Tensile Fracture Properties of Sulfonated Polystyrene Ionomers. 1. Effect of Ion Content

M. Bellinger, J. A. Sauer, and M. Hara*

Department of Mechanics and Materials Science, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855-0909

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ABSTRACT: Tensile fracture behavior of sulfonated polystyrene (SPS) ionomers was investigated as a function of ion content. Both tensile strength and toughness increased slightly at low ion content (below ca. 4 mol %) and increased significantly at higher ion content above 4 mol %, although some reduction of these values was observed at an ion content of 8.8 mol %. The deformation mechanism of the thin film SPS ionomers also changed: from crazing only at low ion content to crazing plus shear deformation at high ion content. Furthermore, the width of hackle bands observed on fracture surfaces decreased with increasing ion content. These observations are interpreted as the effects of ionic aggregates on deformation and fracture behavior of ionomers: at low ion content, small ionic aggregates (multiplets) work as weak cross-links, while at higher ion content, large ionic aggregates (clusters) offer more effective cross-links, and these cross-links enhance craze stability, somewhat like covalent cross-links, leading to better fracture resistance under simple tension.

Introduction

Ion-containing polymers provide a means of modifying various properties by controlling molecular structure through the utilization of ionic interactions. In recent years, a considerable amount of research has been devoted to the structure and properties of ionomers.[1–12] Ionomers are polymers that have a small amount of ionic groups (up to 10–15 mol %) distributed along a nonionic hydrocarbon chain. It has been demonstrated that the change in properties of ionomers in the solid state is due to the clustering of ion pairs in a medium of low dielectric constant. According to a widely used model,[2] two types of ionic aggregates are considered to exist: multiplets, consisting of a small number of ion pairs that work as physical cross-links, which dominate at low ion contents, and ionic clusters, comprised of microphase-separated ion-rich regions and portions of the hydrocarbon chains, which are the dominant morphological feature above a critical ion content. Since these ionic aggregates control much of the physical properties of ionomers, it is essential to understand the change in properties of ionomers in terms of the microstructure of these materials.

Although many investigations have been conducted to elucidate the structure–property relationships of ionomers, most of the reported works have concentrated on the physical properties of ionomers in the rubbery or flow regions, such as the glass transition temperature, the high-temperature (or rubbery) modulus, and the melt viscosity.[1–12] Only recently has work been reported about the glassy state properties, such as the deformation and fracture behavior of ionomers.[13–17]

In recent years, glassy polymers are finding increasing use in a wide range of engineering applications, but the use of these materials is still limited by their tendency to fail in a brittle fashion with no large-scale plastic deformation. Therefore, there exists a great need to understand the micro- and macroscopic mechanisms by which glassy polymers respond to mechanical (monotonic and cyclic) loading and to find ways to improve mechanical properties. Recently, methods to improve the mechanical performance have received great interest due to a better understanding of the relationship among molecular structure, mechanical properties, and the micromechanisms of deformation and fracture behavior.[18–23]

For glassy (amorphous) polymers, the importance of the microscopic deformation processes occurring on a molecular level, such as crazing and shear yielding, as precursors to crack initiation and propagation, has been well established. Both of these deformation mechanisms represent a major source of energy absorption of amorphous polymers and involve localized (inhomogeneous) plastic deformation. Kramer and his co-workers have shown that, for various homopolymers, copolymers, and miscible polymer blends, the nature of the deformation prior to fracture is governed by the molecular entanglement network, characteristic of a given polymeric material.[22–24] As the entanglement density is increased, more energy is required to form craze fibrils in glassy polymers; therefore, the crazing stress increases with entanglement density, while the shear yield stress is less affected by the change of the entanglement density. As a result, crazing is suppressed in favor of shear yielding with increasing entanglement density. For example, polymers with a high entanglement density, such as polycarbonate, deform by shear yielding and exhibit a significant amount of plastic deformation prior to fracture at ambient temperature. However, polymers with a low entanglement density, such as polystyrene, deform by crazing and fracture in a relatively brittle fashion.

The concept of entanglement density, which can be applied to thermoplastics, has been extended to include the effect of covalent cross-links.[24] The concept of strand ("effective" entanglement) network density, which is the sum of physical entanglements and covalent cross-links, is used to correlate the deformation behavior. Therefore, one way to enhance fracture properties involves the chemical modification of the polymer to introduce a small degree of covalent cross-linking. Transmission electron microscopy (TEM) observations on thin films of cross-linked PS demonstrate the suppression of crazing in favor of shear deformation with increasing the strand density to some optimal value.[24] This is a useful method of improving the mechanical properties.

Another potential method of increasing the mechanical performance of glassy polymers is by increasing the strand

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* To whom all correspondence should be addressed.

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density through the introduction of ionic cross-links due to ionic aggregate formation. Recently, Hara et al. have investigated the deformation mechanisms and fatigue properties of ionomers to understand the role of the ionic aggregates in modifying the mechanical properties of these materials.[13-17] Deformation studies of thin films under simple tension by TEM have shown the suppression of crazing in favor of localized shear deformation for SPS ionomers with monovalent Na ions at higher ion contents.[14] In addition, research on the fatigue behavior of ionomers has shown an increase in fatigue lifetime for the same ionomers at higher ion contents.[15] In both of these investigations, the increase in mechanical performance is attributed to the effect of ionic clusters dominating at higher ion contents and providing more effective cross-links than multiplets.

In the present study, we report the results obtained from an investigation of the tensile fracture properties of ionomers as a function of ion content. Tensile properties of bulk ionomers are discussed in terms of the microstructure of ionomers and are also compared with results obtained by simple tension of thin films.

Experimental Section

Materials. Lightly sulfonated polystyrene (SPS) was prepared by sulfonation of polystyrene according to the procedure described by Makowski et al.[25] The ion content was controlled by adjusting the amount of sulfonating agent, acetyl sulfate. Ionomers used to investigate the bulk tensile properties were prepared from a starting polystyrene (Polysciences) with a molecular weight of 125 000–250 000. After the sulfonation reaction was terminated by the addition of methanol, a small amount of sample was removed from the reaction mixture before neutralization, and the ion content was determined by titration of the acid groups. Then, a calculated amount of sodium hydroxide (NaOH) dissolved in methanol was added to completely neutralize the acid groups. The ionomers were recovered by steam stripping in boiling water and dried under vacuum at 85 °C for 48 h and then at 120 °C for an additional 24 h. The ion content of the resulting SPS ionomers ranged from 1.0 to 8.8 mol %.

Ionomers used to study the deformation mechanisms of thin films were prepared from standard polystyrene (Pressure Chemical) with a molecular weight of 400 000 and a sharp molecular weight distribution of $M_w/M_n = 1.06$. After the sulfonation reaction was terminated by the addition of methanol, the acid copolymer was recovered by steam stripping and then freeze-drying from a benzene/methanol (90/10, v/v) solution. The ion content was determined by titration of the acid groups. A calculated amount of NaOH in methanol was added to completely neutralize the acid groups. The ionomer was again freeze-dried, followed by drying under vacuum at room temperature for a week. These SPS ionomers had ion contents of 3.6 and 7.5 mol %.

Tensile Measurements. Tensile specimens were directly machined from compression-molded rectangular bars into hourglass-shaped round samples with threaded ends (3 in. long, $^1/_5$ in. diameter at the middle, and $^1/_2$ in. diameter at the ends). Tensile measurements were conducted on an Instron tensile testing machine at room temperature using a crosshead speed of 0.005 in./min. The fracture surfaces were examined by a scanning electron microscope (SEM; ETEC) after coating them with a thin layer of gold.

Transmission Electron Microscopy. Thin films were cast from a 3 wt % THF solution on glass microscope slides. After drying, the films were cut into small squares and then floated off the glass slides onto the surface of distilled water. Sections of the film were then picked up on a copper grid and dried under vacuum at room temperature for at least 48 h. After the copper grid was deformed by simple tension, the microstructure of the deformed thin films was examined by a transmission electron microscope (TEM) (JEOL 100CX II). Details of the procedure are described elsewhere.[14]

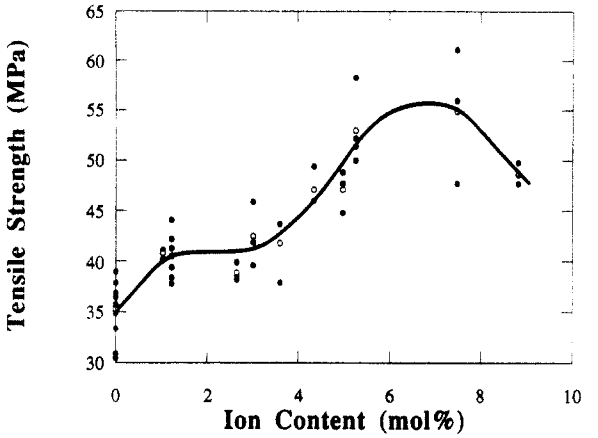


Figure 1. Effect of ion content on the tensile strength of ionomers: closed circles represent individual data points, and open circles represent average values.

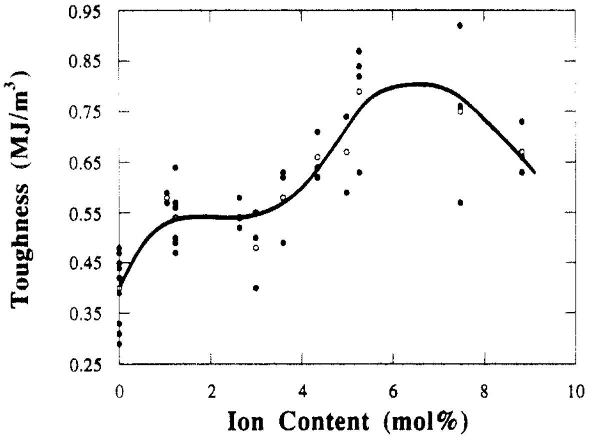


Figure 2. Effect of ion content on the toughness of ionomers: closed circles represent individual data points, and open circles represent average values.

Results and Discussion

Bulk Tensile Properties. The stress–strain curves for both the ionomers and unmodified polystyrene show typical brittle behavior of glassy polymers. It is evident, however, that the introduction of ionic interactions, especially to ionomers with higher ion contents, produces significant changes in the mechanical properties, such as appreciable increases in fracture strain, tensile strength, modulus, and toughness (defined as the area under the stress–strain curve) compared with unmodified polystyrene.

Figures 1 and 2 show the tensile strength and toughness, respectively, for SPS ionomers as a function of ion content. Open circles represent the average value of at least three different specimens. As shown in Figure 1, a slight enhancement in the tensile strength occurs at low ion contents (less than ca. 4 mol %). At higher ion contents, a significant increase occurs in the strength of these materials. However, this increase seems to level off at ion contents above ca. 8 mol % and even decreases at 8.8 mol %. Similar trends are observed for the toughness as a function of ion content as shown in Figure 2.

This behavior may be interpreted in terms of the changes in the microstructure of the ionic aggregates found in random ionomers as the ion content passes through some critical value:[2,26-28] at low ion contents, (below ca. 4 mol %), the small ionic aggregates, multiplets, are dominant, and they increase the strand density of the glassy polymer to some extent by acting as (weak) ionic cross-links. As evidenced by inflection points in stress relaxation curves[29] and by enhancement of both the rubbery plateau and T_g

in dynamic mechanical data,[30-32] SPS ionomers show a cross-linking effect at low ion contents due to multiplet formation. At intermediate ion contents (4–8 mol %), larger ionic aggregates, ionic clusters, dominate, and they provide more effective ionic cross-links between chains, increase the strand density of the polymer, and constitute a small second phase, which may act as a reinforcing filler. This is reflected by a significant enhancement in the tensile strength and toughness. From other studies on polystyrene-based ionomers, it has been established that the ionic clusters play a crucial role in determining the physical properties and that a transition in properties occurs at a critical ion content of 4–6 mol %.[2,27] The data presented here on the tensile properties of SPS ionomers seem to be in good agreement with these previously established values.

At even higher ion content (over 8 mol %), the amount of material that is clustered is increased and, as a result, the mobility of the polymer chains becomes more restricted.[28] The loss of chain mobility due to extensive ionic cross-linking may be responsible for the observed decrease in mechanical properties. Similar decreasing trends in tensile properties were observed for covalently cross-linked polystyrene and were attributed to restricted chain mobility and reduced plastic deformation.[13] However, the decrease in both tensile strength and toughness may be a result of sample preparation and thermal history, as changes in these conditions can cause a reduction in modulus. To provide sufficient thermal energy to form ionic clusters in high ion-content Na-salt ionomers, molding at high temperatures for several hours is required as indicated by the dynamic mechanical data,[30-32] and this may have resulted in some decomposition of the hydrocarbon backbone chains, leading to poorer mechanical properties, including the reduction in modulus. Since only one high ion content (8.8 mol %) was investigated in this study, this discussion is rather speculative.

Fracture Surface Morphology. To study the fracture processes, the tensile fracture surfaces were observed by SEM. The overall fracture surface for unmodified polystyrene is shown in Figure 3. Fracture surfaces show characteristic features that can be related to the processes of crack initiation and propagation, as previously reported for polystyrene.[33-37] Three distinct regions, a smooth initiation region, a series of hackle bands, and a very rough region, can be observed (see Figure 3a): the first region is related to the early stages of crack propagation through the preexisting craze, the second region is associated with bifurcation and branching of the crack, and the last region is associated with final, rapid crack propagation through the undeformed material.[33]

In a simple tensile test, craze formation precedes fracture, and initial stages of crack propagation in polystyrene involve a process in which the crack propagates through the existing craze, frequently jumping from one craze/bulk interface to another, resulting in the formation of so-called *patch patterns*,[33,35-39] as seen in Figure 3b. As the crack propagates and reaches some critical speed, the craze ahead may detach from the bulk.[36,37] The crack tip then sharpens, and the stress at the tip rises. New crazes are nucleated in planes slightly above or below the crack plane. This blunts the crack and momentarily slows its progress. Then, one of the new crazes grows and fractures, and the entire process repeats. The successive crack jumps then give rise to the formation of periodic *hackle bands* as shown in Figure 3c. On the basis of this model, the length of these bands would be determined by the length of the preexisting crazes and the local stress field near the propagating crack tip. This procedure is repeated until the material can no longer withstand the applied stress and catastrophic failure occurs, as characterized by the rough regions of the fracture surface.

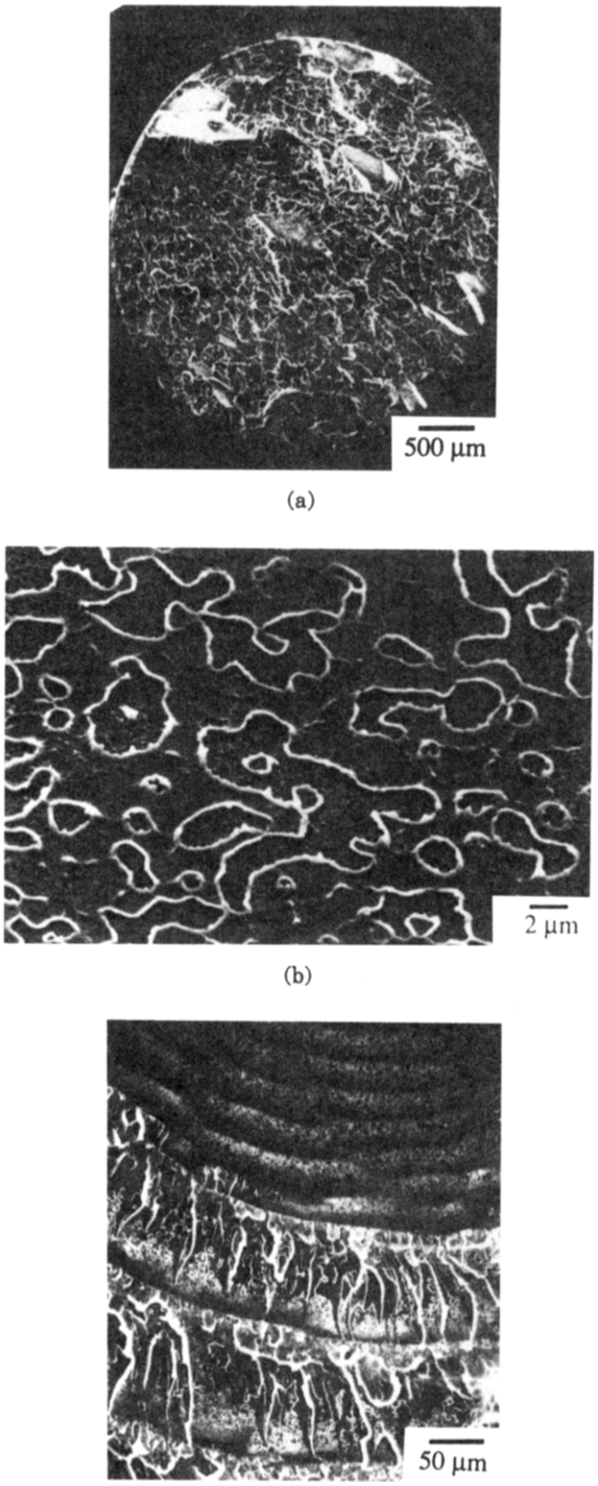
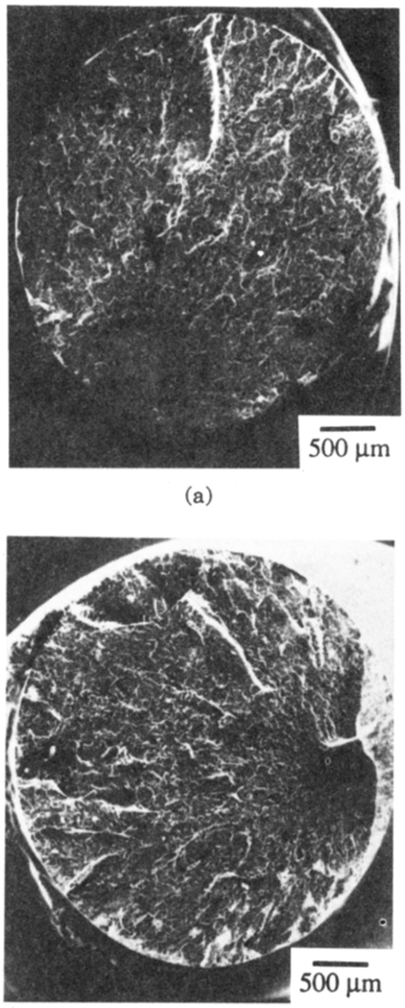


Figure 3. Tensile fracture surface of polystyrene: (a) overall view; (b) patch patterns; (c) hackle bands.

In general, ionomers show a similar fracture surface morphology to that found in polystyrene, as observed in Figure 4. In both of these micrographs, the three distinctive regions can be identified. However, the microstructure and size of these markings change as a function of the ion content of the material. The initiation regions of the ionomer samples with both low (2.7 mol %) and high (7.5 mol %) ion contents reveal patch patterns as



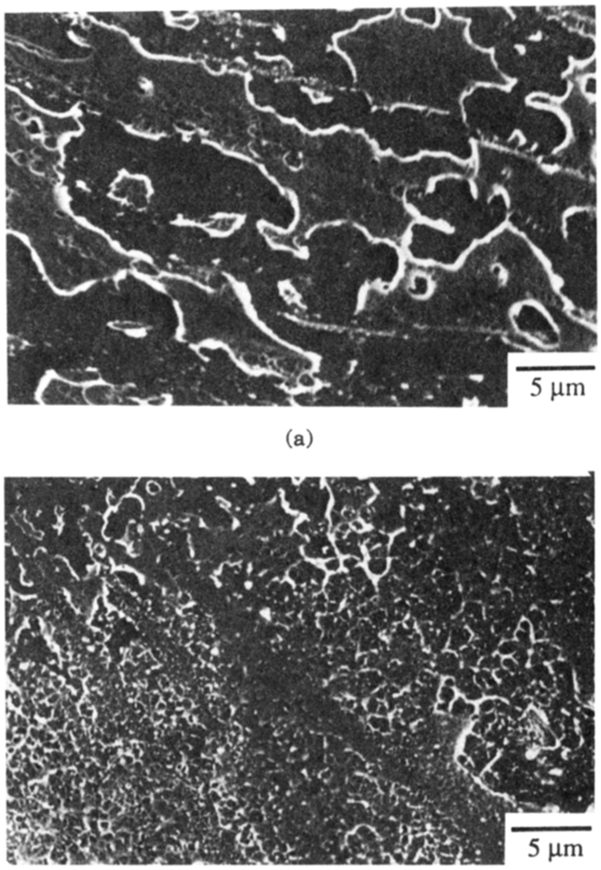
(b)

Figure 4. Tensile fracture surface (overall view) of ionomers with ion contents (a) 2.7 mol % and (b) 7.5 mol %.

shown in Figure 5, similar to those found in polystyrene (see Figure 3b). However, one should note the differences in texture of the two patch patterns. At low ion contents, the pattern is almost identical to that found in PS. At ion contents above 5 mol %, a finer texture in the patch pattern is observed. Although the significance of these differences in the two types of patterns is not clear, they both suggest that the ionomers deform primarily by crazing prior to crack nucleation, and they are consistent with the microstructural features found in PS[33-35] and previous studies on the deformation behavior of ionomers.[14]

The most prominent feature that changes as a function of the ion content is the width of the bands in the hackle region, as observed in the SEM micrographs of Figure 6. Examination of the hackle bands in ionomers as a function of the ion content reveals significant reduction in the width of the first band ranging from 110 μm at low ion content to only 30 μm at the higher ion content. Figure 7 summarizes the width of the first hackle band for ionomers with various ion contents: the hackle bandwidth decreases as the ion content of the material increases. This suggests that, at low ion contents, long crazes are present prior to craze breakdown, while at higher ion contents the crazes are much shorter in length before breakdown begins to occur.

Thin Film Deformation. The relationship between the bandwidth and preexisting craze is better understood by examining the deformation behavior prior to fracture.



(b)

Figure 5. Tensile fracture surface (patch pattern) of ionomers with ion contents (a) 2.7 mol % and (b) 7.5 mol %.

Examination by TEM of SPS ionomer thin films subject to simple tension shows a change in the deformation mechanisms with ion content, as illustrated in Figure 8, which is also consistent with the results reported previously:[14] at low ion content, crazing is the major deformation mechanism, similar to that observed in unmodified polystyrene. Upon increasing the ion content, the deformation behavior changes from crazing only to a combination of crazing and shear deformation. As observed in Figure 8b, short crazes are blunted at the tips by localized shear bands or diffuse shear deformation zones that act to stabilize the material against craze growth. Similar interactions between crazes and shear bands (zones) have been observed in other glassy polymers.[24,40,41] The best example is given by the work on lightly cross-linked polymers by Henkee et al.[24] They have studied the effects of covalent cross-linking on the deformation modes of polystyrene thin films under simple tension and have shown a change in the deformation mechanism from crazing only, to crazing plus shear deformation, and to shear deformation only with increasing covalent cross-link density and therefore strand density. Similarly, the formation of ionic clusters also leads to changes in deformation modes from crazing only to a combined crazing and shear deformation:[14] as the ion content is increased, the total strand density will rise by adding ionic cross-linking sites to the existing entanglement sites. Although ionic cross-linking is not as effective as covalent cross-linking, it provides somewhat similar effects to radiation-induced cross-links.[24]

On the basis of the influence of strand ("effective" entanglement) density on the growth and breakdown of crazes,[22,23] it is suggested that the increase in tensile strength and toughness of bulk ionomer samples with ion

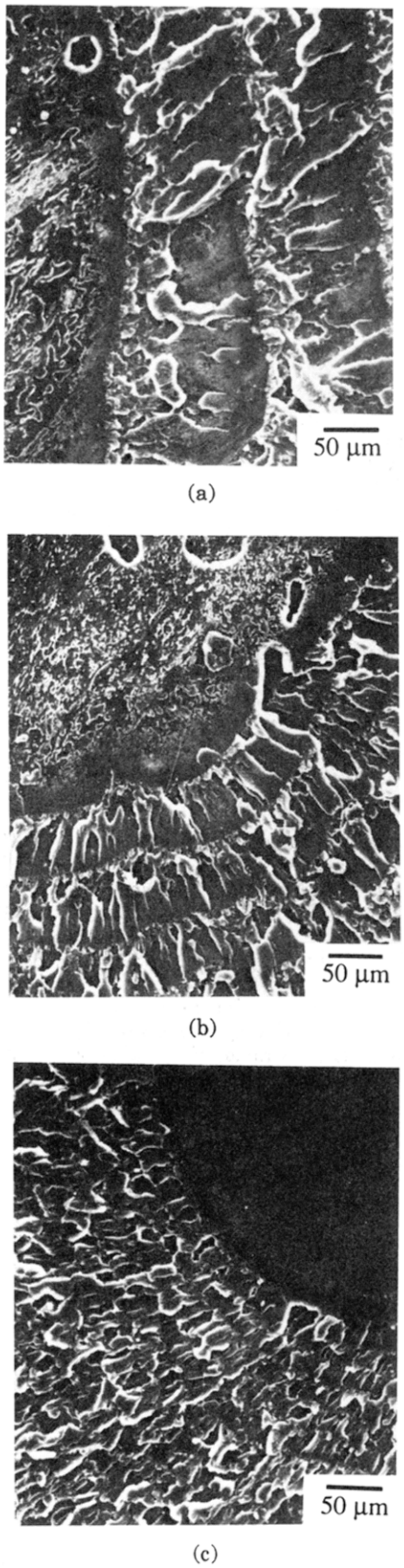


Figure 6. Tensile fracture surface (hackle bands) of ionomers with ion contents: (a) 2.7 mol %, (b) 5.0 mol %, and (c) 7.5 mol %.

content is associated with greater craze stability, which leads to enhanced fracture resistance. These are reflected in changes of deformation modes and in the reduction in hackle bandwidth on the tensile fracture surface.

Conclusion

The tensile fracture properties of sulfonated polystyrene ionomers are enhanced over that of unmodified polystyrene. At low ion contents (below ca. 4 mol %), where the microstructure is comprised primarily of multiplets, a slight enhancement in the tensile strength and toughness of these materials is observed. A significant increase in mechanical properties occurs at ion contents above 4 mol %, where ionic clusters presumably begin to dominate over multiplets. At even higher ion contents (above ca. 8 mol %), the tensile strength and toughness decrease as well as the modulus, which may be due to thermal degradation of ionomer samples at high temperature needed to mold high ion-content specimens. The tensile fracture surface morphology of bulk specimens also reflects a change in the deformation behavior as a function of the ion content: the hackle bandwidth decreases with increasing the ion content, which may be associated with

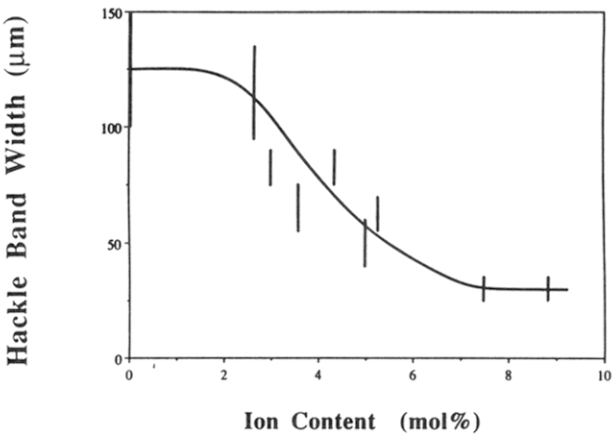


Figure 7. Effect of the ion content on the hackle bandwidth of ionomers.

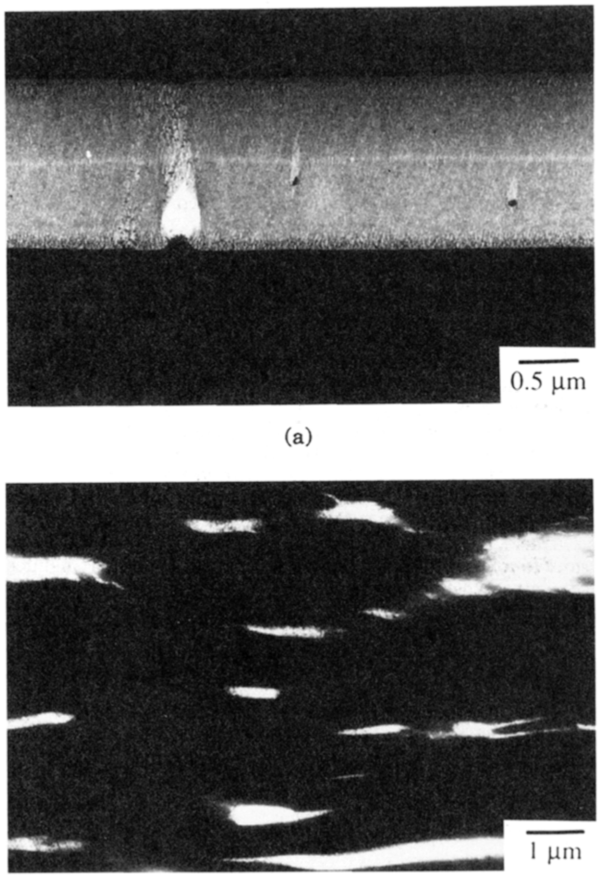


Figure 8. TEM micrograph of the deformation behavior of ionomers with ion contents (a) 3.57 mol % and (b) 7.5 mol %.

greater craze stability and enhanced fracture resistance. The observed tensile behavior is consistent with the investigation of deformation modes of thin films under simple tension: as the ion content is increased, the deformation of ionomers changes from crazing only to a combined crazing plus shear deformation.

These results on the deformation and fracture behavior of ionomers under monotonic loading are also consistent with previous results on the behavior of ionomers under fatigue loading. The explanations as to the role of ionic aggregates seem plausible; at low ion contents, a weak cross-linking effect due to small ionic aggregates (multiplets) takes place, whereas at higher ion contents, ionic clusters offer more effective ionic cross-links, as well as a reinforcing filler effect. Now it seems possible to systematically explain the effect of ion content on the various fracture (bulk tensile and fatigue and thin film tensile) behavior of glassy PS ionomers in terms of ionic aggregate structures.

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