

Proton Conducting Materials Based on Thermoplastic Elastomers Silica Composites

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ABSTRACT: In this research, ionomeric composites based on organophilized silica (SIL) and a thermoplastic elastomer (HSBR), were prepared and characterized from a microstructural and electrical point of view. DSC was used to confirm silica sulfonation and FTIR to characterize the polymer before and after sulfonation reaction. DSC and DMA analysis show that T_g^{HPB} remains constant in all the samples studied. T_g^{PS} measured through DMA presents an increase of about 40°C in the sample containing both the sulfonated filler and the sulfonated polymer matrix. The resulting ma-

terials can be easily processed to yield thin films (thickness 0.2–0.4 mm) with outstanding proton conducting properties ($10^{-2} \text{ S} \cdot \text{cm}^{-1}$). The suitability for film formation and good electrical properties is indicative of their potential use as electrolytes in polymer fuel cells. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2715–2720, 2003

Key words: silicas, thermoplastics; elastomers; composites; ionomers

INTRODUCTION

Among all the inorganic fillers being used in rubber composites, amorphous silica, thanks to their fine particle segmentation, are the ones that achieve good reinforcing properties in the end product. The state of particle segmentation, specific surface, as well as porosity, are relevant elements that together determine its reinforcing properties, apart from the most decisive one, that is, the chemical affinity of the silica surface to the polymer, due to the presence of active centers positioned on the filler surface. The drawback with amorphous silica, however, is, on the whole, that it is an affinity-poor material, due to the small number of active functional groups. The only ones to be found are silanol groups, of an acid nature. On the other hand, these silanol groups possess an important property: that of being able to react with bifunctional organosilane compounds. Hence, one of the silane functions will react with the silanol groups, the other function remaining free, which allows obtaining silica with new reaction potentials.

In this work silica was organophilized by allowing it to react with bis-[3-(Triethoxilyl)-propyl] tetrasulfane. Then it was characterized by means of DSC. The resulting material was incorporated as a fine powder into a thermoplastic elastomer: a hydrogenated poly-(butadiene-styrene) block copolymer (also sulfonated and not sulfonated). The blends were subsequently

characterized from a microstructural and electrical point of view. In addition, the composites obtained were tested for their suitability for film formation, in view of their potential use as electrolytes in polymer fuel cells.

As is commonly known, a fuel cell^{1–5} essentially consists of two electrodes (anode and cathode) separated by an electrolyte (a special polymer or any other ion-conducting and electron-blocking material). A hydrogen-rich fuel flows towards the anode, where the hydrogen releases electrons and deposits positive charge ions. The electrons will travel along the outer circuit, whereas the ions will be diffused through the electrolyte. At the cathode the electrons are bonded to the hydrogen ions and oxygen to form water as a byproduct. The reaction is usually accelerated by means of a platinum-like catalyst. In this sense fuel cells and batteries can be likened, as they both depend on electrochemical processes. In the former, however, it is the hydrogen fuel and the oxidant that react, while in the latter the reaction takes place in the electrode materials (i.e., nickel, cadmium, and their derivatives).

This clean and silent operational technique would be ideal for many modern applications, such as mobile phones, lap top computers, automobiles, and household generators. Yet many hurdles will still have to be taken. First and foremost, there are the problems related to the fuel itself. Liquid hydrogen, which possesses a great energy potential, has to be stored at prohibitive temperatures, practically around absolute zero. Platinum and the proton-conducting polymer film rank second as troublemakers,^{6–8} as their price/performance ratio is totally unbalanced. Especially the

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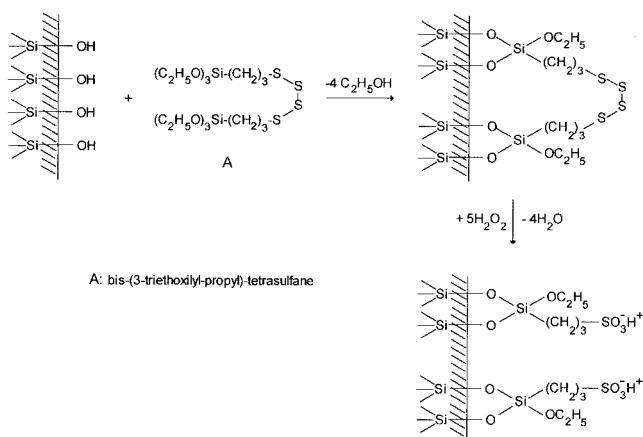


Figure 1 Scheme of sulfonation reaction of silica.

polymer membrane performs very poorly, regarding dimensional stability. This is why there is an interest in the development of new and more stable materials, which is also the purpose of this research.

EXPERIMENTAL

Materials

Hydrogenated poly(butadiene–styrene) block copolymer (HSBR) Calprene CH-6120 was provided by Repsol and containing 30 wt % styrene units. Sulfonating reagent was acetyl sulfate prepared by the reaction of acetic anhydride and concentrated sulfuric acid (96%). 1,2-Dichloroethane (DCE) was previously dried using molecular sieves. Silica (SIL) was supplied by Degussa with the commercial trade of Ultrasil VN3. Bis-[3-(Triethoxilyl)-propyl] tetrasulfane (Si-69) was also provided by Degussa.

Homogeneous HSBR sulfonation procedure (HSBR-SO₃H)

The sulfonating reagent (acetyl sulfate) was prepared by gradually adding 0.84 mol sulfuric acid onto 0.14 mol of acetic anhydride. The reactor was cooled below

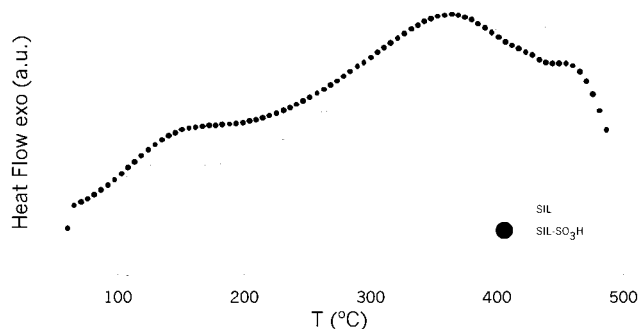


Figure 2 DSC thermograms of SIL and SIL-SO₃H.

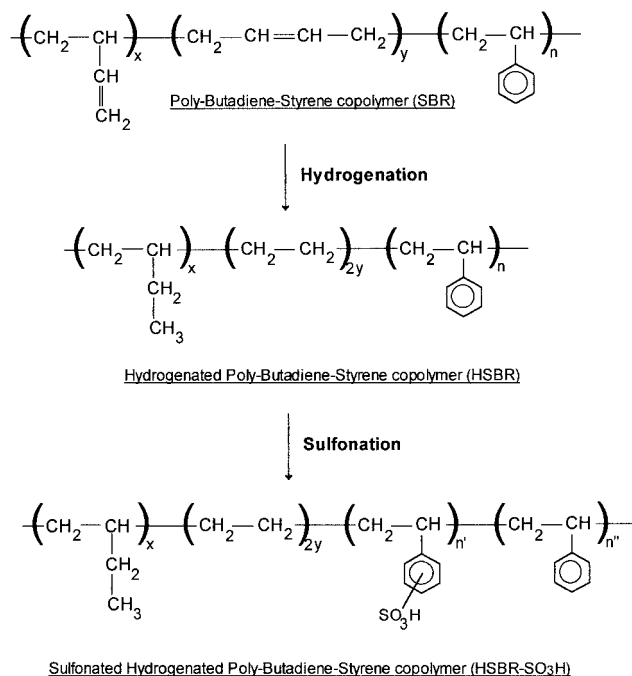


Figure 3 Chemical mechanisms of sulfonation reaction of HSBR.

−10°C. Subsequently, the solution was diluted by 20 mL 1,2-dichloroethane (DCE). The product obtained was maintained at 0°C in an ice bath, until its addition to the reaction medium.

HSBR sulfonation reaction was carried out according to the procedure described by Makowski et al.^{9,10} In an agitated reactor, the polymer (20 g) was dissolved in 200 mL DCE at 52–56°C and purged with nitrogen. Then acetyl sulfate, prepared as described above, was slowly added to the polymer suspension over a drop dispenser. The reaction was allowed to continue for 1 h at 55°C under vigorous stirring and purging with nitrogen. Samples were removed at the desired reaction times and precipitated in methanol or desionized water (1 L per 10 g of the polymer used). The highly sulfonated polymer was partially soluble in methanol or water, which was recovered by steam stripping, and vacuum dried at 50–60°C for a few days.

The complete removal of residual acid from the final product after sulfonation is important because it can interfere with the properties of the final product. The dried polymer was cut into small pieces, washed once with boiling desionized water, and then washed many times with cold water until neutral pH of the sewage was obtained. It was finally vacuum dried at 50–60°C for the last time.

The titration of the polymer against a standard potassium hydroxide solution (0.1N) using phenolphthalein as an indicator shows a sulfonation level higher than 15%.

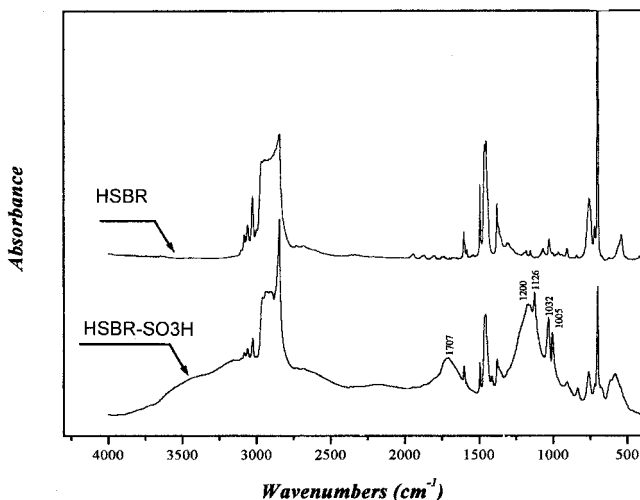


Figure 4 FTIR spectra of HSBR and HSBR-SO₃H.

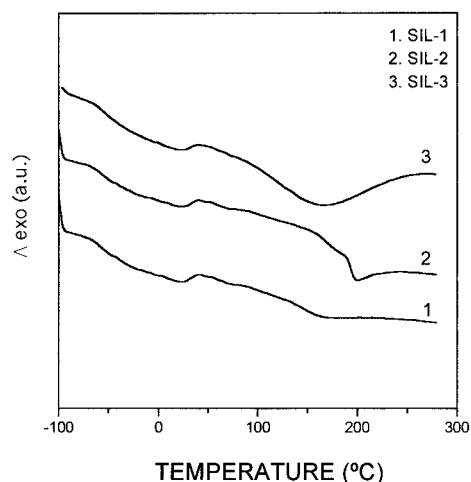


Figure 5 DSC thermograms of the different samples.

Silica sulfonation procedure (SIL-SO₃H)

An ethanol/water solution (95/5) is prepared adjusting the pH between 4.5–5.5 with acetic acid (HAc). Then silane Si-69, dissolved in ethanol, is gradually added under stirring, which latter is continued for 5 further min to ensure homogeneous blending. Then, and without interrupting, the stirring process the silica is added (Ultrasil VN3), the silane/silica ratio being 0.2 g silane per 1 g mineral. The materials are blended under magnetic stirring for 30 min, after which time the dispersion is filtered and the solid is washed in ethanol. Subsequently, the solid matter is dispersed again in 100 mL adding a 30% hydrogen peroxide solution (H₂O₂) in ethanol, the silane/H₂O₂ ratio being 1/5. The reaction is heated to the boiling point and held at that temperature for 30 min. Then it is filtered and the solid is again washed in ethanol. Finally, it is dried at ambient temperature for 24 h.

Blending procedure

An open two-roll mill was utilized to blend HSBR/SIL (SIL-1), HSBR/SIL-SO₃H (SIL-2), and HSBR-SO₃H/SIL-SO₃H (SIL-3). A conventional mixing procedure and ambient temperature was used; the blending time was 20 min to maximize intermixing of the components.

Heterogeneous sulfonation procedure

Samples SIL-1 and SIL-2 are immersed in the sulfonation solution (0.2 M chlorosulfonic acid dissolved in 1,2-dichloroethane) and held there for different sulfonation times (3, 6, 9, and 24 h). Each sample, when taken out of the sulfonation bath, is superficially dried and subsequently washed, first in acetone and then in Milli-Q desionized water. Finally, the samples are air dried for 8 h.

Analysis

A Nicolet 520 Fourier-transform IR (FTIR) spectrometer was used to record the infrared spectra of HSBR before and after sulfonation. A resolution setting of 4 cm⁻¹ and 32 scans were utilized. Samples were KBR pellets.

A Mettler 4000 Differential Scanning Calorimeter (DSC) was used for the thermal analysis of the different samples. The temperature range was from -100 to 280°C for polymer composites and from 60 to 500°C for silica samples before and after sulfonation. Heating rate was 10°C · min⁻¹ for all the samples.

Dynamic mechanical analysis (DMA) measurements were performed with a Viscoanalyseur Metravib RA C815A. Specimens were compression moulded in a Collin press at 130°C and 200 bars obtaining thin

TABLE I
DSC and DMA Transition Temperatures

Sample	Composition				DSC			DMA		
	HSBR wt %	HSBR-SO ₃ H wt %	SIL wt %	SIL-SO ₃ H wt %	T ₁ (°C)	T ₂ (°C)	T ₃ (°C)	T ₁ (°C)	T ₂ (°C)	T ₃ (°C)
SIL-1	70	—	30	—	-47.5	170.2	—	-43.4	110.5	—
SIL-2	70	—	—	30	-47.0	166.6	199.1	-43.8	112.6	141.0
SIL-3	—	70	—	30	-45.2	165.2	—	-45.3	151.6	171.5

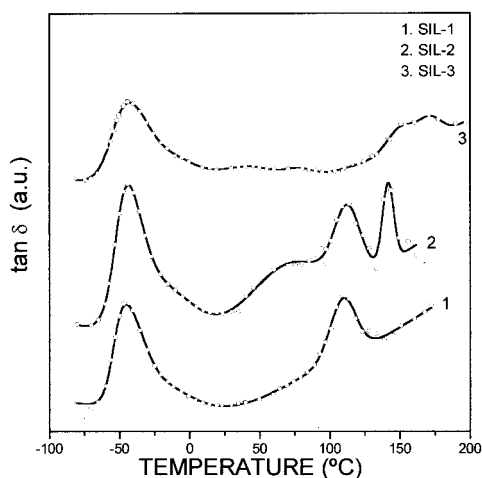


Figure 6 DMA relaxation spectra of the different samples.

films of 0.2–0.4 mm thickness. They were analyzed in the compression mode at a deformation frequency of 5 Hz and using a temperature range from -100 to 200°C .

Complex impedance spectroscopy was carried out using a Hewlett Packard 4192A impedance analyzer; frequency range used was 0.01–10,000 kHz. Samples were immersed in desionized water at 50°C for 1 h. Before measuring they were dried up superficially and rapidly placed into the measurement cell, which was also set up at 50°C . The cell was suspended above liquid water in a tightly closed beaker and the beaker was placed in a temperature bath at 50°C to maintain that temperature in the vapor space.

RESULTS AND DISCUSSION

Sulfonated silica: characterization

Both the pure (SIL) and the sulfonated silica (SIL-SO₃H) samples were characterized by means of differential scanning calorimetry (DSC). The sulfonation reaction of the silica, the procedure of which was described above in the experimental part, follows a process outlined in Figure 1.

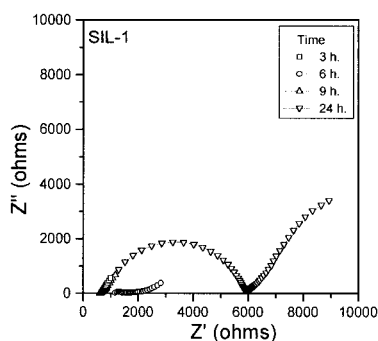


Figure 2 shows the DSC thermograms obtained for SIL and SIL-SO₃H. This technique allows detecting a variation of the calorific capacity in the range between 100 and 200°C due to the loss of adsorbed water. In the case of the silanized and sulfonated silica, this loss is detected at higher temperatures as compared to the reference sample, which is indicative of higher water molecule adsorption energy, due to the presence of sulfonic groups on the silica surface. In the region between 400 and 500°C there appears a broad endotherm in the untreated silica, attributable to loss of the water generated by the surface silanol groups, which begin to condense and form siloxane groups and water. In the treated sample this endotherm is much less prominent, as there are fewer silanol groups present, since most of them have reacted with the silane.

Sulfonated HSBR: characterization

As described in the experimental part, HSBR was sulfonated and the titration of the polymer shows a sulfonation level higher than 15%. The sulfonation reaction occurs as outlined in Figure 3. FTIR was used to confirm the sulfonation of the styrene groups of the HSBR polymer. Figure 4 compares a series of FTIR spectra before and after sulfonation. The changes in the combination vibrations (finger bands) can be clearly detected between 1950 cm^{-1} and 1650 cm^{-1} and are particularly characteristic of the phenyl group. The band centred on 1200 cm^{-1} is characteristic of the O=S=O asymmetric stretching vibration. Absorbencies at 1005 cm^{-1} and 1126 cm^{-1} result, respectively, from the vibrations of the phenyl ring substituted by a sulfonated group and sulfonated anion attached to the phenyl ring.

Microstructural analysis of the membranes

The membranes were microstructurally analyzed by means of DSC and DMA. Table I and Figure 5 show

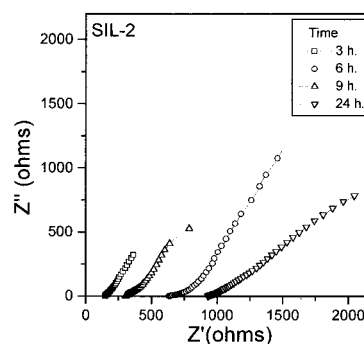


Figure 7 Impedance plots at different sulfonation times for SIL-1 and SIL-2.

the transitions observed at DSC. The transition at the lowest temperature corresponds to the glass transition temperature of hydrogenated polybutadiene (T_g^{HPB}) defined at the midpoint of the transition. As can be observed, it remains practically constant in all samples, except for a slight increase by 2°C in sample SIL-3, that is, the sample for which the sulfonated silica filler was incorporated into the HSBR-SO₃H matrix. Yet, in general, it is legitimate to state that sulfonic group incorporation has no effect on T_g^{HPB} .

At higher temperatures there appear endothermal transitions, whose position and shape vary according to sample composition. Sample SIL-1 shows a single transition at 170.2°C. For SIL-2 this transition occurs at a slightly lower temperature (166.6°C), yet it shows a second and well-defined transition at a higher temperature (199.1°C). This latter transition relates to the electrostatic aggregation of the ionic groups present in the sample, which gives rise to the formation of a new polymer phase, the so-called cluster phase. Finally, and in the case of sample SIL-3, a single, however, considerably wider, transition at 165.2°C is shown, which, again, is attributable to the cluster phase.

Dynamic mechanical analysis (DMA) shows similar results. Table I compiles the relaxation temperatures observed, and Figure 6 shows the dynamic mechanical relaxation spectra of the samples. As found at DSC, also here the first relaxation occurs at the glass transition temperature of hydrogenated polybutadiene (T_g^{HPB}), which remains practically constant for all three samples of our series, thus confirming that sulfonation of one or both components has no effect on T_g^{HPB} . DMA shows another relaxation, which corresponds to the glass transition temperature of polystyrene (T_g^{PS}) and was not detectable by means of DSC. This latter relaxation increases considerably with the ion content in the system, about 40°C for SIL-3, that is, the sample containing HSBR-SO₃H and SIL-SO₃H.

TABLE II
Sulfonation Kinetics of the Samples and Conductivity Analysis

Sample	Composition			Sulfonation time (h)	σ (S · cm ⁻¹)
	HSBR wt %	SIL wt %	SIL-SO ₃ H wt %		
SIL-1	70	30	—	0	10 ⁻⁷
				3	1.00 · 10 ⁻²
				6	2.89 · 10 ⁻³
				9	1.72 · 10 ⁻²
				24	1.97 · 10 ⁻⁴
SIL-2	70	—	30	0	10 ⁻⁷
				3	2.26 · 10 ⁻²
				6	2.67 · 10 ⁻²
				9	1.22 · 10 ⁻²
				24	7.86 · 10 ⁻³

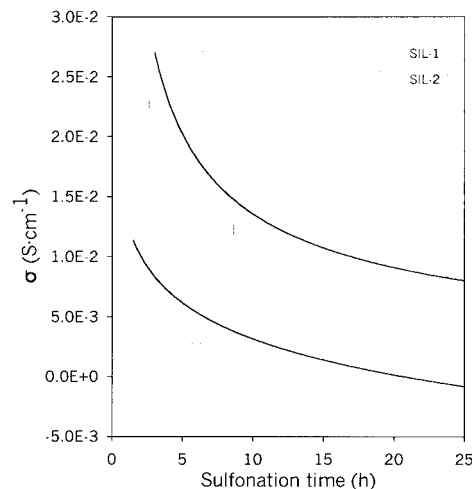


Figure 8 Ionic conductivity as a function of sulfonation time for SIL-1 and SIL-2.

The incorporation of sulfonate groups restricts the segmental movements of the styrene blocks of the copolymer. In addition, sample SIL-3, as well as SIL-2, show both a third relaxation at high temperatures, which DSC could only detect for sample SIL-2. This third relaxation, which increases proportionate to ion content, is attributable to the presence of clusters in the films, as a result of ionic aggregates due to the effect of electrostatic forces.

Electrical analysis of the membranes

Ionic conductivity was determined by means of complex impedance spectroscopy after 1 h hydration at 50°C of the film, obtaining very low values (10⁻⁷ S · cm⁻¹) for all three samples, which are characteristic of insulating materials.

To the purpose of improving these results the kinetics of heterogeneous sulfonation were determined for samples SIL-1 and SIL-2, measuring their ionic conductivity at different sulfonation times and after 1 h hydration at 50°C. Figure 7 shows the impedance diagrams of the two samples as a function of sulfonation time. The results obtained are compiled in Table II. Several aspects deserve to be highlighted. First and foremost, heterogeneous sulfonation proves to be effective already at short sulfonation times, i.e., conductivity is improved by up to five orders of magnitude at 3-h reaction time. Second, the highest values are obtained for sample SIL-2, i.e., the sample that originally contained silica with sulfonic groups. Finally, at the longest sulfonation time (24 h) conductivity does not improve. Moreover, and as can be seen in Figure 8, it diminishes considerably. This decrease goes hand in hand with a remarkable material deterioration of the samples.

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