Polymeric Proton Conducting Systems Based on Commercial Elastomers. III. Microstructural and Electrical Characterization of Films Based on HSBS/EPDM/PP/PS/Silica

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ABSTRACT: This study goes on with the microstructural and electrical characterization of the films, object of our study, containing hydrogenated poly(butadiene-styrene) block copolymer (HSBS). Ethylene–propylene terpolymer (EPDM), and a third component, polypropylene (PP), polystyrene (PS), or silica, crosslinked with peroxides and heterogeneously sulfonated. This process pursues the obtaining of materials with high proton conductivity and great dimensional stability, suited for application in a variety of electronic devices. The structural characterization consists of the study of the dynamic mechanical properties of all the samples, before and after the sulfonation, and also the checking of their structure by infrared spectroscopy. The analysis of the electrical properties of the films hydrated is achieved by electrochemical impedance spectroscopy. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 13–21, 2006

Key words: membranes; conducting polymers; FTIR; DMA; impedance spectroscopy

INTRODUCTION

A polymeric membrane cell consists of an electrode-membrane-electrode assembly held between two bipolar graphite plates. For this appliance to become marketable, new materials have to be synthesized, which can overcome the inconvenience that are known for Nafion, i.e., they must be inexpensive and easy to eliminate or degrade within conventional urban or industrial waste treatment.[1,2]

The proton conducting film is an essential component in a proton exchange membrane fuel cells (PEMFC) and has important tasks to fulfil: to allow for proton crossover (when hydrated), to act as a barrier (blocking crossover) between the gaseous fuel (hydrogen, etc.) and the oxidant gas (oxygen, air, etc.), and, last but not least, to act as an electronic insulator between the two electrodes. As a general rule, the proton conducting polymers used for this purpose are based on polymeric ionomers, as is the case for sulfonated polymers.

The aim of our research is to prepare new polymeric membranes possessing high proton conductivity, as well as high chemical and dimensional stability, to solve the problems presented by Nafion, which is currently used in PEMFCs, such as its high price, its deficient dimensional stability, and its toxicity. To this end, we have further pursued a previous line of research of membrane characterization, utilizing poly(butadiene-styrene) block copolymer, ethylene–propylene terpolymer, polypropylene, polystyrene, and silica blends, at different compositions and subjected to curing and heterogeneous sulfonation later on.[3,5]

EXPERIMENTAL

The following initial materials were used: hydrogenated poly(butadiene-styrene) block polymer (30/70) (HSBS), 2.6% insaturation, Calprene BB13 CH 6110, Repsol ($T_{g\text{-butadiene}} = -56.12°C$ and $T_{g\text{-styrene}} = 95.31°C$); ethylene–propylene terpolymer (EPDM) BUNA G 3850 ($T_g = -51.48°C$); polypropylene (PP), 099 ISPLEN, Repsol ($T_m = 164.97°C$ and $T_g = 123.13°C$); polystyrene (PS), POLYSTYROL 143 E. Basf ($T_g = 88.52°C$); and silica, ULTRASIL VN3, Degussa. Table I compiles the blend compositions under study.

For blend curing, dicumile peroxide was added.

The films from the crosslinked materials were obtained by compression molding, to obtain films that present a mean thickness of 100–150 μm.

The heterogeneous sulfonation reaction was achieved by placing the films in chlorosulfonic acid dissolved in 0.2M dichbroethane.

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TABLE I
Blend Compositions from Initial Materials

Sample	HSBS (wt %)	EPDM (wt %)	PP (wt %)	PS (wt %)	Silica (wt %)
BG-01	45	45	10	—	—
BG-02	40	40	20	—	—
BG-11	45	45	—	10	—
BG-12	40	40	—	20	—
BG-21	45	45	—	—	10
BG-22	40	40	—	—	20

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TABLE II
DMA Analysis of the Initial Materials

Frequency (Hz)	Relaxation HSBS	Relaxation EPDM	Relaxation PP	Relaxation PS
1	−36.16	−38.62	2.32	92.70
5	−32.44	−33.52	3.49	91.54
10	−31.29	−32.39	4.68	93.12

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Dynamic mechanical analysis (DMA) of our samples was implemented on a Mettler DMA 861-e analyzer at three frequencies: 1, 5, and 10 Hz and within a temperature range of −100 and 130°C for the cured samples, or else 300°C for the sulfonated samples at 2°C/min. The geometry used was the stress pattern. The strength applied was 10 N, the shifts varying between 8 and 10 μm, depending on the individual case. Figure 1 shows the spectra corresponding to the base materials, and Table II compiles the values found for the respective relaxations, which, in all cases, coincide with the T_g of each polymer.

Sulfonation of the polymeric films cause their T_gs to rise, as this process triggers deep changes in the physical properties of these composites, as a consequence of the formation of ion associations, such as clusters, multiplets, etc., which, in turn, are accountable for backbone mobility losses.[4]

IR analysis was implemented by means of Fourier transform spectroscopy utilizing a FTIR spectrophotometer, model Nicolet 520. This technique allows for better insight into the structure of these materials, as well as for the verification of the degree of sulfonation in the different films.

Analysis of the electrical properties of the sulfonated samples was implemented by means of impedance spectroscopy, using a Hewlett–Packard 4192-LF
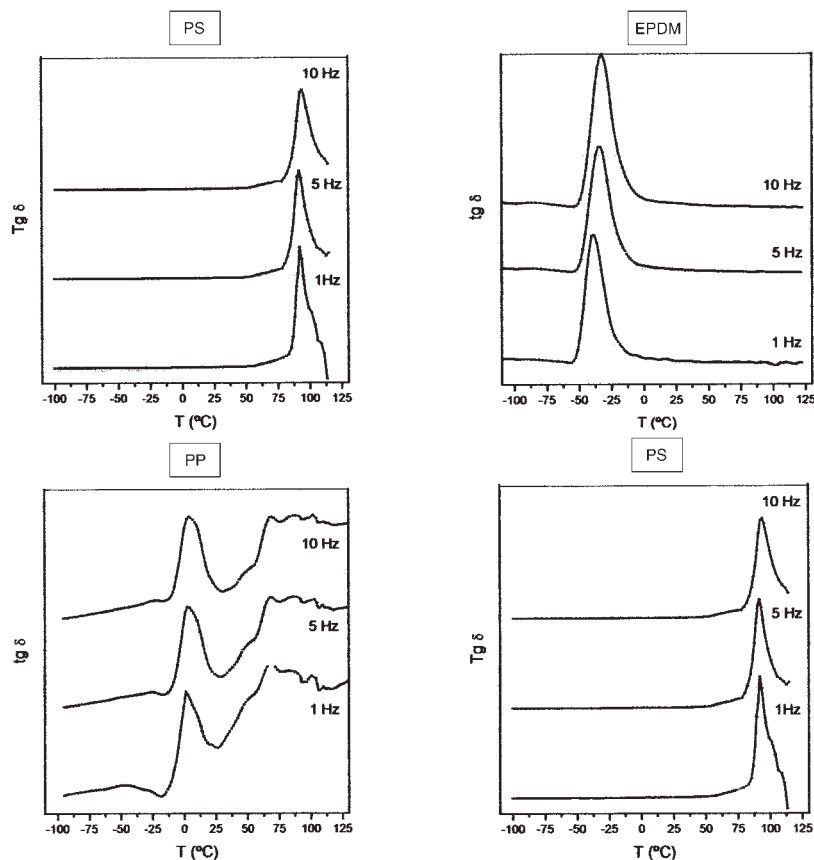

Figure 1 DMA spectra of the initial materials.

TABLE III
Results of DMA Analysis for the PP Samples

Sample	Relaxation 1		
	1 Hz	5 Hz	10 Hz
BG-01V	−37.67	−34.18	−33.19
BG-01Vslf	−30.84	−28.39	−27.55
BG-02V	−36.85	−33.43	−31.62
BG-02Vslf	−27.47	−26.40	−24.57

impedance analyzer with a frequency range of 5–13 Hz. Each sample was held in a water bath at two working temperatures, 60 and 80°C, favoring humidity uptake by means of an N_2 current throughput and measuring at different hydration times.

Hydration is the principal condition for these polymers to show their conductive properties. In the presence of water they swell, due to the strong hydrophilic character of the clusters. The hydrophilic dominions carry water and the proton charge, whereas the hydrophobic dominions confer stability to the material.

RESULTS

The HSBS/EPDM/PP system

The samples were analyzed microstructurally by means of DMA. Table III compiles the values of the relaxations recorded. In addition, the spectra obtained for the cured and sulfonated samples, implemented according to the method described in the Experimental section, are reproduced in Figures 2 and 3, respectively, where the loss factor is plotted against temperature for the three experimental frequencies and the two samples with a different PP portion.
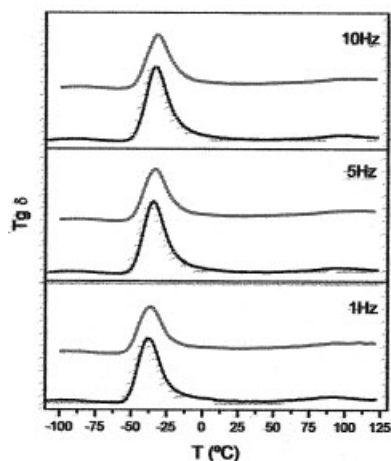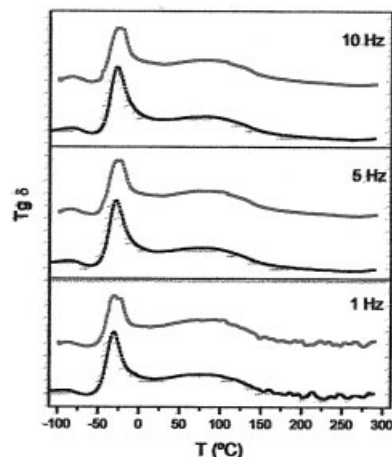

Figure 3 DMA spectra for the sulfonated BG-01 and BG-02 samples.

In these samples, a remarkable relaxation is observed around −35°C (varying slightly as a function of the measuring frequency) in the zone, where the T_g of butadiene of HSBS tends to appear, as well as that of EPDM, both of them probably overlapping.

With sulfonation, this transition is shifted to higher temperatures, since the SO_3H groups incorporated produce a restriction on the chain movements, as a consequence of cluster formation. In addition, two further relaxations are observed, which did not appear prior to sulfonation and are attributable to relaxations of the ionic clusters. One appears at low temperature in the range between −80 to −90°C, slightly blurred in this case and because of the more rigid part of these formations, i.e., the interface of the cluster with the rest of the material. The high temperature relaxation is associated
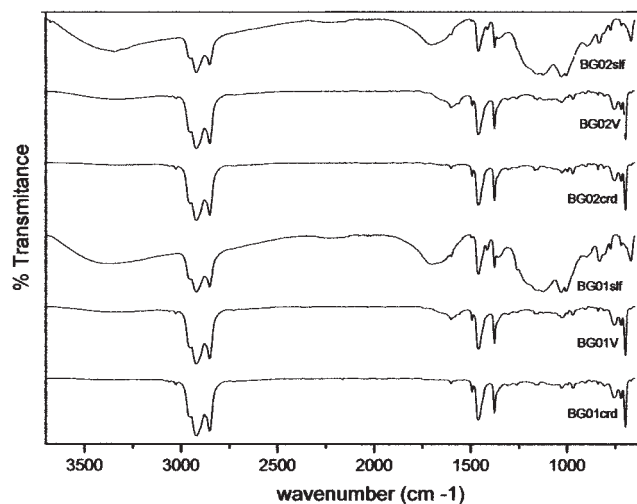

Figure 2 DMA spectra for the cured BG-01 and BG-02 samples.

Figure 4 FTIR spectra of the PP blends, before and after crosslinking and sulfonation.

TABLE IV
Conductivity Values of the Samples with PP, at the Two Working Temperatures

$t_{hydration}$ (h)	T = 60°C		T = 80°C	
	BG-01Vslf σ (S/cm)	BG-02Vslf σ (S/cm)	BG-01Vslf σ (S/cm)	BG-02Vslf σ (S/cm)
Dry	1.72×10^{-6}	1.87×10^{-6}	1.27×10^{-6}	1.14×10^{-3}
0.5	1.03×10^{-2}	2.11×10^{-3}	2.21×10^{-3}	4.58×10^{-3}
1	6.71×10^{-2}	2.25×10^{-3}	2.62×10^{-3}	3.35×10^{-3}
2	2.75×10^{-3}	1.93×10^{-3}	3.96×10^{-3}	5.02×10^{-3}
3	8.57×10^{-3}	1.95×10^{-3}	2.11×10^{-3}	5.86×10^{-3}
4	8.83×10^{-3}	3.12×10^{-3}	3.22×10^{-3}	5.38×10^{-3}
5	5.35×10^{-3}	2.01×10^{-3}	5.19×10^{-3}	5.44×10^{-3}
6	4.91×10^{-3}	2.05×10^{-3}	0.93×10^{-3}	5.12×10^{-3}
7	—	—	1.33×10^{-3}	4.27×10^{-3}

with the proper cluster. According to literature, this relaxation is broad and usually located in the 50–125°C temperature range.

Subsequently all the blends were IR-analyzed, before and after crosslinking and sulfonation. Figure 4 shows the respective FTIR spectra. The characteristic absorption bands of the polymers under study are visible. Between 1000–1250 cm^{-1}, there appears a band assigned to a bond of the R—SO$_2$—OR type. Around 1700 cm^{-1}, a band assigned to styrene sulfonation can be observed, which is typically absent in the nonsulfonated samples. The band at 2900 cm^{-1} shows two peaks, which is characteristic of the
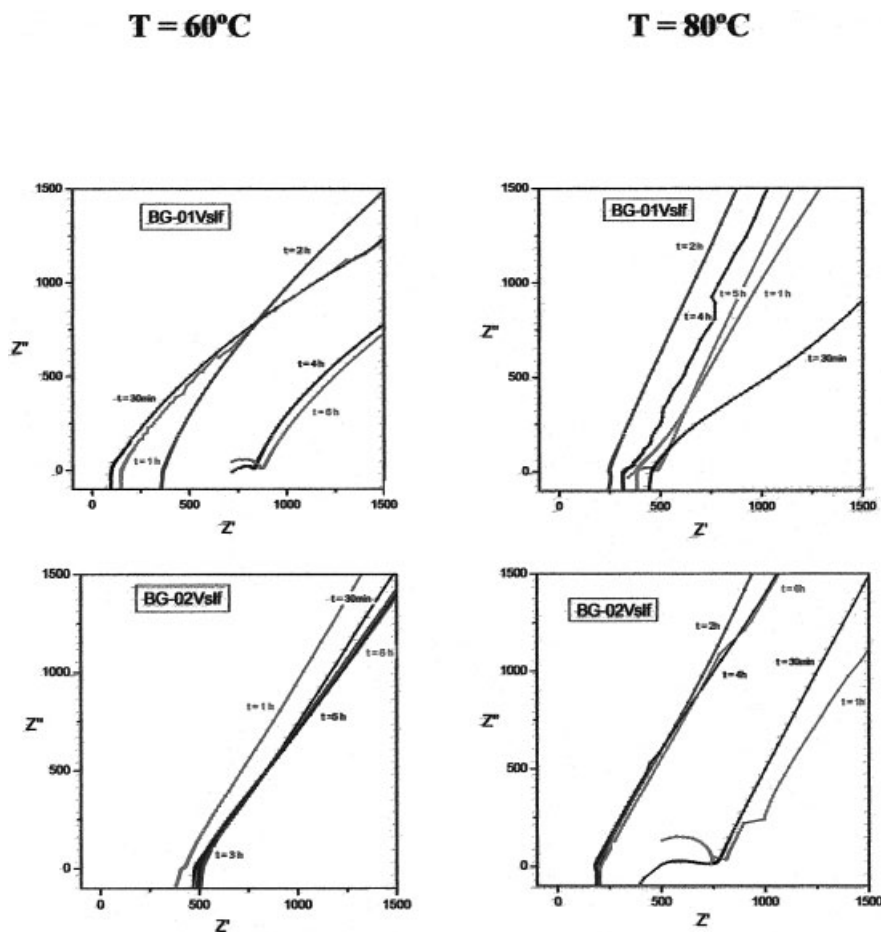

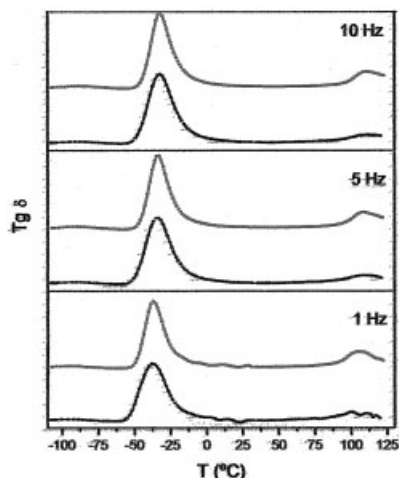**Figure 5** Impedance graphs obtained for blends with PP.

Figure 6 DMA spectra for the cured BG-11 and BG-12 samples.

Figure 8 FTIR spectra of the PS blends, before and after crosslinking and sulfonation.

double CH=CH$_2$ bond. At 3500 cm^{-1}, there appears an absorption band attributable to the OH— of the R—SO$_2$—OR groups and to the water produced.

Regarding the study of the electrical properties, Table IV shows the results obtained at different hydration times. Figure 5 compiles the impedance plot obtained, most of them showing a semicircle at high frequency, due to the contribution of the membrane followed by a
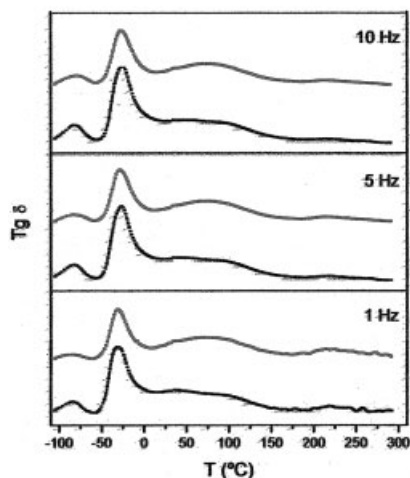
Warburg corresponding to the membrane–electrode interface.

While unhydrated, the films are practically insulators. Yet, upon hydration with steam at 60 and 80°C, respectively, a rapid increase in conductivity can be observed in the order of 10^{-3} S/cm, both samples showing analogous values, which remain stable during the measuring time.

The HSBS/EPDM/PS system

Figures 6 and 7 show the plots of the loss factor against temperature, as obtained by means of DMA of the PS-containing samples, while Table V compiles the relaxations found for these materials.

In this case, the HSBH and the EPDM relaxation is observed to overlap in the same temperature range as in the previously discussed case, as well as their shift to higher temperatures upon sulfonation.

In addition, there appears a relaxation at 105°C, because of the PS present in the samples. It is brighter in the samples containing a higher PS portion. In the sulfonated samples, this latter peak is not observed, probably due to the appearance of the two relaxations

Figure 7 DMA spectra for the sulfonated BG-11 and BG-12 samples.

TABLE V
Results of DMA Analysis for the PP Samples

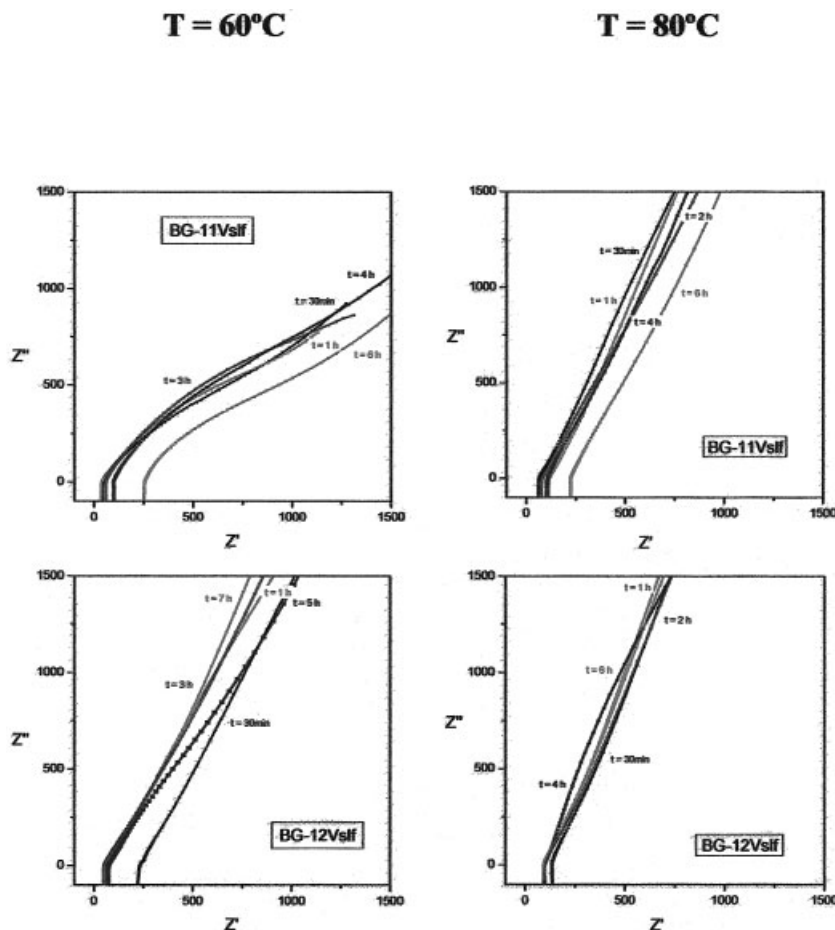| Sample	Relaxation 1			Relaxation 2			Relaxation 3		
	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz	1 Hz	5 Hz	10 Hz
BG-11V	—	—	—	−37.01	−34.18	−32.28	—	110.11	112.66
BG-11Vslf	−85.06	−83.24	−81.27	−30.61	−26.92	−25.91	—	—	—
BG-12V	—	—	—	−37.02	−33.81	−32.06	105.07	108.77	110.88
BG-12Vslf	−86.79	−83.77	80.53	−31.17	−28.12	−27.25	—	—	—

T = 60°C   **T = 80°C**

Figure 9 Impedance graphs obtained for blends with PS.

already commented on and associated to cluster formation, one centering around −85°C and the other between 50 and 125°C, which is also the range where there appears the PS T_g.

Figure 8 shows the FTIR spectra of all the samples under study. As in the previous case, the absorption bands characteristic of the polymers under study can be clearly observed, in particular the bands appearing as a consequence of sulfonation: one between 1000 and 1250 cm^{-1} assigned to the R—SO$_2$—OR bond and the other at 1700 cm^{-1} due to styrene sulfonation.

The impedance spectroscopy graphs are shown in Figure 9, and the respective conductivity values resulting from the graphs are compiled in Table VI.

TABLE VI
Conductivity Values of the Samples with PS, at the Two Working Temperatures

| $t_{hydration}$ (h) | $T = 60°C$ | | $T = 80°C$ | |
	BG-11Vslf σ (S/cm)	BG-12Vslf σ (S/cm)	BG-11Vslf σ (S/cm)	BG-12Vslf σ (S/cm)
Dry	8.77×10^{-5}	5.79×10^{-5}	3.73×10^{-5}	1.39×10^{-5}
0.5	2.40×10^{-2}	4.31×10^{-3}	1.61×10^{-2}	7.52×10^{-3}
1	2.60×10^{-2}	1.40×10^{-2}	8.86×10^{-3}	1.05×10^{-2}
2	7.80×10^{-3}	1.87×10^{-2}	1.30×10^{-2}	1.07×10^{-2}
3	1.73×10^{-2}	1.98×10^{-2}	8.09×10^{-3}	1.84×10^{-2}
4	1.02×10^{-2}	1.70×10^{-2}	9.56×10^{-3}	1.04×10^{-2}
5	3.54×10^{-3}	1.42×10^{-2}	3.85×10^{-3}	2.47×10^{-2}
6	3.95×10^{-3}	1.87×10^{-2}	4.48×10^{-3}	1.07×10^{-2}
7	1.94×10^{-3}	2.00×10^{-2}	—	1.17×10^{-2}
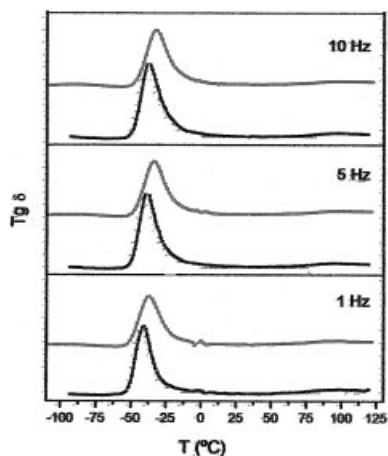
Figure 10 DMA spectra for the cured BG-21 and BG-22 samples.

TABLE VII
Results of DMA Analysis for the PP Samples

| Sample | Relaxation 1 | | |
	1 Hz	5 Hz	10 Hz
BG-21V	−40.42	−38.85	−37.58
BG-21Vslf	−39.89	−37.93	−35.92
BG-22V	−37.57	−33.99	−32.17
BG-22Vslf	−31.85	−29.40	−27.89

With this sample family, and similar to the other blends, only one T_g relaxation can be observed, as there is again an overlap of HSBS and EPDM T_gs. In the sulfonated samples, there appear, in addition, the relaxations resulting from cluster formation. However, the one recorded for the higher working temperature is straightforward only for the sample containing the smallest silica portion. On the other hand, at low temperature, the cluster relaxation is observed only for the sample with the largest silica portion and in that temperature range.

Figure 12 shows the results of IR analysis for all the samples. The spectra show the same characteristic absorption bands as for the other families, especially those due to sulfonation.

In the silica blends, there appears, between 1000 and 1250 cm^{-1}, in addition to the typical band mentioned for the other families, a strong absorption band due to the presence of silica in these blends.

Finally, the impedance spectroscopy study of the electrical properties of the films yield the conductivity values as compiled in Table VIII. The spectra recorded for the sulfonated samples are shown in Figure 13.

As was demostrated for the previously discussed blends, the conductivity values of these materialslikewise increase in several orders of magnitude with hydration, remaining stable during the measuring time. The values are similar at both working temperatures. For the sample containing 20% PS the absolute optimum in conductivity is obtained across the whole sample series, reaching 2×10^{-2} S/cm.

The HSBS/EPDM/silica system

By means of DMA analysis of the silica-containing samples, the loss factor values can be plotted against temperature, as shown in Figures 10 and 11 for the cured and sulfonated samples. In Table VII, the values of the relaxations of the different samples are indicated.
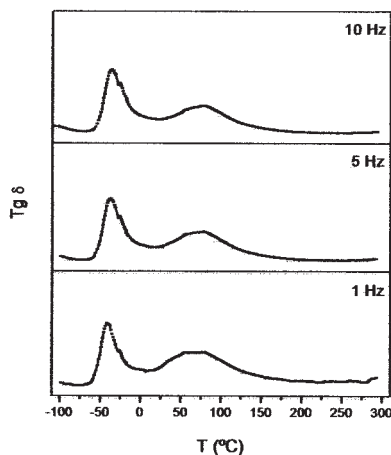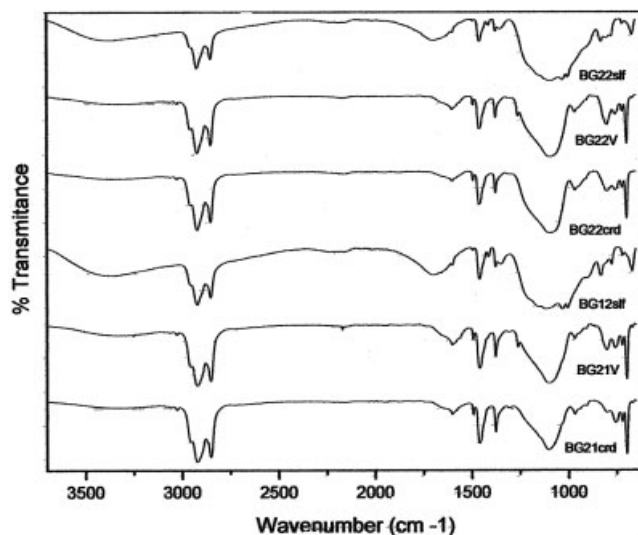

Figure 11 DMA spectra for the sulfonated BG-21 and BG-22 samples.

Figure 12 FTIR spectra of the silica blends, before and after crosslinking and sulfonation.

TABLE VIII
Conductivity Values of the Samples with Silica, at the Two Working Temperatures

$T_{hydration}$ (h)	$T = 60°C$		$T = 80°C$	
	BG-21Vslf σ (S/cm)	BG-22Vslf σ (S/cm)	BG-21Vslf σ (S/cm)	BG-22Vslf σ (S/cm)
Dry	1.07×10^{-6}	1.87×10^{-5}	1.32×10^{-6}	6.83×10^{-6}
0.5	1.45×10^{-2}	1.08×10^{-2}	1.21×10^{-2}	1.12×10^{-2}
1	8.51×10^{-3}	4.77×10^{-3}	9.10×10^{-3}	9.66×10^{-3}
2	9.38×10^{-3}	3.68×10^{-3}	6.13×10^{-3}	5.33×10^{-3}
3	4.97×10^{-3}	2.34×10^{-3}	3.19×10^{-3}	5.76×10^{-3}
4	3.81×10^{-3}	2.97×10^{-3}	2.64×10^{-3}	5.39×10^{-3}
5	2.86×10^{-3}	3.01×10^{-3}	2.49×10^{-3}	3.82×10^{-3}
6	2.64×10^{-3}	3.06×10^{-3}	2.62×10^{-3}	2.68×10^{-3}
7	—	—	2.25×10^{-3}	2.89×10^{-3}

As in the other blends, the conductivity values obtained move in the order of magnitude of 10^{-3} S/cm with hydration, and remain stable over time with no significant difference between one and the other sample.

CONCLUSIONS

In the light of the results obtained, it is legitimate to state that we are dealing with stable materials from a thermal and a chemical point of view, no degradation-proneness being observed.

The impedance spectroscopy values obtained for the different blends allow for the conclusion that, under optimum hydration conditions, good conductivity values can be achieved, similar to those known for the commercial Nafion 117 films. This is especially true for the 20% PS sample, which reaches the best results, as
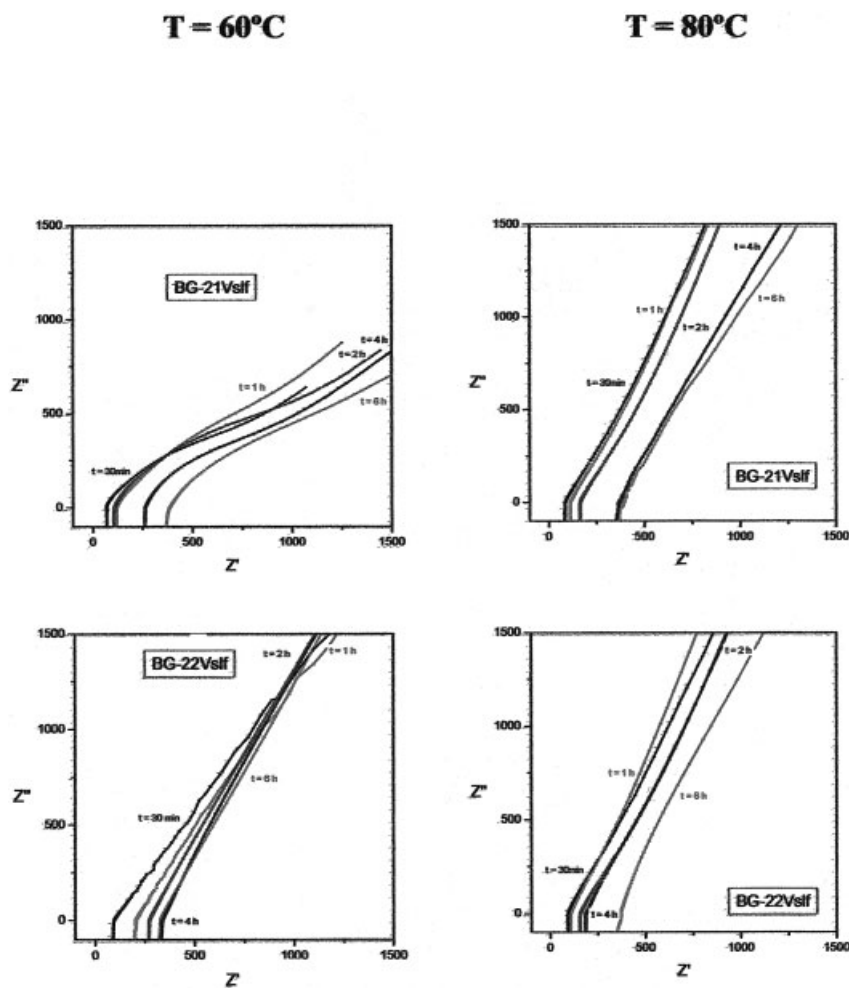

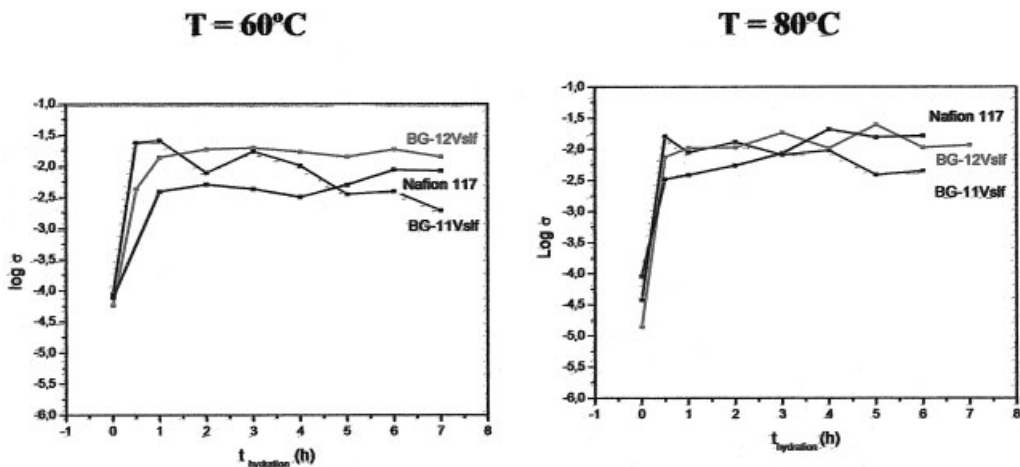**Figure 13** Impedance graphs obtained for blends with silica.

Figure 14 Plot of log σ against hydration time for the PS-containing samples.

the incorporation of this polymer increases its positions susceptible for sulfonation.

Figure 14 shows a plot of log σ against hydration time for the PS-containing samples at the two temperatures under study. The figure shows the increase in conductivity for the hydrated films and values remains stable over time, the same behavior detected for commercial Nafion 117 sample.

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