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Poly(methyl methacrylate) Ionomers. 2. Deformation Modes under Simple Tension

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ABSTRACT: Deformation mechanisms of poly(methyl methacrylate) (PMMA)-based ionomers subject to simple tension were studied by transmission electron microscopy (TEM). The deformation mechanism changed from crazing only for PMMA to crazing plus shear deformation for the Na-PMMA ionomer with 6.0 mol % ion content and to shear deformation only for the Na-PMMA ionomer with 12.4 mol % ion content. Such changes with ion content are similar to those observed for polystyrene (PS)-based ionomers and can be understood as arising from an increased "effective" strand density due to the ionic cross-linking effect. It was also observed that a divalent Ca salt ionomer having an ion content of only 0.8 mol % induced shear deformation in addition to crazing. This is understood as arising from an increased effective strand density due to the formation of stronger ionic cross-links for the Ca salt ionomer as compared with the Na salt ionomer. Deformation mechanisms were also found to depend on thermal treatments of the ionomer specimens. When thin films were cast by a polar solvent, such as dimethylformamide (DMF), ionic aggregates were destroyed but a suitable annealing treatment permitted recovery of ionic aggregates, comparable to those formed in bulk ionomer specimens, and thereby altered the deformation mode.

Introduction

Although polymers are finding increasing use in engineering applications because of their many advantages, such as low density, low cost, ease of fabrication, and unique properties not found in other materials, their use is limited by the tendency of many of these polymers to fail in a brittle fashion.[1] An important consideration for the use of polymers in engineering applications is an understanding of the way they respond to mechanical loading, including both small-strain and large-strain properties, deformation mechanisms, and ultimate failure modes.

It is well-known that amorphous glassy polymers exhibit two types of plastic deformation.[2,3] One is shear yielding, which occurs essentially at constant volume and leads to a permanent change in shape. Shear yielding can take place in either highly localized shear bands or diffuse shear deformation zones.[4] Another is crazing. Unlike shear yielding, crazing is a cavitational process, leading to an increase in volume. Brittle polymers, such as polystyrene (PS), usually deform by crazing, while tougher polymers, such as polycarbonate, usually deform by shear yielding. Although extensive crazing can be beneficial for improving toughness, as in rubber-toughened polymers,[1,5,6] in glassy polymers cracks can propagate readily through crazes and thereby decrease fracture resistance.[7] It is believed that there is a close relationship between crazing and fracture of amorphous polymers. Although crazes are load bearing, as they consist of many small oriented fibrils, with diameter in the range of 5–30 nm, interspersed with voids, cracks may be formed within the craze by breakdown of the fibril structure. Therefore, one way to make polymers more fracture resistant is to control crack nucleation in crazes by suppressing craze formation in favor of shear deformation.[3]

There has been considerable progress over recent years in the study of molecular mechanisms involved in craze nucleation, craze growth, and fracture, as reviewed by Kramer.[2,3] Many factors can influence deformation behavior; some of these are test conditions, such as temperature, stress state, strain, strain rate, and thermal history. When sample preparation and test conditions are chosen to be the same, the effect of molecular variables can be determined. It is now well established that (network) *strand density* plays an important role in determining the deformation mechanisms and in affecting the craze–shear deformation transition. The network strand density of linear polymers, which is simply the (physical) entanglement density calculated from the entanglement molecular weight, a characteristic value for any specific polymer, is considered to be a material constant. The strand density of cross-linked polymers is defined as the sum of the entanglement density and the covalent cross-link density.[8] Kramer and co-workers[2,3,8–10] have found that the deformation mechanism of amorphous glassy polymers changes from crazing only to crazing plus shear yielding, to shear yielding only, and finally to no plastic deformation, as the strand density of the polymer network is increased. These findings appear applicable not only to homopolymers and copolymers but also to miscible polymer blends, such as PS/poly(phenylene oxide) (PPO) blends, and (lightly) cross-linked polymers, such as covalently cross-linked PS. The craze–shear transition may be predicted by a craze growth model.[2]

We can further extend the concept of *strand density* to include the *ionic cross-linking effects* observed in ionomers.[11] Ionomers, usually containing ionic groups up to 10–15 mol % along backbone chains, possess ionic aggregates such as multiplets and clusters. These aggregates function as ionic cross-links as well as reinforcing fillers.[12–19] Therefore, for linear ionomers, the ionic cross-linking effect due to ionic associations should be considered in addition to the entanglement

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density of the base polymers. Recently, Hara et al. have found that the introduction of ionic interactions into PS, i.e., formation of sulfonated PS (SPS) ionomers, can alter the deformation mechanisms induced in strained thin films.[11,20-22] While crazing is the only observed deformation mechanism of PS, the introduction of ionic groups leads to the development of smaller, more stable crazes and, at ion contents of about 6 mol % or above, shear deformation develops in addition to crazing. The changes in deformation mechanisms observed in thin films[11,20,21] suggest that beneficial changes may also occur in mechanical properties of bulk specimens, and this has been observed in both tensile[23,24] and fatigue[25,26] studies of PS ionomers. The altered properties are explained primarily as arising from changes in the effective strand density. The strand density is increased through an ionic cross-linking effect, which raises the crazing stress as compared with the shear yield stress and thereby enhances the fracture resistance of these polymers. While many studies have been conducted on the structure–property relationships of ionomers,[12-19] there has been relatively little information about deformation and fracture mechanisms of glassy ionomers prior to these recent reports. A review concerning the influence of various variables on the mechanical properties of ionomers is available.[11]

To gain a more thorough understanding of how ionic cross-links (and ionic aggregates) affect the deformation mechanisms of ionomers, in this study we examine poly(methyl methacrylate) (PMMA)-based ionomers and compare results obtained on this type of amorphous ionomer with results previously obtained on PS-based ionomers. The dynamic mechanical properties and morphology of these PMMA ionomers have been recently described.[27] Since the structure of ionic aggregates and/or the strength of ionic bonds can be altered through changes in the *ion content* or the *nature of the counterion*,[11] we have investigated the effect of these molecular variables on the relationship between deformation mechanisms and ionic interactions in PMMA-based ionomers. In addition, we have studied the effect of thermal treatment on the deformation mechanisms of these ionomers, since such treatment is critical to preparing good ionomer specimens and to controlling their properties.

Although the ionic interactions that give rise to cross-linking in ionomers are not as thermally stable as covalent cross-linking, they do give rise to a network structure, which, in some respects, is akin to that produced by chemical cross-linking. Common features, aside from a rise in the rubbery plateau modulus with an increase of entanglement density, are an increase in the matrix T_g with increasing ion content, as noted in both PS ionomers[13] and PMMA ionomers,[27] and a rise in the glass transition temperature with an increase in the degree of cross-linking, as observed for chemically cross-linked PS[28] and covalently cross-linked PMMA.[29] While an increase in T_g may lead to an increase in the shear yield stress measured at ambient temperature, an increase in entanglement density, which has little or no effect on shear yielding, will increase the craze stress.[2] It appears that the second effect is dominant both in covalently cross-linked PS[8] and in ionically cross-linked PS[11,20] as, in both cases, shear deformation begins to compete with crazing as a deformation mode when the entanglement strand density is increased. Somewhat similar changes are anticipated for PMMA ionomers, although the transition from one mode to the other may occur at different, and probably higher, values of entanglement density because ionic cross-links are not as stable as covalent ones and also because the shift of T_g with ion content for the PMMA ionomers, which is about 5.5 °C/mol,[27] is much higher than the value for PS ionomers of about 3.2 °C/mol.[30]

Experimental Section

Materials. PMMA ionomers having a low ion content (0.8 mol %) were made by hydrolysis of PMMA and those having higher ion contents (6.0 and 12.4 mol %) were made from random copolymers of methyl methacrylate and methacrylic acid. The PMMA homopolymer (obtained from Polysciences, Inc.) had a weight-average molecular weight of 1.35×10^5, obtained by low-angle light scattering measurements in dimethylformamide (DMF). The preparation and characterization of the PMMA ionomers are described elsewhere.[27]

Transmission Electron Microscopy (TEM). TEM specimens were prepared by solution casting,[20] somewhat similar to the procedure used by Lauterwasser and Kramer.[31] Thin film samples were cast from ionomer solutions on glass microscope slides. The slides were then dried in a bell jar, in which a container of the solvent was placed to decrease evaporation rate. Drying time was chosen in the range from 2 to 4.5 h according to the solvent used. The films were cut into small squares (1.5 × 1.5 mm) with a razor blade and floated off the glass slides onto distilled water. The pieces of a polymer film were then picked up on copper grids and dried under vacuum at room temperature for at least 48 h. The thickness of the films was kept constant by choosing the pieces with the same color; dark gold films with a thickness of around 1500 Å were chosen in this study.[32] Some TEM specimens were heat treated under vacuum before observation. The thin film specimens clamped in folding copper grids were deformed under simple tension by slow stretching of the grids. The polymer deformation, maintained by the plastically deformed copper grids,[31] was observed for the strained specimens with a transmission electron microscope (JEM-100CXII) operating at an accelerating voltage of 100 kV.

The Na-PMMA ionomer samples of 6.0 and 12.4 mol % were prepared by solution casting from dimethylformamide (DMF). Because DMF is polar, having a high boiling temperature (153 °C), it is difficult to remove DMF completely by a normal drying procedure.[30] Therefore, to determine the deformation mechanisms induced in the strained PMMA ionomer films, the residual solvent must be removed: this was done by giving the samples a heat treatment at 160 °C under vacuum for 48 h, after a normal drying process at ambient temperature. Thin films of PMMA and the Ca-PMMA ionomer of 0.8 mol % ion content were prepared by solution casting from methylene chloride; and deformation modes were examined both before and after being heat treated at 100 °C under vacuum for 8 h.

Kramer et al. have investigated extensively the deformation mechanisms of polymers by using cast films,[2,3,8-10] while Michler et al. have used microtoming to prepare thin films.[33-35] Beahan et al. found that the craze structures developed in cast thin films and those in microtomed films were comparable to those produced in bulk materials.[36] Donald et al. studied the effect of film thickness on the craze microstructure of PS and found that the craze structures observed in films with thickness of 1500 Å or larger were the same as those in bulk PS.[37] Since PMMA is like PS in being a brittle, transparent polymer with a comparable T_g value, the results of our deformation studies on thin films may also be indicative of the behavior of bulk samples.

Dynamic Mechanical Measurements. These measurements were made as a function of temperature on specimens having a length of 12.5 mm, a width of 2.5 mm, and a thickness of 0.5 mm. The specimens were made from compression-molded plates and were polished prior to testing. The tests were carried out on a Piezotron (Toyoseiki, Japan), and the heating rate was maintained at 4 °C/min. The test frequency was 1 Hz. More complete information concerning these measurements is given in a separate publication.[27]

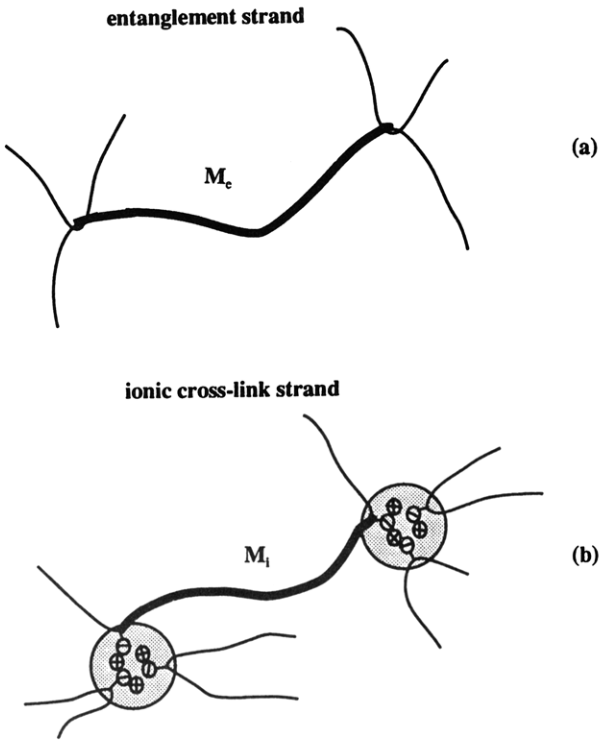

Figure 1. Schematic figures indicating (a) an entanglement strand and (b) an ionic cross-link strand.

Strand Density of Ionomers. Since we make use of the concept of molecular entanglements, or strand density, for understanding the deformation modes of ionomers, some basic relations are explained here. For linear polymers, such as homopolymers and copolymers, the strand density, ν_e, is defined as

$$\nu_e = \varrho N_A / M_e \tag{1}$$

where ϱ is the density of the polymer (g/cm^3), N_A is Avogadro's number, and M_e is the entanglement molecular weight[2,3] (see Figure 1). In a similar fashion, we can define an ionic cross-link strand density, ν_i, as

$$\nu_i = \varrho N_A / M_i = f \varrho N_A / M_0 \tag{2}$$

where M_i is the average molecular weight between ionic groups (see Figure 1), f is the ion content (fraction), and M_0 is the repeat unit molecular weight. By combining these two quantities, the (apparent) strand density may be obtained as

$$\nu = \nu_e + \nu_i \tag{3}$$

Here, ν represents the total (network) strand density, defined as the number of strands (molecular chains separated by two junction points that include physical entanglements and ionic cross-links) per unit volume. Such a relation has been used for describing the deformation modes of covalently cross-linked polymers by using ν_x (covalent cross-link strand density) instead of ν_i by Henkee and Kramer;[8] they found that, for polymers with $\nu < 4 \times 10^{25}$ chains/m^3, crazing was the only observed deformation mechanism. For polymers with $4 \times 10^{25} < \nu < 8 \times 10^{25}$ chains/m^3, both crazes and shear deformation zones were normally observed, with some exceptions, such as PMMA that only crazes despite its high ν_e value (7.8×10^{25} chains/m^3 obtained from eq 1 using an M_e value of 9150[9]). For polymers with $\nu > 8 \times 10^{25}$ chains/m^3, only shear deformation zones were observed, but, at high cross-link densities, fracture occured without any significant plastic deformation.

Although eq 3 seems useful, we must modify it for ionomers, since, as described in the Introduction, the strength of ionic bonds in ionomers is generally smaller than that of covalent bonds. Therefore, what is important in ionomers may be an effective strand density, ν_{eff}, defined as

$$\nu_{\text{eff}} = \nu_e + k \nu_i \tag{4}$$

In eq 4, ν_{eff} is considered to be the strand density normalized in terms of the strength of the covalent bonds. Here, k is a coefficient reflecting the effectiveness of ionic cross-links as compared with covalent cross-links or physical entanglements (at temperatures far below T_g); therefore, the range of k is $0 < k < 1$.[38] It may be expected that the k value of monovalent (e.g., Na) salt ionomers will be low (hence, ν_{eff} will tend to be low), while the k value of divalent (e.g., Ca) salt ionomers of the same ion content is expected to be higher, leading to higher ν_{eff} values. Therefore, it is anticipated that the replacement of counterions from monovalent to divalent may lead to a change in the deformation mode.[11] In addition, since $\nu_i \propto f$ as seen from eq 2, the ν_{eff} value will increase with increasing ion content f, and this increase is expected to produce changes in the deformation modes of the ionomers.[11]

Finally, a combination of eqs 1, 2, and 4 leads to

$$\nu_{\text{eff}} = \varrho N_A (1/M_e + fk/M_0) \tag{5}$$

With known values of ϱ, M_0, and M_e, i.e., material constants for a base polymer, and ion content, f, of an ionomer, we can, in principle, determine k values of a given ionomer by comparing the ν values corresponding to the craze–shear transitions (a transition from crazing only to crazing plus shear occurring at $\nu = 4 \times 10^{25}$ and a transition from crazing plus shear to shear only occurring at $\nu = 8 \times 10^{25}$), which have been obtained from the results on various polymers.[8] One difficulty in carrying out this assignment for PMMA ionomers is that the PMMA homopolymer appears to be an exception to the general rule in that, based on its ν_e value of 7.8×10^{25} chains/m^3, it would be expected to show both shear deformation and crazing but, instead, it only crazes. In view of this, eq 5 will only be used to make an estimate of the effectiveness coefficient, k, of PMMA ionomers by comparing strand density values for the transition from shear deformation to brittle failure, which, for cross-linked PS samples, occurs at $\nu = 14\nu_e$.[8]

Results

Figure 2 shows TEM micrographs of a tensile-strained, cast thin film of PMMA. Similar micrographs were obtained after annealing the films for 8 h at 100 °C. In the low magnification scan (Figure 2a), many individual crazes are seen, aligned, as usual, perpendicular to the applied stress direction, which is indicated by the arrow. A high magnification scan of a typical craze is shown in Figure 2b. Although the fibrillar elements of crazes in PMMA are not as well-defined as those in PS, as also noted by Michler[33] from observation of deformed ultramicrotomed PMMA samples, the induced deformation pattern is considered to be crazing rather than shear deformation for several reasons. First, note the presence of a lighter, thin section in the middle of the craze. This midrib is a typical microstructural feature of crazes grown in glassy polymers. It arises because of high stresses existing near the tip of the craze, which produce a greater initial fibril extension ratio than exists in the remainder of the mature craze. Second, a craze with microstructure similar to that of Figure 2b was obtained by Donald and Kramer[9] in a cast thin film (0.8 μm thick), and, from densitometry measurements, they determined the craze fibril extension ratio, λ_{cr}, and found it to be, as for many other glassy polymers, about $0.8\lambda_{\max}$, where $\lambda_{\max}$ is the maximum extension ratio of the entanglement network. Third, a craze of comparable morphology has been observed by Berger[40] in a cast PMMA film (0.6 μm thick), and its microstructure has been explored by means of low-angle electron diffraction. From the

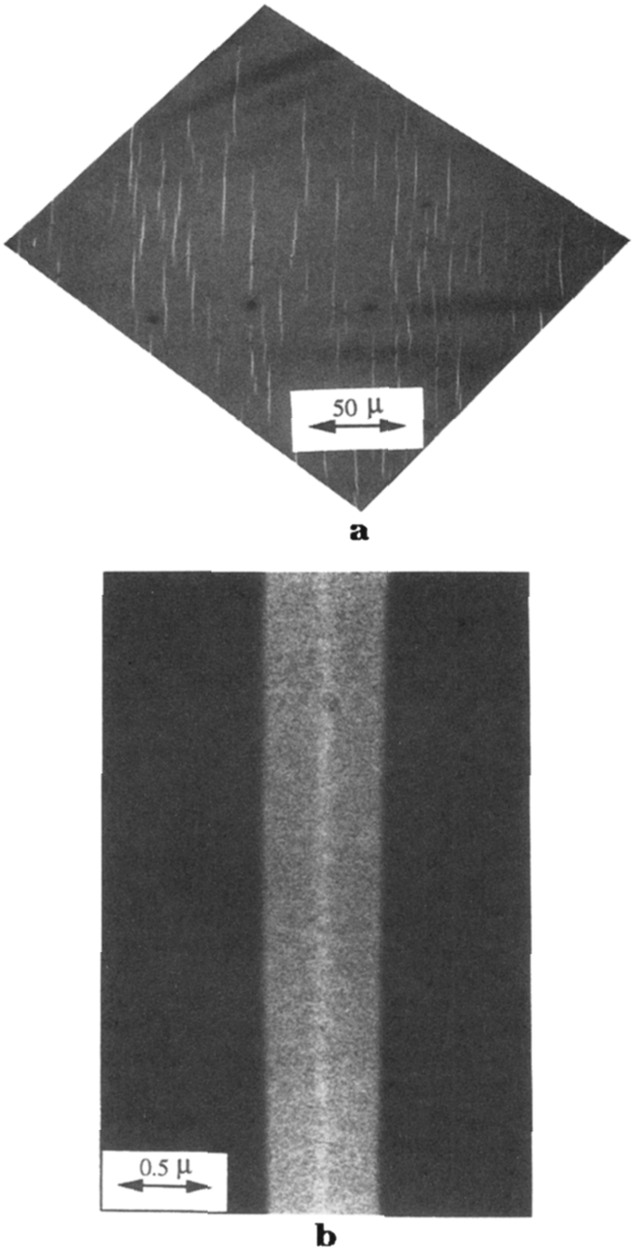

Figure 2. TEM micrographs of a deformed PMMA thin film cast from methylene chloride: (a) overall view at low magnification; (b) a central region of a craze.

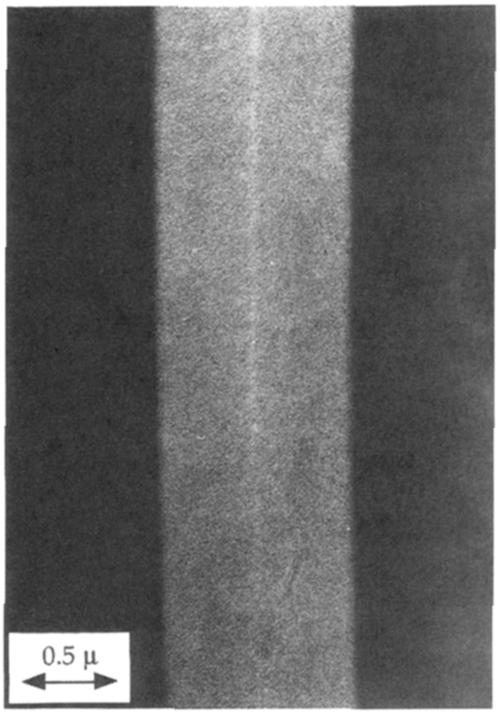

Figure 3. TEM micrograph of the central region of a craze in a deformed thin film of Na-PMMA ionomer having an ion content of 6.0 mol % cast from DMF.

diffraction pattern, Berger was able to determine both the average craze fibril diameter (~13 nm) and the average fibril spacing (~18 nm). Hence, the evidence is strong that, in tests of strained PMMA films at ambient temperature, we are encountering fibrillated crazes, even though the fibrils in the craze are not clearly delineated.

Figure 3 shows a micrograph of a typical craze in a deformed Na-PMMA ionomer, a 6.0 mol % ion content sample cast from DMF, which has been given a normal drying process (vacuum drying at room temperature for 48 h). A low magnification scan (not shown) reveals that many well-developed crazes have formed. The crazes have sharp craze–matrix interfaces, a typical midrib section, and a tapered tip, similar to those seen in unmodified PMMA thin films (see Figure 2b).

It is known that additional thermal treatment or aging can have an effect on the ionic microstructure[30] and on the deformation mechanisms of deformed PS ionomers;[21] hence, it is of interest to examine its effects on PMMA ionomers. When a PMMA ionomer with 6 mol % ion content was heat treated at 160 °C for 48 h, the low magnification scan showed fewer, and shorter, crazes; at high magnification, both crazes, as in Figure 4a, and shear deformation bands interconnecting crazes, as in Figure 4b, were observed. Also, elements of retracted craze fibrils are visible in part of the craze that has fractured. The coexistence of, and interactions between, crazes and shear deformation zones or bands has been noted by Donald and Kramer in drawn thin films of poly(styrene-*co*-acrylonitrile) and of PS/PPO blends.[10,41]

When the ion content of un-heat-treated PMMA ionomer films cast from DMF was increased to 12.4 mol % and subjected to a normal vacuum-drying process at room temperature for 48 h, crazing appeared to be the dominant plastic deformation process; in low magnification scans, many isolated crazes were seen. A high magnification scan of one of these crazes is shown in Figure 5. Although no fibrillar elements can be seen spanning the craze, there is a hint of a thin midrib section. However, the almost homogeneous nature of the deformed zone may indicate that some shear component is also present. Deformation zones, containing a central craze region lying within a shear deformation zone, have been observed both in poly(styrene-*co*-acrylonitrile)[10] and in a Ca-PS ionomer of 4.1 mol % ion content,[21] but, in these instances, the fibrillar nature of the central craze was quite evident. After heat treating the 12.4 mol % PMMA ionomer film for 48 h at 160 °C, we observed no evidence of crazing after tensile straining and fracture appeared to occur without significant plastic deformation; but, upon examination of the strained film at high magnification (Figure 6), some smaller shear deformation zones appeared to be present.

Figure 7 shows the TEM micrographs of a deformed sample of a Ca-PMMA ionomer of 0.8 mol % ion content, which has not been heat-treated. A low magnification

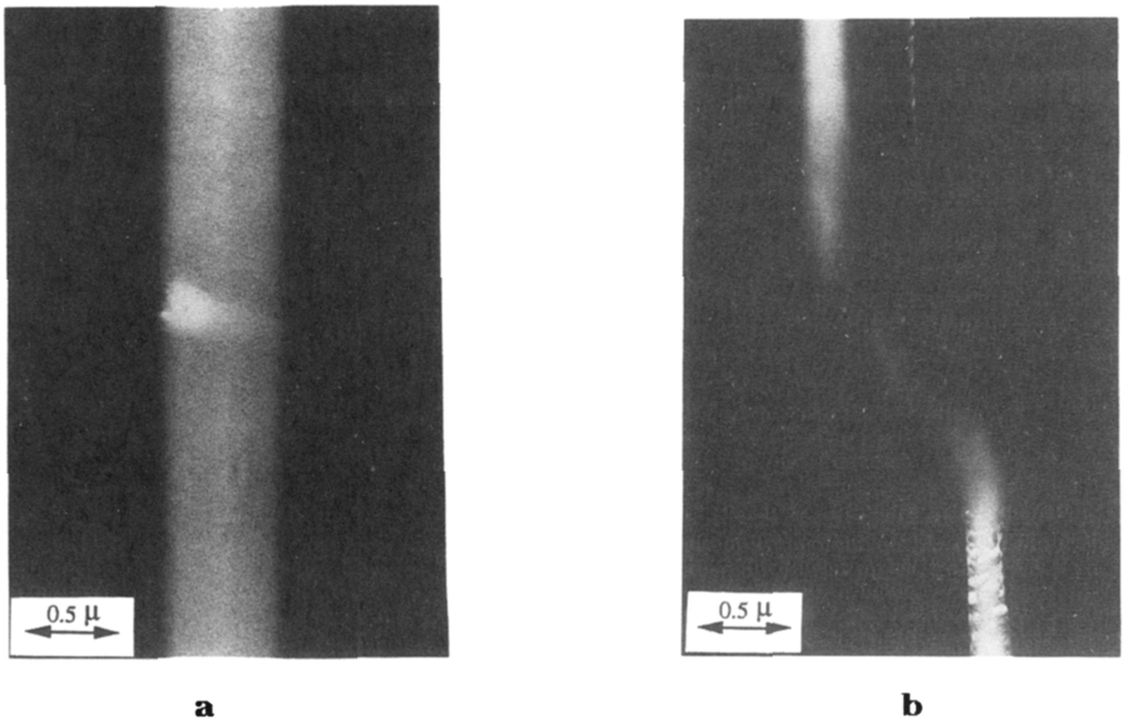

Figure 4. TEM micrographs of a deformed thin film of Na-PMMA ionomer having an ion content of 6.0 mol % cast from DMF, followed by thermal treatment at 160 °C for 48 h: (a) a typical craze; (b) crazes interacting with shear bands.

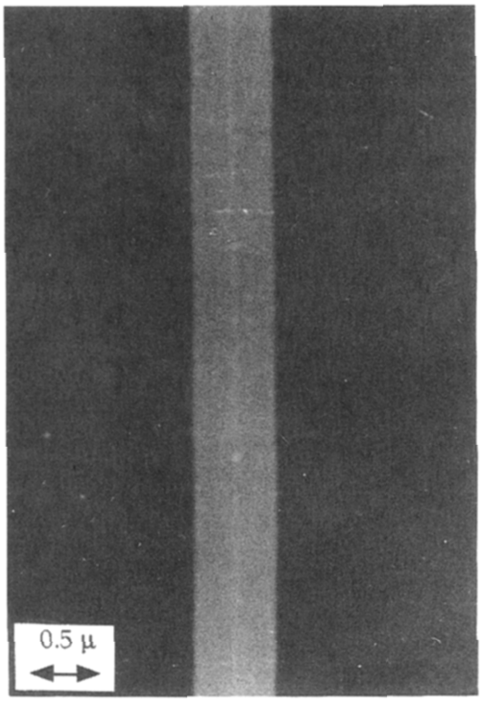

Figure 5. TEM micrograph of the central region of a craze in a deformed thin film of Na-PMMA ionomer having an ion content of 12.3 mol % cast from DMF.

scan (Figure 7a) shows that the main deformation mechanism is crazing; a high magnification scan (Figure 7b) shows the craze to possess morphology similar to that of PMMA (see Figure 2b). Figure 8 shows the deformation behavior of a specimen, after it was heat-treated at 100 °C for 8 h. The change in the deformation mode due to thermal treatment is clear: in Figure 8a, there are many short crazes in contrast to the fewer long crazes seen in Figure 7a. Also, in Figure 8b, we see small crazes interacting with shear deformation zones.

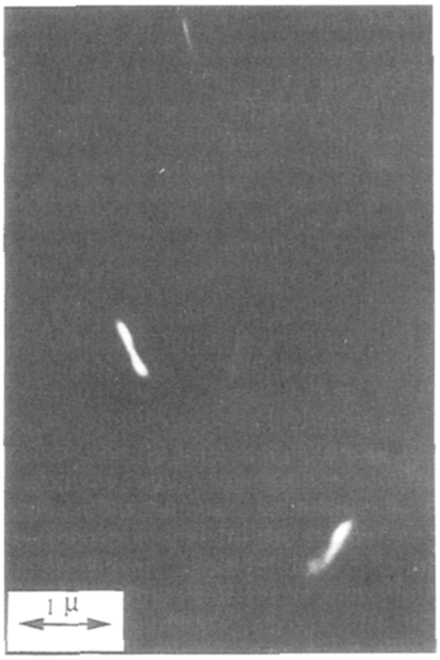

Figure 6. TEM micrograph of a deformed thin film of Na-PMMA ionomer having an ion content of 12.3 mol % cast from DMF, followed by thermal treatment at 160 °C for 48 h, showing small shear deformation zones.

Discussion

Effect of Ion Content and Thermal Treatment on Na-PMMA Ionomers. Before discussing the results obtained on the PMMA ionomers, the deformation modes in strained thin films of PS ionomers will be briefly described, since the PS ionomers have been extensively studied.[11] Typical changes with ion content in deformation mechanisms of PS ionomers are as follows: unmodified PS, and PS ionomers of low ion content, deform only by crazing; as the ion content increases above some critical value, which is about 6

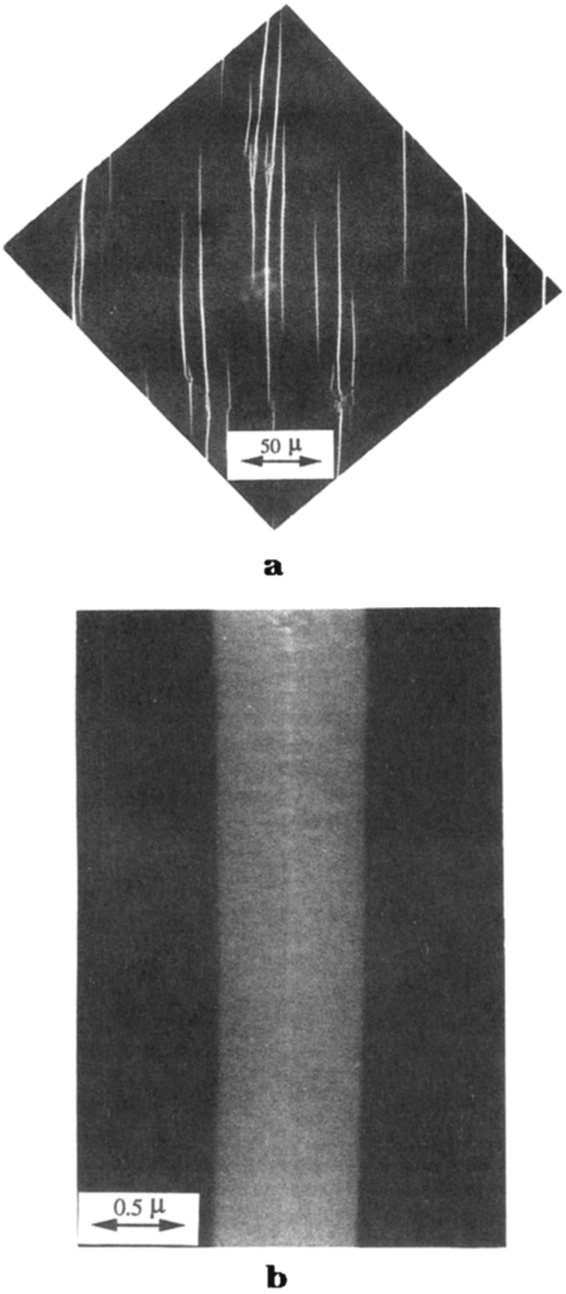

Figure 7. TEM micrographs of a deformed thin film of Ca-PMMA ionomer having an ion content of 0.8 mol % cast from methylene chloride: (a) overall view at low magnification; (b) a central region of a craze.

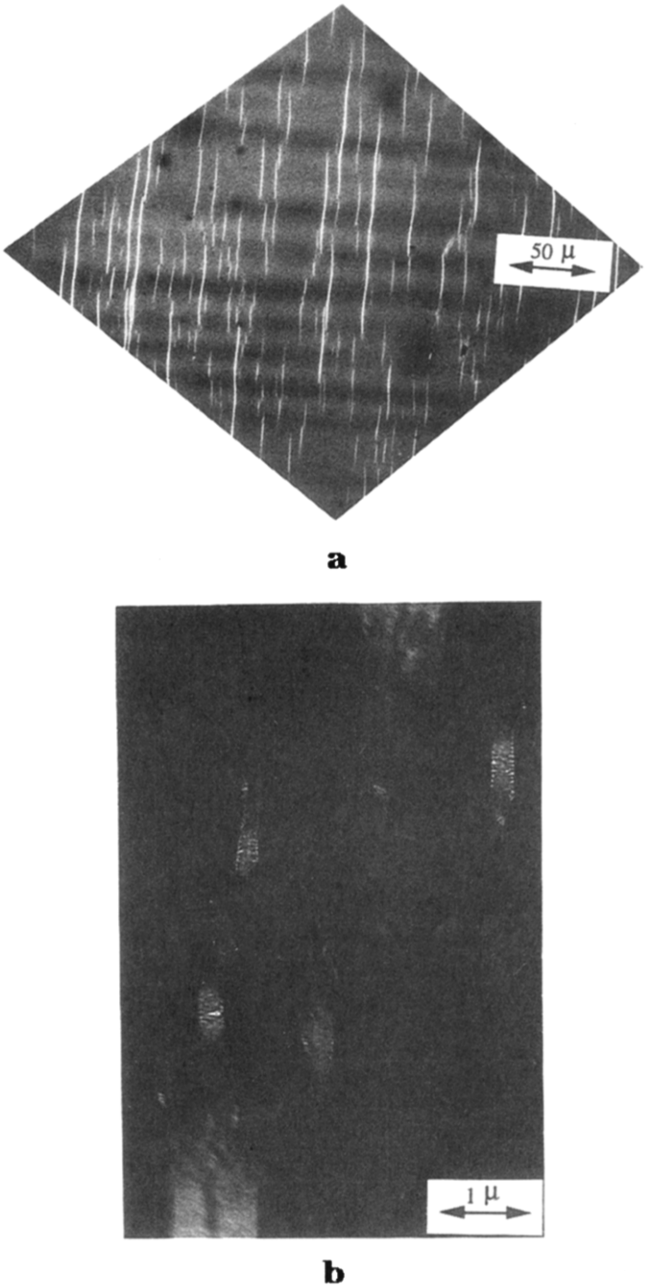

Figure 8. TEM micrographs of a deformed thin film of Ca-PMMA ionomer having an ion content of 0.8 mol % cast from methylene chloride, followed by thermal treatment at 100 °C for 8 h: (a) overall view at low magnification; (b) crazes interacting with shear bands.

mol % for Na-PS and K-PS ionomers, shear deformation components are present and a transition of the deformation pattern occurs from typical long crazes to short curved/branched crazes and to crazes mixed with shear deformation zones. This behavior is generally observed for both SPS ionomers[11,20,21] and poly(styrene-*co*-sodium methacrylate) ionomers.[42]

To investigate the generality of our observations and interpretations on the effects of ionic cross-links (aggregation) on the deformation modes of amorphous polymers, ionomers based on other amorphous polymers than PS need to be investigated; therefore, we have studied PMMA-based ionomers in this investigation. It should be stressed, however, that a study of the deformation mechanisms of PMMA and its ionomers with TEM is much more difficult than for PS and its ionomers. This is because PMMA is more susceptible to beam damage; for example, the amount of byproducts produced by irradiation of PMMA is 2 orders of magnitude larger than that for PS.[43] It is also reported that the dosage of high-energy electrons for changing the mechanical properties of PMMA is only 1/500 of that of PS.[33] Despite these problems, reasonable pictures of deformed thin films of PMMA and its ionomers, as shown in the previous section, have been obtained.

A second problem that arises in studying thin films of PMMA ionomers, especially those of high ion content, is that a polar solvent, such as DMF, is usually needed to dissolve the ionomer. Such polar solvents are known to solvate and destroy the ionic aggregates. Also, any solvent remaining in the cast film will act as a plasticizer, reduce T_g, and increase chain flexibility. For example, it has been shown from dynamic mechanical thermal analysis (DMTA) of SPS ionomers of 8.5 mol

Table 1. Strand Densities and Deformation Modes of PMMA Ionomers

ion content (mol %)	ionic strand density (ν_i)[a] (chains/m^3)	total strand density (ν) (chains/m^3)	deformation mode	
			as-cast	heat-treated
0	0	7.8×10^{25}	crazing	crazing
6.0 (Na salt)	43×10^{25}	51×10^{25}	crazing	crazing plus shear
12.4 (Na salt)	89×10^{25}	97×10^{25}	crazing	shear only

[a] Assuming that all ionic groups are participating in ionic aggregate formation.

% ion content cast from DMF that the usual upper temperature loss peak, indicative of the presence of an ion-rich second phase, is missing and that the lower temperature loss peak, associated with the T_g of the matrix phase, is shifted to lower temperatures.[30] However, when similar samples are given an additional elevated temperature aging treatment (at 200 °C for 41 h), the two DMTA-observed loss peaks are restored to the usual temperature positions found in compression-molded samples.

The deformation modes of thin films of an 8.5 mol % SPS ionomer sample cast from DMF are also altered by a thermal aging treatment.[21] They changed from crazing only for an as-cast specimen to combined crazing and shear for a heat-treated specimen. Effects of thermal treatment on the microstructure of Mn-SPS ionomers of 7.6 mol % ion content, cast from tetrahydrofuran/water (90/10), have been observed in studies by small-angle X-ray scattering.[44] In as-cast specimens no ionic peak was present; but after the samples were annealed for 4 days at 120 °C, the ionic peak, due to the presence of an ion-rich second phase in the sample, was developed.

A summary of our test results on the Na-PMMA ionomer specimens, cast from DMF, is presented in Table 1 both for normally dried samples and for samples given an additional heat treatment. In addition, we have listed estimated values of the ionic strand density and the (apparent) total strand density for each ion content. These estimates have been made on the assumptions that all ion pairs participate in creating ionic cross-links and that the ionic cross-links are comparable to covalent or entanglement cross-links.

Inspection of Table 1 permits us to draw several conclusions with regard to the Na-PMMA ionomers. First, for the untreated cast films, the only observed mode of deformation is crazing, even for samples having high ion contents of 6.0 and 12.4 mol %. This situation is analogous to that found in the Na-SPS ionomer of 8.5 mol %, also cast from DMF. The null effect of ion content on the deformation mechanisms of these PMMA ionomers is a direct result of casting from a polar solvent, thereby destroying the ionic aggregates (cluster).

For the cast films that have been heat treated, the mode of deformation changes with increasing ion content. It varies from pure crazing for PMMA to crazing plus shear deformation at an ion content of 6 mol % and then to essentially localized shear zones at an ion content of 12.4 mol %. Although it would be helpful to have more data at different ion contents, in general the results obtained on the influence of ion content on deformation modes, in these thermally equilibrated Na-PMMA ionomers, are rather similar to those obtained earlier on PS ionomers.

It appears from Table 1 that a transition in the deformation mode from only crazing to crazing plus shear occurs near a total strand density of 51×10^{25} chains/m^3 and that the transition to only shear deformation comes at a total strand density somewhere between 51 and 97×10^{25} chains/m^3. These values for Na-PMMA ionomers are considerably greater than the corresponding values reported by Henkee and Kramer[8] for covalently cross-linked PS of 4 and 8×10^{25} chains/m^3. There are several reasons for this. First, although ionic cross-linking does provide somewhat similar effects to covalent cross-linking, such as a shift of T_g to higher temperatures and a rise in the rubbery plateau modulus, as shown for Na-PMMA ionomers in Figure 9, ionic cross-links are not as strong and stable as covalent cross-links, as they can be overcome at sufficiently high temperatures. The dissociation and reassociation of monovalent ion pairs is expected to be much easier than chain scission, involving primary bond breakage. Also, the contribution of an ionic network to the craze surface energy, a key parameter in determining when craze development becomes unfavorable to shear deformation,[2] will be less than that for a covalently cross-linked network. Hence, for the Na-PMMA ionomers, the effective entanglement strand densities will be smaller than the values cited in Table 1, based on the assumption that ionic cross-links are comparable to covalent ones.

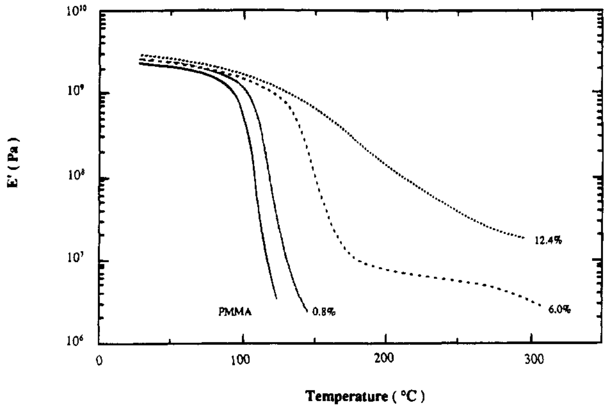

Figure 9. Storage modulus vs temperature curves for Na-PMMA ionomers, showing a shift of T_g to higher temperatures and a rise in the rubbery plateau modulus.

A second reason why the strand density values of Table 1 for the transition from crazing only to crazing plus shear, and for the transition to shear only, are higher than the anticipated values based on results obtained on a number of polymers, including irradiated PS, is that PMMA itself appears to be an exception to the general rule. For example, while many different polymers having an entanglement strand density of about 4×10^{25} chains/m^3 or above develop combined crazing and shear deformation on being deformed, PMMA thin films seem to exhibit only crazing, even though its entanglement strand density has the value of 7.8×10^{25} chains/m^3. Hence, it is not possible to determine the effectiveness coefficient, k, of eqs 4 and 5, based on the use of strand density values for the transition from crazing to crazing plus shear deformation determined from covalently cross-linked PS.[8]

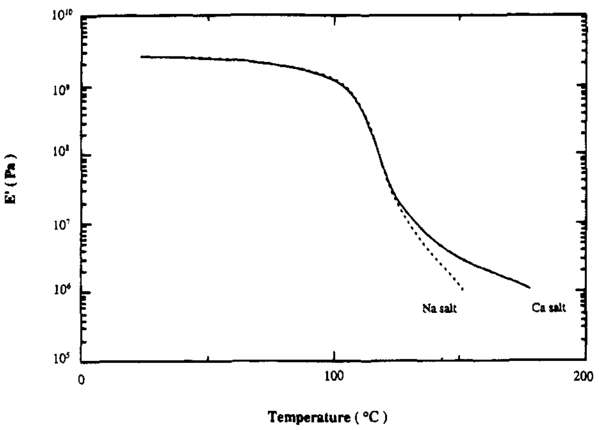

Figure 10. Storage modulus vs temperature curves for Na-PMMA ionomer and Ca-PMMA ionomer with 0.8 mol % ion content.

At very high ion contents where the ν_e term contributes only a small proportion of the total strand density, it may be possible to obtain a rough value of the effectiveness coefficient by comparing values for the transition in deformation mechanisms from only shear to fracture without plastic deformation. For covalently cross-linked PS, Henkee and Kramer give a value of $\nu = 14\nu_e$, corresponding to a total strand density of about 50×10^{25} chains/m^3.[8] Our tests on the Na-PMMA ionomers extended only to ion contents of 12.4 mol %, and it appears from our results that the transition from shear only to fracture will occur at somewhat higher ion contents. However, since only a small amount of localized shear deformation is present at this ion content, the estimated total strand density for the transition to fracture without plastic deformation will probably be slightly above 100×10^{25} chains/m^3. If we assume it to occur at 100×10^{25} chains/m^3, the corresponding ionic strand density would be 92×10^{25} chains/m^3. Inserting this value for ν_i in eq 4 and using the Henkee and Kramer value of 50×10^{25} chains/m^3 for the value of ν_{eff}, corresponding to the transition to fracture without plastic deformation, we find the effectiveness coefficient, k, to have the value 0.46. Hence, on the basis of the strand density needed to effect the transition from shear only to fracture without shear or crazing, ionic cross-linking would appear to be somewhat less than half as effective as covalent cross-linking.

Effects of Counterion on Deformation Modes. The "effective" strand density of ionically cross-linked PMMA ionomers can be increased, as indicated by the data given in Table 1, by an increase of ion content. Another way to do so is, for a given ion content, to replace monovalent counterions by (non-transition) metal divalent ions, as divalent ions are known to form stronger and more stable ionic cross-links than monovalent ions,[12,13] thereby increasing the effective strand density. This is evident from the storage modulus vs temperature measurements of Figure 10, made on compression-molded samples of PMMA ionomer of 0.8 mol % ion content, having respectively monovalent Na and divalent Ca as the counterions. Both types of ionomers have the same glass transition temperature, but the Ca ionomer develops a more extended rubbery plateau; it also shows, in mechanical loss measurements, a small higher temperature loss peak, indicative of the presence of some second-phase ionic aggregates, that is not present in the corresponding Na-PMMA ionomer.[27] The higher stability of the ionic cross-links for the divalent ion ionomer may also imply that there will be a greater resistance to fibril formation and crazing upon subjecting thin films of Ca-PMMA to applied tension.

To investigate this possibility, thin films of PMMA ionomer of 0.8 mol % ion content were cast from methylene chloride. One set of samples had monovalent Na as the counterion and the other set had divalent Ca. In the as-cast condition, both sets of samples exhibited only crazing at this low ion content, and Figure 7 shows the deformation pattern and the typical craze morphology for the Ca-PMMA sample. However, since the dynamic mechanical tests made on compression-molded samples of the 0.8 mol % samples showed that only the samples containing the divalent Ca ion developed a two-phase microstructure containing ion-rich aggregates, it was decided to subject the Ca-PMMA thin films to an additional heat treatment to see whether this would develop the equilibrium microstructure and perhaps change the deformation mode. When this was done, as shown by the deformation patterns of Figure 8, both crazing and interacting shear bands were found to be present. Furthermore, these deformation patterns for the thermally equilibrated Ca-PMMA ionomers of 0.8 mol % ion content were found to be rather similar to those noted in a heat-treated sample of the Na-PMMA ionomer of 6 mol % and in a thermally annealed sample of poly(styrene-*co*-sodium methacrylate) ionomer of 4.8 mol % ion content.[42] These results indicate that ionic groups of about 1 mol % ion content, having divalent Ca as the counterion, may be as effective in modifying deformation behavior as 5–6 mol % ionomer samples with monovalent Na as the counterion. Also, in a study of the deformation modes in a PS ionomer of 4.1 mol % ion content, it was noted that only crazing was observed when the counterion was monovalent K, while combined crazing and shear deformation were present when the counterion was divalent Ca.[21]

For the Ca-PMMA ionomer of 0.8 mol % ion content, the calculated total strand density (the sum of the entanglement density and the ionic cross-linking density) is 14×10^{25} chains/m^3 according to eq 3, again assuming that all ionic groups function as effective cross-links. This value is high enough, according to the concepts enunciated by Henkee and Kramer[8] in their study of covalently cross-linked PS, to expect that only shear deformation or brittle fracture will be present, while we find that both crazes and shear deformation zones coexist. However, as already noted, PMMA is an exception to the general rule, and the calculated value of the strand density may be high, since there may be some ionic groups not involved in bonding and since divalent ionic cross-links, although much stronger than monovalent ion-pair associations, are still not as strong as covalent cross-links.[45]

Conclusions

Unmodified PMMA deforms only by crazing, but when ionic interactions are introduced, the deformation mode changes: crazing and shear deformation coexist at an ion content of 6.0 mol % and localized shear deformation becomes the only deformation mode at an ion content of 12.4 mol %. This general trend is consistent with that observed for PS ionomers. It is believed that ionic cross-links in ionomers, although not as effective as covalent cross-links or physical entanglements (at temperatures far below T_g), are responsible for these changes: the effective strand density is increased upon introduction of ionic cross-links, thereby making crazing more difficult to occur as compared with shear deformation. Divalent Ca ions have a much stronger effect than Na ions; for example, the Ca-PMMA ionomer having an ion content of only 0.8 mol % induces shear deformation in addition to crazing, a comparable effect on the deformation behavior to that observed for the Na-PMMA ionomer having an ion content of 6 mol %.

Thermal treatment plays an important role in determining deformation behavior of the ionomers, particularly when a residual polar solvent, e.g., DMF, preferentially solvates ionic groups in ionomers and effectively destroys the ionic cross-links. With proper thermal treatment, the ionic aggregates can be recovered, leading to significant changes in the observed deformation behavior.

The concept of an effective strand density, ν_{eff}, has been introduced to consider the generally weaker ionic bonds formed in ionomers as compared with covalent bonds. The quantitative evaluation of the coefficient, k, reflecting the strength of the ionic entanglements, may, in principle, be obtained from observations of transitions in deformation patterns of strained thin films of ionomer samples of varying ion contents. The k values obtained could then be compared with model calculations of electrostatic interactions in ionic aggregates, which would be useful to further advance our understanding of the effect of ionic bonds on the deformation behavior of ionomers; these tasks are the subject of future work.

This study on PMMA ionomers has confirmed our previous conclusion, drawn from test results on PS ionomers, that the introduction of ionic groups into glassy polymers can shift the deformation mode from crazing toward shear deformation, thereby potentially increasing the fracture resistance of the base polymers. Since ionic aggregates are thermolabile, such an approach may be a useful one to enhance mechanical properties of glassy polymers without losing melt processability.

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