculation:

$$K_I = [P_Q/(wt)](\pi a)^{1/2} g(a/w) \quad (1)$$

$$g(a/w) = 1.12 - 0.231(a/w) + 10.55(a/w)^2 - 21.72(a/w)^3 + 30.39(a/w)^4 \quad (2)$$

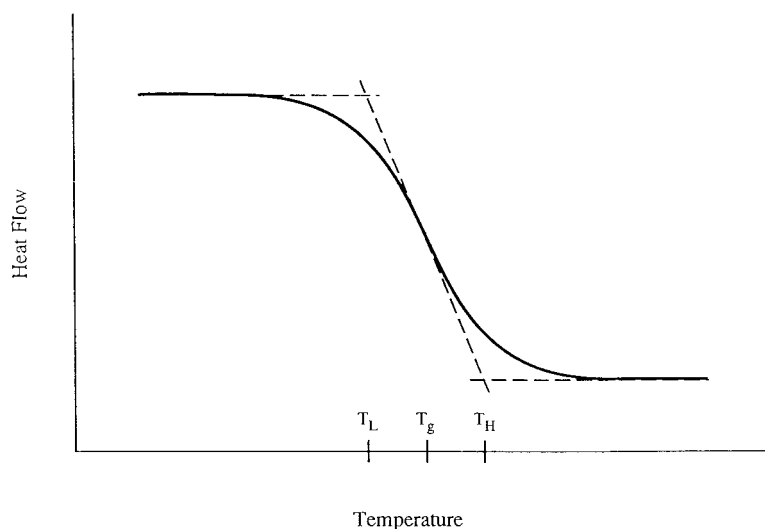


Figure 2 Schematic diagram showing the measurement of T_L , T_g , and T_H on the DSC thermogram.

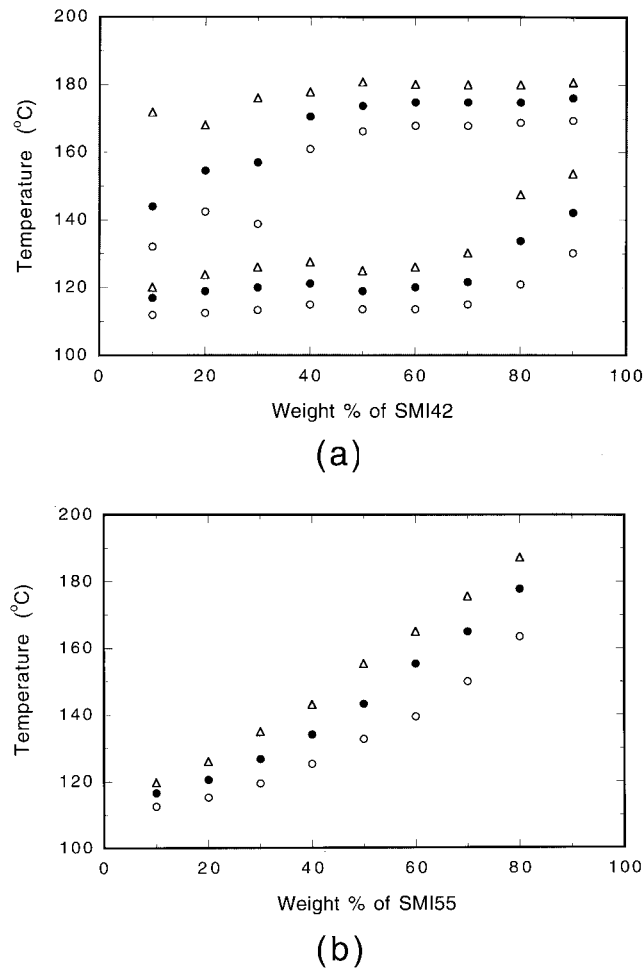


Figure 3 (Δ) T_H , (\bullet) T_g , and (\circ) T_L of SMI/SAN blends as a function of SMI content: (a) SMI42/SAN28; (b) SMI55/SAN28.

where a is the crack length; t , the specimen thickness; and w , the specimen width.

RESULTS AND DISCUSSION

DSC

The values of T_H , T_g , and T_L , defined in Figure 2, as a function of the mixing ratio for SMI42/SAN28 and SMI55/SAN28 are shown in Figure 3, and as a function of acrylonitrile content in SAN at a mixing ratio of 50 : 50 in Figure 4. In Figure 3(a), the SMI42/SAN28 blends showed two glass transitions for the whole range of the mixing ratio, suggesting that the two constituents are immiscible. Values of T_g and the difference between T_H and T_L ($T_H - T_L$) for the upper glass transition are nearly constant when the SMI content is above 50 wt %, but below 50 wt %, T_g

decreases and $T_H - T_L$ increases with decrease of the SMI content. A reversed trend was observed for the lower glass transition but the critical SMI content is 60 wt %, that is, T_g and $T_H - T_L$ are constant for blends with an SMI content below 60 wt %, above which T_g and $T_H - T_L$ increase with increase of the SMI content. Such an effect of the mixing ratio on polymer miscibility was also reported by Aoki³ for a study on blends of poly[styrene-co-(maleic anhydride)] and SAN. This phenomenon is possibly due to the effect of the environment on molecular relaxation during the glass transition, leading to a change of the glass transition temperature. For SMI55/SAN28 blends, Figure 3(b) shows only one glass transition, suggesting that SMI55 and SAN28 form miscible blends in the whole range of the mixing ratio.

Figure 4 shows the T_g 's of the SMI/SAN blends as a function of the acrylonitrile content in SAN. Two glass transitions were observed in blends

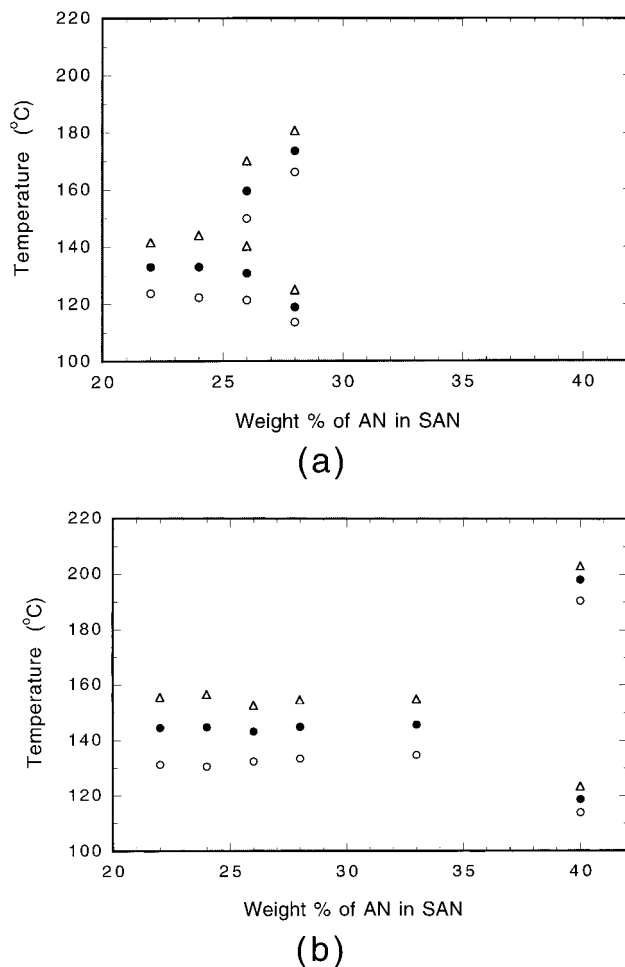


Figure 4 (Δ) T_H , (\bullet) T_g , and (\circ) T_L of SMI/SAN blends with a mixing ratio of 50 : 50, plotted as a function of AN content in SAN: (a) SMI42/SAN28; (b) SMI55/SAN28.

containing SAN of high acrylonitrile content, 41 wt % for SMI55/SAN blends and above 25.9 wt % for SMI42/SAN blends. With decrease of the acrylonitrile content, the two glass transitions merged into one, suggesting that the miscibility improves with decrease of the acrylonitrile content in SAN. The figure also shows that increase of the PMI content in SMI, from 40 to 53 wt %, enhances the miscibility of SMI with SAN of high acrylonitrile content.

Although this study used the glass transition temperature to characterize polymer miscibility, it should be noted that two polymers that form a blend with a single T_g may not be completely miscible. As suggested by Boyer⁷ and Warfield and Hartman,⁸ the glass transition is related to the cooperative segmental motion of the molecular chains, which involves roughly 50–100 backbone-carbon atoms in a domain of roughly

2–3 nm in diameter. A single T_g only suggests that the blend be homogeneous to the scale of the domain size.

FE-STEM

FE-STEM micrographs for the blend morphology are shown in Figures 5 and 6. Figure 5 is for blends of SMI42 and SAN28 at various mixing ratios, and Figure 6, for blends of SMI42 with SANs of various acrylonitrile contents at a fixed mixing ratio of 50 : 50.

As shown in Figure 5, phase separation occurred in the SMI42/SAN28 blends at all mixing ratios, consistent with the results in Figure 3. Since SMI42 has a higher density than that of SAN28, 1.15 and 1.07 g/cm³, respectively, the dark regions in the micrographs represent the SMI42-rich phase, and the bright regions, the

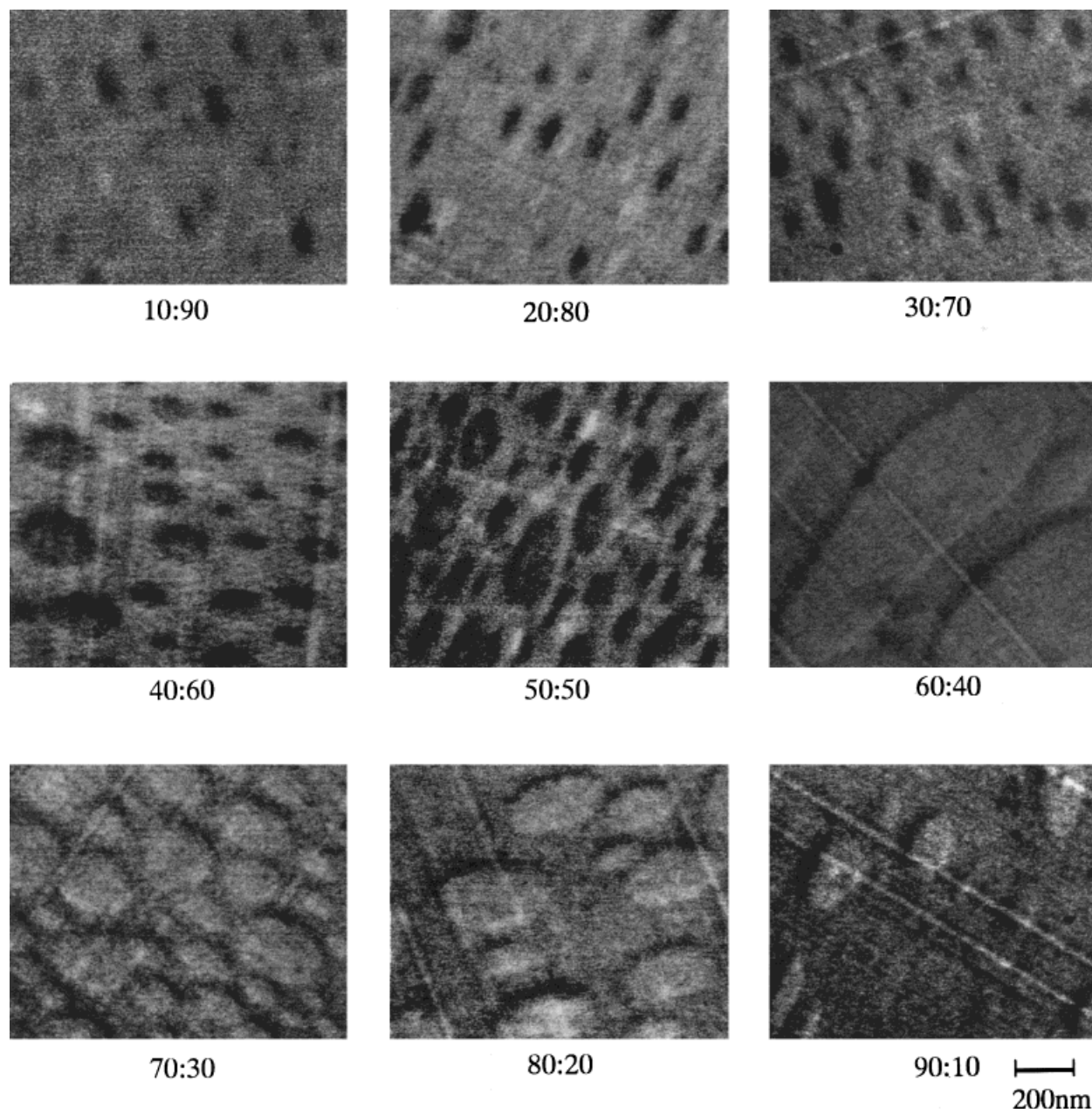


Figure 5 FE-STEM micrographs of SMI42/SAN28 at various mixing ratios.

SAN28-rich phase. The micrographs suggest that the morphology consists of a dispersed spherical phase with diameters in submicrometers. The transition of the blend morphology from a dark dispersed phase to a bright dispersed phase occurred at about 50 wt % of SMI, below which the bright phase is the continuous phase. It should be noted that the dimension of the dispersed phase is processing-condition-dependent, especially in blends with mixing ratios near 50 : 50.

The blend morphologies of SMI42 with SANs

of various acrylonitrile contents are shown in Figure 6. For blends containing SAN26 and SAN28, phase separation is clearly indicated by the dispersed SMI-rich phase submicron in diameter, but for blends containing SAN22 and SAN24, the micrographs in Figure 6 show a two-domain morphology, the dispersed domain having a diameter of roughly 30 nm. Since the blends of SMI42/SAN22 and SMI42/SAN24 show a single T_g (Fig. 4), the dispersed domain of 30 nm in diameter could be an indication of phase separation only

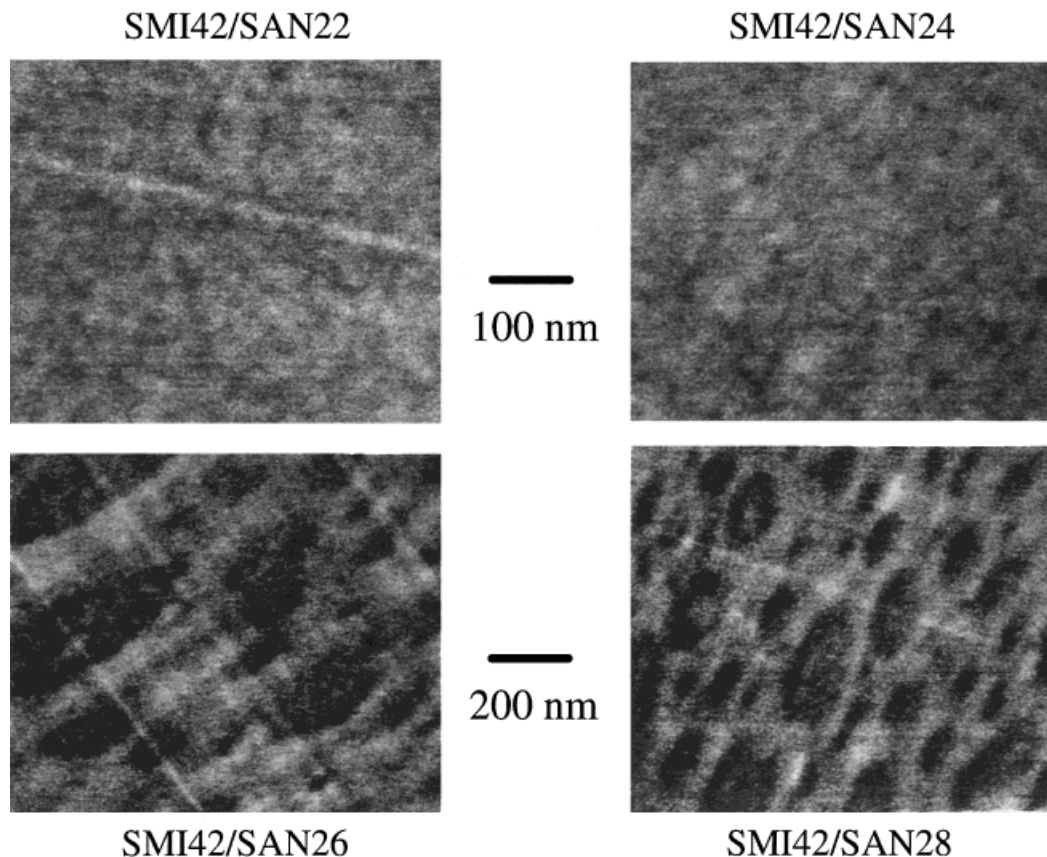


Figure 6 FE-STEM micrographs of SMI42/SAN blends of various acrylonitrile contents in the SAN.

if the domain size for the cooperative molecular motion during the glass transition was larger than 30 nm, which is much larger than the size suggested previously.^{7,8}

Kaplan⁹ and Bair and Warren¹⁰ proposed that the glass transition involves a much larger domain size, with diameters to 15 nm. Based on their prediction, it is possible that the dispersed phases shown in the micrographs for SMI42/SAN22 and SMI42/SAN24 are an indication of phase separation in the blends. To verify whether this morphology represents a “microphase separation,” an FE-STEM study was also conducted on the SMI55/SAN28 blends with different mixing ratios. For all blends, including pure SMI55 and pure SAN28, the micrographs showed similar features as those from SMI42/SAN22 and SMI42/SAN24. Since the pure copolymers should not exhibit “microphase separation,” it is concluded that the feature of the dispersed domain with a diameter of around 30 nm is not an indication of “microphase separation,” but defects that might have been created in the FE-STEM.

It should be noted that the FE-STEM micrographs for SMI42/SAN22 and SMI42/SAN24 in Figure 6 were taken at a magnification of 100,000 times. At such a high magnification, a very large dose of electrons was focused on a small area of the specimen, resulting in a short lifetime (around 1 min) for the sample before being burned by the electrons. This limited the total time allowed for focusing and photographing the images. Although we managed to take the photographs within a very short period (less than 30 s) during which the sample appeared to be quite stable, it is plausible that the quickly accumulated electrons might have created charging that led to the reduction in image resolution, thus preventing the observation of genuine, fine dispersed regions in the blends, if they did exist. Although the above argument did not exclude the possibility of microphase separation in the SMI/SAN blends that show a single T_g , it is concluded that the micrographs for SMI42/SAN22 and SMI42/SAN24 do not represent the true morphology of the blends.

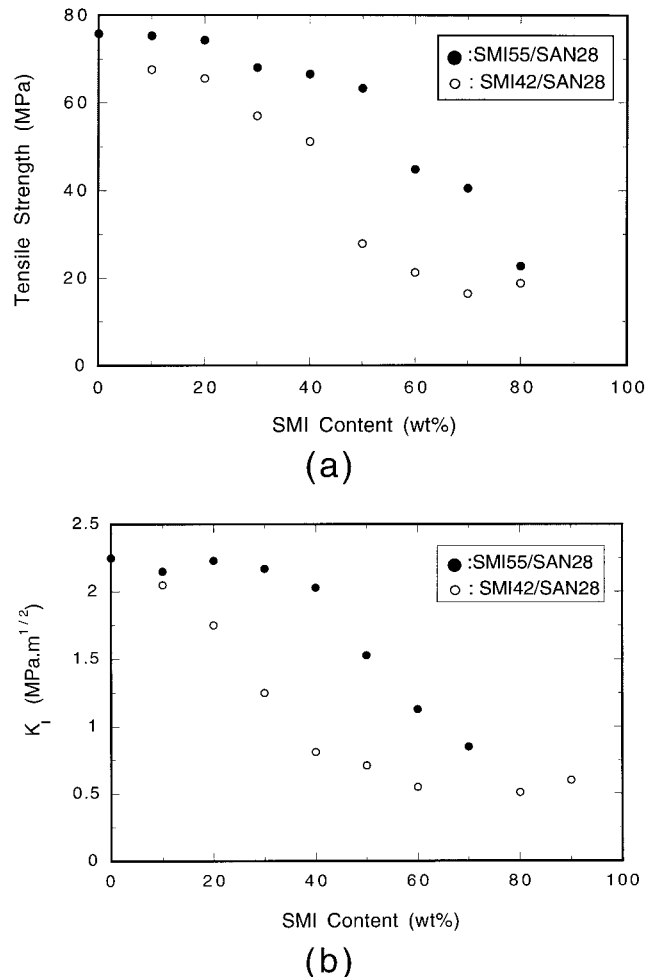


Figure 7 (a) Tensile strength and (b) K_I of (●) SMI55/SAN28 and (○) SMI42/SAN28 as a function of SMI content in the blends.

Mechanical Testing

The tensile strength and K_I value for the SMI55/SAN28 and SMI42/SAN28 blends are given in Figure 7(a) and (b), respectively. The figures suggest that strength and toughness decrease with increase of the SMI content in the blends and that at a given mixing ratio the miscible blend is always better than is the immiscible counterpart in tensile strength and toughness.

It should be noted that the way the K_I value decreases with increase of the SMI content for SMI42/SAN28 (immiscible blend) is different from that for SMI55/SAN28 (miscible blend). For SMI42/SAN28, K_I decreases quickly when the SMI content increases from 0 to 60 wt % and remains constant with further increase of the SMI content. For SMI55/SAN28, K_I decreases only slightly with increase of the SMI content from 0 to around 50 wt % and much faster with further

increase of the SMI content. By extrapolating the results in Figure 7(b) to 100 wt % of SMI, the K_I for pure SMI55 is estimated to be slightly lower than that for SMI42.

The values of tensile strength and the K_I for the SMI/SAN blends are summarized in Figure 8(a) and (b), respectively. The values were plotted as a function of the acrylonitrile content in SAN only for convenience in identifying the SAN used in the blends. Genuine parameters involved in the figure are (i) the type of SMI used in the blend (SMI55 and SMI42), (ii) the molecular weight of SAN, and (iii) the acrylonitrile content of SAN. Figure 8(a,b) clearly show that the tensile strength and K_I for miscible blends are larger than those for immiscible blends, suggesting that the miscibility of the polymers affects their tensile strength and toughness.

The effect of the acrylonitrile content in SAN

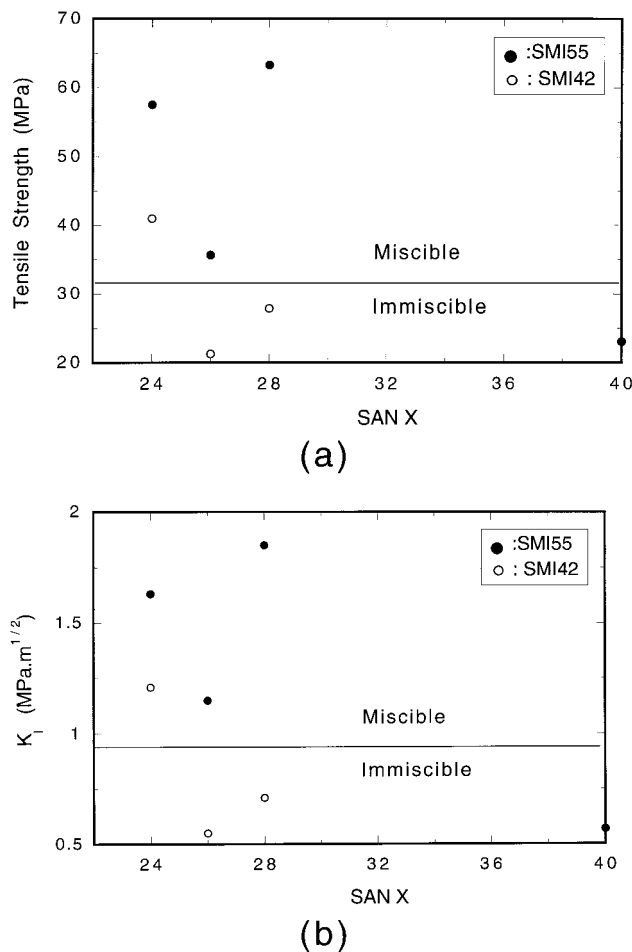


Figure 8 (a) Tensile strength and (b) K_I as a function of SAN used in the blends. Mixing ratio is 50 : 50. (●) Blends containing SMI55; (○) blends containing SMI42.

on the tensile strength and K_I can be seen from the results for SMI55/SAN24 and SMI55/SAN28, which contain SAN of similar molecular weight, 1.94×10^5 and 1.85×10^5 , respectively. The main difference between SMI55/SAN24 and SMI55/SAN28 is the composition of SAN, that is, the acrylonitrile content of 23.7 wt % for SAN24 and 28.8 wt % for SAN28. As shown in the figure, by increasing the acrylonitrile content from 23.7 to 28.8 wt %, the tensile strength increases from 57.5 to 63.3 MPa and the K_I value from 1.65 to 1.85 MPam^{1/2}.

The effect of the SMI type in the blend on the strength and the K_I values can be seen from the results for SMI42/SAN24 and SMI55/SAN24. The tensile strength and K_I values for the former are smaller than those for the latter, 41 MPa and 1.2 MPam^{1/2} and 57.5 MPa and 1.64 MPam^{1/2}, respectively. This is believed to be due mainly to

the difference in the molecular weight of SMI42 and SMI55.

Figure 8 also shows the effect of the molecular weight for SAN on the tensile strength and K_I value for the SMI/SAN blends. SAN24 and SAN26 have significantly different molecular weights, of 194,000 and 126,000, respectively, but only a 2.2 wt % difference in the acrylonitrile content. The tensile strength and K_I value for SMI55/SAN24 are 57.5 MPa and 1.64 MPam^{1/2}, respectively, which are higher than are those for SMI55/SAN26, 35.7 MPa and 1.15 MPam^{1/2}. This is due to the molecular weight of SAN24 being higher than that of SAN26. It should be noted that if SAN26 and SAN24 had the same molecular weight the tensile strength and K_I value for SMI55/SAN26 would be expected to be slightly higher than those for SMI55/SAN24, due to the slightly higher acrylonitrile content of SAN26.

It should be noted that the results suggest that the PMI content in SMI may cause decrease of the toughness for pure SMI, although it enhances the SMI's miscibility with SAN of higher acrylonitrile content, thus yielding blends for better mechanical strength and toughness. The enhancement of the miscibility between SMI and SAN by increase of the PMI content in SMI can be concluded from the fact that SAN28 is miscible with SMI55, but not with SMI42.

It is also believed that increase of the PMI content lowers the toughness of SMI. Such an effect can be seen from the comparison of the published K_I values for polystyrene (SMI with 0% of PMI content) with that for SMI42. The former is around 1 MPam^{1/2},¹¹ but the latter is only 0.5 MPam^{1/2} [from Fig. 7(b)]. As a result, it is expected that increase of the PMI content in SMI lowers the toughness of the SMI/SAN blends. However, results from the study cannot provide supporting evidence for the speculation, as the two SMIs used in the study have different molecular weight.

Discussion

Although the results presented in the article show a consistent trend in the tensile strength and K_I value, they are contradictory to those reported by Aoki.⁵ In Aoki's study, the miscible blends of SMI (with a PMI content of 43.3 wt % and molecular weight of 169,000) and SAN (with acrylonitrile content of 26 wt % and molecular weight of 163,000) exhibited a smaller tensile strength than that for each of the pure components. It was also noted that the tensile strength for their SMI (60 MPa) is much higher than that reported here for SMI42 (estimated to be 20 MPa).

The difference in mechanical properties between the two studies is believed to be due mainly to the SMI used. The SMI used in Aoki's study is a copolymer of styrene and *N*-phenylmaleimide that was synthesized through radical copolymerization of the two monomers, while the SMI used in our study was made through postimidization of poly(styrene-*co*-maleic anhydride).² As the postimidization process cannot completely convert maleic anhydride into *N*-phenylmaleimide, the SMI molecule consists of three monomers, styrene, maleic anhydride, and *N*-phenylmaleimide, with approximately 2 wt % for maleic anhydride. Aoki³ reported that poly(styrene-*co*-maleic anhydride) and poly(styrene-*co*-*N*-phenylmaleimide)

have very different miscibility with SAN, indicating that the monomers have a different interaction with SAN. It is therefore believed that the presence of maleic anhydride affects the entanglement between SMI molecules and SAN molecules, changing the mechanical properties of the SMI and its blend with SAN. Further study is being carried out to quantify the interaction among the four monomer units: styrene, maleic anhydride, *N*-phenylmaleimide, and acrylonitrile. The results are expected to lead us to the understanding of the discrepancy between Aoki's results and ours.

CONCLUSIONS

The miscibility, morphology, and mechanical properties of SMI/SAN blends were studied using DSC, FE-STEM, a tensile test, and the SENT test. The results suggest that the miscibility between SMI and SAN is sensitive to the monomer composition of the constituent polymers. For immiscible blends, FE-STEM micrographs suggest that the blend morphology consists of a dispersed spherical phase with diameters in the submicron range. For miscible blends, the observed microdomains of around 30 nm in diameter were proven not to be an indication of microphase separation.

The mechanical test results suggest that the miscible blends are superior to the immiscible counterparts in tensile strength and toughness. The results also suggest that the tensile strength and K_I value for miscible blends are affected by the monomer composition and molecular weight of the constituent polymers.

The results provide a basis for future work on the selection of the monomer composition and of the mixing ratio between SMI and SAN for optimization of the mechanical strength and toughness of the blends. However, it should be noted that the SMI used in the study contains 2 wt % maleic anhydride, resulting in different mechanical properties from the pure SMI. Therefore, caution should be taken when the results are applied to blend design.

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