Fatigue Behavior of Ionomers. 3. Effect of Excess Neutralizing Agent on Sulfonated Polystyrene Ionomers

M. Hara,* P. Jar, and J. A. Sauer

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

Received November 10, 1989; Revised Manuscript Received March 20, 1990

ABSTRACT: The effect of excess neutralizing agent (NaOH) on fatigue properties of lightly sulfonated polystyrene ionomers was studied. It was found that the fatigue lifetime of ionomers at 100% excess level was longer than that of ionomers without excess NaOH. This was attributed to the presence of small particles in the size range 0.1–0.5 μm made mainly of excess NaOH, which showed good adhesion with the matrix material and probably impeded crack propagation. When the NaOH was added in excessive amounts (300%), larger particles (1–5 μm) with poor adhesion to the matrix were formed and the materials became less resistant to fatigue fracture. The results obtained are consistent with the known better fatigue performance of ionomer samples made by a precipitation method, as this method can lead to retention of some of the neutralizing agent (NaOH) and thereby influence physical properties. The fracture surface of ionomers made by the precipitation method shows a similar morphlogy to that observed for the 100% excess samples, and both surfaces show features indicative of the formation of a second phase consisting mainly of NaOH.

Introduction

Various methods to improve the mechanical properties of glassy polymers have received the attention of research scientists. This is not only because more and more polymers are being used in load-bearing applications but also because a better understanding of the relationship between mechanical behavior and the molecular (or micro) structure of polymers has recently been developed.[1-4] For example, the nature of the deformation/fracture modes that are encountered in a given polymer can be generally defined in terms of the maximum extension ratio (or contour length) that is present in the glassy polymer. Also, the relationship developed appears to apply not only to homopolymers but to copolymers and cross-linked polymers as well. As a result, significant improvements in the mechanical properties of polymers have been obtained by decreasing the contour length and by increasing the network density to some optimum value.[5]

Another potential method of improving the mechanical properties is by the introduction of ionic groups (or ionic bonding) into the polymers, as has been achieved in ionomers. Ionomers are organic polymers having a small number of ionic groups per chain, generally less than 10–15 mol %.[6-10] Many studies on properties of ionomers have been conducted in the rubbery or flow region of the ionomers, and many applications have been found for ionic elastomers. However, little information has been reported about the mechanical properties of glassy ionomers, and few ionomers have been used in the glassy state.

The fracture properties of sulfonated polystyrene (S-PS) ionomers have recently been studied in our laboratory.[11-13] It has been found that when the ion content level is higher than some critical value (about 4–5 mol % for PS-based ionomers containing no excess neutralizing agent), the resistance to fracture is greater than that of the ionomer precursor (PS). This effect is attributed to the dominant effect of ionic clusters at high ion content. TEM observations of thin films subject to simple tension show that craze stability decreases with ion content below the critical content but it increases with ion content above that critical value.[12] Evidently, ionic clusters provide more effective ionic cross-linking than smaller multiplets or ion pairs, which are dominant at low ion contents, and they raise the value of the craze stress and allow shear deformation to compete with crazing as the preferred mode of deformation. In fact, both crazing and shear deformation have been observed in samples having an ion content above the critical value.[12]

It has also been observed that the resistance to fatigue fracture, under tension–compression cycling, is inferior to that of PS at low ion contents and decreases with ion content; but above the critical ion content, fatigue lifetimes were greater than that of PS and they increased with ion content.[13] Cycles to fatigue crack initiation also varied with ion content in a similar manner, probably reflecting changes in craze stability. It appears therefore that the presence of ionic clusters has a stabilizing effect on both tensile- and fatigue-induced crazes and leads to increased resistance to fracture.

In other studies in our laboratory on S–PS ionomer samples having a low ion content (2.8 mol %, Na salt), it was noted that fatigue lifetimes, under alternating tensile stresses, were higher than those of the PS precursor.[11] This result appears to be in contradiction to the findings for the Na salt ionomer system discussed above. The difference in behavior between these two investigations is believed to be due to the different methods of preparation that were used to prepare the samples. A precipitation method was used to prepare the 2.8 mol % ionomer sample,[11] while a steam stripping method was used to investigate the influence of ion content.[13] It was subsequently found that excess neutralizing agent (NaOH in this case) was retained in the ionomer samples during the process of precipitation. In the steam stripping method, with careful washing with water, there is essentially little excess neutralizing agent present.

To obtain more information about the possible role of excess neutralizing agent, in the present study we report on the result of two sets of additional experiments. In one set, carried out at a given stress amplitude under tension-compression cycling, fatigue lifetime data have been acquired on samples of two different ion contents (1.5 and 2.8 mol %) prepared by the precipitation method. Results obtained can then be compared directly with previous results acquired on samples prepared by the steam stripping method. In the second set of experiments, fatigue

---

* To whom correspondence should be sent.

0024-9297/90/2223-4964$02.50/0

lifetime data have been obtained on ionomer samples of 3.5 mol % ion content, containing respectively 0, 100, and 300% of excess neutralizing agent.

Experimental Section

Materials. Ionomer samples, lightly sulfonated polystyrene, were prepared by solution sulfonation in dichloroethane according to the method by Makowski et al.[14] The starting polystyrene (Mobil PS 1800) had a weight-average molecular weight of 3.09 $\times 10^5$ and a number-average molecular weight of 1.41 $\times 10^5$ ($M_w/M_n = 2.2$). Two different procedures were used in this study to recover polymers. The first method was a precipitation method: after the sulfonation reaction was terminated, a large amount of NaOH (dissolved in methanol) was added to the reactant, followed by precipitation into nonsolvent (methanol). The polymer was collected by filtration and dried at 80 °C for 48 h. This procedure was used for only low ion content samples (1.5 and 2.8 mol %). The second method was a steam stripping method: after the termination of the sulfonation reaction to give an ion content of 3.5 mol %, the calculated amount (i.e., 0, 100, and 300% excess) of NaOH was added to the reactant, followed by steam stripping in boiling water. In order to keep excess NaOH in the samples, the polymer was not washed repeatedly by water, as is usually the case. It should be mentioned, however, that some of the excess NaOH added at the beginning was washed out during the steam stripping process. Therefore, the sample with 100% excess means that 100% excess NaOH was added to the acid solution at the beginning and does not reflect the exact amount (somewhere between 0 and 100%) of NaOH retained in the polymer. The recovered polymer was first dried at 80 °C and then at 120 °C for about 1 week to remove residual water.

All fatigue specimens were made by compression molding. They were molded into a 15 cm × 1.6 cm × 1.6 cm rectangular bar and then machined 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 grip ends). All specimens were carefully polished by using fine grades of emery papers (400, 600, 0000, in that order) and, finally, by lens polishing papers until no scratches were detectable under the optical microscope. Usually, five samples were tested for each ion content or each excess NaOH amount.

Measurements. Fatigue measurements were carried out on an Instron Servohydraulic testing machine (Model 1350) at room temperature. Since previous test results on samples prepared by the precipitation method were made only under tension cycling,[11] it was decided to test precipitated samples (1.5 and 2.8 mol % ion content), under the same test conditions used for samples prepared by the steam stripping method (viz., tension-compression cycling at maximum and minimum stress values of +11 and −11 MPa, using a sinusoidal wave form at a frequency of 5 Hz). In a second set of measurements designed to study the effects of excess neutralizing agent, samples of 3.5% ion content were prepared by the steam stripping method and tested under tension–compression cycling at a stress amplitude of 16.5 MPa and at 5 Hz.

After the samples had fractured as a result of many cycles of fatigue loading, fracture surfaces were examined by a scanning electron microscope (SEM) (Etec) after the surfaces were coated with a thin film of gold. Pictures were taken from various angles by tilting the specimen. In our fatigue experiments, any temperature rise due to hysteresis of the ionomer specimens, as well as of the PS samples, is expected to be small in view of the very low tan δ value at room temperature for these samples.[15,16] Therefore, failure is a result of mechanical fatigue involving both a crack initiation phase and a crack propagation phase.

Results

Precipitated Samples. Figure 1 shows S–N curves for ionomer samples, with 2.8 mol % ion content, prepared by the precipitation method, and for PS samples.[11] Although only a relatively small number of specimens were tested, it appears that the fatigue lifetimes of the ionomer samples are considerably longer than the samples of the precursor, PS, under the testing conditions employed (tension cycling and a frequency of 0.5 Hz). The results of additional tests on this same ionomer, and of other ionomer samples having 1.5 mol % ion content, are shown in Figure 2. These measurements were made under tension–compression cycling at a stress amplitude of 11 MPa and at 5 Hz. The stars on this graph represent data obtained on the precipitated samples, and the closed squares represent previous data obtained on steam-stripped samples with no excess NaOH.[13] It is evident that samples obtained by the precipitation method show better fatigue performance than their PS precursor, even though samples of comparable ion contents obtained by steam stripping show poorer performance than PS.

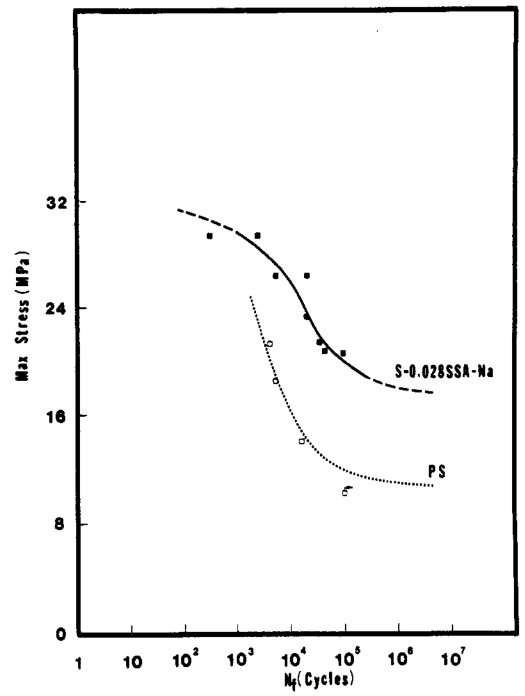

Figure 1. Applied stress vs number of cycles to fracture for ionomer samples with 2.8 mol % ion content (made by precipitation) and for samples of PS, all tested at 0.5 Hz.

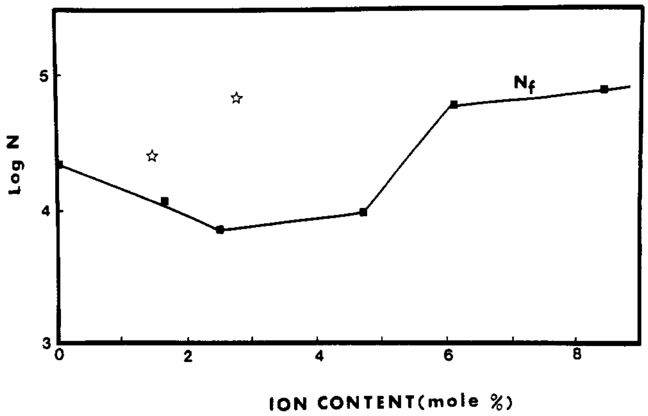

Figure 2. Effect of ion content on cycles to fracture, N_f, for ionomer samples made by steam stripping (closed squares) and by precipitation (stars) and tested under tension–compression cycling at a stress amplitude of 11 MPa and at 5 Hz.

The fatigue results described above were obtained under load-controlled conditions; i.e., specimens were cycled from a maximum to a minimum, controlled-stress amplitude. However, because the maximum stress employed in the fatigue experiments was relatively low and because the stress–strain relation is essentially linear (as shown by test records acquired under simple tension), it is expected that similar fatigue results, and similar fatigue rankings, would

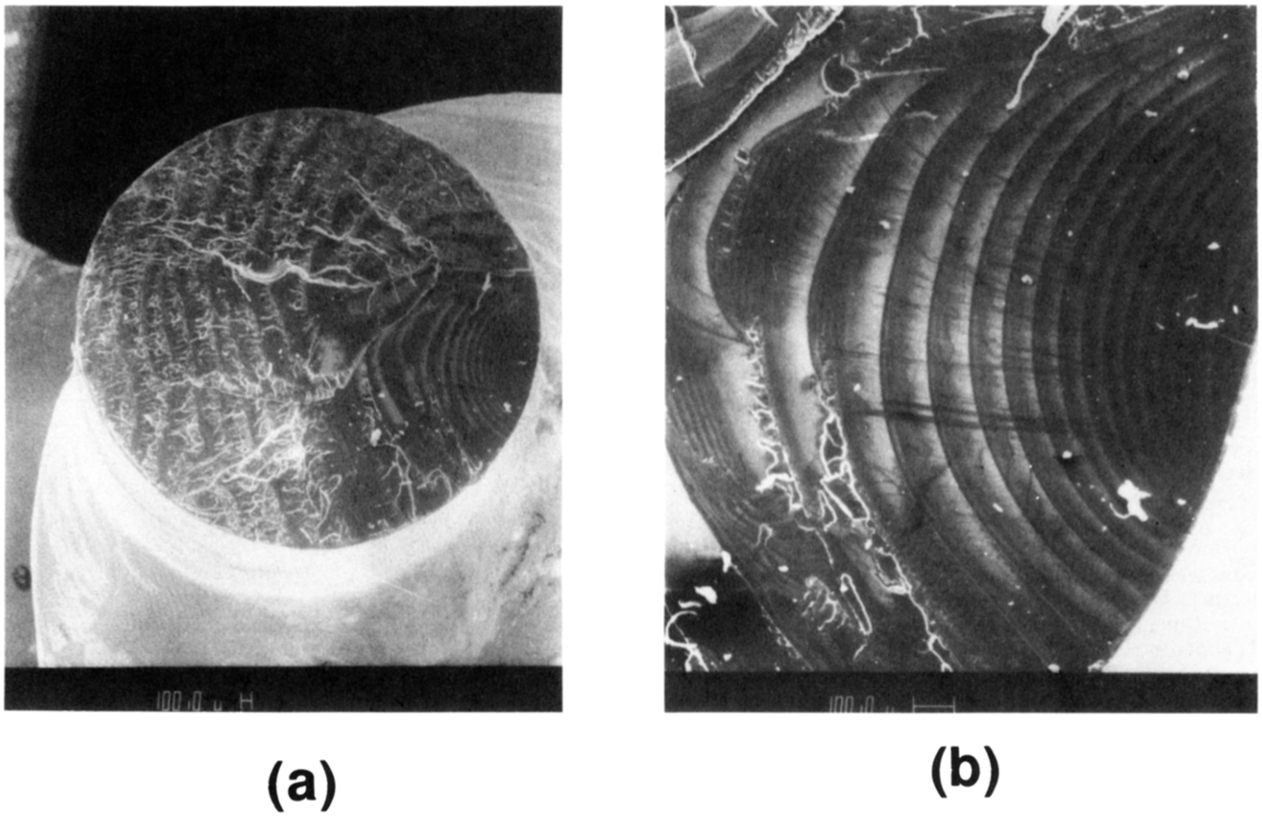

Figure 3. Fatigue fracture surface of an ionomer precursor (PS) tested under tension cycling at 0.5 Hz and at a maximum stress of 13.8 MPa: (a) entire fracture surface; (b) region near the fracture source, showing DCG bands.

also be obtained for tests performed under controlled-strain cycling.

To obtain information about deformation and fracture modes operative during cyclic loading, fracture surface morphologies were examined by SEM for samples of the PS homopolymer and for S–PS samples prepared by both the precipitation and the steam-stripping methods. Figure 3 shows the fracture surface of a specimen of the homopolymer, PS, tested in cyclic tension at a maximum stress of 13.8 MPa and at 0.5 Hz. Figure 3a is a scan of the entire fracture surface, and Figure 3b shows the region surrounding the fracture source. The fatigue fracture surface is typical of that of many glassy polymers.[16–18] In the region near the crack initiation site, one sees a series of so-called discontinuous crack growth (DCG) bands whose spacing increases with depth of the crack. These bands arise from periodic crack propagation through a steadily growing areal craze.[4,18] When sufficient fatigue-induced damage is done to the craze ahead of the crack tip, the crack jumps forward into the damaged craze and then arrests. With continued cycling, this process repeats. Beyond the DCG band region lies a rougher region, which arises from fast crack propagation during the late stages of fracture.

Figure 4 shows the fracture surface morphology of an ionomer sample of 2.8 mol % ion content, prepared by the precipitation method, and tested at 0.5 Hz and at a maximum stress of 22 MPa under tension cycling. For this sample, which has about the same lifetime as that of the PS sample shown in Figure 3, most of the fracture surface possesses a lightly textured morphology (Figure 4a) and a small, slow-growth region appears to be present near to the crack initiation site (Figure 4b). Also, in this region near the fracture source, no DCG bands are observed.

Figure 5 shows a high-magnification scan of the fracture surface morphology near the fracture source for the ionomer sample with 2.8 mol % ion content, prepared by the precipitation method. This sample was tested at a stress amplitude of 11 MPa under tension–compression cycling and at a frequency of 5 Hz. Many small second-phase particles, generally in the size range from 0.1 to 0.5 μm, are present. These particles are considered to arise from the excess NaOH incorporated during the preparation procedure since the fracture surface, for the same ionomer without excess NaOH, does not show any second phase. The particles are clearly not ionic clusters, as it is known from the results of SAXS measurements made on ionomer samples that the size of such clusters is much smaller (in the range from 10 to 100 Å).[6,10]

Samples Prepared by Steam Stripping. Table I summarizes the fatigue lifetime data obtained on steam-stripped samples having various amounts of excess NaOH. These results were obtained on specimens of 3.5 mol % ion content, tested in tension–compression cycling at a stress amplitude of 16.5 MPa and at 5 Hz. The data show that samples having 100% excess NaOH have an average fatigue lifetime, N_f, that is about 5 times better than that of the samples having no excess neutralizing agent. However, when too much excess NaOH (300%) is present, the fatigue performance is inferior to that at the 0% excess NaOH level.

The fracture surface morphology, especially when viewed at high magnification, also appears to vary with the amount of excess NaOH that is present. For the sample containing 100% excess NaOH, two high-magnification scans are shown in Figure 6. Figure 6a reveals the presence of many small particles, in the size range 0.1–0.5 μm, that appear to be well bonded to the matrix. Figure 6b shows both the small, essentially spherical particles as well as what appear to be collapsed craze fibrillar elements. The small particles are believed to arise from the excess NaOH that was intentionally added to the system before steam

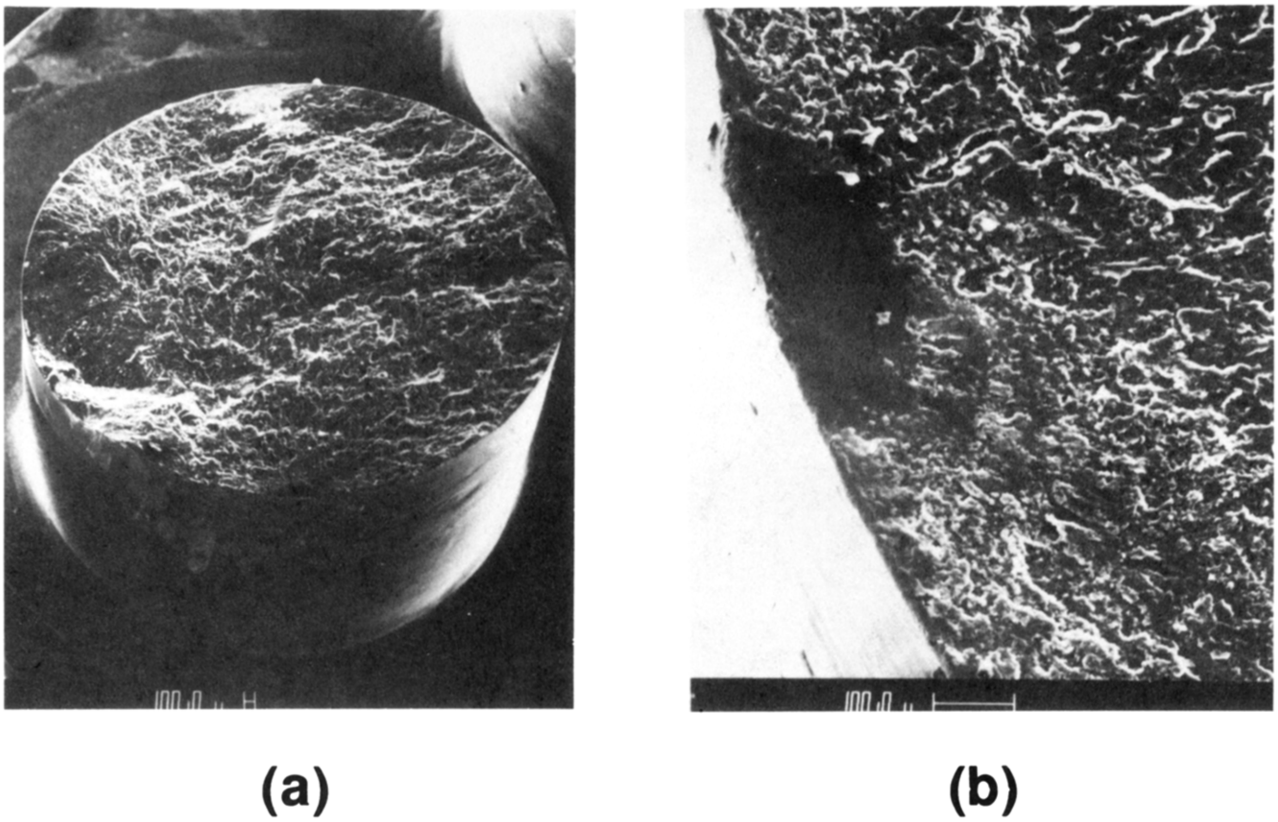

Figure 4. Fatigue fracture surface of a precipitated sample of 2.8 mol % ion content tested under tension cycling at 0.5 Hz and at a maximum stress of 22 MPa: (a) entire fracture surface; (b) region around the fracture source.

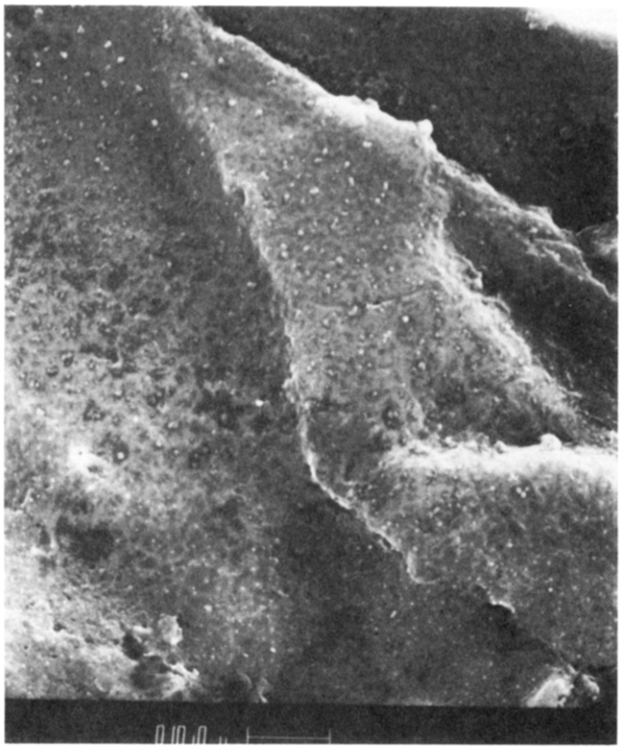

Figure 5. High-magnification view of a portion of the fatigue fracture surface near the fracture source for an ionomer sample of 2.8 mol % ion content (made by precipitation) and tested under tension–compression cycling at 11 MPa and at 5 Hz.

stripping. Very few, if any, such particles are seen on the fracture surfaces of samples having no excess neutralizing agent.

Table I
Effect of Excess NaOH on the Number of Cycles to Fracture, N_f, for Ionomer Samples Subject to a Stress Amplitude of 16.5 MPa at 5 Hz

excess amount of NaOH, %	N_f	excess amount of NaOH, %	N_f
0	3.3×10^4	300	1.9×10^4
100	1.5×10^5		

Figure 7 is a high-magnification scan of a portion of the fracture surface of a sample containing 300% excess NaOH. Small particles, in the size range 0.1–0.5 μm, are present as well as some larger particles. The small particles, as noted above, appear to be attached to the matrix material, but the irregularly shaped, larger particles, which on this SEM scan are about 1 μm in size and which generally fall in the range from 1 to 5 μm, appear to be poorly bonded to the matrix.

Discussion

In samples having no excess neutralizing agent, enhancement of fatigue performance can be realized, as the data of Figure 2 shows, by increasing the ionic content to 5 mol % or higher. This result has been attributed, as noted in the Introduction, to the presence in these samples of ionic clusters that increase network density and raise the stress required for development of craze deformation.[13] As a result, some shear deformation as well as some crazing is present. This allows a greater number of cycles to occur prior to crack formation and fracture and causes the fracture surface to be considerably rougher than that of the precursor, PS.

However, our principle interest in the present study is not with the effects of ion content but with the influence of excess neutralizing agent on the mechanical behavior of S–PS ionomer samples. All our tests have been carried out on ionomer samples that have less than the critical ion content (~5%) at which ionic clusters become dominant.

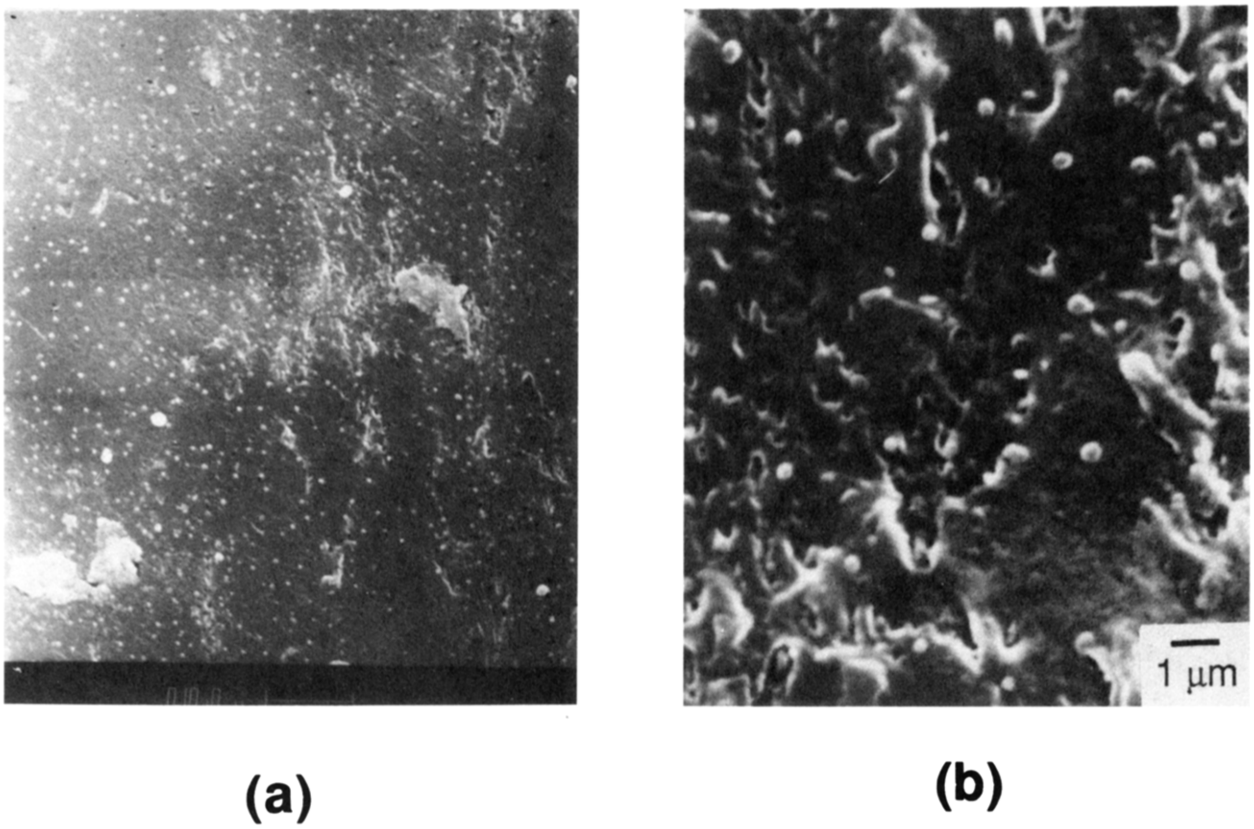

Figure 6. Fatigue fracture surface of an ionomer sample of 3.5 mol % content and 100% excess NaOH (made by stem stripping) and tested at a stress amplitude of 16.5 MPa and at 5 Hz: (a) high-magnification view of a region near the fracture source; (b) a still higher magnification view of a portion of (a).

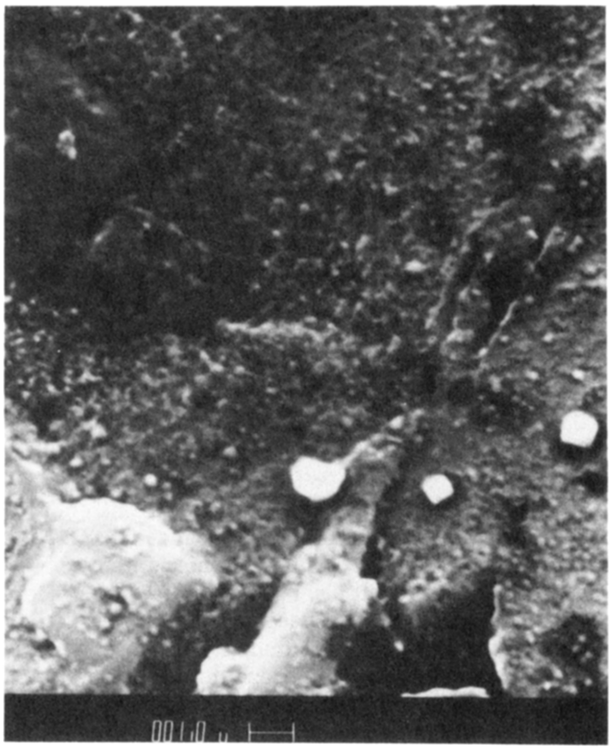

Figure 7. High-magnification scan of a portion of the fatigue fracture surface near the fracture source of an ionomer sample of 3.5 mol % ion content and 300% excess NaOH (made by steam stripping) and tested at a stress amplitude of 16.5 MPa and at 5 Hz.

For such samples that have no excess NaOH, the data of Figure 2 show that average lifetimes to failure are less than that of PS samples. But, when these results are compared with results obtained under the same test conditions on precipitated samples, which do contain excess neutralizing agent, it is evident from the fatigue data of Figure 2 that fatigue lifetimes have been considerably extended. In the samples with no excess NaOH, the inferior fatigue performance is attributed to a decrease in chain mobility, caused by the development of some degree of ionic cross-linking, and to more rapid craze breakdown and crack formation. In this connection, it may be noted that, in strained thin film specimens of similar ionomers, earlier craze formation and more rapid crack development have been observed.[12]

The question that remains to be considered is why is fatigue performance improved significantly when some excess neutralizing agent is present? Although the answer to this question is not yet clear, it is suggested that when there is an excess of neutralizing agent, the additional ions are attracted to the ionic multiplets and to any ionic clusters that may be present. The excess NaOH may then serve to bond some of the swollen multiplets or clusters together to form larger size particles, such as those seen on the fracture surface of the 2.8 mol % samples shown in Figure 5. Since similar second-phase particles are not seen on the fracture surface of the steam-stripped samples, it is reasonable to conclude that these arise from the presence of excess neutralizing agent. The small, second-phase particles, which appear to be well-bonded to the matrix, probably enhance fatigue performance by providing resistance to crack propagation. It may be noted that the presence of small, dispersed particles (rubber particles in this case) also increases the resistance to fatigue crack propagation in ABS.[4,18] In the S–PS ionomers, the small particles, consisting mainly of excess NaOH, may also act as sites of localized shear deformation and thereby contribute to craze stability and to greater resistance to crack initiation.

Additional support for the interpretation of the fatigue results shown in Figure 2 comes from the results of the second set of experiments in which tests were made on steam-stripped samples in which different amounts of excess NaOH were intentionally added. As the data of Table I show, an appreciable increase in fatigue life has been realized in the ionomer samples having 100% of excess NaOH. Again, examination of fracture surfaces by SEM (Figure 6) shows that many small dispersed particles, similar in size to those noted on the fracture surface of the precipitated samples shown in Figure 5, are present. Thus enhanced fatigue performance has been achieved in precipitated samples, having an unknown amount of excess neutralizing agent, and in stream-stripped samples containing 100% excess NaOH. In both instances, fracture surface examination shows the presence of coherent small particles that provide some resistance to fatigue crack propagation and thus enhance fatigue lifetimes.

It is pertinent to compare our result, obtained on glassy ionomers, with literature accounts of the effects of excess neutralizing agent on the properties of elastomeric ionomers. For example, Bagrodia et al.[19] have studied the effects of excess neutralizing agent on the properties of sulfonated, polyisobutylene telechelic ionomers. They observed an increase in high deformation properties in samples containing excess neutralizing agent and proposed that the additional ions from the excess neutralizing agent resided at the ionic sites and strengthened the degree of ionic cross-linking. In another study, Duvdevani et al.[20] investigated the effects of excess zinc stearate on the properties of a sulfonated EPDM (ethylene–propylene–diene) ionomer. They reported that the excess zinc stearate formed a second crystalline phase, with size ~1 μm, which acted as a reinforcing filler and enhanced the tensile properties. Both of these studies involved elastomeric ionomers, and, therefore, the reinforcing mechanisms may be different from those in glassy ionomers, such as the sulfonated polystyrene ionomers that we have studied. Nevertheless, it is now apparent for both rubbery and glassy ionomers that the presence of small, second-phase particles, formed from the excess neutralizing agent, can significantly enhance mechanical performance.

The results of the present study also show that while some excess neutralizing agent is beneficial to performance, too much excess neutralizing agent can be harmful. For example, when samples of the 3.5 mol % ionomer were given 300% excess NaOH, the average fatigue life, as Table I indicates, dropped significantly and fell below that of samples with no excess neutralizing agent. The poorer performance of these samples is attributed to the presence of relatively poorly bonded particles, in the size range from about 1 to 5 μm. Some of these large inclusions are seen on the SEM scan of Figure 7. These poorly bonded particles act as stress raisers, cause earlier craze initiation, and are not effective in impeding crack propagation. Hence, when too much excess neutralizing agent is present, fatigue life is reduced.

Conclusions

The fatigue behavior of sulfonated polystyrene ionomers was studied as a function of the amount of excess neutralizing agent (NaOH). It was found that the fatigue performance of ionomers with 100% excess NaOH was better than that of ionomers with no excess NaOH because of the enhanced resistance to crack propagation provided by the presence of small particles of 0.1–0.5 μm made mainly of NaOH. However, when an excessive amount of neutralizing agent was added (300%), larger particles with relatively poor adhesion to the matrix were formed and the materials became less resistant to fatigue fracture.

These results help to explain the observed better fatigue performance of ionomer samples made by the precipitation method and tested under tension cycling (Figure 1) or tension–compression cycling (Figure 2). Here, too, examination of fatigue fracture surfaces indicates that small, second-phase particles, similar to those observed in the 100% excess NaOH samples, were dispersed throughout the material. This is a clear indication that the precipitation procedure introduces excess NaOH into the samples; and this excess neutralizing agent then forms a second phase in the material and makes the material more resistant to fatigue fracture. The results obtained in this study are interesting from the viewpoint of structure–property relationships, and they are also significant to the practical use of ionomers as engineering plastics.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the U.S. Army Research Office is also gratefully acknowledged. M.H. also acknowledges the support provided by the Trustees Research Fellowship Award from Rutgers University.

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) Hertzberg, R. W.; Manson, J. A. *Fatigue of Engineering Plastics*; Academic: New York, 1980.
(5) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *52/53*, 1.
(6) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.
(7) MacKnight, W. J.; Earnest, T. R. *Macromol. Rev.* **1981**, *16*, 41.
(8) Wilson, A. D.; Prosser, H. J., Eds. *Development in Ionic Polymers*; Applied Science: New York, 1983.
(9) Eisenberg, A., Bailey, F. E., Eds. *Coulombic Interactions in Macromolecular Systems*; ACS Symposium Series 301; American Chemical Society: Washington, DC, 1986.
(10) Pineri, M., Eisenberg, A., Eds. *Structure and Properties of Ionomers*; NATO Advanced Study Institute Series; Plenum: New York, 1987.
(11) Hara, M.; Jar, P. *Polym. Commun.* **1987**, *28*, 52.
(12) Hara, M.; Jar, P. *Macromolecules* **1988**, *21*, 3187.
(13) Hara, M.; Jar, P.; Sauer, J. A. *Macromolecules* **1988**, *21*, 3183.
(14) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3870841, 1975, assigned to Exxon Research and Engineering Co.
(15) Sauer, J. A.; Hara, M. *Adv. Polym. Sci.* **1990**, *91/92*, 69.
(16) Sauer, J. A.; Richardson, G. C. *Int. J. Fract.* **1980**, *16*, 499.
(17) Hertzberg, R. W. *Deformation and Fracture Mechanics of Engineering Materials*; Wiley: New York, 1983.
(18) Sauer, J. A.; Chen, G. C. *Adv. Polym. Sci.* **1983**, *52/53*, 169.
(19) Bagrodia, S.; Tant, M. R.; Wilkes, G. L.; Kennedy, J. P. *Polymer* **1987**, *28*, 2207.
(20) Duvdevani, I.; Lundberg, R. D.; Wood-Cordova, C.; Wilkes, G. L. *ACS Symp. Ser.* **1986**, *302*, 184.

Registry No. NaOH, 1310-73-2.