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Fatigue behaviour of sulfonated polystyrene ionomers and their blends with polystyrene

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The resistance to fracture under alternating cycles of stress is examined for sulfonated polystyrene (SPS) ionomers. The influence of ion content on the number of cycles to failure and on fracture surface morphology has been determined. At low ion contents below 3 mol%, the fatigue resistance was found to be essentially unaffected, or slightly increased; but, in the range of ion contents from 4 to 6 mol%, cycles to failure increased appreciably. This behaviour, rather similar to the known influence of ion content on tensile strength, is attributed to the importance of a growing ionic cluster phase that leads to an increased strand density. Fatigue tests were also run on two series of blends of the SPS ionomer with polystyrene. In the first series, as the concentration of the SPS ionomer component (2.65 mol%) was increased, the average fatigue lifetimes were reduced with an apparent minimum at 30 wt%. In the second series of blends, containing 10 wt% of SPS ionomer, the fatigue resistance decreased as the ion content of the ionomer was increased. These results are discussed in terms of the two-phase nature of the blends and the influence of alternating stressing on the extent of bonding between the SPS ionomer particles and the polystyrene matrix. Copyright © 1996 Elsevier Science Ltd.

(Keywords: fatigue behaviour; sulfonated polystyrene ionomer; blend of sulfonated polystyrene ionomer and polystyrene)

INTRODUCTION

It is well established that an introduction of ionic groups into a polymer has a significant effect on microstructure and on properties[1–8]. As originally proposed by Eisenberg[9], the interaction between ionic groups leads to the formation of multiplets, containing a small number of ion pairs, and ionic clusters, which constitute a second phase and which contain many multiplets as well as portions of the hydrocarbon chains. This multiplet-cluster model of ionomers has been recently refined to accord more fully with results obtained from both dynamic mechanical data and from studies of small-angle X-ray and neutron scattering; it is now generally referred to as the EHM model[10]. In this model, the meaning of the multiplet is the same as in the original model: an aggregate of several ion pairs. However, the meaning of the cluster is modified: the cluster is considered to be a contiguous region including many multiplets, chain mobility around which is reduced, and is now large enough to have its own T_g. As a result of their 'two phase' microstructure, ionomers develop two glass transition temperatures, one associated with the multiplet-containing matrix, and a second one, at a higher temperature, which is associated with onset of mobility in the ionic cluster 'phase'. The ionic interactions act rather like physical cross-links. With increasing ion content, the rubbery plateau modulus and both glass transition temperatures increase in value.

For sulfonated polystyrene (SPS) ionomers, it appears that there is a critical ion content, about 6 mol%, where the ionic cluster phase becomes dominant over the multiplet-containing matrix phase[10–12]. This has important implications for mechanical properties as well as for elevated temperature relaxation behaviour[4]. For example, as the ion content approaches the critical value, not only is there a rise in the rubbery plateau modulus but there is a change in the deformation mode of strained thin films from crazing only to combined crazing and shear[13,14], and a significant increase in the tensile strength and toughness (the energy to fracture)[15]. The enhancement in mechanical properties is attributed to the effects of an intensifying ionic cluster 'phase' which, by providing more effective entanglement, increases craze stability and leads to a greater resistance to fracture. The significant role played by molecular entanglements in determining deformation modes and resistance to fracture has been recently described by Kramer and coworkers[16,17]. They have shown that in amorphous polymers, including homopolymers, random copolymers, and miscible blends, a determining factor governing the deformation mode is strand density[16]. The strand density is defined as the number of strands (a chain segment bounded by cross-links or entanglement points) per unit volume; here, polymers are considered to consist of a network of molecular strands[17]. We have extended the concept of the strand density to include an ionic cross-linking effect[18] by considering the fact that the effectiveness of cross-linking is less for ionic cross-links than for covalent cross-links. We have also pointed out

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that the effectiveness of ionic cross-links (due to multiplets) depend on their locations, i.e., whether they are in a matrix phase or in a cluster phase: the effectiveness of the latter case should be higher, as seen in changes of deformation modes as well as of bulk mechanical properties.

One purpose of the present paper is to examine how the presence of ionic groups in SPS ionomers affects another important mechanical property, viz. the resistance to fracture under repetitive loading. Under reversed stressing, to which many polymer products are subject in actual applications, failure generally takes place in a brittle manner with little or no plastic deformation. Failure occurs, even at relatively low stress amplitudes, after some critical number of cycles[19,20]. Hence, the effect of any material variable on fatigue performance may differ from its effect on static tensile properties.

One investigation of the influence of ion content on the fatigue behaviour of SPS ionomers has been reported[21]. In this study, the ionomer samples were prepared from a polystyrene (Mobil PS1800) that is thought to contain some mineral oil as a processing agent, and all samples were moulded at relatively low temperatures. Since both of these factors may have significant effects on the results, it was decided to do a new study in which the polymer was free of additives and in which appreciably higher moulding temperatures were used so as to more fully develop the equilibrium microstructure of the ionomers. Processing conditions and sample history are known to have a significant effect on microstructure and properties of ionomers[22]. For example, a sulfonated polystyrene ionomer (Na salt) containing 2.5 mol% ion content, and moulded at a relatively low temperature (135°C), exhibited no rubbery plateau region above its T_g; but, after the sample was given an additional treatment, it developed an extended rubbery plateau region and displayed a second T_g, indicative of the presence of an ionic cluster phase, near 225°C. For some ionomers, such as those based on poly(ethylene-*co*-methacrylic acid), even simple aging at ambient temperature can influence the mechanical behaviour[23].

A second purpose of the present study is to investigate the fatigue properties of blends of SPS ionomer with polystyrene (PS). Because the two components of these blends are immiscible due to the difference in polarity of the two polymers, the ionomer component micro-phase separates when added in small amounts (less than 30 wt%) and appears as small dispersed particles in the PS matrix. In such blends interesting synergistic effects arise and addition of even a small amount (5–10 wt%) of the ionomer component can significantly increase the tensile strength and toughness of polystyrene[24]. Scanning electron microscope (SEM) scans of the tensile fracture surfaces show that there is good interfacial adhesion between the two components and that the rigid, second-phase ionomer particles share in carrying the applied load. Whether this good adhesion can be maintained under severe conditions of alternating loading and whether fatigue lifetime, like tensile strength, can be enhanced by blending, are questions to be investigated.

EXPERIMENTAL

Materials

Lightly sulfonated polystyrene (SPS) was synthesized from a polystyrene homopolymer (Polysciences, PA, USA), free of additives, and with a molecular weight in the range 125 000 to 250 000. Sulfonation was carried out by the procedure described by Makowski *et al.*[25]. Acid groups of the SPS were fully converted to the Na-salt form by appropriate addition of sodium hydroxide (NaOH) dissolved in methanol and the ionomers were recovered by steam stripping. Na-salt SPS ionomers with ion contents of 2.65, 4.35, 5.26, and 7.48 mol% were selected for this study. For preparing blends of the SPS ionomer with PS, each component was dissolved in a solvent mixture of 1,2-dichloroethane (DCE)/methanol (90/10 v/v) and the blend material recovered by steam stripping. More details of the preparation procedure have been given elsewhere for both the SPS ionomer[15] and the SPS ionomer/PS blends[24].

Fatigue measurements

Samples for fatigue studies were machined from compression moulded bars to specimens of 7.62 cm in length, 1.27 cm in diameter at the threaded ends and 0.51 cm in diameter at the reduced central section. SPS ionomer samples were made by compression moulding at a pressure of 750 psi for 45 min at a specific moulding temperature and then cooled under pressure to 85°C. Because of the increased melt viscosity of the SPS ionomers as ion content rises, the moulding temperatures chosen for this study were successively raised from 130°C for the PS to 190°C, 210°C, 210°C and 225°C for the SPS ionomer samples having respectively 2.65, 4.35, 5.26, and 7.48 mol% ion contents. SPS ionomer/PS blend samples were made by compression moulding at a pressure of 500 psi for 30 min at a specific temperature and then cooled under pressure to 85°C. To remove surface scratches, all samples were carefully polished with successive finer grades of emery paper. The fatigue tests were carried out in a sinusoidal, tension-compression mode on an Instron servohydraulic testing machine at a stress amplitude of 11 MPa and a frequency of 5 Hz.

Scanning electron microscopy

The fatigue fracture surfaces of many ionomer samples and blend specimens were coated with a thin layer of gold and then examined in an ETEC scanning electron microscope.

RESULTS AND DISCUSSION

Sulfonated PS ionomers

Figure 1 shows how the average fatigue lifetime to fracture, N_f, varies with ion content for the SPS ionomers. The solid points represent average values based on the testing of three or four specimens, except for an ion content of 4.35 mol% where only two specimens were tested. The vertical bars signify mean deviations about the average. As usual for fatigue tests, there is an appreciable scatter in the data caused by the presence of stress concentrating surface imperfections. Although it would be desirable to have data on more specimens and at more ion contents, it is evident from *Figure 1* that a significant contribution to fatigue resistance occurs for ion contents above 4 mol%, with a possible a maximum lifetime being reached in the range of 5–6 mol%.

Before discussing the fatigue fracture surface morphology of the ionomer samples, we briefly review what

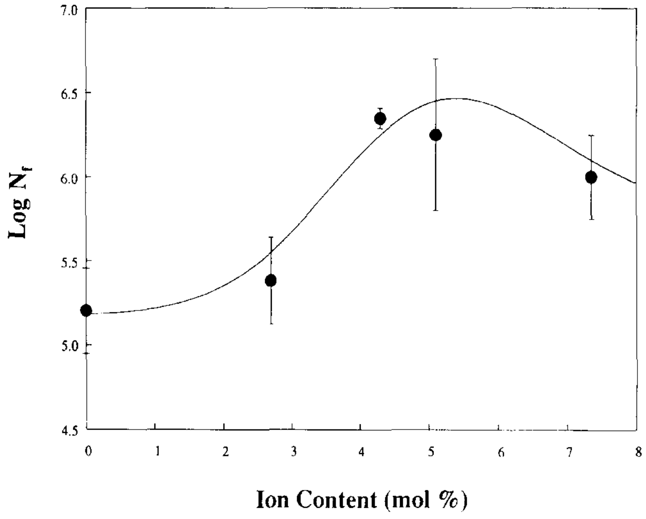

Figure 1 Log N_f vs. ion content for SPS ionomers. A curve is drawn to guide the eye

is known about the nature of fatigue fracture in PS. This polymer has been thoroughly investigated at many different stress amplitudes and over a wide range of frequencies[19,20,26]. In general, especially at relatively low frequencies and stress amplitudes, four distinct regions appear on the fatigue fracture surface[26]. First, there is a smooth mirror-like region surrounding the fracture source, which frequently contains a series of discontinuous crack growth (DCG) bands indicative of periodic crack movements through a single growing areal craze. This region is generally followed by a fairly smooth region exhibiting parabolic features caused by intersection of the primary crack front with secondary cracks induced by heterogeneities lying ahead of the crack front. A less smooth region where the crack front may bifurcate, by breaking through crazes that developed slightly above or below the main crack plane, then follows. The last region of rapid crack growth has a rough surface and, at its inception, one may see a series of hackle bands similar in nature to those seen on tensile fracture surfaces.

Figure 2 is a low magnification scan of the fatigue fracture surface of an SPS ionomer sample of 5.26 mol%. A similar fracture surface morphology was observed for the 4.35 mol% samples. The four regions of different topology, described above for PS, are also present on the fatigue fracture surface of these ionomers. However, there are some differences. First, the smooth regions for the ionomer samples of high ion content are greater in extent than for samples of PS or of SPS samples containing an ion content of 2.65 mol%. The larger extent of the smooth slow growth regions is indicative of a longer lifetime to fracture for ionomer samples that contain a significant amount of the ionic cluster phase in their microstructure. Another difference is that DCG bands are apparently not present in the mirror-like region of the fracture surface of the ionomer samples. This may be a result of an ionic cross-linking effect which, by increasing the entanglement density, hinders the growth of large crazes.

Figure 3 is an SEM scan of a region on the fracture surface at the onset of rapid crack growth for an SPS ionomer sample of 5.26 mol% ion content. The bands seen here are not DCG bands as such bands are seen only in the mirror-like region surrounding the fracture source[19]. Instead, they are hackle bands typical of those seen in tensile fracture. They result from instabilities in the rapid crack growth process[27], which here occurs in the last tensile cycle prior to failure. The width of these bands appears to decrease with increase of ion content and this fact was also noted from SEM scans of tensile fracture surfaces of the SPS ionomers[15]. The decrease in hackle band width as ion content rises and the fatigue crack grows longer, is probably a reflection of a higher crack tip stress, and hence a more rapid craze

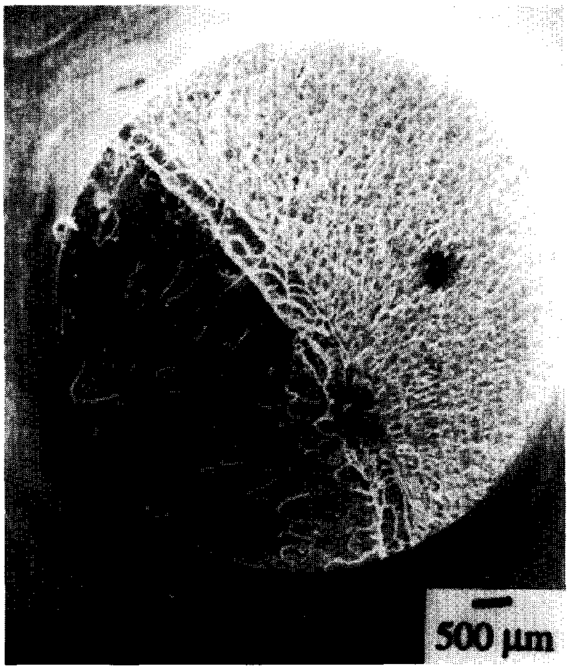

Figure 2 SEM scan for fatigue fracture surface of an SPS ionomer containing 5.26 mol% ion content

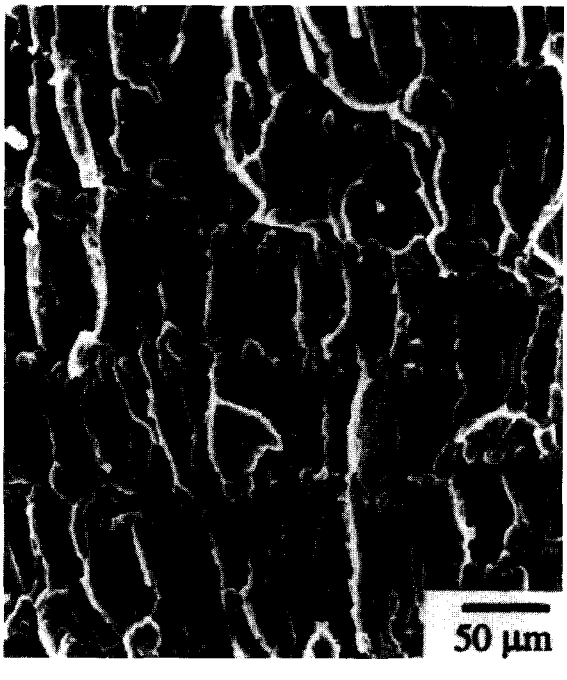

Figure 3 SEM scan showing hackle bands on fatigue fracture surface of an SPS ionomer containing 5.26 mol% ion content

breakdown, at the start of the rapid fracture crack advance.

It is interesting to compare the influence of ion content on fatigue lifetime, as shown in *Figure 1*, with prior results obtained on tensile properties of SPS ionomers[15]. There too, properties, such as tensile strength and toughness (energy to fracture), increased significantly as ion contents rose above 4 mol% and also a maximum in properties seemed to be achieved at higher ion contents of about 6–7 mol%. This enhancement in performance, in both fatigue and tensile tests, is attributed to the increasing presence of ionic clusters in the microstructure of these ionomers as ion content rises. It is known, from dynamic mechanical measurements, that the ionic cluster phase begins to dominate over the multiple-containing matrix phase at an ion content of about 6 mol%[11,12] and this is essentially the ion content at which one obtains the optimum results in both fatigue and tensile tests. Ionic clusters apparently provide more effective chain cross-linking than ion pairs or multiplets; and the resulting increased entanglement density is beneficial to mechanical properties.

A comparison of present results with those of a previous study[21] on fatigue behaviour of SPS ionomers shows some significant differences as well as some similarities. First, with regard to the similarities, both studies show that increasing the ion content to about 6 mol%, where the ion-rich cluster phase begins to dominate the microstructure, results in a significant enhancement of cycles to fracture as compared to the PS homopolymer. Another similarity is that a decreasing hackle band width with increasing ion content was also noted in the prior studies[28].

One difference in behaviour between the present and prior fatigue study of SPS ionomers[21] occurs in the low ion content range. In the prior study, it was observed that, in this range of ion contents, the fatigue life decreased with increasing ion content; while, in the present study, no decrease was found. This difference in behaviour is believed to be due to the low compression moulding temperatures used for the 2.5 mol% sample in the earlier study. For example, the moulding temperature for the 2.5 mol% sample was 135°C as compared to 190°C for the 2.65 mol% samples of the present study. Also, for the 4.8 mol% samples of the prior study, the moulding temperature was 155°C as compared to 210°C for the 4.35 mol% samples of the current investigation. It is concluded that the higher moulding temperatures, and the longer times at elevated temperature during the cooling process, are conducive to the development of the ionic cluster phase and thereby lead to an enhanced fatigue lifetime.

Another difference in behaviour is that the average lifetimes to fracture in the present study are a decade or more higher than the lifetimes of corresponding specimens in the prior study. One reason for this result is that the starting polystyrene of the earlier study was believed to contain mineral oil. The additive, by acting as a plasticizer, apparently causes a reduction in strength and resistance to fracture. A second reason is that already mentioned above, viz. the higher moulding temperatures of the present study are more conducive to the development of an equilibrium microstructure containing an appreciable fraction of the ionic cluster phase.

SPS ionomer/PS blends

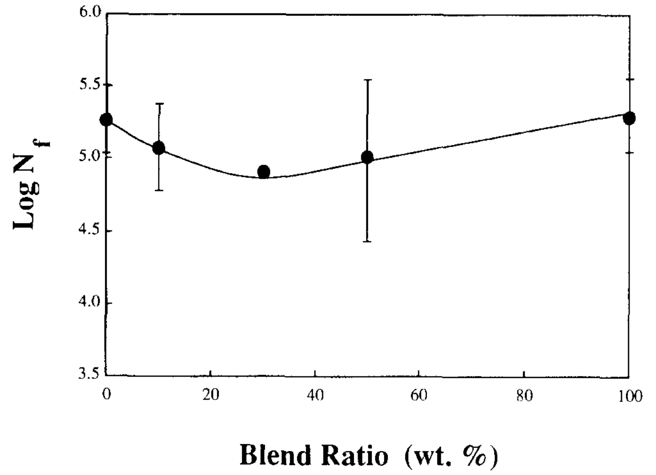

Figure 4 Log N_f (average value) vs. blend ratio for blends of SPS ionomer (2.65 mol%) and PS

Two types of SPS ionomer/PS blends were prepared. In the first series, the ion content of the ionomer component was kept constant at 2.65 mol% and fatigue tests were made on blend specimens having 10, 30, and 50 wt% of the SPS component. In the second series, the blend ratio of ionomer to PS was kept constant at 10/90 and tests were made on samples which had ion contents of 2.65, 5.26, and 7.48 mol%.

The results obtained in the first series of tests are shown in *Figure 4*, where the average lifetime to fracture is plotted against the wt% of the ionomer component. Three specimens were tested at each blend ratio, except for the 30 wt% ionomer blend where only one sample was tested. There is apparently no dramatic change in lifetime with blend ratio; but, from the limited data available, it appears that log N_f initially decreases somewhat and then increased slightly. In contrast to these fatigue results, tensile measurements have shown that there is a significant enhancement in tensile strength and energy to fracture upon addition of as little as 5–10 wt% of the ionomer[24]. It appears from these contrasting results that repetitive cycling may be producing some change in the microstructure of the blends that is harmful to performance.

Further information about the influence of blending comes from examination of both low and high magnification scans of the fatigue fracture surfaces. For a blend sample containing 10wt% of the ionomer component, SEM scans of the fracture surface are shown in *Figure 5*. At low magnification, *Figure 5a*, the general topology is rather similar to that of the SPS ionomer samples already described. At high magnification, *Figure 5b*, some dispersed, second phase particles, about 2–3 μm in size, are visible on the fracture surface. The presence of drawn material on their surface indicates that some degree of adhesion existed at the interface between the dispersed particles and the matrix. At the base of the SEM scan of *Figure 5b*, one can also see a 2–3 μm size cavity where the fatigue crack appears to have run around a previously imbedded particle. It is suggested that the good initial interfacial bonding between the SPS ionomer particles and the PS matrix, which is evident from examination of strained thin films[29] and from the fracture surface morphology of tensile fractured samples[24], may have been reduced by the repetitive stressing and this reduction in bonding is probably

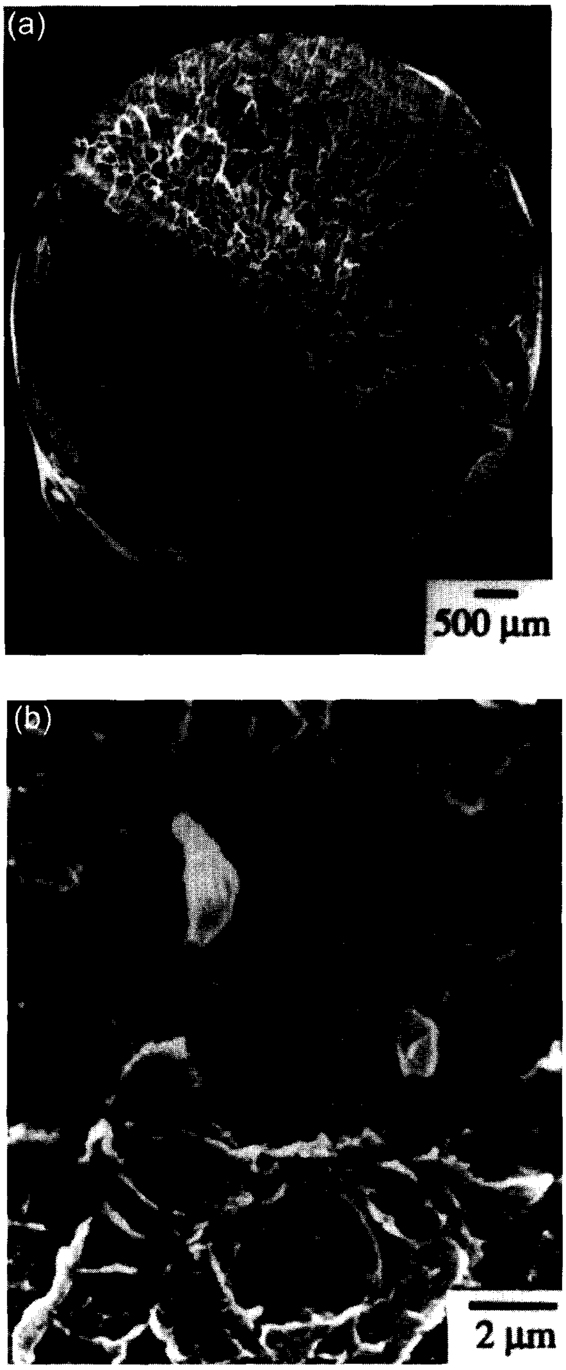

Figure 5 SEM scans of fatigue fracture surface of a 10/90 blend of SPS ionomer (2.65 mol%) and PS: (a) entire fracture surface; (b) high magnification scan showing two-phase nature of blend

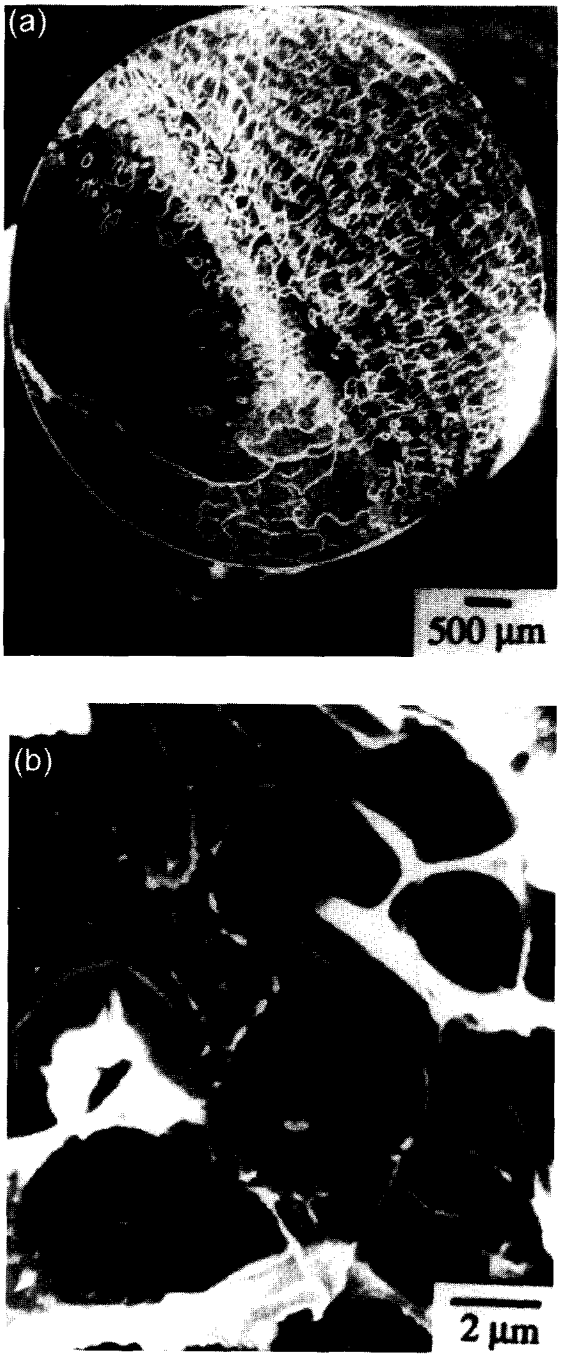

Figure 6 SEM scans of fatigue fracture surface of a 30/70 blend of SPS ionomer (2.65 mol%) and PS: (a) entire fracture surface; (b) high magnification scan showing two-phase nature of blend

responsible for the reduced fatigue life of the blends compared to that of the PS homopolymer.

SEM scans of the fatigue fracture surface of a sample containing 30 wt% of the ionomer component are shown in *Figure 6*. The low magnification scan, *Figure 6a*, shows that the extent of the comparatively smooth area prior to rapid fracture is smaller than that of the blend sample containing 10 wt% of the ionomer. This is another indication of a reduced lifetime to fracture as shown in *Figure 4*. The high magnification scan shows that the dispersed particles are somewhat larger (3–4 μm in size) than those for the 10/90 blend; and this may be a contributing factor to the lower number of fatigue cycles found for the 30/70 blend. For example, it has been reported for blends of glass beads with an elastomeric matrix, that the stress for debonding decreases as the particle size increases[30]. Also, in studies of thin films of blends of polystyrene and poly(2-vinylpyridine) by Creton *et al.*[31], it has been observed that, for larger size particles, voids form more readily at a craze-matrix interface and lead to earlier fracture.

Another factor contributing to a lower fatigue life upon blending appears to be the influence of repetitive stressing on the interfacial bonding between the ionomer, second-phase particles and the PS matrix. Under simple tension loading, this bonding is sufficient to give the SPS ionomer/PS blends a higher strength and toughness than the PS homopolymer[24]; and this beneficial result is

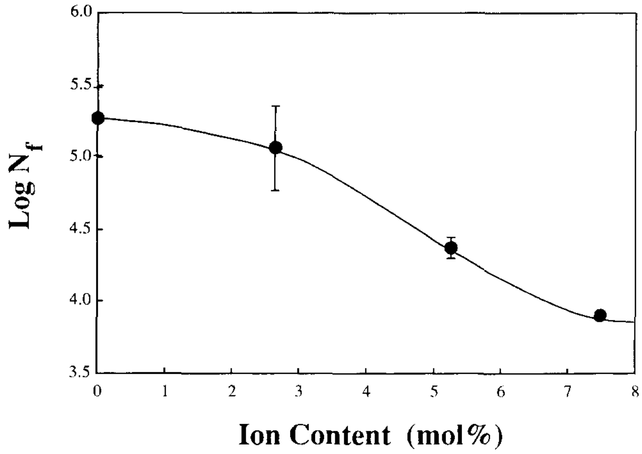

Figure 7 Log N_f (average value) vs. ion content of the SPS ionomer component in 10/90 blends of SPS ionomer and PS

attributed to a higher stress for crazing of the ionomer particles as a result of ionic cross-linking and a higher entanglement density[15]. However, as noted by Manson and Hertzberg[32], repetitive loading tends to be more damaging to interfacial adhesion than does static loading. A similar type of behaviour was noted in composites of nylon 66 containing coated glass beads; the tensile yield stress increased with filler concentration but the fatigue resistance decreased[33]. The effect of alternating stress on adhesion is also evident by comparing the high magnification SEM scan of the fatigue fracture surfaces of the 30/70 blends (*Figure 6b*) with the corresponding scans of tensile fracture of similar blends (Figure 8a of ref. 24). In the latter case, the SPS particles appear to be bound to the matrix while, in the former case, as illustrated in *Figure 6b*, the surfaces of many of the second phase particles are comparatively smooth. This is an indication that the interfacial bonding has been sufficiently reduced by the long-time repetitive cycling to permit the fracture crack to essentially bypass many of the particles.

For the 50/50 blend, SEM scans of the fracture surface show no evidence of distinct second phase particles; instead, the ionomer phase and the matrix phase appear to be intricately mixed at this composition (i.e., formation of so-called modulated structure). However, the extent of the comparatively smooth region surrounding the origin is reduced compared to that of PS and this is a fracture surface manifestation of a lower fatigue life as noted in *Figure 4*.

Results of the second series of fatigue tests on the SPS ionomer/PS blends are shown in *Figure 7*. Three specimens were tested for each ion content, except only one was tested at 7.48 mol% ion content. The average lifetime to fracture decreases as the ion content of the ionomer component increases. Also, there are some changes in the fracture surface morphology. For the blends with a 2.65 mol% ion content in the ionomer component, the fracture morphology is evident from the SEM scans of *Figure 5*. For blends in which the ionomer component has an ion content of 7.48 mol%, SEM scans showing the fatigue fracture surface morphology are given in *Figure 8*.

Comparison of the two low magnification scans (*Figure 8a* vs. *Figure 5a*) shows that the higher ion content sample has a smaller slow growth region; and this is an indication of a reduced fatigue life, as illustrated by the graph of *Figure 7*. Comparison of the high magnification scans (*Figure 8b* vs. *5b*) reveals that the dispersed SPS particles are much larger (~ 10 μm) for the blend samples containing the ionomer phase of higher ion content. Hence, interfacial bonding between the two phases, which is reported to vary inversely as the square root of the particle size[30], will be more easily overcome by alternating stressing, and lifetime to fracture will be reduced.

Another factor that may contribute to a reduction in adhesion between the two phases as the ion content of the ionomer component rises, is that a higher ion content SPS ionomer phase has less affinity for the PS matrix.

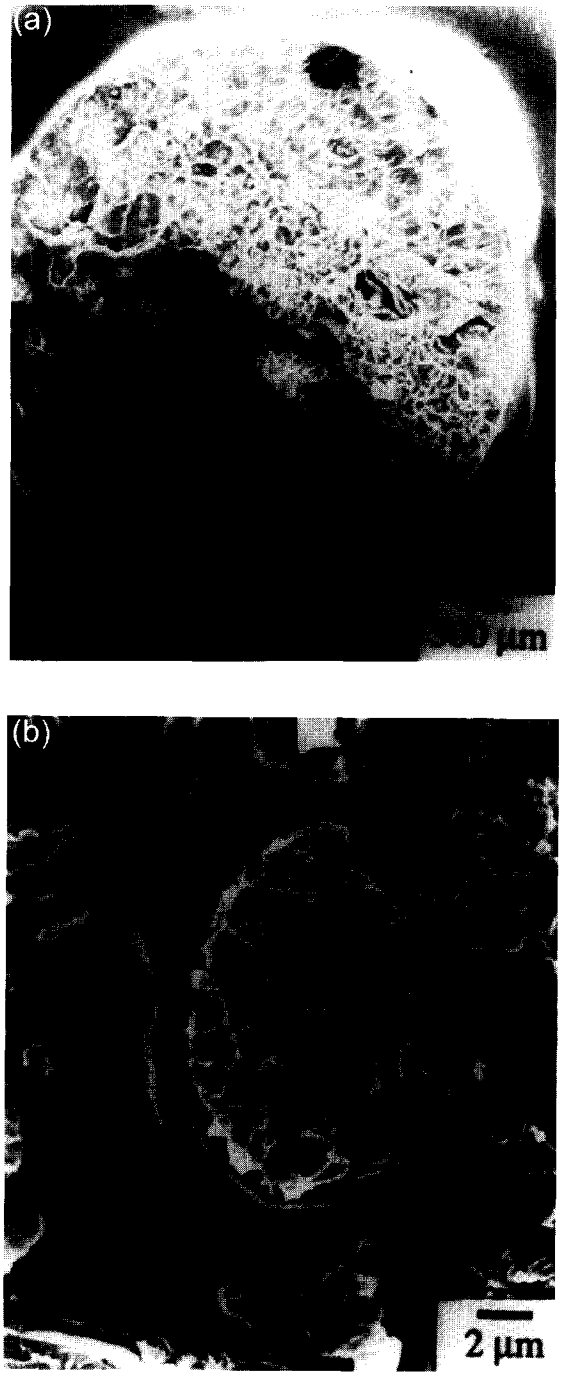

Figure 8 SEM scans of fatigue fracture surface of a 10/90 blend of SPS ionomer (7.48 mol%) and PS: (a) entire fracture surface; (b) high magnification scan showing a large ionomer particle

Also, as noted in the discussion of the first series of tests, repetitive stressing, by itself, is more damaging to interfacial bonding than slowly applied tensile loading. Hence, this factor, as well as a larger particle size and a reduced affinity between the two phases, all contribute to the reduced fatigue lifetime noted in *Figure 7* as the ionomer ion content increases.

It is recognized that many different factors are involved in determining the mechanical properties of polymer/polymer blends. Hence, it is not too surprising that altering the ion content of the ionomer component may affect different mechanical properties in different, or even reverse, ways. As noted earlier, at least three different factors are important, viz. interfacial adhesion of the second phase particles to the matrix, the inherent higher entanglement density of the ionomer phase, and the influence of particle size. For tensile properties, it appears that any deleterious effect of an increased particle size, as blend ratio or ion content are increased, is more than compensated by good bonding between the two phases and by an inherent greater resistance to fracture of the more highly entangled ionomer phase. Hence, tensile strength is enhanced by blending ionomer with PS, and even more by raising the ion content of the ionomer phase. However, the inherent greater resistance to fracture of the SPS ionomer phase as ion content is raised is of little value if good bonding is not maintained between the phases. Under continued, repetitive stressing for many cycles, the degree of bonding between the ionomer phase and matrix tends to reduce; hence any inherent superior properties of the ionomer phase, such as enhanced craze stress and tensile strength, are not utilized. As a result, SPS ionomer/PS blends show less resistance to fatigue fracture than does the polystyrene homopolymer.

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