Deformation and tensile fracture behaviour of sulfonated polystyrene ionomers: effects of counterion and excess neutralizing agent

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The mechanical behaviour of sulfonated polystyrene ionomers can be altered by changing the nature of the counterion and by addition of excess neutralizing agent. Enhanced tensile strength and greater energy to fracture have been obtained by changing the counterions from monovalent Na to divalent Ca. The Ca ions create stronger ionic crosslinks that result in a more effective entanglement network. Increases in both tensile strength and toughness have also been obtained in an Na salt sulfonated polystyrene ionomer by addition of a 100% excess of neutralizing agent. The enhancement in properties is thought to arise from the presence of a small, coherent second phase that acts as a reinforcing filler and increases resistance to crack propagation.

(Keywords: sulfonated polystyrene; ionomers; mechanical behaviour)

INTRODUCTION

The introduction of ionic groups into polymers provides a unique opportunity to modify their molecular structure and physical properties[1–6]. The resulting materials, which generally have less than 15 mol% of ionic groups, are referred to as ionomers. Interaction between the ionic groups modifies and strengthens the existing entanglement network and leads to two different types of ionic aggregates, viz. multiplets and ionic clusters. According to a widely used model of ionomer microstructure, multiplets are small ionic aggregates consisting of a small number (eight or less) of interacting ion pairs, which act rather like physical crosslinks, and clusters are larger aggregates of phase-separated ion-rich regions that also contain segments of hydrocarbon chains[2,6–8]. Evidence in support of the crosslinking effect of ionic interactions is a continued rise in the value of the glass transition temperature with increasing ion content and a steady increase in the rubbery modulus and in the melt viscosity. The presence of ionic clusters as a second phase receives support from the observation of a second higher-temperature glass transition in dynamic mechanical data and from the presence of a low-angle, so-called ionic peak in small-angle X-ray or neutron-scattering data[6].

Structure–property relationships in ionomers have been studied by many investigators, but until recently most of the reported studies have been concerned with the physical properties of these materials in the rubbery or flow state. Much less attention has been given to the mechanical properties in the glassy or solid state[9,10]. An important variable affecting the performance of ionomers is ion content. For example, for Na salt sulfonated polystyrene (SPS) ionomers, it has been shown that with increasing ion content the deformation modes in thin-film samples subject to tensile loading change from crazing only at low ion contents to crazing plus shear deformation at high ion contents[11], a finding similar to that observed by increase of radiation-induced crosslinking in polystyrene[12]; also, in bulk samples, both the tensile strength and toughness of SPS ionomers increase appreciably above some critical ion content where ionic clusters begin to control the microstructure[13,14].

Aside from ion content, two other variables that are known to have an effect on some properties of ionomers are the nature of the counterion and the presence of excess neutralizing agent[2,10,15]. The present study is concerned with the influence of these two variables on the mechanical behaviour of SPS ionomers. We have investigated the effect on deformation modes and on stress–strain response of changing the counterion from monovalent Na or K to divalent Ca, as divalent Ca ions are known to lead to stronger ionic bonds than monovalent ions[2]. Also, since it has been reported that excess neutralizing agent can raise the tensile strength of elastomeric ionomers[15] and of telechelic polyisoprene ionomers[16], another purpose of the present study is to investigate the influence of excess neutralizing agent on the mechanical properties of a glassy-type ionomer, such as sulfonated polystyrene ionomer.

EXPERIMENTAL

Lightly sulfonated polystyrene samples were prepared by sulfonation of polystyrene according to the method

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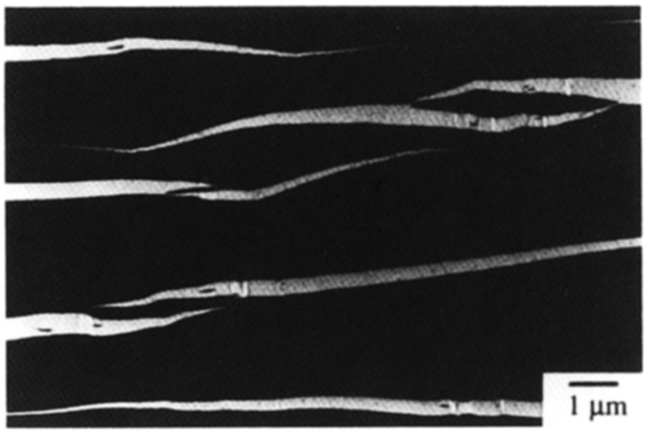

Figure 1 TEM micrograph of a strained thin film of a Ca salt SPS ionomer (2.6 mol% ion content) cast from tetrahydrofuran solution

described by Makowski *et al.*[17]. Two different grades of polystyrene were used as the starting polymer. For the deformation studies on thin-film specimens, the polystyrene (Pressure Chemical) was a narrow molecular weight distribution polymer ($M_w = 400\,000$, $M_w/M_n = 1.06$). For the study of the mechanical behaviour of bulk samples, a broad molecular weight distribution polymer (Polysciences) with a molecular weight in the range 125 000–250 000 was used.

After the sulfonation reaction was terminated, the partially sulfonated polystyrene was recovered by steam stripping in boiling water. A small amount of the acid copolymer was removed and the ion content was determined by titration of the acid groups. To neutralize the acid groups, or to obtain samples of desired excess neutralizing agent, a calculated amount of metal hydroxide (NaOH or $Ca(OH)_2$) was added to the acid copolymer. For the study of deformation modes in thin-film samples, the ionomer sample was obtained by freeze drying from benzene/methanol (90/10 v/v) solution followed by vacuum drying for one week at room temperature. For the study of the mechanical behaviour of bulk samples, the ionomer sample was dried, after steam stripping, under vacuum for 48 h at 85°C and then for an additional 24 h at 120°C, and subsequently compression moulded into bars.

The thin-film samples were prepared by casting onto glass microscope slides. They were subsequently dried, cut into small squares (2 × 2 mm) and floated on distilled water. Sections of the film were picked up on a copper grid, further dried for 48 h under vacuum at room temperature and then deformed in tension by stretching the copper grid. After straining, the microstructures of the deformed samples were examined by means of a transmission electron microscope (JEOL-100 CXII) operating at 100 kV. This method of approach has been previously described in detail by Kramer and coworkers[18,19].

For the measurements of the stress–strain characteristics of bulk samples, tensile tests were made on hourglass-shaped samples (3 in long, with a 0.2 in diameter in the gauge section and a 0.5 in diameter at the ends) machined from compression-moulded bars. All tests were performed on an Instron tensile-testing machine at a crosshead speed of 0.005 in min^{-1}. Tensile fracture surfaces were coated with a thin layer of gold and examined by an ETEC scanning electron microscope.

RESULTS AND DISCUSSION

Effects of the counterion on deformation modes in thin films

Previous tests carried out on SPS ionomers, neutralized with monovalent Na or K ions, have shown that thin-film samples deform only by crazing at low ion contents but that when the ion content reaches about 6 mol% or higher both crazing and shear deformation are present[10,11]. For example, shear deformation zones were observed at the tips of crazes in Na salt SPS ionomers having an ion content of 7.5 mol%[14], and inclined shear zones have been seen, in addition to crazes, in samples having an ion content of 8.5 mol%[20,21].

In the present study on Ca salt SPS ionomers, only localized crazing was observed in a sample with an ion content of 2.6 mol%, and this is illustrated in the transmission electron microscopy (TEM) micrograph of *Figure 1*. However, at an ion content of 5.2 mol%, as the TEM micrograph of *Figure 2* suggests, crazes interact with the shear deformation zone (DZ). We have also previously observed the formation of a shear deformation zone in Ca salt SPS samples having an ion content of 4.1 mol%[20]. These shear deformation zones are similar to those seen in tensile-strained thin films of poly(styrene-*co*-acrylonitrile), in which the low entanglement density of polystyrene was increased by copolymerization[22]. In contrast to the above-mentioned results on Ca salt ionomers, a K salt ionomer, also of 4.1 mol% ion content, exhibited only crazing[20], as did also an Na salt ionomer with an ion content of 4.3 mol%[11].

It is evident from these results that when the counterion is divalent Ca the ion content at which the transition occurs from crazing only to crazing plus shear deformation is significantly lower than when the counterion is monovalent Na or K. The results indicate that a stronger and more effective crosslinked ionic network is present when the divalent Ca ion is substituted for monovalent ions. A greater stability of Ca salt ionomers as compared to monovalent salt ionomers of comparable ion content is also evident from the results

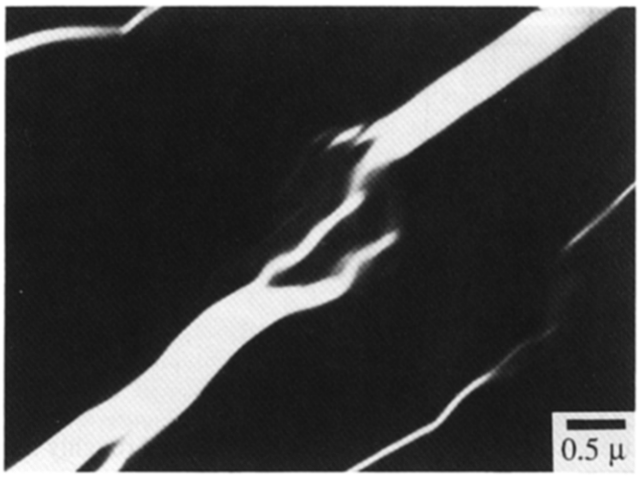

Figure 2 TEM micrograph of a strained thin film of a Ca salt SPS ionomer (5.2 mol% ion content) cast from tetrahydrofuran solution

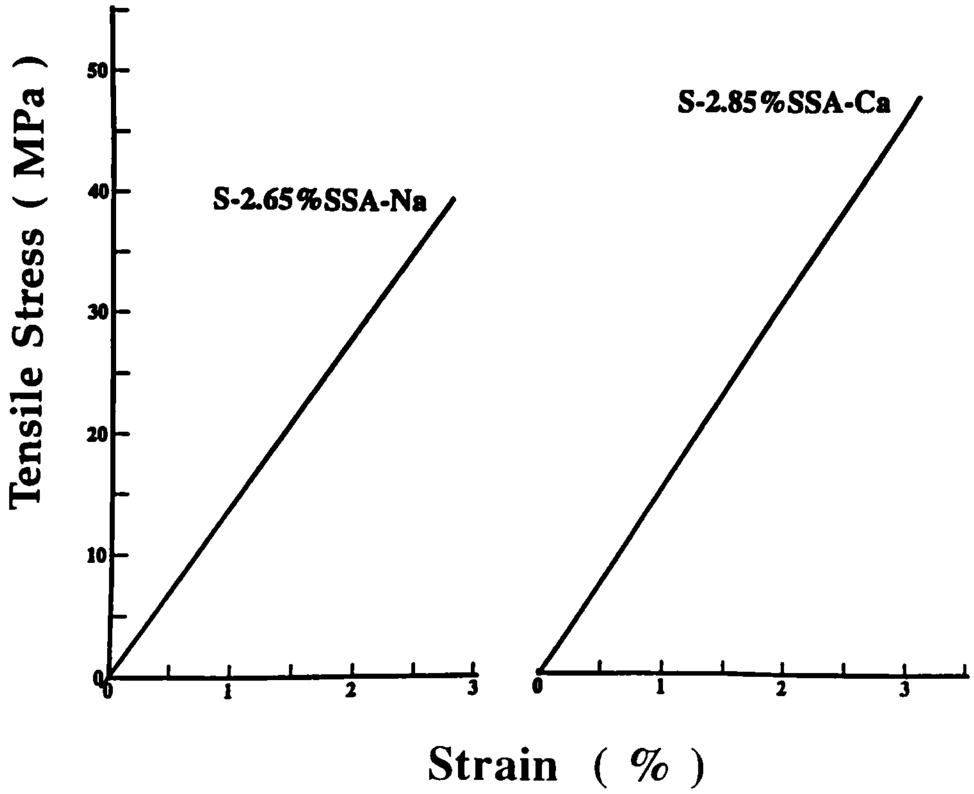

Figure 3 Typical stress–strain response curves for a Ca salt SPS ionomer (2.85 mol% ion content) and an Na salt SPS ionomer (2.65 mol% ion content)

of dynamic mechanical measurements; the rubbery plateau modulus of Ca salt SPS ionomers is essentially constant with increasing temperatures to well above 250°C, while for monovalent salt ionomers the rubbery modulus drops significantly with increasing temperature above 150°C[20].

Effects of the counterion on the mechanical behaviour of bulk samples

All of the Ca salt SPS ionomer samples failed in a brittle manner when tested in tension under conditions of plane strain. There was a considerable degree of scatter in the data obtained on individual samples, presumably because of the presence of varying degrees of surface defects (samples were carefully machined but not polished). Tensile strength generally increased with ion content and appeared to reach an optimum value at about 3 mol%, as compared to about 6 mol% for Na salt SPS samples[14]. An observed drop in strength at higher ion contents may result from some degree of thermal degradation, as the samples of high ion content had to be moulded at high temperatures after prolonged heating. For example, the sample having an ion content of 5.75 mol% was moulded at 245°C after heating for 7 h, and this sample exhibited some yellowing indicative of thermal degradation.

At lower ion contents thermal degradation was not a problem and the ionomer samples remained colourless. A typical stress–strain curve for a Ca salt sample of 2.85 mol% ion content is shown in *Figure 3*. The stress–strain curve for an Na salt ionomer of roughly the same ion content is shown for comparison purposes on the same figure. Both samples exhibit an essentially linear response but it takes a greater load to fracture the samples containing the divalent Ca ions. For example, the average tensile strength of the Ca salt samples, based on tests on four separate samples, was 47.6 MPa, as compared to a value of 38.9 MPa for the Na salt samples.

The toughness, or energy to fracture per unit volume, as measured by the area under the stress–strain curve, also increases as divalent Ca ions replace monovalent Na ions. For example, the average value of toughness for the Ca salt samples discussed above was 0.74 MJ m^{-3} compared to a value of 0.54 MJ m^{-3} for Na salt samples. The generally higher values for tensile strength, a 22% increase, and toughness, a 37% increase, for the Ca salt samples are an indication that the ionic crosslinking network that is formed is stronger and more stable than that present in SPS ionomers containing only monovalent ions, such as Na or K.

A scanning electron microscopy (SEM) scan of a portion of the fracture surface for the sample with a 2.85 mol% ion content is shown in *Figure 4*. This sample failed by breakdown of a craze, the only mode of deformation seen in this and other Ca salt samples that were tested. *Figure 4* shows the transition zone between the slow-growth region surrounding the fracture source and the faster-growth region showing typical hackle bands. These bands tend to arise because of instabilities in the fast crack growth process[23,24]. Such bands were also noted on the tensile fracture surfaces of samples of Na salt ionomers, and the width of the first band, indicative of the length of the craze ahead of the crack front, was found to decrease with increasing ion content[14]. For comparable ion contents, the width of the band for the Ca salt ionomers is found to be significantly smaller than that observed for the Na salt ionomers. Stated somewhat differently, the observed band width for

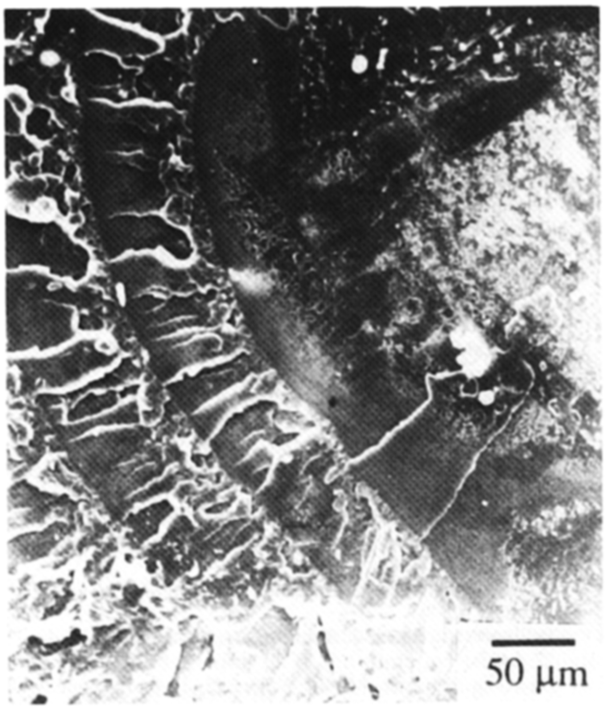

Figure 4 SEM micrograph of a portion of the tensile fracture surface of a Ca salt SPS ionomer (2.85 mol% ion content) sample

Table 1 Effect of excess neutralizing agent on tensile properties of Na salt SPS ionomers (3.6 mol%)

Excess NaOH (%)	Tensile strength (MPa)	Toughness (MJ m^{-3})
0	41.2 ± 1.3	0.57 ± 0.06
100	45.1 ± 0.5	0.65 ± 0.01
300	40.9 ± 2.0	0.54 ± 0.03

the Ca salt ionomer of 2.85 mol% ion content is comparable to the band width to be found in an Na salt ionomer of about 5 mol% ion content or greater. This appears to be another indication of a greater stability to craze breakdown and fracture, probably as a result of a stronger ionic crosslinking network, when divalent counterions such as Ca are used in place of monovalent ions such as Na.

A greater stability to craze breakdown in bulk samples of SPS ionomers containing divalent Ca counterions is also evident from measurements of the lifetime to fracture for samples subject to alternating cycles of stress. Results of such studies have been reported[21]. They show that, for a given ion content of 4.1 mol%, SPS ionomer samples containing divalent Ca ions have an average lifetime to fracture almost three times greater than samples containing monovalent ions. Thus, both from tests made on bulk samples under plane strain conditions and on thin-film samples made under plane stress conditions, it may be concluded that substitution of divalent Ca ions in place of monovalent counterions, such as Na or K, leads to enhanced craze stability, to a more effective crosslinking and entanglement network and to improved tensile and fatigue properties.

Effect of excess neutralizing agent

Samples were prepared of a Na salt SPS ionomer with 0%, 100% and 300% excess NaOH. Tests were made only on samples having an ion content of 3.6 mol%. At this ion content, the microstructure consists primarily of multiplets[25]. Hence, the possible influence of ionic clusters on the test results was appreciably reduced, if not completely eliminated. The choice of 100% and 300% excess NaOH was made so that the present results concerning strength and fracture energy could be compared with previously obtained results on similar samples exposed to alternating cycles of tension and compression[26].

The results obtained from the tensile experiments are given in *Table 1*. The values of tensile strength and toughness given there are average values based on test results obtained on three separate samples.

The data show that the addition of a 100% excess of neutralizing agent enhances both the tensile strength and the toughness compared to samples having no excess neutralizing agent. However, the addition of a 300% excess of NaOH leads to a decrease in properties. These conclusions are similar to those obtained when similar samples were subjected to fatigue cycles of loading[26]. In that study, samples containing 100% excess neutralizing agent only failed after 150 000 cycles of loading, as compared to about 33 000 cycles for samples having no excess NaOH. Here too, addition of a 300% excess of NaOH led to poorer performance.

Examination of the fracture surfaces of failed samples provides some clues as to why a modest amount of excess NaOH is helpful to properties while 300% excess neutralizing agent is detrimental. An SEM scan of a portion of the tensile fracture surface of a 100% excess NaOH sample is shown in *Figure 5*. Finely dispersed second-phase particles, in the size range 0.1–0.3 μm, are present and they appear to be well bonded to the ionomer matrix. These fine particles, which are not seen in the 0% excess samples, may act as a reinforcing filler. Also, the ions of the excess NaOH are probably attracted to and increase the size and the strength of the small ionic aggregates that are already present, as has been proposed when excess neutralizing agent is added to a three-armed star polyisobutylene-based ionomer[27].

A similar fracture surface morphology to that shown in *Figure 5* has also been observed in fatigued samples of Na salt SPS ionomers having 100% excess NaOH, and it was suggested that the fine second-phase particles, which ara a direct result of the addition of the excess

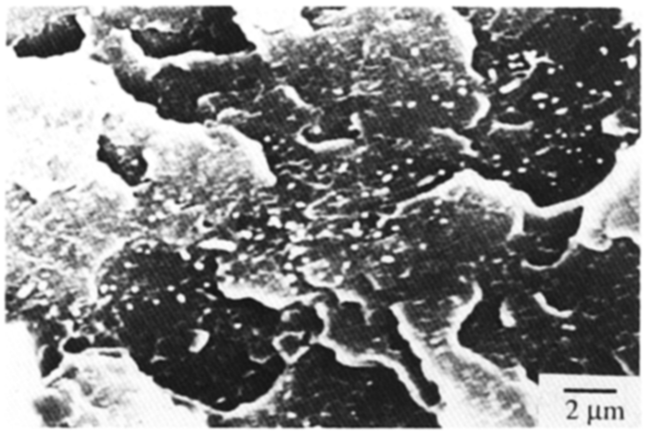

Figure 5 SEM micrograph of a portion of the tensile fracture surface of a Na salt SPS ionomer (3.6 mol% ion content) having 100% excess NaOH

neutralizing agent, may contribute to a greater resistance to crack propagation[26].

For the 300% excess NaOH samples, the tensile fracture surfaces of this study and the fatigue fracture surfaces of the previous study[26] show the presence of considerably larger particles, in the size range 1–5 μm. These larger particles, which appear to be rather poorly bonded to the matrix, can act as stress raisers and thereby cause earlier craze and crack initiation. They are also ineffective in impeding crack propagation.

It is instructive to compare our results obtained on a glassy ionomer with reported literature results on the effects of excess neutralizing agent on some properties of elastomeric ionomers[15,27] and carboxylic polyisoprene telechelic ionomers[16]. In these studies it was found that a significant increase in tensile properties could be obtained by the addition of an excess of neutralizing agent. It was suggested that the enhanced properties resulted when the ions of the neutralizing agent joined with the ionic aggregates already present and thereby strengthened the ionic network. An enhancement in ultimate properties has also been reported when excess neutralizing agent (zinc stearate) is added to a sulfonated ethylene/propylene/diene ionomer[16]. In this case, the added zinc stearate formed crystalline second-phase particles (about 1 μm in size) which led to a reinforcing filler effect.

Although the chemical compositions, the microstructures and the physical properties of glassy ionomers, elastomeric ionomers and telechelic ionomers can be significantly different, it may be concluded that in all of these materials an enhancement of mechanical properties can be achieved by addition of a proper excess of neutralizing agent.

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