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Deformation and Fracture of Ionomers under Simple Tension. 1. Sulfonated Polystyrene Film from THF Solution

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ABSTRACT: Deformation and fracture behavior was studied for ionomer thin films (sodium salt of partially sulfonated polystyrene) subject to simple tension. The craze structures of these ionomers with low ion content (less than 5 mol %) showed typical structural features of those of glassy polymers. It was observed that the craze stability decreased with increasing ion content at low ion content, which may be due to the ionic cross-linking produced by small ionic aggregates (multiplets). At higher ion content (more than 6 mol %), fewer crazes were seen, craze growth was suppressed, and localized shear deformation appeared. These changes in deformation mode seem to relate to the microstructure of ionomers, such as cluster formation.

Introduction

In recent years, there has been a tremendous increase in the use of polymers as structural engineering polymers.[1] Therefore, it is very important to know the performance of polymers under external (monotonic and cyclic) loadings. Fracture is the phenomenon where materials suffer failure under external loading.[2] It is well-known that the development of cracks in metallic components of structures has led to disastrous consequences. Although much information is available concerning the deformation and fracture studies of metals, there is a need for more knowledge and understanding of the mechanical properties of polymeric materials. It is well established that two major micromechanisms are involved in the crack propagation process of glassy polymers. These are crazing and shear yielding. Both involve localized (inhomogeneous) plastic deformation, and in both, some energy is dissipated during the deformation process.[3–6]

Deformation and fracture under external loading are affected by various aspects of the molecular structure of polymers,[3–8] such as molecular weight, molecular weight distribution, cross-linking, rubber inclusion, etc. Another interesting molecular structure feature that could change the deformation and fracture properties of polymers is the presence of ionic aggregates. These exist at various levels of concentration in ionomers.

It is widely recognized that the incorporation of ions into organic polymers modifies their physical properties dramatically.[9–12] For example, the modulus of styrene copolymerized with ca. 9 mol % sodium methacrylate is ca. 10^8 N/m^2 at 180 °C, while pure polystyrene of a comparable molecular weight is an oil at the same temperature.[13] Many examples of large changes in properties are cited in recent books and reviews.[9–13] Therefore, the introduction of ionic groups into polymer chains has become an interesting and useful approach to modifying the various properties of polymers. Ionomers are ion-containing polymers which have ions in concentration up to 10–15 mol %, distributed in nonionic backbone chains. The change in properties of ionomers in the solid state is due to the clustering of ion pairs in the medium of low dielectric constant. Two types of ionic aggregates are proposed to exist according to ion content:[10] (1) below a certain ion content, multiplets consisting of a small number of ion pairs, which work as physical cross-links, dominate; (2) above that critical ion content, clusters consisting not only of ion pairs but also of portions of hydrocarbon chains, which bear many of the characteristics of microphase separation, dominate.

Although much work has been done to elucidate the structure–property relationship of ionomers, most of the properties so far discussed, such as the high-temperature modulus, the melt visosity, and the glass transition temperature, relate to the viscous liquid or rubbery phase.[10,11] Little work has been reported about the glassy-state properties, such as deformation and fracture of glassy ionomers.

In this paper, we report the results of a study on the deformation and fracture behavior of ionomers under simple tension. Recently,[14–16] we reported the fatigue properties (deformation and fracture under cyclic loading) of ionomers and suggested that there may be a signficant change in deformation and fracture behavior due to ionic aggregation. In this work, the deformation/fracture mechanisms of a sulfonated polystyrene ionomer under simple tension are studied as a function of ion content by examination of deformed thin films by transmission electron microscopy (TEM). It has been shown that TEM observation of deformed thin films of glassy polymers under simple tension can provide basic information concerning deformation/fracture mechanisms.[6,17] Prior to this study, little was known about the mechanisms of deformation and fracture of ionomers. Do they respond by crazing or shear yielding? What is the effect of ionic cross-linking? What is the effect of microphase separation of ionic regions (cluster)? etc. Answering these questions is of interest from the basic research point of view to understand the relationship between deformation/fracture behavior and microstructure of ionomers. Also, it is useful for the application of ionomers as engineering plastics.

Experimental Section

Lightly sulfonated polystyrene (S-SSA) was prepared by solution sulfonation of polystyrene according to the method by Makowski et al.[18] Details of sample preparation were described elsewhere.[14–16] However, in this work, a steam stripping method was used to recover polymer to avoid the possible effect of excess neutralizing agent.[15] All materials used were the same as those for the fatigue studies:[15,16] The starting polystyrene (Mobil PS 1800) had a weight-average molecular weight of 3.09×10^5 and a number-average molecular weight of 1.41×10^5 ($M_w/M_n = 2.2$). Ion contents of ionomers are 1.7, 2.5, 4.8, 6.1, and 8.5 mol %. As a reference material for the known occurrence of localized shear deformation, drawn films of polycarbonate (PC, Aldrich) were also examined.

Thin film samples were cast from THF solution of ionomer (3 wt %) on glass microscope slides. The films were floated off the glass slides onto the surface of a water bath from which they were picked up on a copper grid. These samples were dried at high temperature (200 °C) under vacuum for ca. 8 h. This heat history was chosen to be the same as that for fatigue samples used previously[15,16] in order to compare the results under simple tension with those under repetitive loading. After the copper grid was deformed by simple tension, the microstructure of the deformed

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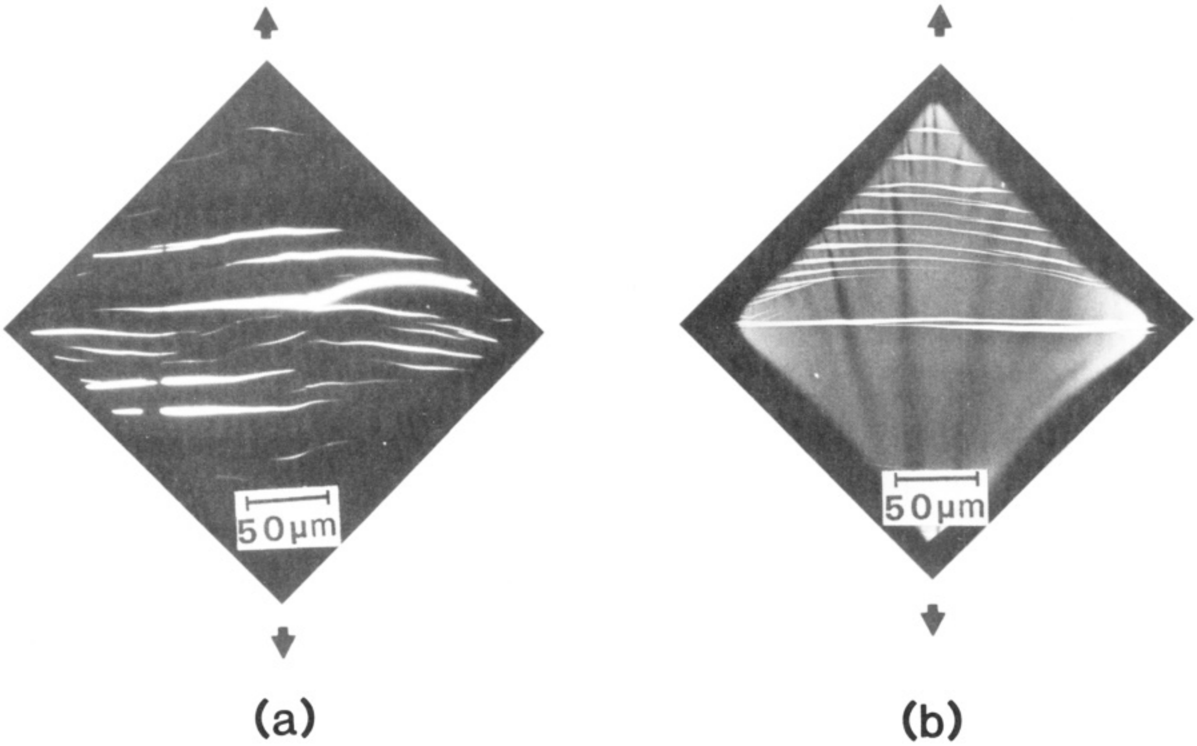


(a) (b)

Figure 1. TEM micrographs (low magnification) for (a) ionomer with 2.5 mol % ion content and (b) PS.

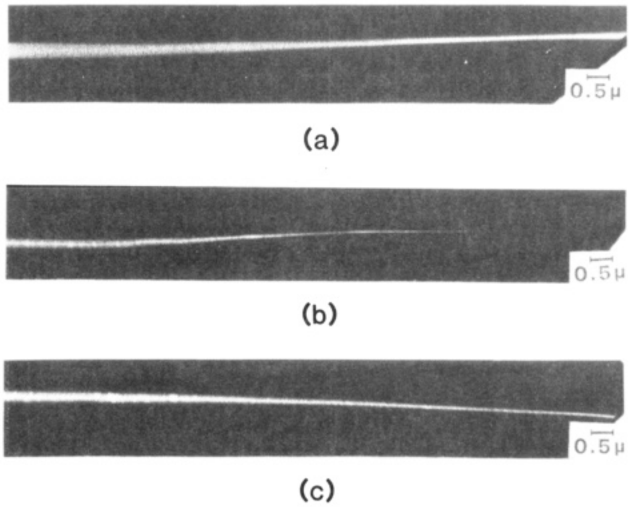
thin film was observed by transmission electron microscope (TEM) (JEM-100CX II) operating at 100 kV.

Results

Samples with Low Ion Content (Less Than 5 mol %). Figure 1 shows the TEM low magnification pictures of the deformed thin films for an ionomer (2.5 mol %) as well as for the starting polystyrene (PS). Figure 2 shows the microstructure of the craze tip region for ionomers with low ion content (2.5 and 4.8 mol %) as well as for PS. Figure 3 shows the middle part of the craze structure of each sample in Figure 2. It is seen that the basic craze structure of ionomers with low ion content (less than 5 mol %) is similar to that in polystyrene.[19] These micrographs clearly show typical structural features of crazes of glassy polymers:[5,20] (1) a midrib of lower fibril density running along the central plane of the craze, (2) sharp craze–bulk interfaces, and (3) development of craze breakdown from the bulk–craze interfaces, where pear-drop-shaped cavities are formed.

However, the following differences are observed. As is seen in Figure 1b, PS tends to form long crazes many of which extend from one end to the other of the grid bars. With increasing ion content, the crazes become shorter; i.e., craze breakdown occurs before the crazes have extended across the grid openings (Figure 1a). Also, the fracture plane within the craze becomes rougher with increasing ion content as is seen in Figure 4. The breakdown of crazes appears to occur by coalescence of pear-drop-shape cavities (seen in Figure 3) to form a larger void and then a crack.[5] If many such localized craze breakdowns occur, the crack surface becomes rougher as is seen in Figure 4b. Therefore, craze stability appears to decrease with increasing ion content.

Samples with Higher Ion Content (More Than 6 mol %). At higher ion content level (6.1 and 8.5 mol %), it is noted that fewer crazes are formed, and the direction of some of these is not perpendicular to the stress axis. Also, bifurcation of crazes is observed (Figure 5). In addition to these anomalies in craze structure, some shear character, such as localized shear deformation, also appears (Figure 6a). For comparison, a TEM micrograph taken for a polycarbonate (PC) sample under the same experimental conditions is shown in the Figure 6b. PC is known to deform by shear deformation at room temperature.[5,21] In Figure 6b, it is seen that shear bands are formed at ca. 45° to the stress direction. Simlar structure features, although in smaller degree, are seen for ionomer samples with high ion content (Figure 6a). Also, in these samples interactions between crazes and shear bands are noted. Interaction effects have been observed in other glassy polymers.[5,22]



(a)

(b)

(c)

Figure 2. TEM micrographs of craze tips for (a) PS, (b) ionomer with 2.5 mol % ion content, and (c) ionomer with 4.8 mol % ion content.

Discussion

So far, the general features of the microstructure for ionomer samples stressed in simple tension were described. Here, possible micromechanisms are discussed. At low ion

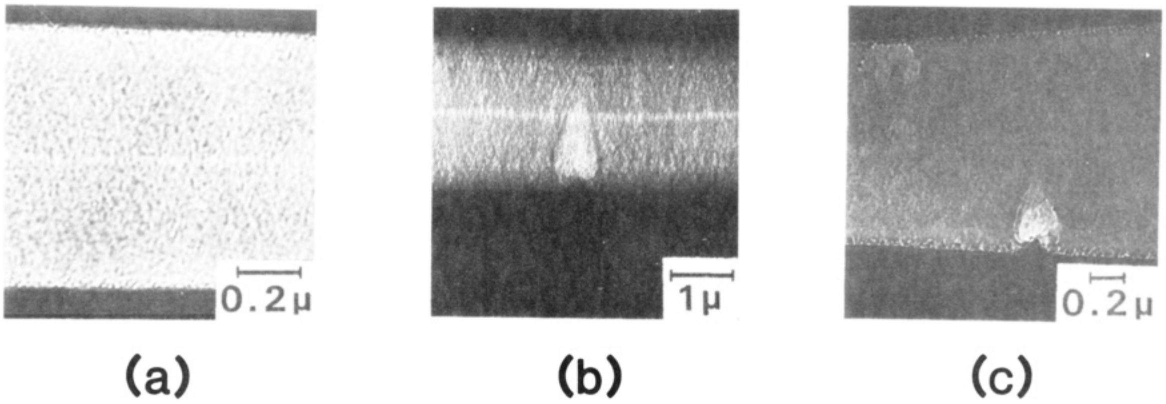


Figure 3. TEM micrographs of regions near the center of the crazes for (a) PS, (b) ionomer with 2.5 mol % ion content, and (c) ionomer with 4.8 mol % ion content.

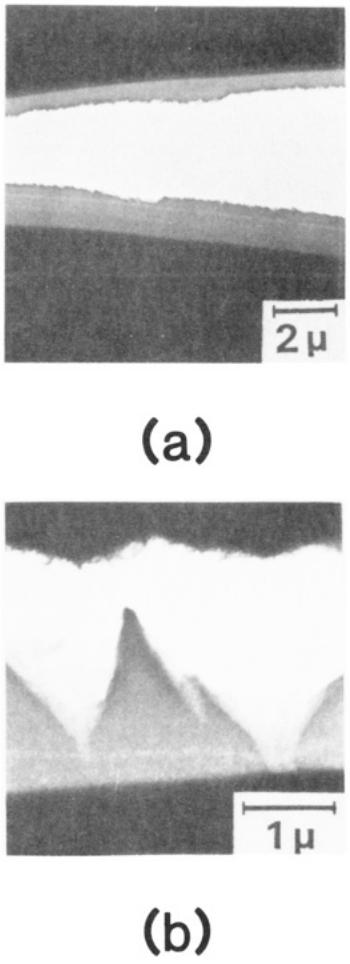


Figure 4. TEM micrographs showing the results from breakdown and crack propagation along crazes for (a) PS and (b) ionomer with 4.8 mol % ion content.

content (less than 5 mol %), only crazes are noted and these appear to become unstable with increasing ion content. This is probably due to the cross-linking effect produced by the ionic multiplets that are present. It has been shown by various experiments that small ionic aggregates (multiplets) are produced due to ionic dipole attractions and that they dominate at low ion content below the critical ion content, acting as ionic cross-links.[10] For polystyrene-based ionomers, such as sulfonated polystyrene or copolymer of styrene with sodium methacrylate, the critical ion content has been shown to be 4–6 mol %. In fatigue experiments for cross-linked polymers (PMMA, epoxy resin, etc.),[7] it has been shown that fatigue performance decreases with increasing cross-link density. Also, it was observed that the fracture energy of cross-linked PMMA decreased with increasing cross-link density.[23] This was attributed to the decrease in chain mobility, which leads to less plastic deformation. Also, the ionomers with low ion content show poorer fatigue performance with increasing ion content.[15,16] Evidently, the loss of chain mobility whether due to ionic cross-linking or to chemical cross-linking causes embrittlement of glassy polymers, and this is probably responsible for the observed effects seen here in ionomer samples with low ion content.

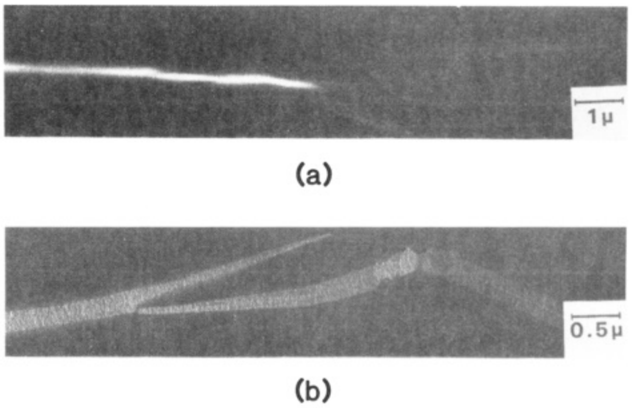


Figure 5. TEM micrographs of crazes for (a) ionomer with 6.1 mol % ion content and (b) ionomer with 8.5 mol % ion content.

However, at higher ion content (above 6 mol %), craze development is partially suppressed and localized shear deformation appears. The observations reported here seem to be consistent with observed fatigue behavior of the same ionomers.[15,16] Both behaviors change significantly at around a critical ion content (ca. 5 mol %).

Henkee et al.[24] have shown that with increasing degree of cross-linking the mode of deformation of covalently cross-linked PS changed from craze to craze/shear, to shear deformation. The formation of ionic aggregates (cluster) also increases the "effective" cross-linking density, which may lead to the changes in deformation mode from crazing only to combined craze/shear deformation. It has also been shown that the clusters developed at ion contents above the critical ion content form a tiny second phase (10–100 Å) and act somewhat like reinforcing fillers.[10] Such clusters may be partly responsible for the presence of anomalous craze structures and shear deformation. More investigation is needed to elucidate this mechanism.

Conclusions

Deformation and fracture modes of sulfonated ionomer thin films subject to simple tension were studied. It was

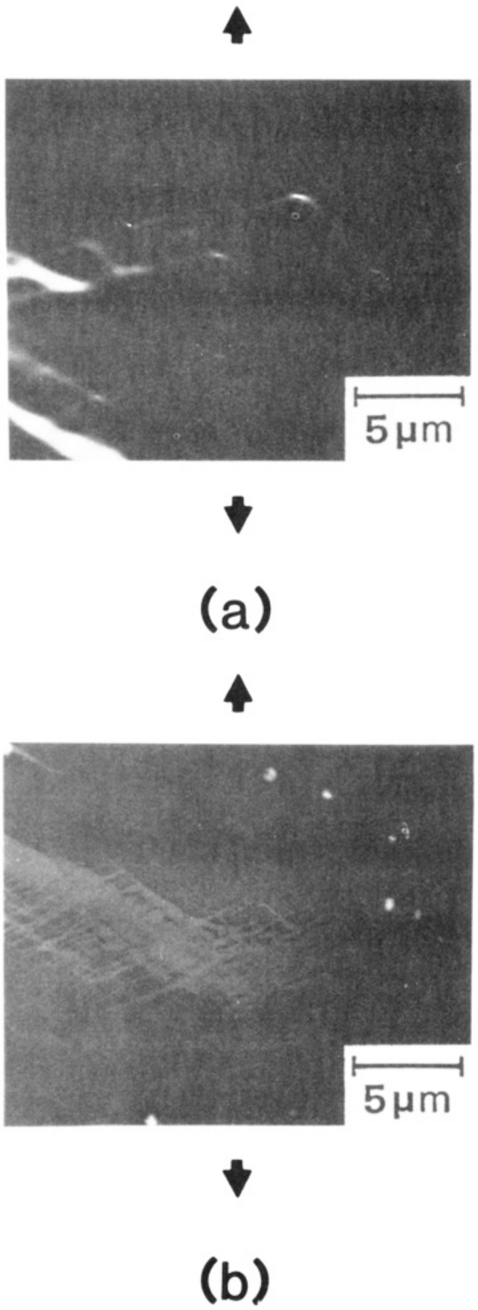


Figure 6. TEM micrographs of localized shear deformation for (a) ionomer with 8.5 mol % ion content and (b) polycarbonate.

observed that craze stability decreased with increasing ion content up to 5 mol %. This may be due to the ionic cross-linking produced by multiplets (small ionic aggregates). The craze structures of these ionomers showed typical structural features of those of glassy polymers. At higher ion content, craze growth was partially suppressed, and localized shear deformation appeared. These changes seem to be closely related to the ionic aggregate structure, although we do not know the exact role of ionic cluster formation in deformation processes at high ion content, which is the subject of future study. The work presented here is the first step in elucidating the basic deformation/fracture mechanisms of ionomers, where the amount and nature of ionic aggregates (multiplets and clusters) change by changing ionic concentration. More systematic and quantitative studies will follow this report.

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