

Mechanical and Chemical Properties of Poly(styrene-isobutylene-styrene) Block Copolymers: Effect of Sulfonation and Counter Ion Substitution

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ABSTRACT: In this study, the mechanical and chemical properties of a series of sulfonated poly(styrene-isobutylene-styrene) (SIBS) block copolymers were evaluated using a combination of nanoindentation, dynamic mechanical analysis (DMA), elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR), water absorption, and small angle X-ray scattering studies (SAXS). The materials properties were characterized as a function of the sulfonation percent in the block copolymers, as well as a result of the counter-ion substitution with Mg^{2+} , Ca^{2+} , and Ba^{2+} . Nanoindentation studies revealed that the elastic modulus (E) and hardness (H) increase with sulfonation up to a certain level, at which point, the effect of water content further hinders any mechanical reinforcement. The incorporation of counter-ions increases E and H , but the results are dependent upon the size of the counter-ion. DMA results showed that the polymer maintained the glass transition temperature (T_g) of the polyisobutylene (PIB) segment ($-60^\circ C$) regardless of the sulfonation level or counter-ion substituted. However, both the shoulder of the PIB T_g ($-30^\circ C$), which was probably caused by a Rouse-type motion, as well as the T_g of polystyrene ($105^\circ C$) disappeared upon sulfonation. Counter-ion substitution increased the storage modulus of the rubbery plateau, which is indicative of a stronger and more thermally stable crosslinked complex formation. Additional unique relaxations were observed with the counter-ions, and could be attributed to the stretching/rotation of the S—O bond and the interaction of the cations with the oxygen in the sulfonic group. FTIR results also revealed a unique shifting of the asymmetric S—O band when counter-ions were added. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40344.

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INTRODUCTION

Proton exchange membranes (PEMs), such as the perfluoro-sulfonate, Nafion®, have unique chemical functional groups and free-volume that allows for the selective transport of some substances, while blocking (or partially blocking) others. PEMs are commonly used in fuel cell applications, such as direct methanol fuel cells (DMFC).^{1–3} Some of the major challenges for the development of DMFC are to overcome the methanol cross-over, which limits cell efficiency and lifetime, and also to maintain or improve the mechanical properties, which can be subject to aging or degradation.^{1–4} Numerous studies have focused on the development of alternative or nanocomposite PEMs that can perhaps allow for significantly different transport mechanisms for protons and methanol,

while still maintaining and/or enhancing the mechanical properties of the material.^{2,3,5–7}

Alternative PEM's are the focus of on-going efforts by this group, one of which involves the chemical modification and structural characterization of an ionomeric polymer, the triblock copolymer poly(styrene-isobutylene-styrene) (SIBS) formed via molecular self-assembly.^{8–12} These studies emphasize the dependence of phase structure and transport properties on intermediate range molecular interactions. Self-assembled morphologies occur in block copolymers that are composed of thermodynamically immiscible constituent blocks. Ordered microstructures that include spheres, cylinders, or lamellae can be observed depending on the chemical composition of the blocks, the sample preparation, interactions between the blocks,

Table I. Sulfonation Levels and IEC for SIBS Membranes

Sample name ^a	Sulfonation level (mol %)	IEC ^b (meq/g)
SIBS-0	NA	NA
SIBS-53	53.1	1.28
SIBS-64	63.8	1.62
SIBS-97	97.3	2.28

^aSIBS: sulfonated poly(styrene-isobutylene-styrene).

^bIEC: ion-exchange capacity.

NA: not applicable.

and/or by the addition of diluent materials/solvents.¹³ Block copolymers in which an amorphous block is present as the primary constituent and a glassy block exists as the minor component, typically exhibit the solid-state properties of thermoplastic elastomers (TPE). When a portion of the polymer chain contains an ionic group, the polymer is classified as an ionomer. Association of ion-rich domains occurs in ionomers and usually results in “physical” crosslinks that affect the block copolymer morphology as well as its thermal and mechanical properties.¹⁴

Chemically modified triblock copolymers comprised of sulfonated polystyrene (PS) components have also been the focus of several investigations.^{5,15–18} The fraction of PS and the sulfonation level control the resulting copolymer morphology (i.e., spheres, cylinders, or lamellae). The triblock copolymer used for this investigation is comprised of ~30 weight percent (wt %) PS and exhibits cylindrical morphology in the PS domains.^{19,20} When the PS component is chemically modified, thus converting a percentage of the PS monomers into styrene sulfonic acid, the resulting morphology includes the formation of ionic “nanochannels” capable of transporting small polar molecules such as water.^{4,20} Those ionic nanochannels are critical for the transport and mechanical properties of the polymer. However, the amount of water swelling, which increases with sulfonation level, could hinder some of the mechanical properties of ionomers. One approach for influencing this effect involves the selective sulfonation of the mid-blocks, rather than the end-blocks, to maintain the mechanical stability of the polymers.^{21–23} Another approach includes the use of organic or inorganic additives to crosslink the micro domains.⁶ Counter-ions are one type of inorganic additives in which the specific chemical interaction with the ionic nanochannel is dependent upon the valence of the ion. For sulfonated ionomers, 2+ cations are considered to perhaps allow for a crosslink between two sulfonic groups, which can influence the chemical, transport, and mechanical properties.

This article focuses on the mechanical and chemical characterization of SIBS with respect to two major variables: sulfonation level (0–97%) and counter-ion substitution (Mg²⁺, Ca²⁺, and Ba²⁺). New mechanical property data is presented and explained in terms of the chemical effects created upon sulfonation and counter-ion substitution. Additional thermogravimetric analysis,¹⁰ and transport properties for DMFC¹² and chemical and biological protective clothing (CBPC)¹¹ for these two variables are presented elsewhere.

EXPERIMENTAL

Materials

The SIBS block copolymer was provided by Kuraray, Tsukuba research laboratories with the reported properties: 30.84 wt % styrene, 0.95 specific gravity, $M_w = 71,920$ g/mol, $M_n = 48,850$ g/mol, and PDI = 1.47. Other chemicals used were as follows: tetrahydrofuran (Burdick & Jackson, HPLC grade, Assay 99.9%), hexanol (J.T. Baker, Assay 99%), toluene (VWR, HPLC Grade), methylene chloride (EM Science, HPLC Grade), barium chloride (Sigma–Aldrich, anhydrous, powder, 99.99%), calcium chloride (Sigma–Aldrich, anhydrous, powder, 99.99%), and magnesium chloride (Sigma–Aldrich, anhydrous, powder, 99.99%).

Processing Conditions and Nomenclature

The sulfonation of SIBS was performed with acetyl sulfate as the sulfonating agent and is described in more detail elsewhere.¹⁷ The mole percent of styrene sulfonated in each copolymer was controlled by the amount of acetyl sulfate used in each reaction and its exact amount was determined via elemental analysis (EA). EA was conducted by Atlantic Microlab, Norcross, Georgia, and the results are listed in Table I. Hereafter, the sulfonated block copolymers will be referred to as SIBS-#, where the succeeding number (#), refers to the mol % of styrene sulfonated. Table I also contains the corresponding ion exchange capacity (IEC) values for the polymers. IEC was obtained by immersing the samples in a 1.0M NaCl solution for 24 h and performing titration on the residual solution with NaOH.

After sulfonation and evaluation, the SIBS samples were solvent casted in a toluene/hexanol (85/15 wt %) solution in an open Teflon Petri dish for several days at ambient conditions. For SIBS-0, pure toluene was used to cast the membranes. The films were then annealed under vacuum at 50°C for an additional two weeks to remove any residual solvent.

The cations selected for crosslinking the sulfonated SIBS were Mg²⁺, Ca²⁺, and Ba²⁺. These were selected to provide a potential interaction with two sulfonic group sites. They were also selected because of their different size and electronegativity. The sulfonated polymers were irreversibly crosslinked by immersing them for several hours in a 1.0M solution of MgCl₂, CaCl₂, or BaCl₂, depending on the desired cation. The cross-linked solutions were washed with deionized water and left to dry for at least 24 h in a vacuum oven at 50°C. The nomenclature for the counter-ion substituted membranes uses the chemical symbol for the ion after the sulfonation percent (e.g., SIBS-64-Mg corresponds to SIBS with 64% sulfonation of available PS and Mg²⁺ as the substituted counter-ion). All the 2+ counter-ions studied in this investigation showed a mole ratio of sulfonate group to counter-ion of 2 : 1 from neutron activation EA.^{11,12}

Nanoindentation Studies (NS)

NS were used to evaluate the effect of sulfonation and counter-ion substitution on the nanomechanical properties of the SIBS polymers. The experiments were performed using a G200 NanoIndenter by Agilent Technologies, equipped with a Berkovich tip (three-sided pyramidal diamond tip). The elastic

Table II. *E* and *H* for SIBS Membranes

Sample name	<i>E</i> (GPa)	<i>H</i> (GPa)
SIBS-0	0.044 ± 0.003	0.011 ± 0.001
SIBS-21	0.114 ± 0.008	0.010 ± 0.001
SIBS-39	0.138 ± 0.070	0.016 ± 0.012
SIBS-53	0.270 ± 0.118	0.017 ± 0.009
SIBS-64	0.641 ± 0.209	0.033 ± 0.019
SIBS-83	0.404 ± 0.178	0.023 ± 0.016
SIBS-90	0.203 ± 0.029	0.017 ± 0.003
SIBS-95	0.181 ± 0.019	0.011 ± 0.001

modulus (*E*) and hardness (*H*) of the samples were calculated from the load (mN) versus displacement (nm) data recorded by the instrument and using the Oliver–Pharr method.^{24–26} A fused silica sample was used as the calibration standard. Polymer films of ~1 cm² were attached to glass slides using Krazy Glue® and then the entire structure was bonded to rigid metallic sample holders for testing. Defect-free areas of the membrane surfaces were selected for testing and always toward the center of the piece to avoid edge effects. For these studies, the G200 Nano Indenter was operated under depth-control and the maximum displacement into the surface was set at 2000 nm. Arrays of 30 indents were performed per sample with a separation of 50 μm between indents. The results for the mechanical properties were averaged over all the indents performed per sample.

Dynamic Mechanical Analysis

The thermoviscoelastic behavior of the SIBS polymers was determined using a Hi-Res dynamic mechanical analysis (DMA) 2980 DMA (TA Instruments) operated at a single frequency of 1.0 Hz. In each experiment, a polymer film of ~15–20 mm long, 7–8 mm wide, and 0.07–0.10 mm thick was used. The storage modulus (*E'*) and loss modulus (*E''*) were measured after thermal equilibrium for 5 min at –100°C, followed by heating to 120°C at 2°C/min. The *E'*, *E''*, and tan δ reported in this investigation correspond to the average over 2–3 measurements made per sample. The results were highly reproducible with a maximum variability of 2–3%.

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra for all the polymer samples were collected using a FTIR spectrometer (Nicolet Magna 560 Series) equipped with a Gateway (Specac) accessory and a 7-reflection ATR crystal (ZnSe, refractive index = 2.4). The accessory contains a pressure mechanism that assures good sample-to-crystal contact. All infrared spectra were collected using 128 scans and 4 cm⁻¹ resolution. The results presented were also proven consistent over 2–3 measurements made per sample.

Water Absorption Studies

Polymer samples of ~50 mg were weighed before and after immersion (for a minimum of one week) in deionized water. Water absorption (also referred as to swelling) is defined here as:

$$wt\% = \frac{(\text{wet polymer wt} - \text{dry polymer wt})}{\text{dry polymer wt}} \times 100 \quad (1)$$

A balance with 0.01 mg precision was used. Experiments were conducted in triplicate for each sample.

Small Angle X-Ray Scattering (SAXS)

A SAXS instrument (Anton-Paar, Graz, Austria) was used for the SAXS experiments. The objective of these studies was to obtain information about the structure and morphology of the membranes. Two-dimensional scattering patterns were collected on a line-collimation system using a Cu Kα source with a wavelength of 1.54 Å. Fujifilm (Greenwood, SC) image plates and a Perkin Elmer (Covina, CA) image plate reader were used to acquire the data. The SAXSQuant software® was used to reduce two dimensional data to one-dimensional intensity versus scattering vector (*q*) plots.

RESULTS AND DISCUSSION

Nanoindentation Studies

Effect of Sulfonation. Nanoindentation was used to measure the *E* and *H* as a function of the sulfonation level in the SIBS copolymers. The results are summarized in Table II. SIBS-0 shows very low values for both *E* and *H* and these results were highly expected because the unsulfonated material is 69.16% polyisobutylene (PIB), which is very elastic. The results show an increasing trend in the mechanical properties up to about 64% sulfonation level and then both *E* and *H* decrease as the sulfonation level is further increased within the copolymer. One possible explanation for these results could be that as the sulfonation increases, both *E* and *H* increase as the sulfonic groups interconnect and result in the creation of ionic nanochannels. However, the saturation and further decrease in the mechanical properties beyond 64% sulfonation could be related to the increase in water absorption induced by the nanochannels (further discussed in a later section). It is possible that beyond a certain concentration the presence of water hinders the mechanical reinforcement initially provided by the ionic nanochannels.

Effect of Counter-Ion Substitution. The effect of counter-ion substitution was studied for three different ions (Mg²⁺, Ca²⁺, and Ba²⁺) and three different sulfonation levels in the range from 39 to 83% sulfonation. The results are presented in Figure 1 for both the *E* and *H* of the different SIBS copolymers. The results show an increase in the *E* as a function of both, sulfonation level and size of the counter-ion (Ba > Ca > Mg) but again, up to a maximum of 64% sulfonation. However, this optimum or saturation value as a function of sulfonation was not observed for Ba. A possible explanation for this behavior could be related to the fact that the membranes containing Ba had the lowest water content observed (further discussed in a later section).

For the counter-substituted samples, the mechanical properties were measured as a function of the displacement into the surface, so the results presented were averaged in the range between 300 and 500 nm. In this range, the values remain relatively constant and are free from any possible surface effects (artifacts). Overall, the measurements were very consistent

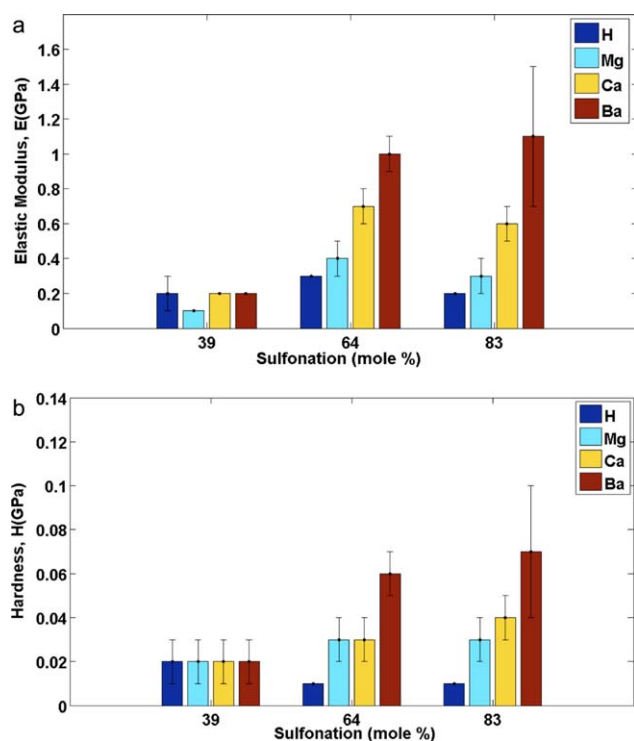


Figure 1. E and H as a function of sulfonation level and counter-ion substitution for SIBS membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

across the 20 indents made per sample as can be seen from the characteristic E versus displacement into the surface plot presented in Figure 2. To further analyze, the variability in the mechanical properties as a function of the different counter-ions, surface maps were prepared using the results from the nanoindentation experiments. The plots are presented in

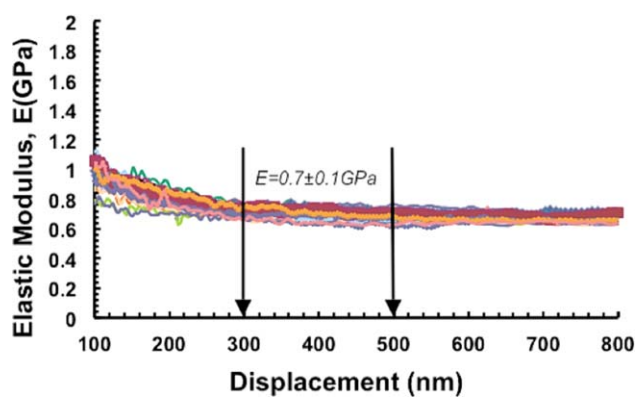


Figure 2. E versus displacement into surface for SIBS-64-Ca. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3. The results illustrate small variations for most of the SIBS samples except in the case of Ba substitution.

Dynamic Mechanical Analysis

Effect of Sulfonation. The E' and the E'' of SIBS vs. temperature in the unmodified and sulfonated forms are shown in Figure 4(a,b). At low temperatures, sulfonation has little effect on E' and E'' , since that region is controlled by the effect of PIB. However, a large increase in both E' and E'' for the sulfonated copolymers in the rubbery plateau region is observed. This increase is due to the increased phase separation of the highly polar sulfonate groups, which act as additional pseudo-crosslinks in the TPE, providing improvements in mechanical properties as well as thermal stability. The sulfonated film still exhibits flexibility and ease in handling. A clearer picture results with the examination of the $\tan \delta$ shown in Figure 4(c). The unsulfonated SIBS has two main transitions, a high

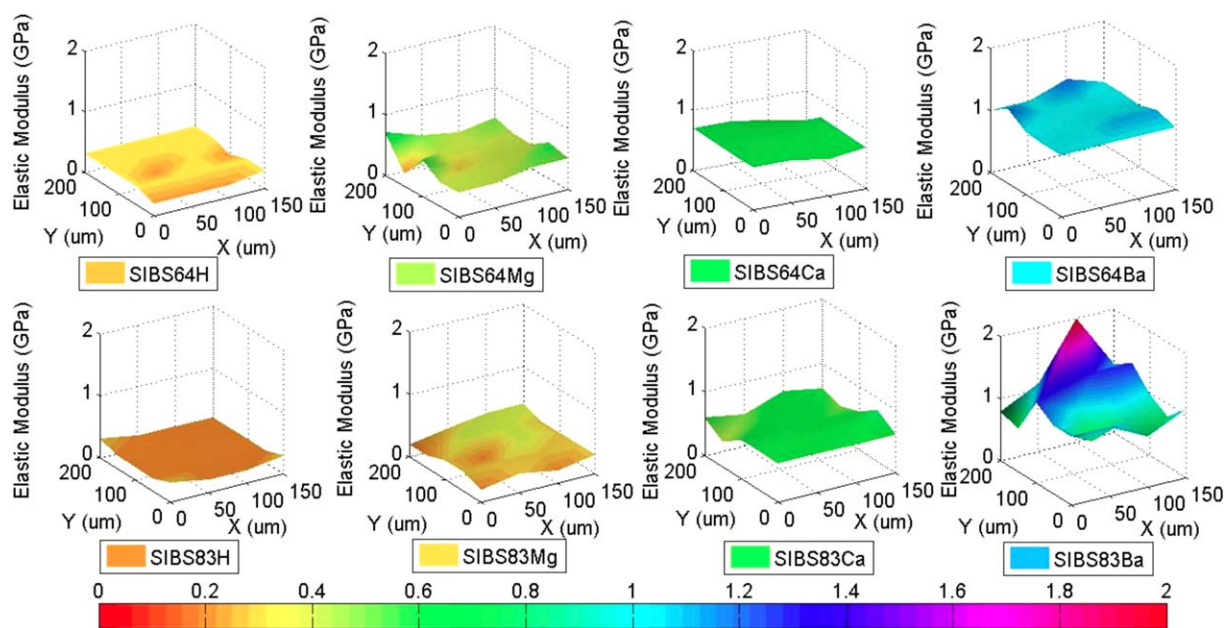


Figure 3. Nanoindentation map for E at 2000 nm maximum depth for SIBS membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

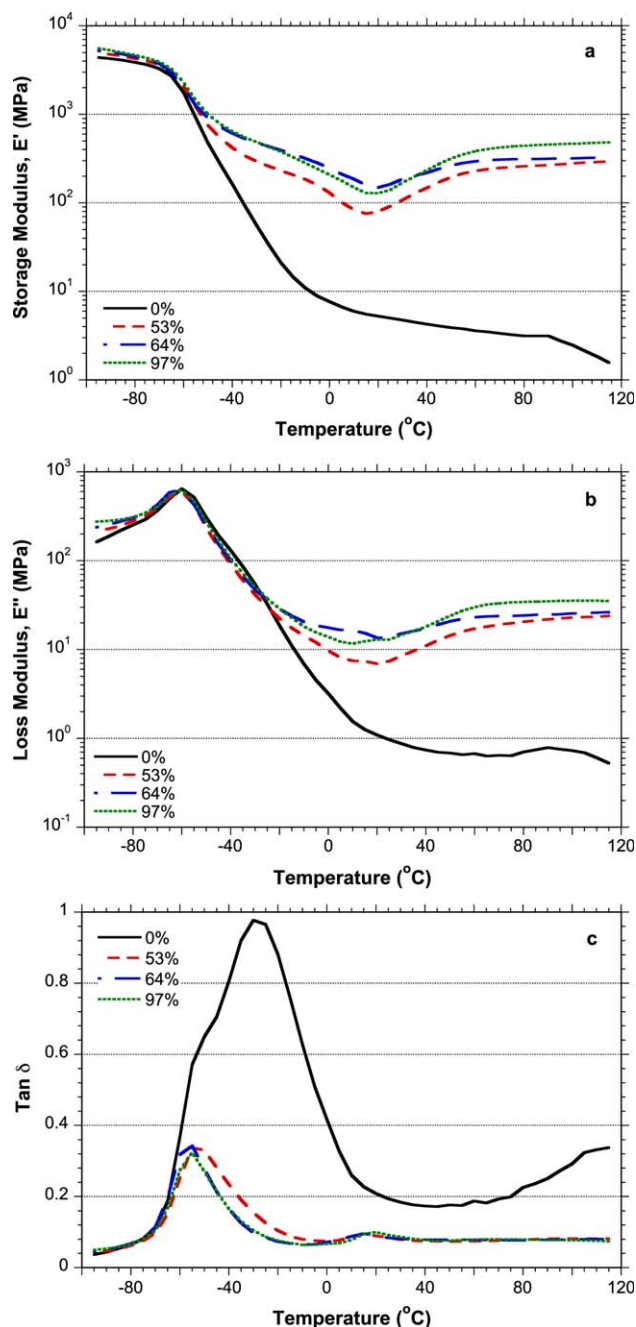


Figure 4. Effect of sulfonation level on E' , E'' , and $\tan \delta$ for SIBS membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature transition corresponding to the T_g of the pure PS phase ($\sim 106^\circ\text{C}$), and a lower temperature transition corresponding to the T_g of the PIB phase (-55 and -30°C). We observe two peaks in the low temperature transition (-55 and -30°C), which have been observed by other authors who have speculated that the transition at -30°C may be due to a sub-Rouse type motion caused by relaxation occurring at longer time scales.²⁷ Thus, the transition at shorter time scales gives rise to the lower temperature PIB transition (-55°C) and the transition at longer time scale gives rise to the higher tempera-

ture PIB transition (-30°C). A more detailed explanation can be found elsewhere.²⁸ For the sulfonated polymers, four significant phenomena are observed. First, the sub-Rouse PIB motion disappears, as only one transition is observed in the highly interconnected network ($\sim 55^\circ\text{C}$). Second, the T_g of the pure PS domains disappears for the range of temperatures studied (up-to- 120°C). Other investigators^{29–31} have observed that the T_g of PS moves to higher temperatures upon sulfonation or ionic incorporation. Third, the $\tan \delta_{\max}$ ($\tan \delta$ at T_g) was significantly reduced upon sulfonation, which is attributed to the stiffening imparted by the ionic domains.³² Finally, a very small additional relaxation is observed around 18°C , which could be due to the stretching, rotation, or deformation of the ionic domains. Additional relaxations attributed to ionic aggregates have been found to occur in the case of rubbery PS ionomers in similar temperature ranges.^{30,31} In the case of sulfonate ions, the relaxation could be related to the limited mobility of the saturated S—O bond adjacent to the ionic aggregates. This hypothesis will be supported ahead with FTIR and water swelling results, as well as the incorporation of counter-ions to the sulfonate ionic domains.

Effect of Counter-Ion Substitution. The effect of counter-ion substitution in the mechanical properties of SIBS-97 can be observed in Figure 5. E' shows an increase in the rubbery plateau, which indicates that the stiffness of the polymers increases for all the cations exchanged [Figure 5(a)]. The plot also shows an improvement in thermal stability (up-to 120°C measured) compared to the acid form of the sulfonated polymer. For both the E' and the E'' the low temperature properties remain unchanged, perhaps since the low temperature behavior depend primarily on PIB and the cations do not interact directly with the PIB. The plot of $\tan \delta$ vs. temperature for SIBS-97 with counter-ions [Figure 5(c)] reveals two major effects upon the incorporation of counter-ions. First, the T_g of PIB shifted slightly to -60°C (from -55°C), regardless of the counter-ion substituted. Second, two additional unique complex relaxations were observed for all the counter-ion substituted samples. These relaxations become more pronounced with concentration (Figure 6), and were reproducible even after several (cooling \leftrightarrow heating) thermoviscoelastic cycles. The unique complex relaxations above the T_g of PIB perhaps describe unique crosslinks between the oxygen of the sulfonic group and each cation. The relaxation temperatures occur at regions with sufficient energy for stretching, rotation or deformation motions to occur. Since neutron activation EA results revealed that the mole ratio of sulfonate group to counter-ion was 2 : 1,^{11,12} the two additional relaxation temperatures could be related to each of the counter-ion-sulfonate group interactions. Each counter-ion presents unique relaxation temperatures related to their unique interaction with the oxygen of the sulfonate group (as it will be supported ahead with FTIR).

The comparison with the state-of-the-art shows that the values of E' for Nafion®,³³ can be several orders of magnitude higher than the value obtained for SIBS. However, the value of E' for Nafion® decreases several orders of magnitude in the 50 – 150°C ,³³ while SIBS maintains the thermal stability of E' in

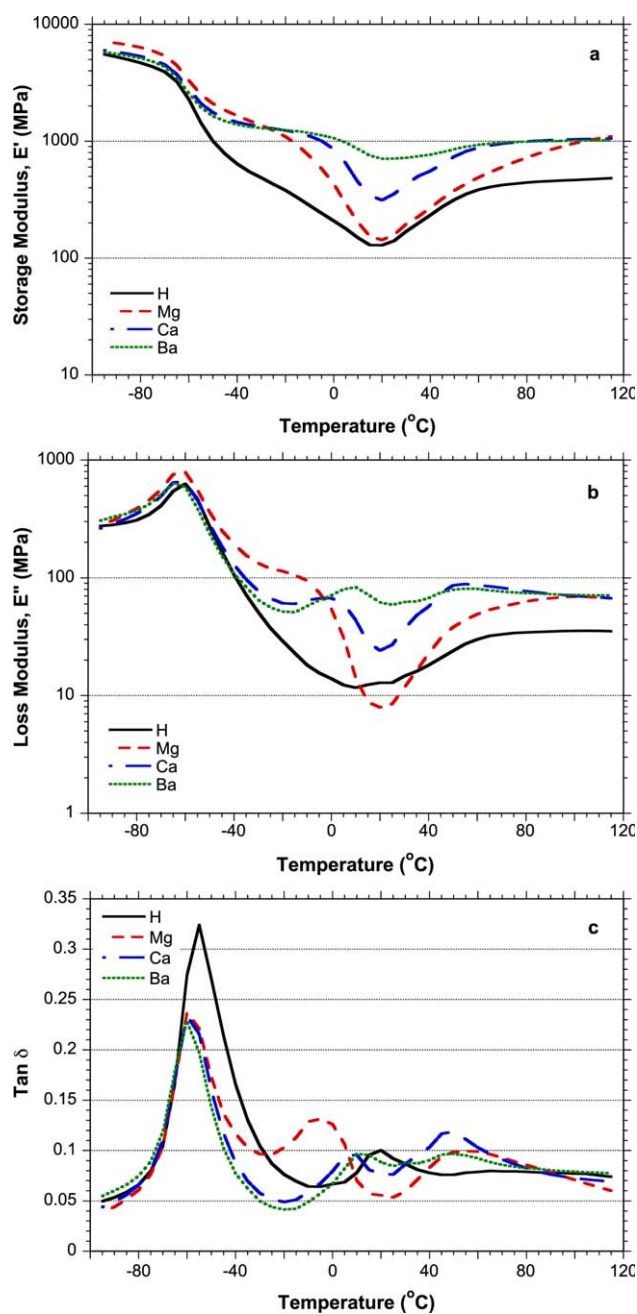


Figure 5. Effect of counter-ion substitution on E' , E'' , and $\tan \delta$ for SIBS membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

this temperature range. The incorporation of counter-ions improves the mechanical properties of SIBS even further, especially its thermal stability over this temperature range making it suitable for DMFC and CBPC applications.

Fourier Transform Infrared Spectroscopy

FTIR was conducted on these polymers in an attempt to identify molecular associations occurring within the polymer domains. Figure 7 shows the FTIR spectra of the acid form and cation exchanged forms for SIBS-97 polymer in the 1000–1300 cm^{-1} region.

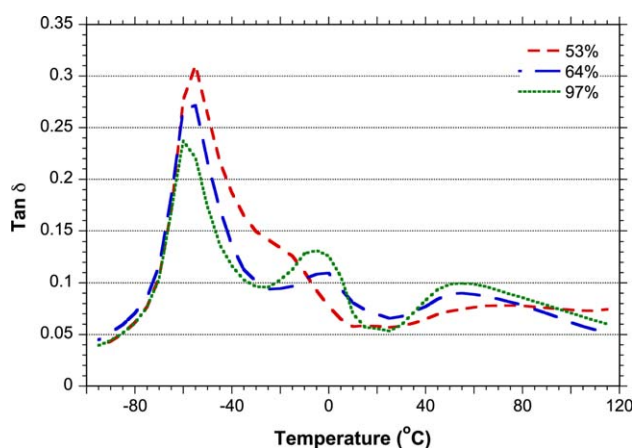


Figure 6. Effect of concentration for Mg substituted SIBS on $\tan \delta$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

There are four bands in SIBS-97 observed at 1156, 1127, 1034, and 1006 cm^{-1} , which are all representative of the stretching vibrations associated with sulfonation.^{10–12,34,35} The bands at 1034 and 1006 cm^{-1} show no change, so they have been excluded from this graph. The bands at 1034 and 1156 cm^{-1} represent the symmetric and asymmetric stretching vibrations of the sulfonate group, respectively.

The spectra reveal various shifts in the 1156 cm^{-1} peak. Specifically, IR peak shifts from 1156 to 1167 cm^{-1} for Ca^{2+} and Mg^{2+} counter ions and to 1160 cm^{-1} for Ba^{2+} . This shift is a direct result of the positively charged metal cation interacting and influencing the stretching of the negatively charged sulfonate group. It is interesting that these ionic interactions shift the IR peaks to a high spectral frequency. Generally, interacting species cause a shift to lower frequencies due to the lowering of the specific energy of the vibration. This shift suggests that the interaction between the sulfonate group and hydrogen (present in the acid form) are stronger than the interaction between the metallic cation and the sulfonic acid groups. Other authors have observed this effect in similar sulfonate-cation systems without any explanation.^{34,35}

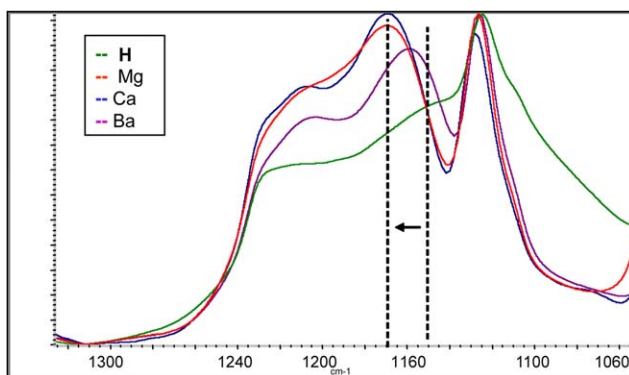


Figure 7. FTIR spectra for counter-ion substituted SIBS-97. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

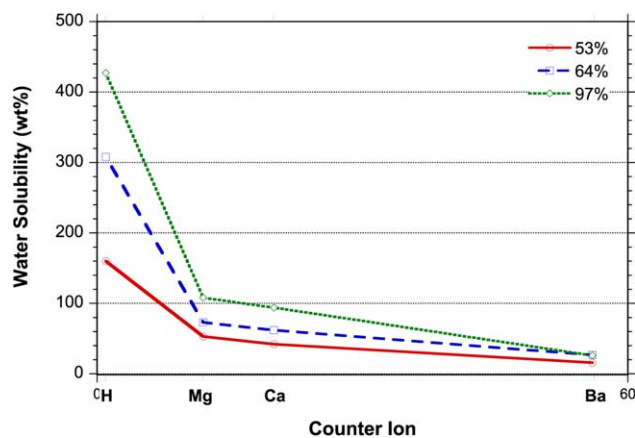


Figure 8. Effect of counter-ion substitution on water swelling for SIBS membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Absorption

One of the proposed applications for polymers of these type are as semipermeable membranes, where water is allowed to readily transport through the membrane while preventing larger organic toxins from passing through. At low sulfonation levels no water transport is achieved³⁶; however, as the sulfonation levels are increased the ionic moieties percolate the membranes and form a continuous domain capable of transporting water and other small polar molecules. A useful method to evaluate this property is to measure the water absorption (or swelling) within the polymer membrane. The water absorption of each polymer is shown as a function of sulfonation level in Figure 8. As expected, increasing the sulfonation level in the polymer results in a significant increase of water swelling. A water uptake of over 400 wt % was measured for SIBS-97, resulting in a polymer that is effectively a gel. The large increase in the water uptake with increasing sulfonation levels suggests that larger ionic domains are being formed. However, the introduction of

2+ inorganic cations results in a membrane with much lower water absorption than its acid counterpart (Figure 8). This incorporation of inorganic counter-ions changes the chemical balance surrounding the ionic domains, which influences the amount of water absorbed in the ionic domains. The SIBS-53 neutralized polymer shows a solubility decrease from 160 to 53% for Mg, 42% for Ca, and 16% for Ba. A more dramatic effect is observed for the SIBS-97 polymers, where the solubility goes from 427 to 108% (Mg), 94% (Ca), and 26% (Ba). Detailed water absorption results are also presented in Table III.

It is tempting to explain this result in terms of the increasing cation size that is acting to block the absorption of water into the existing ionic domains. However, SAXS measurements revealed that the size of the ionic nanochannels, obtained using Bragg's law to the ionomer peak (Figure 9), is only slightly affected by the presence of the cations (54–59 nm), which are significantly smaller (0.15–0.215 nm). Therefore, it is also reasonable to suggest that the incorporation of the cations reduce the ionic charges in the polar domain, resulting in reducing the amount of water capable of clustering near the sulfonic acid groups.

A very interesting observation from the SAXS data is the peak observed at $\sim 0.34 \text{ \AA}^{-1}$ (Figure 9), which is observed for all counter-substituted samples but not for the polymer in its acid form (SIBS-79.3). Bragg's law suggests that this region could have an interstitial distance of $\sim 1.8 \text{ nm}$ and is the same for all counter-ions studied. This distance could be related to the distance for the crosslink between one 2+ counter-ion and two sulfonic groups as suggested by EA, FTIR, water swelling, and DMA. The distance appears to be the same, regardless of counter-ion, perhaps because this distance might be dictated by the crosslink interactions and not the size of the counter-ion, for the counter-ions studied in this investigation. A SAXS and solid-state NMR study conducted with Nafion[®],⁴ concluded that the sulfonic groups self-organize into arrays of hydrophilic water channels of $\sim 2.4 \text{ nm}$ dispersed in a hydrophobic matrix, which are responsible for the transport of ions and the mechanical stability. In our study, the incorporation

Table III. Water Absorption and Mol H₂O/Mol S for SIBS Membranes Studied

Sample name	% (Mass H ₂ O/ mass polymer)	Mol H ₂ O/Mol S
SIBS-0	0	0
SIBS-53	160	69.4
SIBS-53-Mg	53	23.4
SIBS-53-Ca	42	18.7
SIBS-53-Ba	16	7.5
SIBS-64	308	105.6
SIBS-64-Mg	73	25.5
SIBS-64-Ca	62	21.9
SIBS-64-Ba	27	10.3
SIBS-97	427	104.0
SIBS-97-Mg	108	27.0
SIBS-97-Ca	94	24.0
SIBS-97-Ba	26	7.3

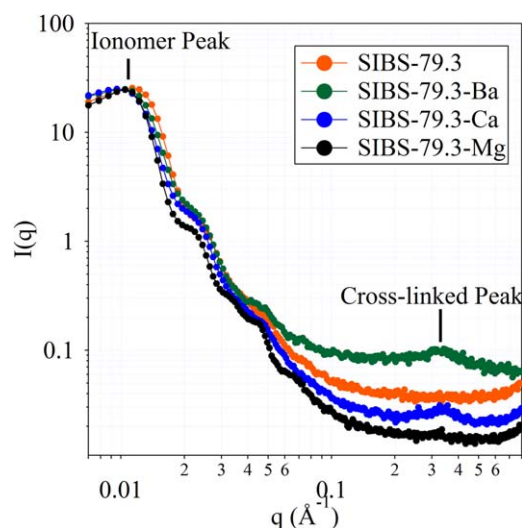


Figure 9. SAXS results for SIBS-79.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of counter-ions creates a crosslink that inhibits the formation of the water channels limiting the transport of ions, but the new crosslink provides improved mechanical properties.

CONCLUSIONS

Mechanical and chemical properties of sulfonated SIBS block copolymers were investigated as a function of sulfonation level and counter-ion substitution. Unsulfonated membranes showed two T_g transitions for the PIB segments (-55 and -30°C), attributed to sub-Rouse motions of longer time scale, and one T_g for PS at 106°C . Sulfonated membranes maintained the -55°C T_g of PIB, while the -30°C transition disappeared regardless of sulfonation level or cation exchanged. Upon sulfonation, the T_g of PS was not longer observed in the range up to 120°C . A small additional relaxation at 18°C was also observed for the highly sulfonated samples and this could be attributed to the restricted mobility of the S—O bond stretching/rotation/deformation. All the mechanical properties studied (E , H , E' , and E'') increased with sulfonation level due to the interconnection of the sulfonic groups throughout the membrane. Some of the mechanical properties, in particular E and H , showed an optimum or saturation level with sulfonation due to the competing effects of nanochannel reinforcement and water absorption. The incorporation of counter-ions into the sulfonated membranes created complex crosslinked domains that exhibited additional unique relaxations between -5 and 50°C . The incorporation of counter-ions also resulted in an increase in the mechanical properties of the ionomers due to the crosslinking between the sulfonic groups and the counter-ions. The water absorption showed a dramatic decrease upon neutralization with inorganic cations due to the reduced polarity of the ionic domains. Finally, FTIR showed molecular evidence of the crosslinking between the sulfonate groups and the counter-ions, by observing a shift in the sulfonate band at 1156 cm^{-1} . These results were also supported with the EA and SAXS studies.

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