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Tensile Fracture Properties of Rigid–Rigid Blends Made of Sulfonated Polystyrene Ionomer and Polystyrene

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ABSTRACT: The tensile fracture properties of rigid–rigid blends made of sulfonated polystyrene (SPS) ionomer and polystyrene (PS) were studied. A positive deviation from the rule of mixtures in both tensile strength and tensile toughness was observed over the entire composition range, and an especially significant enhancement was observed at low ionomer composition (e.g., 10 wt %). This is attributed to a fine dispersion of the rigid ionomer phase in the PS matrix together with good interfacial adhesion between the phases. The adhesion arises from entanglements due to athermal interactions between PS and the styrene units of the SPS ionomer chains. At a constant blend ratio, an increase in ion content of the ionomer component leads to an increase in both the tensile strength and toughness of the two-phase blends. The tensile properties of these blends appear to be determined largely by the resistance to fracture of the ionomer particles. Hence the addition of more fracture-resistant ionomers (e.g., ionomers of high ion content) to PS leads to blend materials of higher strength and toughness. Some enhancement of the mechanical properties may also be attributed to a stress concentration effect of the ionomer second-phase particles, which allow a greater volume of plastic energy to be absorbed in the blend materials. Changing the counterion of the ionomer particles from Na (monovalent) to Ca (divalent) results in a moderate increase in ultimate properties.

Introduction

Glassy polymers are used increasingly as structural materials, either by themselves or with other materials. As a result, there has been a significant interest in the relationship among molecular structure, the micromechanisms of deformation and fracture, and bulk mechanical properties.[1–4] To use polymers in load-bearing applications, their ultimate properties need to be better understood. Since glassy polymers fail in a brittle fashion, it is very important to understand the mechanism of their brittle behavior and to improve the toughness of these polymers.

One method by which the toughness and fracture resistance of glassy polymers have been enhanced is through the incorporation of a second, rubbery phase into a matrix polymer (i.e., creation of *rubber-toughened polymers*), as typically demonstrated for high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) resins.[3,5] A major role of the rubbery particles is to act as stress concentrators, which generate extensive matrix deformation (either by crazing as in HIPS or shear yielding as in rubber-toughened PVC) from many sites rather than from only localized regions around the crack tip.[3] This so-called multiple deformation mechanism leads to a larger degree of plastic deformation prior to fracture, making these modified polymers—most of these are graft copolymers, but some are polymer blends—significantly tougher than their unmodified polymers. Although rubber toughening is a useful method, there are some drawbacks: for example, an increase in toughness is accompanied by a decrease in modulus, yield strength, and creep resistance. In some cases, like highly-cross-linked epoxides, rubber toughening is not very effective.[6]

Another useful approach recently discussed is incorporation of rigid, thermoplastic particles in phase-separated polymer blends (i.e., *rigid–rigid blends*).[7,8] In polymer blends, it is known that miscible, homogeneous blends generally show a negative deviation from the rule of mixtures of toughness, since molecular interactions responsible for miscibility are considered to reduce chain mobility, which leads to higher modulus and yield stress, but lower elongation, craze resistance, and toughness of the blends.[9–12] At best, additive mechanical properties are expected for homogeneous miscible blends that have athermal interactions.[9] However, blending of slightly immiscible polymers (e.g., a creation of rigid–rigid blends) leads to microphase separation and this provides a means for achieving better mechanical properties, especially better toughness.[13] Although rigid–rigid blends, with a potential to enhance toughness, have been used widely in industry, systematic studies to elucidate the mechanisms of deformation and fracture in such blends are lacking. This is partly because these systems are complex, due to possible crystallinity, variable processing conditions, and development of hierarchical structures. Hence the microstructure of rigid–rigid blends is not well-controlled.[14]

As a continuation of efforts to elucidate the deformation/fracture behavior of ionomers, we have investigated simple model blend systems made of SPS ionomers and their precursor polymer, PS.[15,16] In such a combination of (amorphous) ionomer/ionomer-precursor, the degrees of polymerization of both component polymers are identical, no crystalline phase exists, and no hierarchical structure is produced. The use of a simple system and simple processing conditions reduces the complexities associated with many rigid–rigid blend systems. Because of a large difference in polarity between the two component polymers in the blend, even though the ionomer component may have only several mole percent of ionic groups, there is a tendency toward microphase separation,[15,16] leading to the presence of two phases in such rigid–rigid blends. At low ionomer composition, the ionomer second-phase particles are dispersed in the matrix polymer, and ionic aggregates are formed in the ionomer phase. In addition, athermal interactions between the identical repeat units (styrene) on the SPS ionomer and on PS may ensure compatibility at the interface through interpenetration of polymer chains, and development of some molecular entanglements. It is well-known that entanglements are a prerequisite for

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strength in polymer systems, as also is good interfacial adhesion.[17,18] TEM micrographs show that some adhesion is present between the SPS ionomer second-phase particles and the PS matrix.[15,16] Under an applied stress, it was found that the ionomer particles fibrillated, elongated to some extent, and adhered well to the PS matrix, as suggested by the absence of voids associated with debonding. Thus, sufficient molecular entanglements at the interface seem to provide a satisfactory level of adhesion to transmit the applied load.

Ionomers are ion-containing polymers having a small number of ionic groups (<15 mol %) distributed along nonionic hydrocarbon chains, and they provide a means of modifying various properties of the original polymers through ionic interactions. It has been well-established that significant changes in properties of ionomers in the solid state are due to the clustering (aggregation) of ion pairs. While many studies have been conducted on the structure–property relationships of ionomers,[19–25] the work on their large-strain mechanical properties in the glassy state has been reported only recently; these studies include deformation mechanisms of thin films[27–29] and fatigue[30,31] and tensile[32,33] fracture behavior of bulk ionomers. It has been demonstrated that the mechanical properties of glassy ionomers can be altered either by changing the structure of the ionic aggregates or the strength of ionic bonds through changes in the *ion content* or the *nature of the counterion.* The altered properties are explained primarily as arising from changes in the "effective" entanglement network (strand) density. This is increased through an ionic cross-linking effect, which raises the crazing stress compared with the shear yield stress and thereby increases the fracture resistance of these polymers. Therefore, ionic interactions can be used to control the microstructure and mechanical performance of polymers by changing molecular variables inherent to these polymers. A recent review concerning the mechanical properties of ionomers is available.[26]

Recently, ionomers have been used for various polymer blend studies: the major approach of these efforts has been to enhance miscibility by introducing ionic interactions between two otherwise immiscible polymers. The attractive interactions include ion–ion, ion–dipole, and complex formation.[34–40] Our blend system results from a different approach, in that the attractive interactions are at best athermal interactions between the same repeat units (e.g., styrene), and the ionic groups, introduced into one component of the polymer blend, slightly decrease miscibility due to the difference in polarity between the ionomer and the ionomer precursor. This leads to microphase separation, which is considered to be an essential condition for obtaining better fracture properties.[41] In other studies, a PS ionomer, made from poly(styrene-*co*-methacrylate), has been used with PS or PS oligomers to study rheological properties[44] and the plasticization effects by PS oligomers.[45] However, study of the mechanical properties of such mixtures as rigid–rigid blends has not been reported.

In this study, the tensile fracture properties of rigid–rigid blends of SPS ionomer/PS were examined. It was found that significant changes in properties were produced by the addition of a rigid ionomer phase to PS. The influence of ion content and counterion on the tensile properties of these blends was investigated, and there appears to be a strong correlation between the results obtained and the morphology and micromechanisms of deformation and fracture.

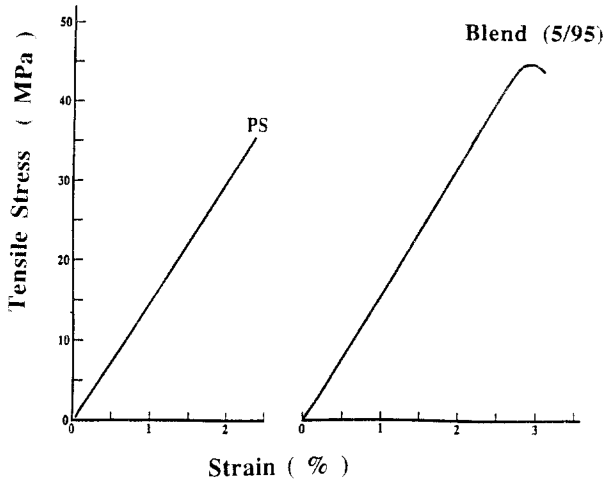


Figure 1. Typical stress–strain curves for polystyrene and the SPS ionomer (5.26 mol %; Na salt)/PS (5/95) blend.

Experimental Section

Materials. Lightly sulfonated polystyrene (SPS) was prepared by sulfonation of starting PS having a molecular weight of 125 000–250 000 (Polysciences), according to the procedure described by Makowski et al.[46] After the sulfonation reaction was terminated by the addition of methanol, a small amount of sample was removed from the reaction mixture to determine the ion content by titration of the acid groups. Then, the calculated amount of sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$) dissolved in methanol or water was added to completely neutralize the acid groups of SPS. The SPS ionomer (salt form) was recovered by steam stripping in boiling water and washed with methanol, followed by vacuum drying at 85 °C for 48 h and then 120 °C for an additional 24 h. The ion content was controlled by adjusting the amount of sulfonating agent: the ion contents of the Na-salt ionomers were 2.65, 5.26, and 7.45 mol %, and the ion content of the Ca-salt ionomer was 2.85 mol %.

Solution blending was used to make SPS ionomer/PS blend samples; a proper amount of each component polymer was dissolved in a solvent mixture of 1,2-dichloroethane (DCE)/methanol (90/10 v/v) and mixed under stirring for 3 days. Then, the blend material was recovered by steam stripping in boiling water, washed with methanol, and dried under vacuum at 85 °C for 3 days.

Testing. Tensile specimens were directly machined from compression-molded rectangular bars into hourglass shaped round samples with threaded ends (7.62 cm long, 0.51 cm diameter at the gauge length, 1.27 cm diameter at the ends). Tensile testing was done on an Instron tensile testing machine at room temperature using a crosshead speed of 0.013 cm/min. The average values of at least three specimens were used for analysis. Fracture surfaces were examined by a scanning electron microscope (SEM) (ETEC) after coating them with a thin layer of gold. Details of tensile samples and experiments are described elsewhere.[32]

Results

Effect of Blend Composition. Figure 1 shows a typical stress–strain curve of the SPS ionomer/PS blend and the curve of PS for comparison. Although both materials show brittle behavior, the blend material exhibits a yield point and some plastic deformation. It is worth noting that the addition of only 5 wt % SPS ionomer to PS causes a significant increase in tensile strength and elongation. Similar curves were obtained for the SPS ionomer/PS blends with blend compositions ranging from 5 to 30 wt % ionomer. The tensile strength and tensile toughness (defined as the energy absorbed per unit volume, and determined by the area under the stress–strain curve), obtained as the average values for at least three samples, are plotted as a function of ionomer content of the blend

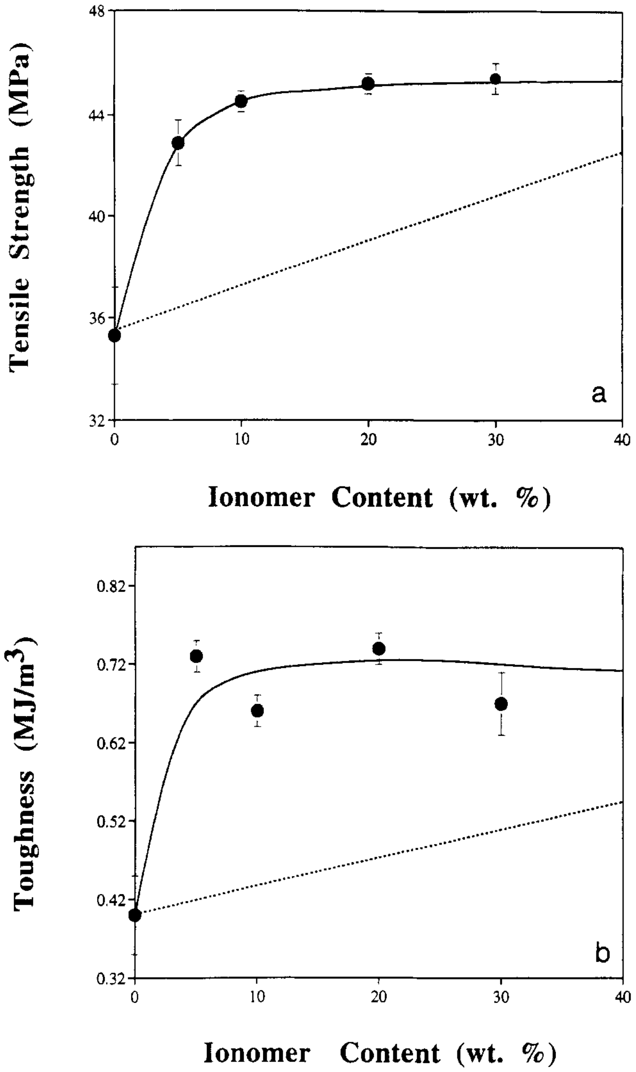


Figure 2. Composition dependence of (a) tensile strength and (b) tensile toughness of SPS ionomer (5.26 mol %; Na salt)/PS blends. Dotted lines represent the rule of mixtures.

in Figure 2. A significant increase in tensile properties is apparent in the low ionomer composition range; the addition of 10 wt % of ionomer to PS has resulted in a 25% increase in tensile strength and a 70% increase in toughness as compared with unmodified PS. Changes in modulus are less significant, however. Beyond 10 wt %, there is little, if any, change in the mechanical performance of these blends. A comparison of the experimental property values as a function of the ionomer content (solid lines) with values calculated from a simple rule of mixtures (dotted lines) clearly shows a positive deviation in tensile strength and toughness of the SPS ionomer/PS blends. There is also a synergistic enhancement for blends in which the SPS ionomer component has an ion content of 2.65 mol %, and as the data of Figure 3 show, the enhancement in both tensile strength and toughness extends over the whole composition range; i.e., all observed values are higher than those of either PS or the SPS ionomer.

When preparing blends from two polymers, opacity is an indication of immiscibility.[47] The relative transparency of the SPS ionomer (5.26 mol %; Na salt)/PS blends, along with the homopolymers, is shown in Figure 4. All compression-molded samples are optically clear as evidenced by the visible grids below each specimen. Other blends of different ion contents (2.65 and 7.48 mol %) are also transparent. While optical clarity is an indication of blend miscibility on a scale down to 0.1 μm, it may also result if the refractive indices of the two polymers are similar

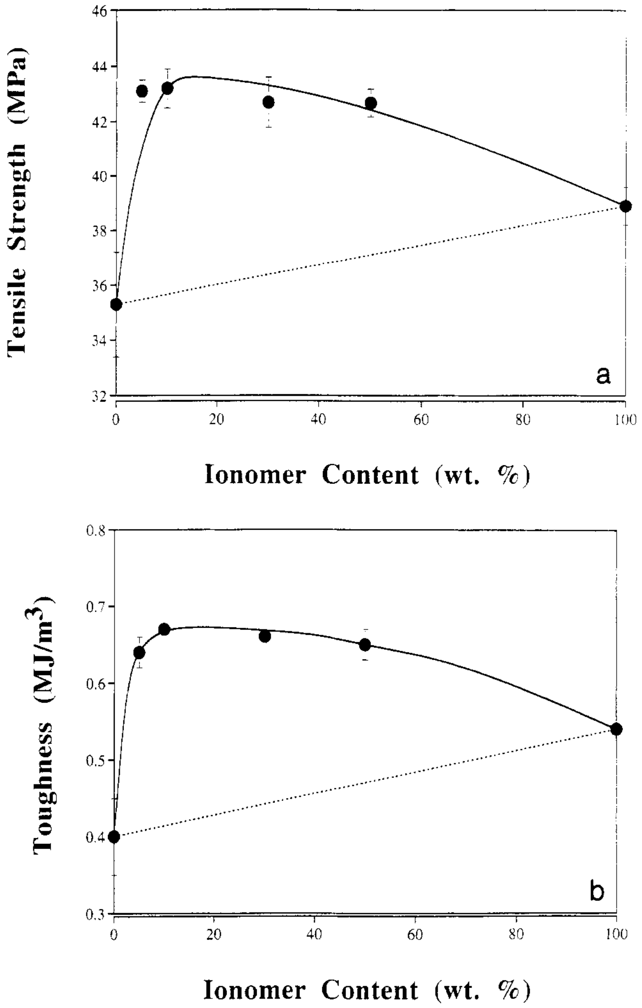


Figure 3. Composition dependence of (a) tensile strength and (b) tensile toughness of SPS ionomer (2.65 mol %; Na salt)/PS blends. The dotted lines represent the rule of mixtures.

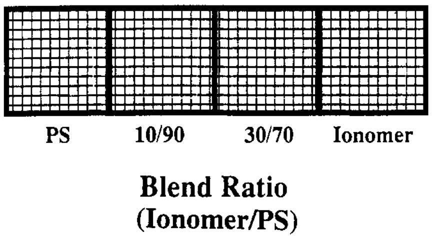


Figure 4. Optical clarity of SPS ionomer (5.26 mol %; Na salt)/PS blends.

($\Delta n < 0.01$), or if the size of the second phase is too small compared with the wavelength of light (order of 0.1 μm) to scatter light.[47] Since the size of the ionomer phase is on the order of 0.1–1 μm, as will be shown later, obviously the former reason is the applicable one for our blend samples. The refractive index of the SPS ionomers is expected to be very close to that of PS; therefore, the second-phase particles cannot be discriminated by light.

The tensile fracture surfaces of the ionomer/PS blends were examined by SEM to observe the failure processes and particle/matrix interactions. Micrographs for PS and the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend are shown in Figures 5 and 6, respectively. Distinct differences in the fracture surfaces of these materials are observed. In PS (see Figure 5a), the tensile fracture surface shows three characteristic regions: a smooth initiation region, a series of hackle bands, and a very rough region. The initiation region is related to the early stages of crack propagation through a preexisting craze. As the crack

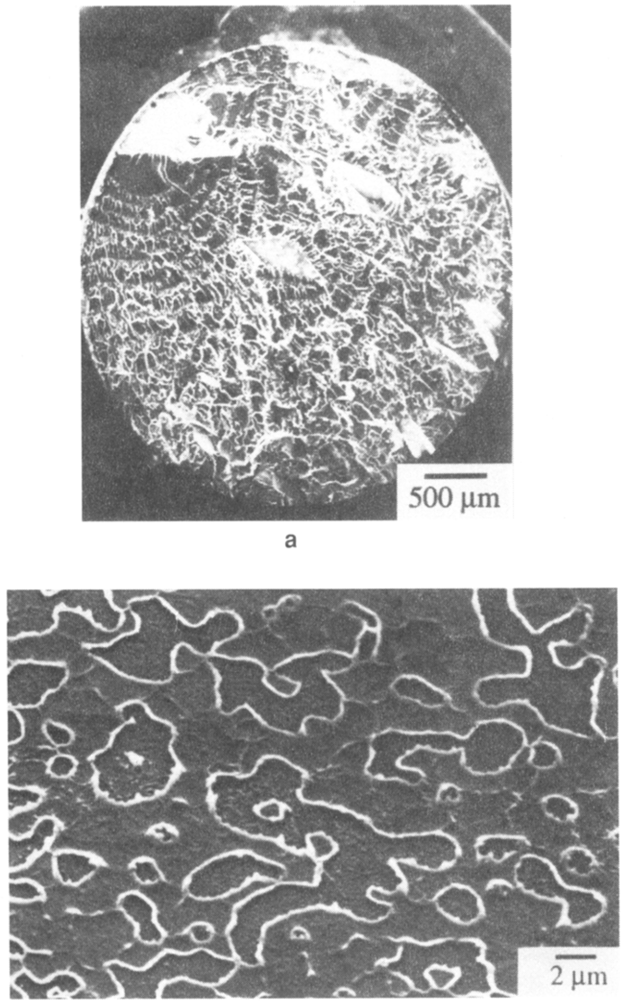


Figure 5. Tensile fracture surface of polystyrene: (a) overall fracture surface; (b) high magnification view showing patch patterns within the initiation region.

propagates through the existing craze, it frequently jumps from one craze/bulk interface to another, resulting in the formation of so-called patch patterns, as observed in the high magnification view of the initiation region (see Figure 5b).[48-51] In contrast, the fracture surfaces of the SPS ionomer/PS blends show two distinct regions (see Figure 6a): a smooth initiation region and a relatively flat region extending throughout the remainder of the fracture surface. Except for the 30/70 blend ratio, the absence of a rough region and the appearance of a very smooth mica-like region due to high reflectivity of the fracture surface suggest that the crack propagated through preexisting crazed regions throughout the entire material before failure occurred. The texture of the fracture surface arises as the crack propagates with incremental jumps from one craze plane to another.

The microstructure of the initiation region of the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend is revealed by the higher magnification scan of Figure 6b. This region shows the existence of some ionomer second-phase particles. Although the particles seem somewhat debonded from the matrix, close examination of the particle/matrix interface shows the presence of adhesion. In multiphase polymers with poor adhesion, as for example in blends of polyamide and polypropylene,[58] the surfaces of the second-phase particles are quite smooth, reflecting fracture through a path along the particle/matrix interfaces. In contrast, the micrograph of Figure 6b shows signs of drawn polymeric material on the fracture surfaces of the second-phase particles. It appears that fracture occurred on a path through the ionomer particles, again indicating a significant amount of adhesion.

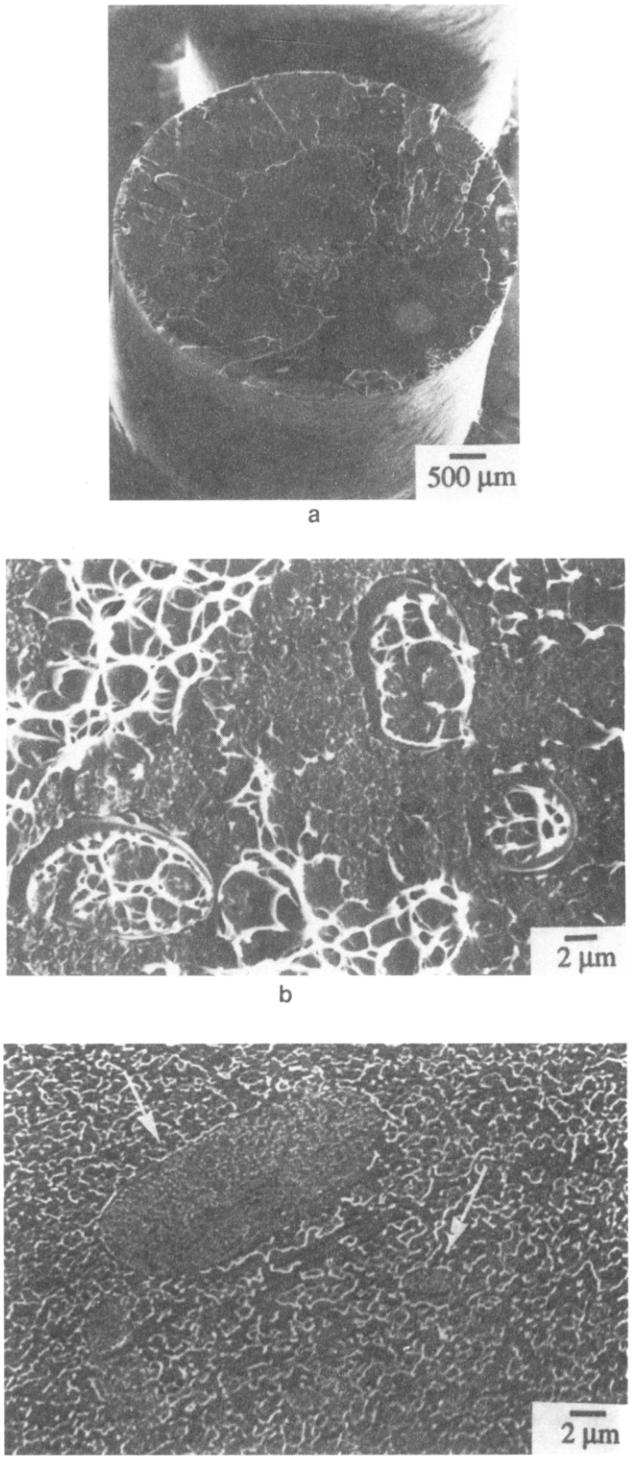


Figure 6. Tensile fracture surface of the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend: (a) overall fracture surface; (b) high magnification view showing particle/matrix interactions within the initiation region; (c) high magnification view of the microstructure within the mica region.

Figure 6c displays the microstructure of the flat mica-like region for the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend. Most of the fracture surface morphology consists of the fracture markings, so-called patch patterns, reflecting the crack propagaging through a preexisting craze as it travels from one craze-bulk interface to another.[48-51] These patch patterns are commonly seen in

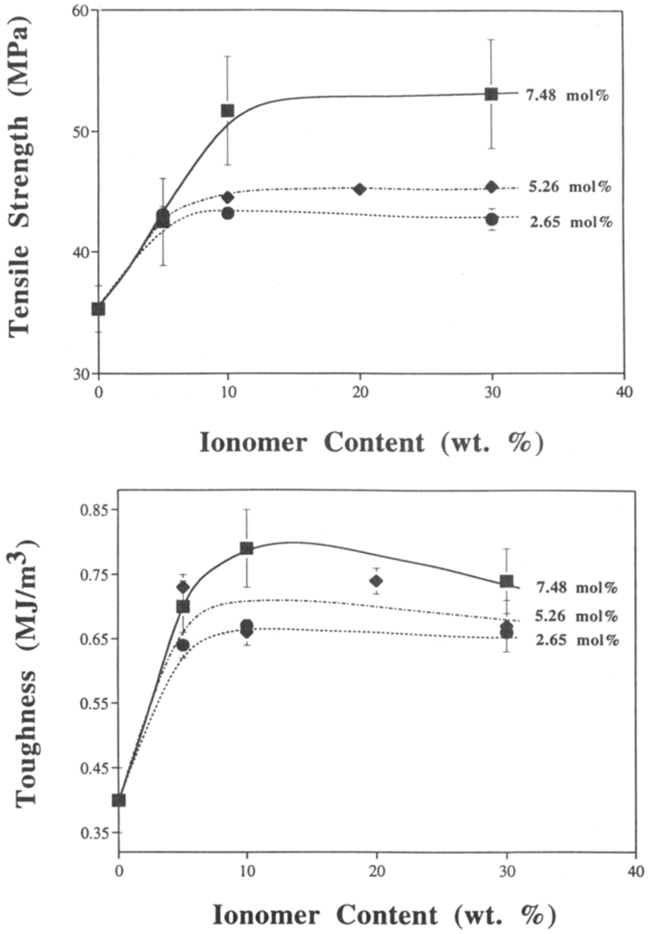
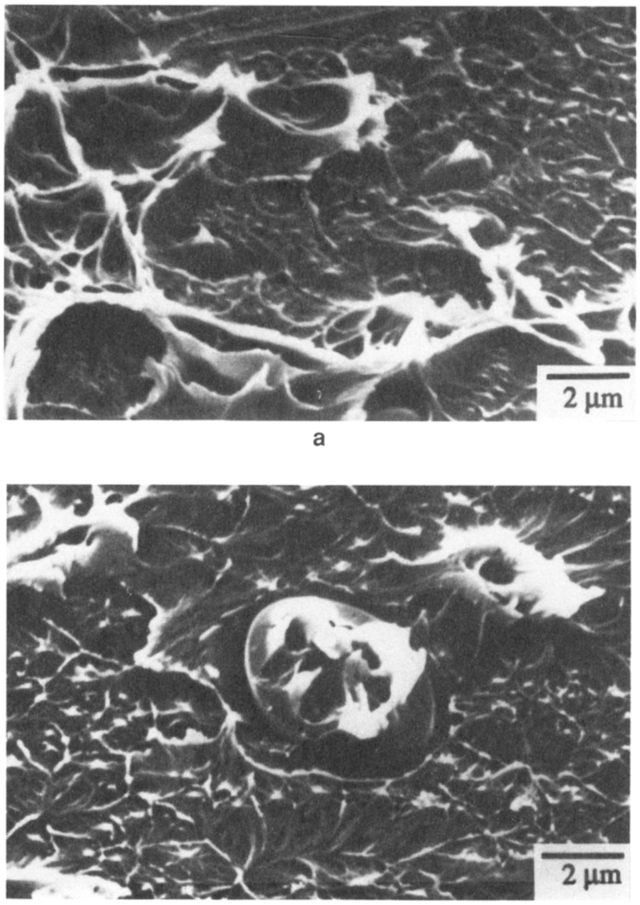


Figure 7. Composition dependence of (a) tensile strength and (b) tensile toughness of SPS ionomer/PS blends for various ion contents.



a

b

Figure 8. High magnification view showing particle/matrix interactions in SPS ionomer/PS (30/70) blends: (a) 2.65 mol %; (b) 7.45 mol %.

PS, and it would be anticipated that they would also appear in the SPS ionomer/PS blends of low ionomer content. Occasionally, large particles of approximately 10 μm are observed. Since these large precipitates are rare, their occurrence may be a result of insufficient mixing during blend preparation; they are not characteristic of the blend system. The patch pattern also shows a specific type of circular marking, as identified by the arrows in Figure 6c. Even within these features, the microstructure of the patch pattern is preserved. These makings arise from the existence of second-phase particles and two possible explanations may be given for their appearance, according to the path of the craze traveling ahead of the crack front. If the adhesion between the particles and matrix is good, the propagating craze may not recognize the interface and move through the particle as if the boundary did not exist. Thus, the patch pattern within the circular markings would be that of the ionomeric material. However, if the adhesion between the two phases is not that good, the propagating craze will prefer to travel along the interface. If the interface has a sufficient number of molecular entanglements to be effective in preventing debonding at the interface, the patch patterns within the circular markings may represent the breakdown of a craze spanning the particle and matrix. Observation from TEM on strained thin films of the ionomer/PS blends favors the first explanation,[15,16] although no evidence is available to contradict the second one.

Effect of Ion Content. Since the tensile fracture properties, such as tensile strength and toughness, of SPS ionomers increase with increasing ion content,[32] it can be anticipated that the ion content of the ionomer component of the blend may also affect the tensile properties of the SPS ionomer/PS blends.

Figure 7 shows how the tensile strength and toughness of the SPS ionomer/PS blends varies with the ionomer content for various ion contents of the ionomer component. For all the ion contents examined, 2.65, 5.26, and 7.48 mol %, a significant increase in both tensile strength and toughness compared with PS is apparent in the low ionomer composition range. However, the degree of the enhancement in properties depends on the ion content; when 10 wt % of a low ion content SPS ionomer (2.65 mol %) is added to PS, a 22% increase in tensile strength and a 68% increase in toughness are observed; upon increasing the ion content of the ionomer component to 7.48 mol %, the enhancement increases to a 46% rise in tensile stress accompanied by almost a 100% improvement in toughness.

The tensile fracture surfaces of the SPS ionomer/PS blends at low (2.65 mol %) and high (7.45 mol %) ion contents of the ionomer component show two distinct regions: a smooth initiation region and an extended flat region, similar to that observed in Figure 6a for the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend. The microstructures within the initiation region of the blends (10/90) are shown in Figure 8. In general, particle/matrix interactions are observed in all the blend materials, regardless of ion content or blend composition. However, the manner in which this interaction occurs differs according to the ion content. In the blends including low ion content ionomer (2.65 mol %), the size of the second-phase particles is ca. 1–2 μm (see Figure 8a), while the blends including high ion content ionomer (7.45 mol %), on the other hand, have larger particles, ca. 5 μm (see

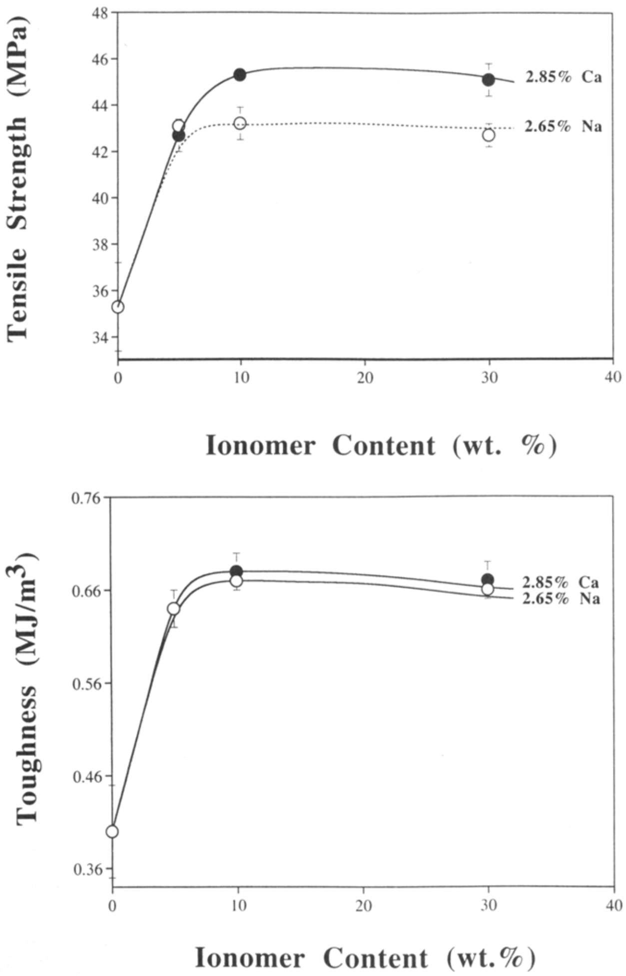


Figure 9. Effect of counterion on (a) tensile strength and (b) tensile toughness of SPS ionomer/PS blends.

Figure 8b). Figure 8 clearly shows signs of adhesion between the ionomer particles and the PS matrix, especially for low ion content blends, in which the second-phase particles are completely embedded in the matrix polymer (see Figure 8a).

The flat region of the fracture surface, at both high and low ion contents, contains patch patterns and circular markings due to the presence of the second-phase particles. These microstructural features are quite similar to those observed for the SPS ionomer (5.26 mol %; Na salt)/PS (10/90) blend of Figure 6c.

Effect of Counterion. Figure 9 shows the tensile strength and toughness of two SPS ionomer/PS blends in which the ionomer components are Na salt (2.65 mol % ion content) and Ca salt (2.85 mol % ion content), at ionomer contents less than 30 wt %. As seen for the Na-salt SPS ionomer/PS blends, the 10 wt % addition of the ionomer to PS leads to maximum tensile properties over this composition range. The replacement of Na with Ca causes a moderate increase in tensile strength and a slight increase in toughness.

Examination of the fracture surface of Ca-salt ionomer blends reveals characteristic features similar to those observed in the Na-salt ionomer/PS blends. In general, the morphology of the Ca-salt ionomer (2.85 mol %)/PS (10/90) blend is quite similar to the features found in Na-salt ionomer/PS blends, as seen in Figures 6. Within the initiation region, as shown in Figure 10, some ionomer second-phase particles, having a size of ca. 2 μm, are observed. The Ca-salt ionomer (2.85 mol %)/PS blend also shows signs of interfacial adhesion between the

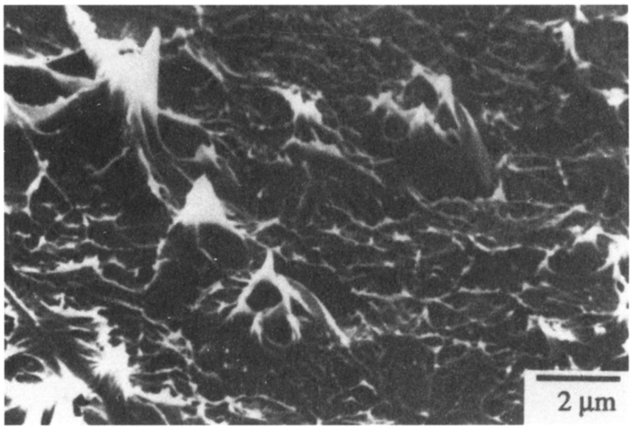


Figure 10. High magnification view showing particle/matrix interactions in the SPS ionomer (2.85 mol %; Ca salt)/PS (10/90) blend.

ionomer particles and the PS matrix. In addition, the flat mica region of the fracture surface contains patch patterns, including circular markings due to the presence of the ionomer particles, similar to the ones observed in the ionomer (5.26 mol %; Na salt)/PS 10/90 blend of Figure 6c.

Discussion

The SPS ionomer/PS blends show significant enhancement in tensile properties compared with PS. The addition of a rigid SPS ionomer to PS causes a positive deviation from the rule of mixtures in tensile strength and toughness, and in some cases (2.65 mol % ionomer blend) synergistic enhancement is observed at low ionomer composition (e.g., 10 wt %). The resulting blend properties may be attributed to several factors: *enhanced fracture resistance of ionomer particles, good interfacial adhesion*, and *a stress concentration effect*.

The most important factor affecting the enhancement in strength and toughness of the SPS ionomer/PS blends is the fracture resistance of the ionomer second-phase particles. As already noted, the ionomer particles have a greater strand density than unmodified polymers due to an ionic cross-linking effect.[26] Even though ionic cross-linking is not as stable as covalent cross-linking, since it can be overcome at sufficiently high temperatures, nevertheless it may be anticipated that it will provide somewhat similar effects to covalent cross-linking, which is known to increase total strand density.[52] In fact, two effects, expected from introduction of covalent cross-links, i.e., a shift of T_g to higher temperatures and a rise in the rubbery plateau modulus, also occur in ionomers.[53] Also, we have observed that the deformation mode of thin films under simple tension changes from crazing only for PS to crazing plus shear deformation as the ion content of the ionomers is increased,[27] a behavior similar to that noted in covalently cross-linked PS.[52] In SPS ionomer/PS blend materials, such an increase in strand density of the iomomer second-phase produces an increase in its craze stress, and when crazing occurs within the second-phase particles, more cross-tie fibrils will be present. This should lead to a greater resistance to the development of damaging cracks in the craze and inhibit early fracture. The importance of the fracture resistance of the ionomer phase is typically seen in the data on the ion content effect in blends with a fixed blend ratio 10/90. At low ion content (2.65 mol %), a 20% increase in tensile strength and a 70% increase in toughness occurs over that of unmodified PS. However, at high ion content (7.48 mol %) where

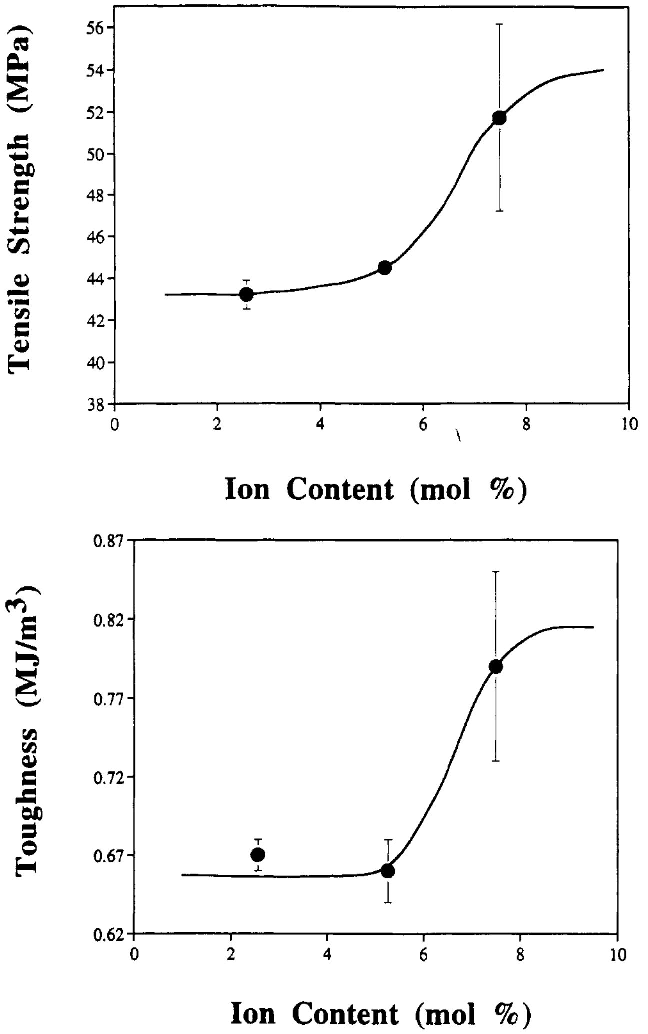


Figure 11. Effect of ion content on (a) tensile strength and (b) tensile toughness of SPS ionomer (Na salt)/PS blends (10/90).

ionic clusters are dominant, the properties are improved, exhibiting a 45% increase in tensile strength and almost a 100% enhancement in toughness.[54]

To understand why the high ion content ionomer component leads to better mechanical properties of the SPS ionomer/PS blends, it is helpful to recall prior studies of the pure SPS ionomers.[32] There it was determined that the degree of enhancement in tensile properties of pure SPS ionomers depends on ion content. At low ion contents, where the microstructure is composed primarily of nanosized multiplets, small increases in tensile strength and toughness were observed. When the ion content was raised above ca. 5 mol %, where ionic clusters became the dominant microstructure,[19-25] a significant improvement in mechanical properties was noted. With an increase in ion content, there is an increase in the "effective" entanglement (strand) density of the SPS ionomer (and of the ionomer particles in the SPS ionomer/PS blends) due to the presence of ionic cross-links. The higher strand density means a higher craze stress to induce fibrillation, as it has been shown, for a variety of polymers that craze, that the crazing stress is directly proportional to the square root of the entanglement density;[57] and the rise in the stress for crazing increases the fracture resistance of these materials. Thus, the effect of ion content on the mechanical performance can be observed in both ionomers and ionomer blends. This is quite clearly seen in Figure 11, which shows that both tensile strength and toughness of the SPS ionomer/PS blends increase significantly above ca. 5–6 mol % ion content. These changes in tensile properties are comparable to those of pure SPS ionomers.[32]

The good interfacial adhesion between ionomer particles and the matrix phase is also an important factor for enhanced toughness. SEM examination of the fracture surface morphology shows the presence of adhesion along portions of the particle/matrix interface (see Figure 8). Also, in TEM pictures of strained thin films of SPS ionomer/PS blends, voids are absent at the poles of the second phase particles and the edges of the crazes are uneven.[15,16] Thus, both TEM and SEM observations suggest that a sufficient level of adhesion is present between the SPS ionomer particles and the PS matrix. This is due to favorable (athermal) interactions between PS and the styrene units of the ionomer chains, which lead to the entanglement of the polymer chains of the blend components at the interface. On the contrary, in two-phase polymer blends with poor adhesion, smooth second-phase particles are observed, reflecting fracture occurring though a path along the particle/matrix interface.[58] Dekkers et al. studied rigid–rigid blends of poly(butylene terephthalate) (PBT) and polycarbonate (PC) and found that good interfacial adhesion between PBT and PC comes from interpenetration of the two polymers at the interface.[7] From the work on the reinforcing effect of block copolymers in two-phase polymer blends, Creton et al. have shown that at least one average "entanglement" is needed between the block copolymer and the homopolymers as well as a sufficient amount of block copolymer at the interface to have good stress transfer across the interface.[18] Therefore, the formation of entanglements between two phases is a necessary condition for good interfacial adhesion in rigid–rigid blends, as shown in our blends.

Another factor affecting the toughness of blends is a stress concentration effect of the second-phase particles. For rubber-toughened polymers, the difference in moduli between the elastomeric particles and the glassy matrix creates a significant stress concentration at the equator of the second-phase particles; and the increase in toughness is due to extensive matrix deformation (crazing, shear deformation, or a combination of the two) initiated by these dispersed rubbery particles.[3,5] The large volume of plastic deformation permits materials, such as HIPS, to reach large elongations (e.g., 50%) before fracture occurs. However, the significant increase in toughness of HIPS occurs as a result of a large increase in elongation, though accompanied by an unfavorable decrease in tensile strength and modulus. In contrast, the SPS ionomer/PS blends show a modest increase in toughness over PS, due to some degree of enhancement in both tensile strength and elongation. Although the SPS ionomer and PS have rather comparable moduli,[32] and the stress concentrating effect of the ionomer-rich second phase particles is less significant, it is evidently not completely eliminated. TEM studies of thin films of the SPS ionomer/PS blend deformed under simple tension have shown that a large number of small crazes have been generated by the presence of the ionomer particles.[15,16] In addition, ionomer particles within the crazed regions have fibrillated and elongated parallel to the tensile axis. Similarly, Pearson and Yee have reported that rigid poly(phenylene oxide) (PPO) particles in an epoxy matrix can initiate shear bands in the matrix despite the small modulus difference between the particles and the matrix polymer.[6] Therefore, additional matrix deformation due to even a mild stress concentration can contribute to increased toughness.

Rigid particulates, such as glass beads, can also act as stress concentrators and induce localized plastic deformation in the matrix material.[59,60] However, they are generally ineffective in increasing toughness due primarily to their postyield behavior;[3] unlike the grafted rubbery particles, which can stretch and remain well-bonded when a load is applied, rigid particulates generally cannot deform sufficiently, become debonded from the matrix, and fail to transmit the applied load. Voids formed at the poles of the second-phase particles then serve as sites for premature crack nucleation. The unique behavior of the SPS ionomer/PS blend system lies in the fact that although the ionomer phase is a rigid phase, some similarities exist in the deformation behavior of these blends and rubber-toughened polymers: in addition to ionomer particles producing a mild stress concentration effect, as already discussed, ionomer chains in the glassy state can undergo crazing and deform significantly, unlike particulate fillers, as typically seen in the high extension ratio of polymer chains observed in crazes.[61] TEM micrographs show that the SPS ionomer particles in strained SPS ionomer/PS blends have appreciably elongated but remained well-adhered to the PS matrix, as suggested by the absence of voids associated with debonding along the particle/matrix interface.[15,16] Thus, in contrast to rigid particulate fillers, a second phase composed of glassy ionomers can be used as a more effective rigid second phase.

Another factor influencing the toughness of the blends with respect to the ion content effect may be the size of the second phase in these blends. As observed in TEM studies of this blend system, the average size of the second-phase particles increases with increasing ion content because of the greater difference in polarity between the SPS ionomer and PS.[15] SEM micrographs of the fracture surfaces of the SPS ionomer/PS blends show similar trends (see Figure 8). It is well-known that for rubber-toughened polymers, such as ABS and HIPS, an optimum particle size exists, leading to maximum toughness.[3,5] On the other hand, it has been shown that the size of the glass beads in glass-bead-filled polymers has no significant effect on dewetting cavitation in these materials.[59] Gent and coworkers[62-63] have shown that the critical stress for debonding of glass beads from an elastomeric matrix is inversely proportional to the square root of the particle diameter. A similar argument was used to explain the size effect of immiscible blends of PS and poly(2-vinylpyridine) (PVP) reinforced by a block copolymer (S-VP);[18] i.e., debonding becomes more favorable for larger particles. Therefore, the debonding is expected to occur more easily with increasing ion content, due to a greater difference in polarity (thus less entanglements at the interface) and a lower critical stress for debonding. However, the degree of adhesion at the interface of the high ion content SPS ionomer/PS blends seems sufficient to cause deformation of these large second-phase particles, as observed in the SEM micrographs (see Figure 8b). Therefore, a possible explanation for changes in tensile properties as a function of ion content lies in the combined effects of particle size, particle/matrix adhesion, and inherent ionomer resistance to craze initiation and fracture.

Changing the counterion of the ionomer particles from Na to Ca shows less significant effects on the mechanical properties; a moderate increase in tensile strength and toughness occurs in the blend when the ion content of the ionomeric particles is below 3 mol %. Somewhat better mechanical properties were anticipated for these materials on the basis of the extent of the increases in tensile properties found in Ca-salt SPS ionomers.[33] Since the size of the second-phase particles of the Ca salt is similar to that of the Na salt (compare Figure 8a with Figure 10), and since the fracture resistance of the Ca-salt ionomer is better than that of the Na-salt ionomer at low ion content, a possible explanation is that the mechanical properties of the Ca-salt ionomer in the blend may not be as good as those found in pure Ca-salt ionomers due to insufficient thermal energy applied during the molding process; the molding temperature of the Ca-SPS ionomer (2.85 mol %)/PS (10/90) blend was 130 °C, while that of the Ca-SPS ionomer (2.85 mol %) was 210 °C. Therefore, ionic aggregates (and hence the ionic cross-linking effect) may be insufficiently developed during this thermal process.[53] In general, Ca-salt ionomers are more difficult to handle due to lower solubility and higher softening temperature compared with Na-salt ionomers; however, this intractability is associated with those characteristics (i.e., stronger ionic bonds) that are responsible for the better fracture resistance of Ca-salt ionomers.[33] More systematic work on processing conditions needs to be conducted to fully take advantage of the good mechanical properties of Ca-salt ionomers in rigid-rigid blends.

Conclusions

The addition of SPS ionomer (<30 wt %) to PS results in a creation of rigid-rigid blends with significant improvements in tensile strength and tensile toughness. The enhancement in tensile properties is a result of a phase-separated blend morphology arising from the difference in polarity of the two component polymers; the ionomer second-phase particles have more fracture resistance and act as stress concentrators, generating some matrix crazing and allowing some plastic energy to be absorbed before failure occurs. The elongation and fibrillation of the ionomer particles, along with the absence of voids at the poles, suggest that a sufficient level of interfacial adhesion exists to transfer the applied stress across the interface. This interfacial adhesion is a result of the favorable (athermal) interactions between the styrene units of both the SPS ionomer and PS, which allows molecular entanglements to occur at the interface.

The changes in the mechanical properties as a function of ion content lie in the combined effects of particle size, particle/matrix adhesion, and fracture resistance of the ionomer phase. As the ion content of the ionomer particles increases, the fracture resistance of the ionomer second phase increases and the average particle size increases without losing good interfacial adhesion; as a result, both tensile stress and toughness increase. A moderate increase in tensile properties is observed by changing the counterion from monovalent Na to divalent Ca, although the effect of counterions on tensile mechanical properties has not been studied as systematically as the effect of ion content. The Ca-salt system needs more systematic study to fully develop the possible effects of the divalent Ca salt, which has the potential to modify properties more effectively than the Na-salt system.

This work has indicated that blending of a small amount (e.g., 10 wt %) of glassy ionomers with unmodified glassy polymers can significantly enhance tensile fracture properties. The rigid-rigid blends are transparent at all compositions and temperatures studied, because of the very close refractive indices of the two component polymers. Since these blend materials retain the transparency of the original polymer, and the total amount of repeat units having ionic groups included in the material is less than 1%, this approach based on the synthesis of rigid-rigid blends of ionomer/ionomer-precursor appears to be a useful one for improving mechanical properties of glassy polymers.

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References and Notes

(1) Rosen, B., Ed. *Fracture Processes in Polymeric Solids*; Interscience: New York, 1964.
(2) Andrews, E. H., Ed. *Developments in Polymer Fracture*; Applied Science: New York, 1979.
(3) Kinloch, A. J.; Young, R. J. *Fracture Behavior of Polymers*; Applied Science: New York, 1983.
(4) Roulin-Moloney, A. C., Ed. *Fractography and Failure Mechanisms of Polymers and Composites*; Elsevier Applied Science: New York, 1989.
(5) Bucknall, C. B. *Toughened Plastics*; Applied Science: New York, 1979.
(6) Pearson, R. A.; Yee, A. F. *Polymer* **1993**, *34*, 3658.
(7) Dekkers, M. E. J.; Hobbs, S. Y.; Watkins, V. H. *J. Mater. Sci.* **1988**, *23*, 1225.
(8) Sue, H.; Yee, A. F. *J. Mater. Sci.* **1989**, *24*, 1447.
(9) Kambour, R. P. In *Polymer Blends and Mixtures*; Walsh, D. J., Higgins, J. J., MaConnachie, A., Eds.; NATO ASI Series; Martinus Nijhoff Publishers: Boston, 1985.
(10) Yee, A. F.; Maxwell, M. A. *J. Macromol. Sci., Phys.* **1980**, *B17*, 543.
(11) Kambour, R. P.; Smith, S. A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2069.
(12) Serrano, A. M.; Welsch, G. E.; Gibala, R. *Polym. Eng. Sci.* **1982**, *22*, 946.
(13) Fayt, R.; Jerome, R.; Teyssie, P. In ref 25, Chapter 2.
(14) Bosnyak, C. P.; Sehanobish, K.; Rightor, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (2), 624.
(15) Hara, M.; Bellinger, M.; Sauer, J. A. *Polym. Int.* **1991**, *26*, 137.
(16) Hara, M.; Bellinger, M.; Sauer, J. A. *J. Colloid Polym. Sci.* **1992**, *270*, 652.
(17) Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* **1993**, *26*, 4155.
(18) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Macromolecules* **1991**, *24*, 1846.
(19) Eisenberg, A.; King, M. *Ion Containing Polymers*; Academic: New York, 1977.
(20) Holliday, L., Ed. *Ionic Polymers*; Applied Science: London, 1975.
(21) MacKnight, W. J.; Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(22) Wilson, A. D., Prosser, H. J., Eds. *Developments in Ionic Polymers*; Applied Science: New York, 1983.
(23) Bazuin, G. C.; Eisenberg, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 271.
(24) Pineri, M., Eisenberg, A., Eds. *Structure and Properties of Ionomers*; NATO Advanced Study Institute Series; Plenum: New York, 1987.
(25) Ultracki, L. A., Weiss, R. A., Eds. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989.
(26) Hara, M.; Sauer, J. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 325.
(27) Hara, M.; Jar, P. *Macromolecules* **1988**, *21*, 3187.
(28) Hara, M.; Jar, P.; Sauer, J. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 223.
(29) Sauer, J. A.; Hara, M. *Adv. Polym. Sci.* **1990**, *91/92*, 69.
(30) Hara, M.; Jar, P.; Sauer, J. A. *Macromolecules* **1988**, *21*, 3183.
(31) Hara, M.; Jar, P.; Sauer, J. A. *Macromolecules* **1990**, *23*, 4465.
(32) Bellinger, M.; Sauer, J. A.; Hara, M. *Macromolecules* **1994**, *27*, 1407.
(33) Bellinger, M.; Sauer, J. A.; Hara, M. *Polymer*, in press.
(34) Smith, P.; Hara, M.; Eisenberg, A. In *Current Topics in Polymer Chemistry*; Ottenbrite, R. H., Utracki, L. A., Inoue, S., Eds; Hauser Publishers: Munich, 1987; Chapter 6.3.
(35) Weiss, R. A.; Beretta, C.; Sasongko, S.; Garton, A. *J. Appl. Polym. Sci.* **1990**, *41*, 91.
(36) Lu, X.; Weiss, R. A. *Macromolecules* **1991**, *24*, 4381.
(37) Molnar, A.; Eisenberg, A. *Macromolecules* **1992**, *25*, 5774.
(38) Molnar, A.; Eisenberg, A. *Polym. Commun.* **1991**, *32*, 370.
(39) Douglas, E. P.; Sakurai, K.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 6776.
(40) Sakurai, K.; Douglas, E. P.; MacKnight, W. J. *Macromolecules* **1992**, *25*, 4506.
(41) Another approach involves introducing ionic groups into one component of already miscible blends, such as a blend made of PS and PPO.[42,43] In this case, nanoscale ionic aggregates are formed in homogeneous blends, in contrast to 0.1–1 μm second-phase particles, which include ionic aggregates, formed in our blends.
(42) Zhao, Y.; Prud'homme, R. E.; Bazuin, C. G. *Macromolecules* **1991**, *24*, 1261.
(43) Tomita, H.; Register, R. *Macromolecules* **1993**, *26*, 2796.
(44) Iwakura, K.; Fujimura, T. *J. Appl. Polym. Sci.* **1975**, *19*, 1427.
(45) Villeneuve, S.; Bazuin, C. G. *Polymer* **1991**, *32*, 2811.
(46) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3,870,841 (assigned to Exxon Research & Engineering Co.), 1975.
(47) Paul, D. R., Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978.
(48) Hull, D. *J. Mater. Sci.* **1970**, *5*, 357.
(49) Doyle, M. J.; Maranci, A.; Orowan, E.; Stork, S. T. *Proc. R. Soc.* **1972**, *A329*, 137.
(50) Beahan, P.; Bevis, M.; Hull, D. *Polymer* **1973**, *14*, 96.
(51) Beahan, P.; Bevis, M.; Hull, D. *Proc. R. Soc.* **1975**, *A343*, 525.
(52) Henkee, C. S.; Kramer, E. J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 721.
(53) Hara, M.; Jar, P.; Sauer, J. A. *Polymer* **1991**, *32*, 1622.
(54) The ionic cross-linking effect leading to enhanced strand density in SPS ionomers appears to be more efficient when ionic clusters, rather than multiplets, are dominant. For example, at low ion content where multiplets dominate, the deformation mode is still crazing, although the shorter craze length suggests more stable craze formation, and at high ion content where ionic clusters dominate, shear deformation begins to appear in addition to crazing.[27] Bulk mechanical properties, such as tensile[32] and fatigue[55] properties, seem to corroborate these changes in deformation modes. Although initial work indicated poor fatigue resistance of SPS ionomers at low ion content,[30] more recent results show a slight increase in fatigue performance at similar ion contents.[55] This is believed to arise from a difference in *thermal history*. The importance of the effect of thermal history on ionomer morphology has been discussed in recent papers;[53,56] if sufficient thermal energy is not applied to ionomer samples, ionic aggregates are poorly developed, and ion pairs even remain isolated,[53,56] which should lead to rather poor mechanical properties. Additional discussion of this topic is given in ref 26.
(55) Bellinger, M. Ph.D. Dissertation, Rutgers University, 1992.
(56) Register, R. A.; Sen, A.; Weiss, R. A.; Cooper, S. L. *Macromolecules* **1989**, *22*, 2224.
(57) Wu, S. *Polym. Eng. Sci.* **1990**, *30*, 753.
(58) Lambla, M.; Yu, R. X.; Lorek, S. In Ref 25, Chapter 3.
(59) Dekkers, M. E. J.; Heikens, D. *J. Appl. Polym. Sci.* **1985**, *30*, 2389.
(60) Dekkers, M. E. J.; Heikens, D. *J. Appl. Polym. Sci.* **1983**, *28*, 3809.
(61) Kramer, E. J.; Berger, L. L. *Adv. Polym. Sci.* **1990**, *91/91*, 1.
(62) Gent, A. N. *J. Mater. Sci.* **1980**, *15*, 2884.
(63) Gent, A. N.; Park, B. *J. Mater. Sci.* **1984**, *19*, 1947.