Block copolymer ionomers: 2. Viscoelastic and mechanical properties of sulphonated poly(styrene-ethylene/butylene-styrene)

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Ionomers prepared from a sulphonated poly(styrene-(ethylene-*co*-butylene)-styrene) triblock copolymer possessed a unique three-phase microstructure that consisted of 3–4 nm ionic domains within 20–30 nm polystyrene domains dispersed in a rubbery continuous phase. The ionic network resulted in an increase of the glass transition temperature, T_g, of the polystyrene-rich phase and the development of a new plateau region in the dynamic modulus above this T_g. The plateau modulus due to the block copolymer microstructure, i.e. the modulus between the rubbery block and polystyrene block T_gs, decreased for the ionomers. These effects were accentuated by increasing the sulphonation level. Room temperature tensile properties were unaffected by sulphonating the block copolymer, but significant improvements were realized in the high temperature (70–200°C) tensile modulus, elongation and ultimate strength. The zinc salts exhibited the best combination of good processability and high temperature tensile properties. The ionomers were more hygroscopic than the unmodified block copolymer, but the reduction in tensile properties of saturated samples was generally <20% of those of the dry ionomer.

(Keywords: ionomers; viscoelasticity; mechanical properties)

INTRODUCTION

Thermoplastic elastomers based on styrenic block copolymers exhibit the melt processing characteristics of thermoplastics and many of the physical properties of vulcanized rubber. This behaviour is a result of the formation of microphase separation of glassy polystyrene (PS) domains that act as physical crosslinks dispersed in the rubbery matrix. At elevated temperatures, above the glass transition of the hard phase, the physical crosslinks are easily deformed and significant creep can occur even at low applied stress. This establishes an upper temperature limit for use of these materials, which is usually low compared with chemically crosslinked rubber. Moreover, the PS domains are relatively non-resistant to hydrocarbon solvents and oils, which further limits the applications of these polymers.

One way to eliminate the above deficiencies of conventional block copolymer thermoplastic elastomers is to crosslink the PS microdomains. If the crosslinks were thermally reversible, the melt processability of the composition could be retained. In particular, functionalization of the PS endblocks of a styrene/diene or styrene/olefin block copolymer with acid or neutralized acid groups may result in intermolecular associations that form a physical network within the PS domains in a manner similar to what commonly occurs in other ionomers[1].

In a previous paper[2], we described a new block copolymer ionomer prepared by sulphonating a poly(styrene-(ethylene-*co*-butylene)-styrene), SEBS, triblock copolymer. In this paper, we report the tensile and dynamic mechanical properties of this material.

EXPERIMENTAL

The starting polymer was a hydrogenated poly(styrene-butadiene-styrene) triblock copolymer, Kraton 1652, from Shell Development Co. After hydrogenation, the midblock was essentially a random copolymer of ethylene (1,4-additions) and butylene (1,2-additions). The polymer had a $M_n = 50\,000$ and contained 29.8 wt% styrene. The preparation of the sulphonated block copolymer ionomers has been described in an earlier paper[2]. The materials used in this study are given in *Table 1*; the sample nomenclature used for the ionomers was X.YM-SBC, where X.Y was the degree of substitution of the styrene (mol% styrene sulphonated) and M designated the counterion. The unmodified copolymer was referred to as SEBS.

Dynamic mechanical analyses (d.m.a.) were performed on compression-moulded films using a Polymer Laboratories dynamic mechanical thermal analyser. The samples were ~1 × 5 × 10 mm. The frequency used was 1 Hz and the temperature was varied from −110 to 250°C at a rate of 3°C min^{-1}.

Tensile property measurements were made on microtensile specimens, cut from ~1.5 mm thick compression-moulded films, with an Instron universal testing machine equipped with a convection oven. Measurements were

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Table 1 Block copolymer ionomers

Material designation	Sulphonation level (mol%)[a]	Cation
SEBS[b]	0.0	–
2.5H-SBC	2.5	H
2.5Na-SBC	2.5	Na
2.5Zn-SBC	2.5	Zn
5.2H-SBC	5.2	H
5.2Na-SBC	5.2	Na
5.2Zn-SBC	5.2	Zn
8.7H-SBC	8.7	H
8.7Na-SBC	8.7	Na
8.7Zn-SBC	8.7	Zn
11.0Pb-SBC	11.0	Pb
11.0Co-SBC	11.0	Co
11.9H-SBC	11.9	H
11.9Na-SBC	11.9	Na
11.9Zn-SBC	11.9	Zn
18.0H-SBC	18.0	H
18.0Na-SBC	18.0	Na
18.0Zn-SBC	18.0	Zn

[a] Calculated from elemental sulphur analysis
[b] Kraton TR70-8819 (Shell Development Co.)

made at 25, 75, 100, 150 and 200°C using a crosshead speed of 12.7 mm min^{-1}. The specimens were conditioned at the test temperatures for 5 min prior to testing.

Small angle X-ray scattering (SAXS) measurements were made on beam line I-4 at the Stanford Synchrotron Radiation Laboratory (SSRL), Stanford, CA, USA. The sample-to-detector distance was varied to cover a range of wavevector, q, from 0.1 to 6.0 nm^{-1}, where $q = 4\pi \sin \theta/\lambda$, 2θ was the scattering angle and $\lambda = 0.143$ nm was the X-ray wavelength. This corresponded to long periods of 1–63 nm. Additional information on the experimental set-up can be found elsewhere[3].

Transmission electron microscopy (TEM) was used to study the microstructures of the SEBS and the ionomers. Analyses were carried out by Structure Probe, Inc. of West Chester, PA, USA, using a Jeol 100CX scanning transmission electron microscope. Specimens were prepared by thin sectioning compression-moulded films (1.5 mm thick) with a diamond knife at liquid nitrogen temperature. The PS phase was stained by exposing the films to RuO$_4$ vapour.

RESULTS AND DISCUSSION

Sample preparation

The sulphonated polymers were more difficult to mould than the unmodified SEBS, and moulding became more difficult with increasing sulphonation. For the highest sulphonation level, 18 mol%, it was not possible to produce good films. In general, the compression-moulded films usually possessed a high degree of moulded-in stresses, which resulted in severe shrinkage of the film at elevated temperatures. This problem was less severe for the zinc salts and the free acids than for the sodium salts. The residual stresses were due to the long relaxation times of the physical network formed by the ionic associations, and these were successfully eliminated by annealing the specimens overnight between spring-loaded parallel steel plates under vacuum near the glass transition temperature, T_g, of the PS phase. This procedure adequately prevented excessive distortion of the specimens at high temperature.

Dynamic mechanical behaviour

The tensile storage modulus, E', and loss modulus, E'', are plotted as a function of temperature in *Figure 1* for SEBS and the zinc salts of the sulphonated polymers. The transition temperatures, defined as the maxima in E'', are summarized in *Table 2*. The glass transition temperature, $(T_g)_{EB}$, increased ~3°C upon sulphonation

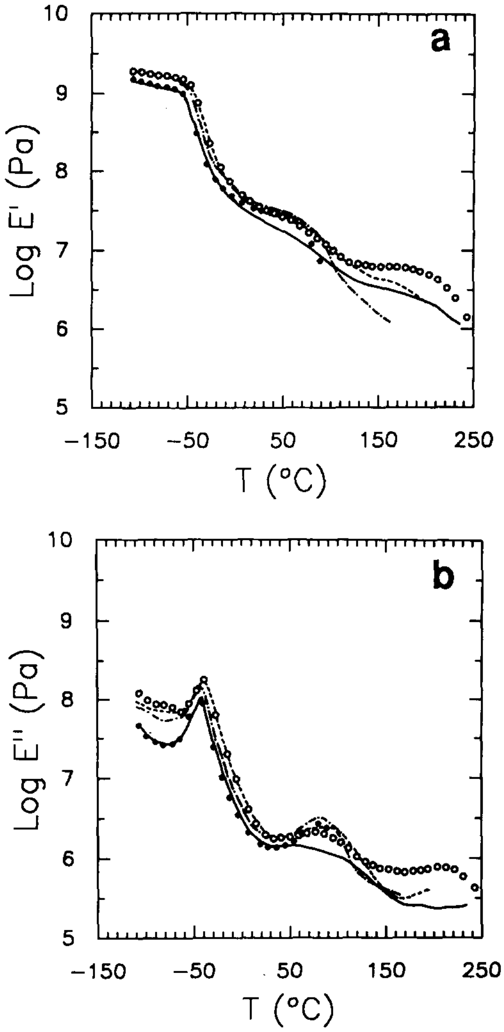

Figure 1 (a) Tensile storage modulus and (b) loss modulus *versus* temperature of the sodium and zinc salts of sulphonated SEBS ionomers: (●) SEBS; (—·—) 2.5Zn-SBC; (---) 5.2Zn-SBC; (——) 8.7Zn-SBC; (○) 11.9Zn-SBC

Table 2 Transition temperatures

Sample	Sulphonate (mol%)	Glass transition temperature (°C) EB	S	Post-T_g transition (°C)
SEBS	0	−41	80	
2.5Zn-SBC	2.5	−38	83	
5.2Zn-SBC	5.2	−38	89	
8.7Zn-SBC	8.7	−40	–[a]	195
11.9Zn-SBC	11.9	−39	80[a]	204

[a] Broad transition

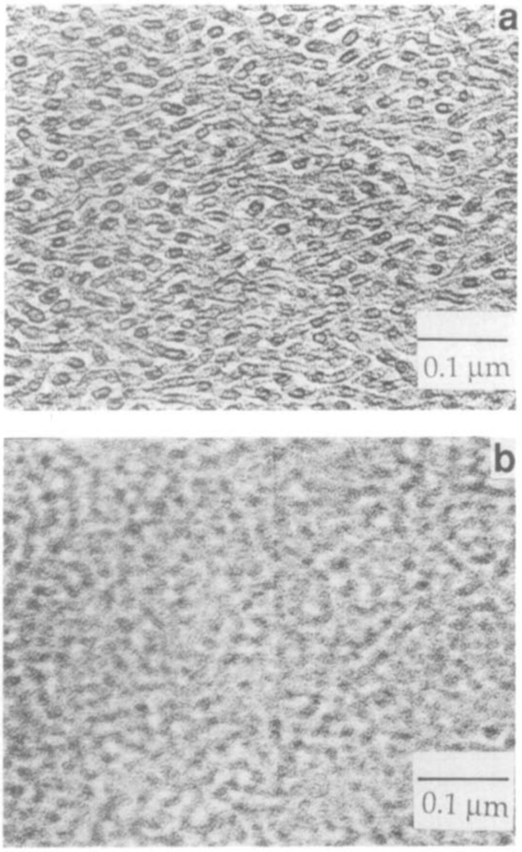

Figure 2 Transmission electron micrographs of (a) SEBS and (b) 11.9Zn-SBC. Dark regions represent the PS-rich phase

of the SEBS, but was insensitive to the degree of sulphonation. In contrast, sulphonation increased $(T_g)_S$ and broadened that transition region, similar to what has been reported[4,5] for sulphonated PS, SPS. As the sulphonation level increased, the PS glass transition became less distinct due in part to the broadening, but also due to the relatively high modulus of the ionomer above $(T_g)_S$. A third relaxation is apparent near 200°C for the two higher sulphonated polymers. Based on a similar post-T_g relaxation observed in SPS, this transition is attributed to motion in the ion-rich phase. The choice of the counterion had little effect on the temperatures of either of the transitions.

No attempts were made in this work to control the morphology of the polymers. Generally for block copolymers, equilibrium morphologies are more easily attained by slowly evaporating off the solvent of a polymer solution. The properties of the materials reported here were obtained on compression-moulded samples. Because the melt viscosities of the unmodified and sulphonated block copolymers were considerably different, it is quite likely that the departure of the morphologies from equilibrium for the various materials differed. This may explain some of the minor differences between the moduli, especially in the plateau region between the two T_gs, which is most sensitive to the block copolymer microstructure. As will be discussed later, microscopy and SAXS analyses indicated that the block copolymer morphology was perturbed by the sulphonation.

The E' for the SEBS decreased rapidly above $(T_g)_S$ as the polymer began to flow. The modulus for the ionomers, however, remained at values between 10^6 Pa and 10^7 Pa above $(T_g)_S$, and E' and the melt viscosity increased with increasing sulphonation. The persistence of a second modulus plateau region above $(T_g)_S$ in the ionomers was due to the development of physical crosslinks in the PS phase from intermolecular ionic associations. Similar behaviour was observed with lightly SPS ionomers[4,5]. The extent of the high temperature plateau region was dependent on the temperature resistance of the ionic network, which became more thermally stable with increasing sulphonation.

It must be stressed, however, that the ionic network resulted from thermally reversible, physical interactions and not from covalent bonding. That is, the pseudo-network behaviour was due to extremely long relaxation times of the electrostatic associations, similar to what has been observed with SPS ionomers[6].

Of course, the block copolymer also possessed thermally reversible crosslinks due to the microphase separation of the PS-rich phase, but this network was manifested below $(T_g)_S$. Thus, the SEBS ionomers possessed two distinct physical networks: one due to the microphase separation of the PS-rich phase and the other due to ionic crosslinking within the PS-rich phase. The first was responsible for the modulus plateau between $(T_g)_{EB}$ and $(T_g)_S$ and the latter for plateau above $(T_g)_S$. Although the transition temperatures for the sodium and zinc salts at identical sulphonation levels were similar, the moduli in the two plateau regions were generally higher for the zinc salts than for the corresponding sodium salts. This was more evident above $(T_g)_S$, which was somewhat surprising considering that the zinc salts were more processable, i.e. had lower viscosities.

Although the moduli of the ionomers remained between 10^6 Pa and 10^7 Pa at temperatures in excess of 200°C, values typical of a rubber-like network, these materials did exhibit melt flow as evidenced by the fact that samples were compression moulded and sometimes remoulded several times. Melt flow of the ionomers involves a relaxation process characterized by the repetitious breaking and reforming of ionic associations, which has been termed 'ion-hopping'[7]. The viscosity of the melt is determined by the kinetics of this process. Since the magnitude of the applied stress probably affects the kinetics of ion-hopping, it is not unreasonable to find that at low stresses, as in the dynamic mechanical experiment, the ionomer had the characteristics of a rubber-like network, and at the higher stresses encountered in typical polymer processing operations, they exhibited viscous flow.

Polymer microstructure

The TEM micrograph of the unmodified SEBS block copolymer (*Figure 2a*) showed a two-phase morphology of PS domains (the dark phase) dispersed in a continuous rubber phase. The texture of the PS phase appeared to be intermediate between spherical and cylindrical, with a characteristic diameter of ~10–15 nm. The microphotograph of 11.9Zn-SBC (*Figure 2b*) was qualitatively similar but the phase boundaries were much less distinct. The average diameter of the phase was estimated to be ~10–15 nm.

The SAXS analysis revealed that the ionomers actually consisted of three phases: a continuous rubber (EB) phase, glassy PS-rich domains and an ion-rich micro-

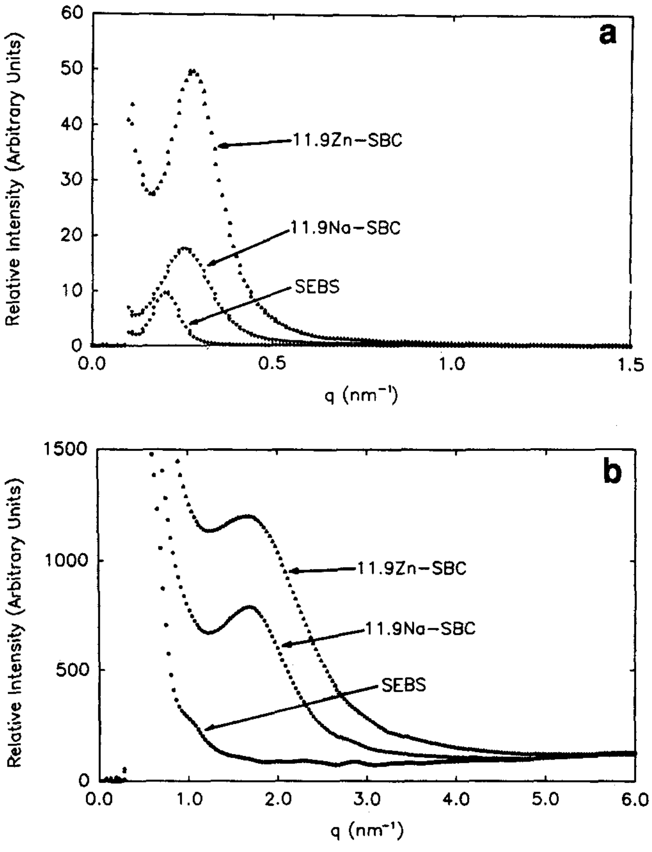

Figure 3 SAXS intensity *versus* wavevector for SEBS, 11.9Na-SBC and 11.9Zn-SBC: (a) $q=0.1\text{–}1.7\,\mathrm{nm}^{-1}$; (b) $q=1.0\text{–}6.0\,\mathrm{nm}^{-1}$

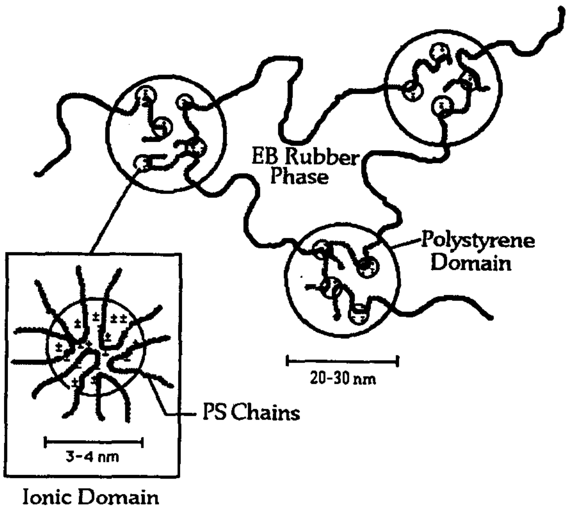

Figure 4 Schematic model of a triblock copolymer ionomer in which only the endblocks are functionalized

phase. The latter existed as a dispersed phase within the PS domains.

The SAXS curves at 50°C for SEBS, 11.9Na-SBC and 11.9Zn-SBC are given in *Figure 3*. *Figure 3a* covers the range $0.1<q<1.5\,\mathrm{nm}^{-1}$ and *Figure 3b* shows the data for $1.0<q<6.0\,\mathrm{nm}^{-1}$. The peak in *Figure 3a* corresponded to the two-phase structure of the block copolymer. When the SEBS was sulphonated, the peak broadened and moved to a higher wavevector, which indicated that the characteristic phase size became smaller and less homogeneous. The long spacing, calculated from the peak position in *Figure 3a* decreased from 30.2 nm for SEBS to 24.8 and 22.1 nm for 11.9Na-SBC and 11.9Zn-SBC, respectively, which roughly agrees with the TEM results.

In addition to the block copolymer SAXS peak, the ionomers also had a much less intense scattering peak at higher angle (*Figure 3b*). This peak was absent in SEBS, and its angular position corresponded to where a similar SAXS peak was observed in SPS ionomers[8]. By analogy, this peak is attributed to ion-rich domains dispersed within the PS microphase.

A schematic model of the microstructure of these ionomers is shown in *Figure 4*. Although the ionic domains are shown as spherical, the actual shape and spatial arrangement of the ionic groups are not known. In general, the microphase structure in ionomers remains an unanswered question. The proposed model in *Figure 4* allows for the presence of contact ion pairs that are not contained within the ion-rich microdomains and that do not constitute a separate phase.

Tensile properties

The tensile stress and elongation at break of the sulphonated ionomers and the base SEBS at various temperatures between 23°C and 200°C are given in *Tables 3* and *4*. At 23°C, there were no differences between the tensile properties of the SEBS and the ionomers. At 75°C, whch was within the transition region of the PS-rich domains (*Figure 1*), the stresses at break of the ionomers were two to six times higher than for SEBS and the elongations were four to six times higher. Both the stress and elongation at break increased with increasing sulphonation level and when the cation was changed from sodium to zinc. Surprisingly, the ultimate strengths and elongations of the acid derivatives at 75°C were similar or even higher than those for the sodium salts.

At higher temperatures, the improvement of the tensile properties of SEBS upon sulphonation became even more apparent. Typical stress–strain curves for SEBS and 11.9Zn-SBC at 100°C are shown in *Figure 5*. At any given temperature, tensile stress and elongation at break

Table 3 Tensile stress at break of sulphonated SEBS ionomers

	Strength at break (MPa)				
Sample	23°C	75°C	100°C	150°C	200°C
SEBS	28.5	1.67	1.03	0.36	0.15
Free acids					
2.5H-SBC	27.9		1.07	0.38	0.17
5.2H-SBC	28.2	4.55	1.21	0.45	0.34
8.7H-SBC	27.6		2.00	0.79	0.45
11.9H-SBC	27.6	5.39	2.62	1.10	0.62
18.0H-SBC	12.4		1.17	0.48	0.28
Sodium salts					
2.5Na-SBC	27.6		1.10	0.45	0.18
5.2Na-SBC	27.6	3.34	1.24	0.60	0.36
8.7Na-SBC	27.8		2.20	1.00	0.55
11.9Na-SBC	27.9	5.00	2.96	1.72	0.86
18.0Na-SBC[a]	13.1		1.31	0.48	0.31
Zinc salts					
2.5Zn-SBC	28.0		1.45	0.59	0.32
5.2Zn-SBC	28.1	4.48	1.72	1.03	0.65
8.7Zn-SBC	27.9		2.76	2.00	1.24
11.9Zn-SBC	28.2	7.58	3.38	2.76	1.79
18.0Zn-SBC	20.7		1.79	1.21	0.69

[a] Partial decomposition of sample occurred during moulding

Table 4 Elongation at break of sulphonated SEBS ionomers

	Ultimate elongation (%)				
Sample	23°C	75°C	100°C	150°C	200°C
SEBS	700	85	70	35	20
2.5H-SBC	695		155	40	25
5.2H-SBC	695	450	175	65	52
8.7H-SBC	680		240	85	52
11.9H-SBC	690	345	300	120	50
18.0H-SBC[a]	210		140	39	32
2.5Na-SBC	690		175	42	28
5.2Na-SBC	680	410	200	70	50
8.7Na-SBC	670		250	100	55
11.9Na-SBC	670	315	390	130	65
18.0Na-SBC[a]	200		150	50	35
2.5Zn-SBC	700		185	50	35
5.2Zn-SBC	690	425	210	88	62
8.7Zn-SBC	670		295	150	85
11.9Zn-SBC	690	485	370	240	110
18.0Zn-SBC	300		200	85	58

[a] Partial decomposition of sample occurred during moulding

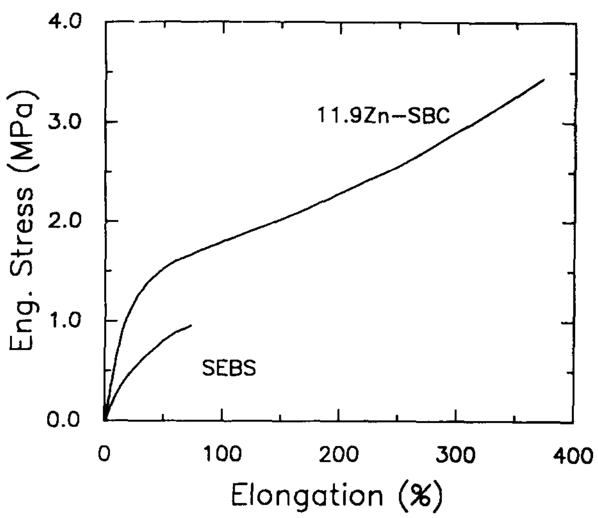

Figure 5 Typical stress *versus* elongation curves at 100°C for SEBS and 11.9Zn-SBC

and tensile toughness (the area under the stress–strain curve) improved with increasing sulphonation, and the zinc salts had the best properties. The tensile properties of the sodium salts were usually slightly better than those of the acid derivatives. The superior properties of the zinc salts may be attributed to higher ultimate elongations than for the other two derivatives. This, in turn, may be due to a weaker network formed by intermolecular hydrogen bonding of the sulphonic acid groups at elevated temperatures for the acid derivatives and, in part, to poorer film integrity of the sodium salts due to the poorer processability of these materials. The tensile stress at break of the SEBS and the zinc ionomers as a function of temperature are plotted in *Figure 6*. Note that the ultimate stress of 11.9Zn-SBC at 200°C was comparable to that of SEBS at 75°C.

The optimum improvement of the tensile properties by sulphonation occurred between 11.9 mol% and 18.0 mol%. In the case of the sodium and acid derivatives, the poor properties of the 18.0 mol% ionomers compared with the 11.9 mol% ionomers may have been due to degradation of the samples during moulding. The properties of 18.0Zn-SBC were better than those of the other two derivatives, but still considerably poorer than those of 11.9Zn-SBC. This might have been due in part to difficulties in moulding this ionomer, which resulted in films of relatively poor quality.

The very small improvement in the properties of the sodium salt over those of the acids was surprising. It is generally believed that because of stronger intermolecular interactions, the mechanical properties of ionomer salts are superior to those of the free acid derivatives[9]. No data is available in the literature, however, comparing sulphonic acid and metal sulphonate functionalized polymers. The absence of information on sulphonic acid derivatives is probably due to concern over the thermal and oxidative stability of these materials. For example, sulphonated EPDM (SEPDM) and telechelic polyisobutylene sulphonates (SPIB) are unstable in the free acid form[10]. There appears, however, to be less evidence to indict the acid derivatives of SPS, yet very few properties of these materials have been reported. In fact, the acid derivatives of SPS and the sulphonated block copolymers of the present study are stable to relatively high temperatures[2], and the data listed in *Tables 3* and *4* indicate that the mechanical property improvements obtained by intermolecular hydrogen bonding of sulphonic acid ionomers are at least of the same order of magnitude as those from electrostatic interactions of metal sulphonates. The higher thermal stability of the free acid derivatives of SPS and SEBS is probably due to the stabilizing influence of attachment to a phenyl ring.

The differences between the tensile properties of SEBS and the ionomers at elevated temperatures resulted from differences in the ability of the PS domains to support a tensile load above $(T_g)_S$. Beecher *et al.*[11] showed that the ultimate tensile failure of styrenic block copolymers resulted from rupture in the PS phase. Hence, restricting the molecular mobility in the PS phase should retard chain slippage and ultimate failure. Slippage of the chains within the PS domains is facilitated at high temperatures, as the viscosity of the PS phase decreases. For both the unmodified and sulphonated block copolymers, the elongation to break and tensile toughness decreased with increasing temperature as a consequence of the increasing ease at which the physical crosslinks due to the PS

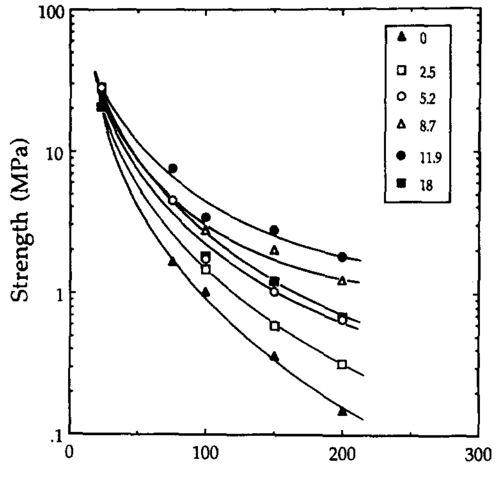

Figure 6 Tensile stress at break *versus* temperature for zinc salts of sulphonated SEBS

domains deformed under an applied load above $(T_g)_S$. The decrease in properties for the ionomers was moderated, however, by the ionic crosslinks that increased the relaxation times required for the PS segments to translate within the PS microdomains. This allowed the material to achieve a higher elongation and, as a result, support a higher stress.

Except for the decrease in E' discussed earlier, the room temperature tensile properties were unaffected by sulphonation, i.e. by the inclusion of ionic crosslinks. At temperatures below $(T_g)_S$ the PS phase was a glass. The molecular mobility within this phase is already low, and the physical crosslinks due to the microphase separation of the PS domains provided an adequate strengthening mechanism.

The sodium and zinc salts were chosen for this investigation, because they represented the two most extensively studied ionomer derivatives[9]. This was especially true for SPS, which is closely analogous to the SPS blocks of the sulphonated SEBS. Zinc salts have the distinction for a variety of ionomers of yielding the best combination of processability and properties. The reason for this is not well established, but has been attributed to the outer shell d-electrons of zinc that form a stronger, more covalent interaction with the sulphonate anion[12]. The data for the sulphonated SEBS polymers reported in this paper also suggest that optimum performance for these ionomers may be attained with the zinc salt.

A limited evaluation of two other counterions, cobalt(II) and lead(II), was performed. These were chosen on the basis that for SEPDM these two salts were reported to have the next best combination of rheology and properties after zinc[13]. The tensile secant modulus measured at 100% elongation, tensile stress and elongation to break at 23°C and 100°C for SEBS and four salts of sulphonated SEBS are compared in *Table 5*. (Note that the sulphonation levels of the sodium and zinc salts were marginally higher than for the cobalt and lead salts.) The improvement of the tensile properties of the ionomers at elevated temperature *versus* the properties of SEBS is clear from the data in *Table 5*, but there were no significant differences between the various salts at 100°C. The lower values of ultimate stress and elongation for the lead and cobalt salts compared with the sodium and zinc salts can probably be explained by their slightly lower sulphonation level. Whereas the 11.9Na-SBC was difficult to mould, the zinc, cobalt and lead salts moulded easily.

Table 5 Effect of the cation on the tensile properties of sulphonated SEBS (sulphonation level of 11–12 mol%)

	23°C			100°C		
Sample	E^a	σ^a	ε^a	E	σ	ε
SEBS	2.00	28.5	700	0.55	1.03	70
11.9Na-SBC	2.41	27.9	670	1.62	2.96	390
11.9Zn-SBC	2.55	28.2	690	1.65	3.38	370
11.0Co-SBC	2.38	27.6	710	1.41	2.69	290
11.0Pb-SBC	2.58	27.9	650	1.72	2.86	280

[a] E = 100% secant modulus (MPa), σ = tensile stress at break (MPa), ε = % elongation at break

Excess neutralization

Mohajer *et al.*[14] reported that the use of excess neutralizing agent increased the melt viscosity and ultimate tensile stress of SPIB ionomers, though the initial modulus was unaffected. They concluded that the excess base was preferentially incorporated at the ionic sites and strengthened and stabilized the ionic network. No similar observation has been reported for other ionomers. In fact, over neutralization of ionomers appears to be a common practice, at least with regard to SEPDM and SPS. For these systems, a slight excess of base was usually added in order to ensure that the acid derivative was fully neutralized.

A limited study of the effect of excess neutralizing agent on the properties of sulphonated SEBS was carried out. The secant modulus and the stress and elongation at break at 23 and 100°C for 5.2Na-SBC and 5.2Zn-SBC that were neutralized with a stoichiometric amount and a 100% excess of sodium hydroxide and zinc acetate, respectively, are compared in *Table 6*. The 100% secant modulus of 5.2Zn-SBC was unaffected by over neutralization, but a small increase of $\sim$20% in strength and 15% in elongation was realized at 100°C by the use of excess zinc acetate. Although these increases were statistically significant (the standard deviation in the ultimate tensile stress measured was $\sim$5% and $\sim$10% for elongation), they are not as dramatic as the increases reported by Mohajer *et al.*[14] for SPIB. Although there are insufficient data here to give a conclusive reason for the differences in the behaviour of the two systems, several explanations are possible. For example, they might be due to inherent differences in the properties of SPIB and SEBS, differences in the molecular architecture (i.e. sulphonated block copolymer *versus* sulphonated homopolymer or star polymer), or differences in the position of the sulphonate groups on the chain (i.e. telechelic *versus* random placement). It is possible that the sulphonated SEBS system would actually yield results similar to

Table 6 Effect of excess neutralizing agent on the tensile properties of 5.2M-SBC

		23°C			100°C		
Sample	Neutralizing agent (% excess)	E^a	σ^a	ε^a	E	σ	ε
SEBS	–	2.00	28.5	700	0.55	1.03	70
5.2Na-SBC	0	2.27	27.6	680	1.07	1.24	200
	100	1.31	1.86	114	–[b]	0.85	52
5.2Zn-SBC	0	2.45	28.1	690	1.38	1.72	210
	100	2.62	28.2	700	1.45	2.10	240

[a] E = 100% secant modulus (MPa), σ = tensile stress at break (MPa), ε = % elongation at break

[b] Sample broke at 52% elongation

Table 7 Tensile properties of water-swollen ionomers

Sample	Water (%)	23°C		75°C	
		σ^a	ε^a	σ	ε
SEBS	0	28.5	700	1.67	85
	0.2	28.0	580	1.65	78
5.2H-SBC	0	28.2	695	4.55	450
	5	25.8	585	3.62	440
5.2Na-SBC	0	27.6	680	3.34	410
	8	23.8	590	2.69	400
5.2Zn-SBC	0	28.1	690	4.48	425
	5	25.1	575	3.51	398
11.9H-SBC	0	27.6	690	5.39	345
	7	23.6	520	4.86	320
11.9Na-SBC	0	27.9	670	5.00	315
	10	17.2	450	2.89	205
11.9Zn-SBC	0	28.2	690	7.58	485
	8	24.2	540	6.34	433

[a] σ = tensile stress at break (MPa), ε = % elongation at break

the SPIB if the measurements were made at higher temperatures. For the SPIB, the mechanical properties were measured ~75°C above T_g, while for sulphonated SEBS measurements were made in the transition region of the sulphonated phase. Another explanation for the differences observed with excess neutralization of the SEBS and SPIB ionomers may be the much lower concentration of ionic groups in the latter materials. This may have allowed a much greater perturbation of the microstructure by the excess salt, which resulted in enhanced properties.

Over neutralization had a distinct detrimental effect on the properties of 5.2Na-SBC at 23 and 100°C. Films of the over-neutralized polymer were non-uniform and contained distinct white contaminants that were most likely precipitated NaOH.

Tensile properties of water-swollen ionomers

The tensile properties of water-swollen samples of SEBS and the ionomers at 23 and 75°C are compared with the dry materials in *Table 7*. Although the water concentrations were not constant within each series of constant sulphonation level, they were probably close enough (5–8% for 5.2M-SBC and 7–10% for the 11.9M-SBC) to allow meaningful comparisons and conclusions. Because the vapour pressure of water at 75°C is fairly high, the swollen specimens most surely lost water during their conditioning for the tensile measurements at this temperature. Therefore, the water concentrations associated with the 75°C data in *Table 7* should be considered an upper limit, since the specimens were not weighed after the test to determine how much water was lost.

The SEBS base resin sorbed very little water and as a consequence its tensile properties were not affected by immersion of the polymer in water. With the exception of the 11.9Na-SBC sample, the effect of water on the tensile properties of all the ionomers tested was similar. At 23°C, the ultimate tensile stress of 5.2M-SBC (M = H, Na, Zn), 11.9H-SBC and 11.9Zn-SBC decreased ~ 2% per wt% water sorbed. Thus, the tensile stress at break of the different ionomers appeared to depend only on the concentration of sorbed water. Similarly, the elongation to break for these materials decreased at a rate of ~3% per wt% water.

At 75°C, again with the exception of 11.9Na-SBC, the reductions in properties for all the materials were similar. Tensile stress at break declined from 10 to 20% with no obvious relation to the water concentration. Similarly, the reduction in ultimate elongation was 2–10%.

For the water-swollen 11.9Na-SBC ionomer, the reductions in the tensile properties were significantly greater, ~40% for the ultimate tensile stress and 35% for the elongation. This material was much more hygroscopic than the other ionomers, and during a 70°C water sorption experiment the test specimens of this ionomer actually broke apart and may have partially dissolved[2]. Thus, one might expect that the physical network in this derivative would be more sensitive to disruption by water. It is also apparent from the data in *Table 7* that even though the ionomers were in general more water sensitive than SEBS, the ionic network was still relatively resistant to solvation, even at elevated temperatures. A striking example of this water resistance is that at 75°C, 11.9Zn-SBC containing ~8% water still exhibited an ultimate tensile stress and elongation four to five times greater than those of the dry SEBS.

CONCLUSIONS

The viscoelastic and mechanical properties of sulphonated SEBS clearly indicated the presence of an ionic network within the styrene-rich phase. This was manifested by an increase in the T_g of the PS-rich phase, $(T_g)_S$, and the development of a high temperature plateau in the dynamic modulus above $(T_g)_S$. These effects were also accompanied by a decrease in the plateau modulus between the T_gs of the rubber and PS phases. Room temperature SAXS measurements indicated that the sulphonated SEBS had a three-phase microstructure consisting of a rubbery EB continuous phase, 20–30 nm PS domains and 3–4 nm ionic domains. A more complete SAXS analysis of these ionomers as a function of composition, counterion, temperature and sample preparation (i.e. compression moulding *versus* solvent casting) is currently in progress and will be reported in a future publication.

Sulphonation of SEBS also resulted in substantial improvements in the high temperature tensile stress and elongation to break. The zinc salts exhibited the best combination of good processability and high temperature tensile properties. The ionomers were more hygroscopic than the base SEBS, but the reduction in the tensile properties at room temperature and at 75°C of ionomers containing up to 8% water were generally <20%.

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