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# Miscibility Behavior of Polybenzimidazole/Sulfonated Polysulfone Blends for Use in Fuel Cell Applications

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ABSTRACT: Polybenzimidazole (PBI) and polysulfone (PSF) compose an immiscible polymer pair; the introduction however of functional groups such as sulfonate groups in the polymeric chain of PSF resulted in the formation of miscible blends with PBI. The miscibility behavior of a series of blends of PBI with sulfonated PSF (SPSF) at various sulfonation levels has been studied by dynamic mechanical analysis (DMA), FT-IR, and FT-Raman spectroscopy. DMA has shown that the sulfonation degree as well as blend composition controls the miscibility behavior of the studied system. In that respect, partially miscible or miscible blends were obtained when the sulfonation level is higher than 10 mol %. Since both polymers exhibit functional groups, which could participate in specific interactions, this possibility has been examined by FT-IR analysis. In absorption FT-IR spectra of PBI−SPSF specimens with high sulfonation degree and high PBI content, band shifts associated with the NH and sulfonate groups are accounted for the induced miscibility in terms of specific interactions. Moreover, a clear red shift of the symmetric vibration of the main chain sulfone group at 1152 $cm^{-1}$ has been also observed in the FT-Raman spectra of miscible PBI−SPSF blends. Careful examination of this spectral feature, assisted by curve-fitting analysis, has revealed that, besides the peaks attributed to pure PBI and PSF, a new scattering contribution, which is accounted for a new associated type of sulfone group, appears as the sulfonation degree of SPSF is increasing. This was partially attributed in terms of specific interactions but also to the Raman sensitivity in the medium polarity changes related to the increase of blend homogeneity. Preliminary results have demonstrated the potential usefulness of the blend polymeric membranes as electrolytes for fuel cells.

## Introduction

Polymer blending is a common and potentially versatile way to develop new materials with desirable properties.[1] However, the development of new useful blends is severely limited by the incompatibility of many polymer pairs of interest.[2] This is mainly due to the small contribution of the entropy of mixing, which leads to phase separation of the blend since enthalpy of mixing and the resulted $\Delta G$ are both positive. An effective way to overcome this problem is to induce specific interactions and thus miscibility between the two polymers. The prerequisite for such specific interactions is the existence or the introduction of the proper functional groups onto macromolecular chains.

In recent years, a lot of scientific interest has been directed to ionomers, e.g., polymers containing a small amount of bonded ionic groups. Ionomers are attractive polymers for promoting miscibility via specific interactions with a wide range of other polymers through ionic functional groups. Some possible interactions are hydrogen-bonding, dipole−dipole, and ion−dipole interactions. Polystyrene (PS)-based ionomers, such as sulfonated PS (SPS), have extensively been used in order to produce new miscible blends. Examples include styrene−methacrylic acid/ poly(alkylene oxide),[3,4] SPS/polyamide,[1,5−8] SPS/polyurethane,[9] and SPS/ethyl acrylate−vinylpyridine copolymer.[10−12] Sulfonated polyesters, such as PET, have also been used in blends with ethyl acrylate−vinylpyridine copolymers.[2,13−15] Other polyester ionomers have been studied in blends with PET and nylons.[16,17] In all above cases, the observed miscibility was attributed to specific interactions between the ionic groups of the ionomer and polar groups of the other polymer. One prominent advantage of this approach is that the strength of the specific interactions, and as a result, the phase behavior of the resulting blends can be tailored by varying the structure of the ionomer, the functionality level, the acid group, and the counterion used.

Aromatic polybenzimidazole (PBI) is a macromolecule that possesses both donor and acceptor hydrogen-bonding sites, which are indeed capable of participating in specific interactions. On the other hand, PBI exhibits high thermal stability, high chemical resistance, and outstandingly high glass transition temperature.[18,26] Moreover, this material possesses ionic conductivity after being doped with phosphoric acid.[19] Recently, doped PBI membranes were found to have promising properties for use as polymer electrolytes in a high-temperature direct methanol fuel cell[20] as well as in $H_2$/$O_2$ fuel cells.[21] PBI has already been used as a component in polymeric blends either with high-$T_g$ polymers[22,23] resulting in high-performance blends or with flexible polymers as a molecular composite.[24,25] In both cases, the miscibility is assisted by specific interactions.[22−26]

Polysulfone (PSF) is an engineering thermoplastic with excellent mechanical properties, good mechanical stability, and toughness. Blends of PSF with PBI form high-performance fibers although the two polymers are

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**Table 1. Blend Composition with Different Sulfonation Degrees**

| blends | composition | blends | composition |
|---|---|---|---|
| PBI−SPSF(Na)20 | 0/100 | PBI−SPSF(Na)44 | 50/50 |
| PBI−SPSF(Na)20 | 50/50 | PBI−SPSF(Na)44 | 75/25 |
| PBI−SPSF(Na)20 | 67/33 | PBI−SPSF(Na)70 | 0/100 |
| PBI−SPSF(Na)20 | 75/25 | PBI−SPSF(Na)70 | 50/50 |
| PBI−SPSF(Na)44 | 0/100 | PBI−SPSF(Na)70 | 67/33 |
| PBI−SPSF(Na)44 | 25/75 | PBI−SPSF(Na)70 | 75/25 |

immiscible.[27] Sulfonation of the PSF[28,30] at various degrees resulted in materials bearing functional groups and having high glass transition temperatures. Since sulfonated polysulfone (SPSF) bears polar groups, it can be considered that the presence of functional groups, which can participate in hydrogen-bonding interactions, is expected to lead to the formation of miscible blends with PBI. Moreover, in applications, where ionic conductivity is needed, sulfonate groups can also promote ion conduction.

In the present work, we report on the miscibility behavior and the interactions observed between PBI and SPSF as a function of the extent of sulfonation and blend composition. The blends have been characterized using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). FT-IR and FT-Raman spectroscopic techniques have been also used for the direct investigation of the existence of specific interactions between blend components. It should be noted that the use of Raman spectroscopy, although a complementary technique to IR, has been underutilized for studying polymer blends. The potential usefulness of Raman spectroscopy in the study of specific interactions of polymer blends has been reported[31,32] in combination with the simplicity of sample preparation, which allow in a more realistic sample examination in polymer blends. Moreover, as it was realized from this study, the progressive homogenization of a blend might be estimated resolving the sensitivity of a vibrational normal mode to the medium polarity changes.

## Experimental Section

**Materials.** PBI was supplied from Aldrich in the powder form. Polysulfone was purchased also from Aldrich with an average $M_n$ ca. 26 000. Sulfonated polysulfone (SPSF) was prepared by using chlorosulfonic acid as a sulfonated agent in a dichloroethane solution following the procedure of Johnson et al.[28] The sulfonation levels determined by $^1$H NMR and FT-Raman measurements were 10, 20, 36, 44, and 70%. The sodium salt SPSFNa was prepared by neutralizing the solution of SPSF with a methanol solution of sodium hydroxide under vigorous stirring. The precipitated product was filtered, washed, and dried at 100 °C in high vacuum.

**Sample Preparation.** Blends were prepared by dissolving the two polymers (1% w/v) in dimethylacetamide (DMAc) at the desired ratio for 1.5 h at 160 °C. Films of the blends were cast by pouring the solution into a glass plate at 80 °C for 24 h. To remove any excess of solvent, the films were dried under vacuum at 200 °C for 3 days. Films were examined by Fourier transform infrared spectroscopy (FT-IR) in regards to the peak at 2940 cm$^{-1}$ of DMAc to ensure that there was no residual solvent present. The studied blends with different sulfonation degrees are given in Table 1.

**Characterization Techniques.** Differencial scanning calorimetry (DSC) thermograms were obtained using an SP plus calorimeter equipped with the Autocool accessory from Rheometrics Scientific Ltd. The heating rate was 20 °C min$^{-1}$ and covered the range from −50 to 450 °C.

DMA measurements were carried out with a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz. Specimen dimensions were $2.5 \times 0.5 \times 0.02$ cm$^3$.

To determine the sulfonation degree of SPSFs, $^1$H NMR measurements were performed by using a Bruker Avance DPX 400 MHz spectrometer. The samples were dissolved in deuterated dimethyl sulfoxide ($d_6$-DMSO), and the measurements were performed at 65 °C.

Infrared spectra were measured in the transmission mode on a Bruker Equinox 55 Fourier transformed mid-IR spectrometer with sealed and desiccated optics. All spectra were measured at room temperature; the spectra of PSF and SPSF have been measured at a resolution of 0.5 cm$^{-1}$ and represent the average of 400 scans, while all other spectra represent the average of 50 scans at a resolution of 2 cm$^{-1}$.

Raman spectra have been recorded with the FT-Raman FRA-106-S module of the Equinox 55 FT-IR spectrometer of Bruker using NIR excitation at 1064 nm. The curve-fitting analysis shown as an inset in Figure 13 has been performed using the PeakFit v4.0 software of Jandel Scientific.

**Fuel Cell Test.** Platinum catalysts (20% Pt) supported by carbon black (Vulcan XC-72R, Cabot) were prepared by chemical reduction of platinum chloroacid. The catalysts were applied onto a wet-proofed carbon paper (Toray TGP-H-120) by a tape-casting technique. Assemblies from the acid-doped polymer membranes and electrodes were prepared by means of hot press at 150 °C.

A single test cell (5 cm$^2$) was made of graphite plates with gas channels. Two aluminum end plates with attached heaters were used to clamp the graphite plates and collect current. Fuel and oxidant gases were supplied by means of mass flow controllers. Performance curves were obtained by a current step potentiometry. Potential values at various current densities were then taken from chronopotentiometric curves when a steady state was reached.

## Results and Discussion

**Dynamic Mechanical Properties.** The miscibility of an ionomer with another polymer is often[1] very sensitive to the counterion chosen for the ionomer if the miscibility is due to specific interactions. In this study, we have used the sodium salt of the sulfonated polysulfone since preliminary work has shown that blends of PBI with sulfonated polysulfone in the acidic form were immiscible.

The thermal examination of the studied blends was attempted using DSC and DMA. The DSC thermograms, recorded for up to four subsequent scans, increased monotonically without showing transition up to 450 °C. As is known from the literature, for both blend constituents[28,30,33,34] special drying and heating conditions were applied in order to get well-defined reproducible glass transition temperatures; in our case, however, they have proved insufficient. Most of our effort was concentrated on the dynamic mechanical analysis, but in that case, plasticization effects due to remaining solvent, especially in blends with high PBI content, were also encountered. To obtain reliable results, casted blends were subjected to prolong drying (at least 3 days at 200 °C); the presence or absence of the dimethylacetamide solvent was confirmed by FT-IR analysis based on the peak at 2940 cm$^{-1}$, which is assigned to the stretching band of the dimethylacetamide methyl group.[22]

Having the samples exhaustedly dried, dynamic mechanical analysis was performed. At first the influence of the sulfonation degree (s.d.) on the miscibility was examined at the 50−50 blend composition. Blends of PBI with SPSF of 10, 20, and 44% s.d. have been tested, and the results in terms of the temperature dependence of $E'$ and $E''$ are shown in Figure 1, in comparison with pure SPSFs. As we can see, the blend with 10% s.d. gives $T_g$ at the temperature where the $T_g$ of the pure SPSF appears, showing that the 10% s.d. is not enough

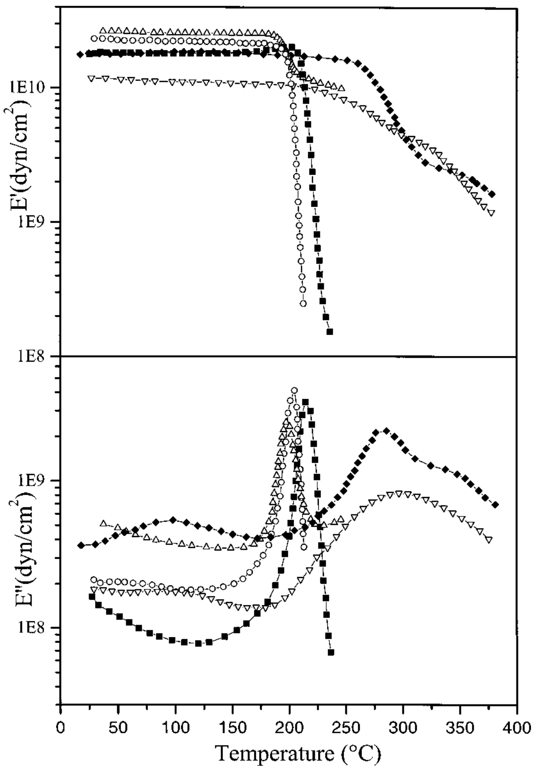

**Figure 1.** Temperature dependence of the storage ($E'$) and loss ($E''$) modulus of PBI−SPSF(Na)$X$, $X$ = 10, 20, 44 blends: (△) $X$ = 10, 0/100; (○) $X$ = 10, 50/50; (■) $X$ = 20, 0/100; (▽) $X$ = 20, 50/50; (♦) $X$ = 44, 50/50.

to induce miscibility. The same miscibility behavior was obtained when the system PBI−SPSF(Na)10 was examined in the whole composition range. The blends with higher sulfonation degrees (20% and 44%) show broad $T_g$'s, in the region between the $T_g$'s of the pure polymers. These broad $T_g$'s might be considered as two converging $T_g$'s as well, indicating miscibility or partial miscibility between the blend components at these sulfonation degrees. Further improvement of the miscibility by increasing the sulfonation degree cannot be tested using this method since sulfonated polysulfones with higher sulfonation degrees do not form self-supported films. Ng and Mac Knight[2] have already reported that sulfonation degree higher than 10% was needed to obtain miscible blends for the sulfonated PET−poly(ethyl acrylate-*co*-vinylpyridine) system.

Having examined the effect of the sulfonation degree on the miscibility of our system, the dependence of the composition on miscibility has also been considered. In that respect, blends of PBI with a sulfonated polysulfone of intermediate sulfonation degree (44%) were selected. The results in terms of the temperature dependence of $E'$ and $E''$ are depicted in Figure 2. As is shown there, the blend with low PBI content is immiscible since it shows a glass transition at the same temperature as the respective pure SPSF. In blends with higher PBI contents, broad $T_g$'s shifted to higher temperatures, indicating miscibility based on the single $T_g$ criterion. More careful examination at the $E''-T$ curve shows the appearance of a shoulder, which could also denote the existence of a second PBI rich phase, leading to a partially miscible system. On the basis of the storage modulus values presented in Figure 2, blends with high modulus up to 300 °C are obtained in the cases where PBI content is 50% and 75%. So, the temperature up to which these blends can be used is much higher that the one for the polysulfone polymer, and thus, high-performance blends were obtained by this method. Two common theoretical equations were used to correlate the $T_g$ and the composition of the miscible blends.

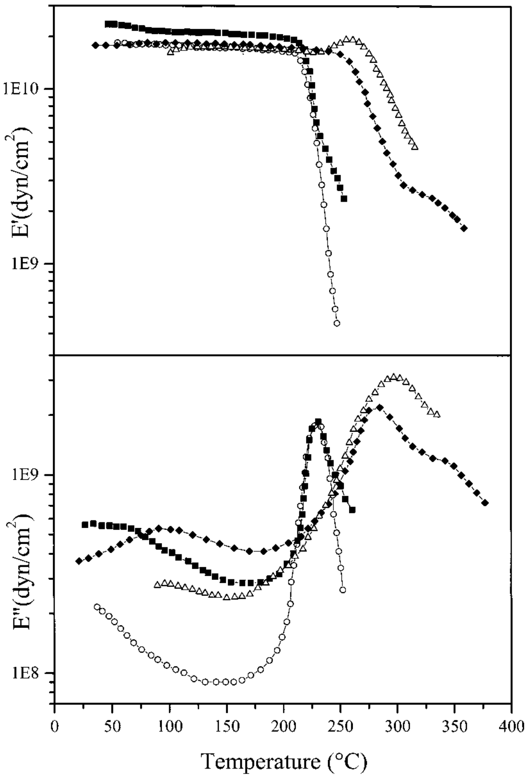

**Figure 2.** Temperature dependence of the storage ($E'$) and loss ($E''$) modulus of PBI−SPSF(Na)44 blends: (○) 0/100; (■) 25/75; (♦) 50/50; (△) 75/25.

**Table 2. Experimental versus Theoretical $T_g$'s Using the Fox and Utracki Equations for the PBI−SPSF(Na)44 Blends**

| blends | composition | $T_g$(exptl) (K) | $T_g$(Fox) (K) | $T_g$(Utracki) (K) |
|---|---|---|---|---|
| PBI−SPSF(Na)44 | 75−25 | 297 | 359 | 356 |
| PBI−SPSF(Na)44 | 50−50 | 285 | 309 | 305 |
| PBI−SPSF(Na)44 | 25−75 | 231 | 266 | 264 |

$$\text{Fox equation: } \frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

$$\text{Utracki equation: } \ln T_{gb} = \frac{w_1 \ln T_{g1} + k w_2 \ln T_{g2}}{w_1 + k w_2} \tag{2}$$

where $w_i$ is the weight fraction and $T_{gi}$ is the glass transition temperature of polymer $i$. $k$ is an empirical parameter describing deviation from the assumed negligibility of the entropy of mixing and usually taken equal to $k = \rho_1 T_{g1}/\rho_2 T_{g2}$ and $p_i$ is the density of polymer $i$. The results for the PBI−SPSF(Na)44 blends are depicted in Table 2. This treatment shows that the best fit to the experimental data is accomplished by the Utracki equation. Among the studied compositions, only the 50−50 composition is adjusted well with both equations while the PBI-rich blend show a much lower $T_g$ value than the expected value, and the SPSF-rich blend is immiscible. Attempts to measure the $E'$ and $E''$ at higher temperatures in order to ensure whether other PBI rich phases exist or not have been made without success.

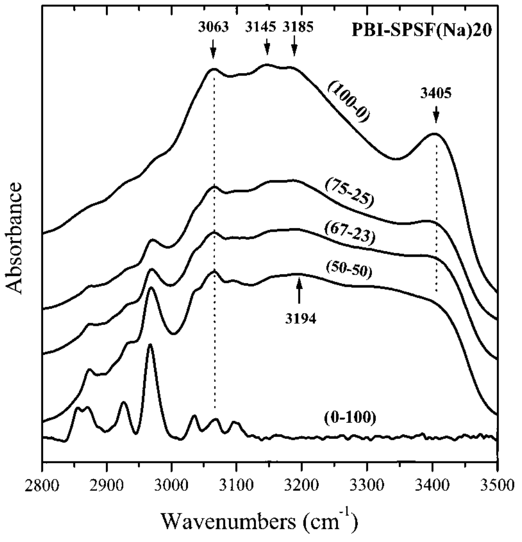

**Figure 3.** FT-IR spectra of PBI−SPSF(Na)20 blends in the N−H stretching region.

Although specific interactions are expected to be responsible for the observed miscibility behavior of our system, the obtained $T_g$ values are lower than the ones expected according to the Fox equation. This is in contradiction with other systems where specific interactions have led to a synergistic effect on the $T_g$ dependence on composition.[18] To clarify the existence of specific interactions in the studied polymer system, a systematic examination of blends of PBI with polysulfone at various sulfonation degrees as well as at various compositions has been conducted utilizing FT-IR and FT-Raman spectra.

**FT-IR Examination.** Since the interactions in PBI blends have been extensively examined[22−26,35,36] by FT-IR, it is well-known that most of the information is based on the N−H stretching region. Thereby, in present work, the complex high-frequency absorption spectrum of PBI has been separated into three distinguishable contributions shown in top spectrum of Figure 3:[26] (a) a relatively sharp peak at 3405 cm$^{-1}$ attributed to non-hydrogen-bonded “free” N−H groups, (b) a broad absorption at ~3145 cm$^{-1}$ attributed to self-associated hydrogen-bonded N−H groups with a high-frequency counterpart at ~3185 cm$^{-1}$ tentatively attributed to a vibrational overtone of the conjugation between benzene and imidazole rings located at ~1600 cm$^{-1}$, although both bands have been also suggested as strongly dependent on the presence of residual solvent as well as on adventitious water,[22] and (c) a third peak at 3063 cm$^{-1}$ well attributed to the stretching modes of the aromatic C−H groups.

In sulfonated polysulfone, a doublet at 1295 and 1325 cm$^{-1}$ and an absorption band at 1152 cm$^{-1}$ are attributed[28] to the asymmetric and symmetric stretching vibration of sulfone group, respectively. Moreover, the infrared absorption bands located at 1014 and 1363 cm$^{-1}$ were assigned to the symmetric stretch of diphenyl ether units along the macromolecular chain or/and the in-plane vibrations of para-substituted benzene rings[28,29] and the symmetric C−H bending deformation in methyl group of aliphatic isopropylidene units,[28] respectively. These two bands, which should be more or less insensitive to the sulfonation, may be used as internal standards in the FTIR spectra of SPSF to identify the absorption bands due to the sulfonate. In this context, the FTIR spectra of the polysulfone and the sulfonated polysulfones with sulfonation degrees 10, 20, 36, 44, and 70% were recorded, and two representatives are depicted in Figure 4 in the spectral window of sulfur−oxygen stretching. The bands at 1028, 1093, and 1190 cm$^{-1}$ are associated with the sulfonate anion. The peak at ~1028 cm$^{-1}$ may be well assigned as the symmetric stretch of the sulfonate group. More and above that, the well-shaped and resolved absorption peak at ~1028 cm$^{-1}$ might be used to match interactions that involve the $-SO_3^-$ group.[38] In general, all absorption bands, either of sulfone or sulfonate groups, might be considered as sensitive to interactions with their environment. To get an inside on these specific interactions, we have focused on three spectral windows of Figure 4, related to the well-resolved peaks of the symmetric vibration of sulfonate (Figure 5) and sulfone (Figure 6) groups and the asymmetric stretching of sulfone group (Figure 7) as well. To facilitate comparison, all spectra have been normalized so that the intensity of the 1014 cm$^{-1}$ band is the same in all spectra. In Figure 5, a slight red shift of the sulfonate symmetric stretch takes place at a high sulfonation degree. This indicates that sulfonate group most probably interacts with the main chain sulfone group as it has been also observed in the case of blends of sulfonated polystyrene with polysulfone.[37] Having a look in the corresponding symmetric stretch region of polysulfone at ~1152 cm$^{-1}$, shown in Figure 6, we can distinguish that SPSF(Na)70 sample exhibits also a slight red-shift compared with the corresponding samples

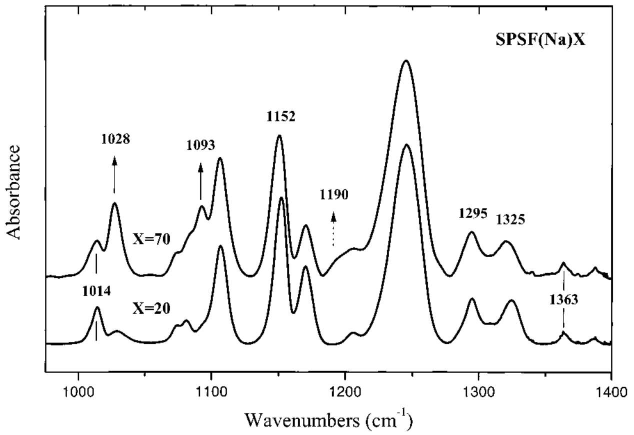

**Figure 4.** FT-IR spectra of sulfonated polysulfones at two sulfonation degrees in the sulfur−oxygen stretching region.

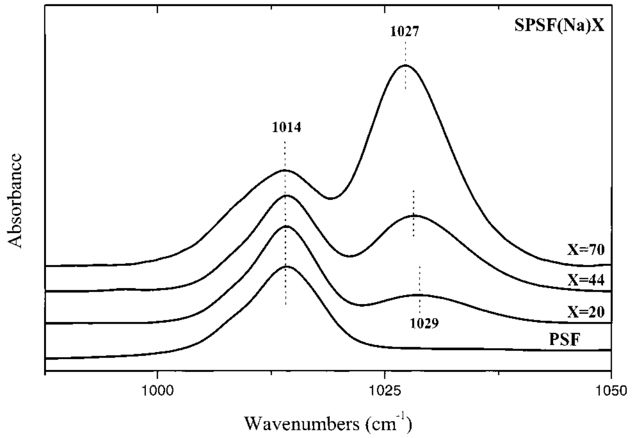

**Figure 5.** FT-IR spectra of polysulfone and sulfonated polysulfones at various sulfonation degrees in the symmetric stretch region of sulfonate ($SO_3^-$) group.

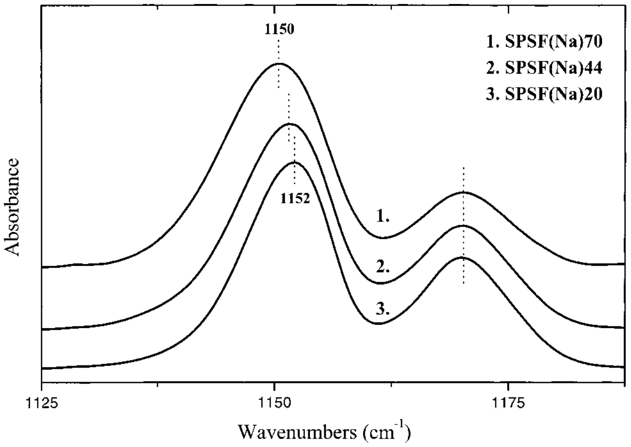

**Figure 6.** FT-IR spectra of sulfonated polysulfones at various sulfonation degrees in the symmetric stretch spectral region of sulfone group.

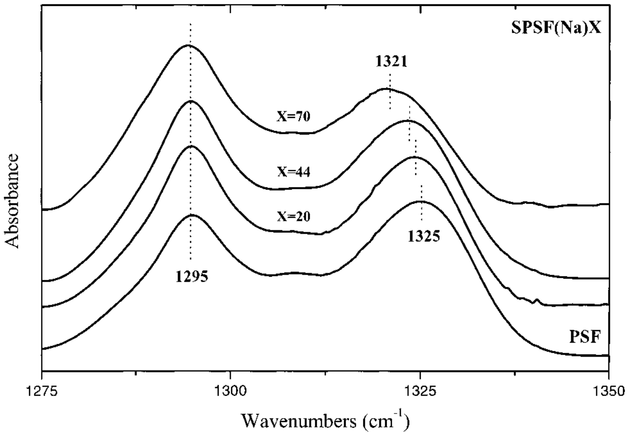

**Figure 7.** FT-IR spectra of polysulfone and sulfonated polysulfones at various sulfonation degrees in the antisymmetric stretch spectral region of sulfone group.

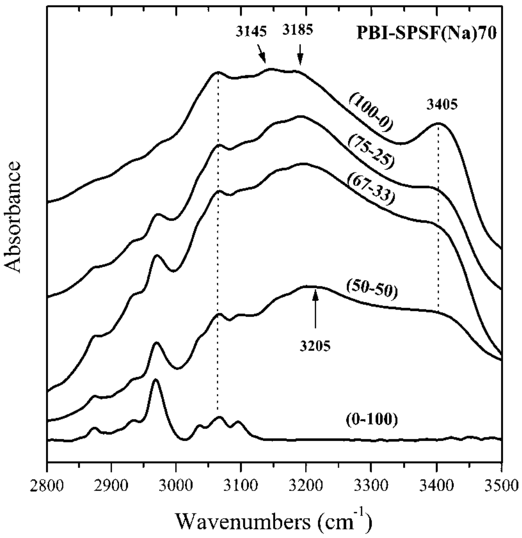

**Figure 8.** FT-IR spectra of PBI−SPSF(Na)70 blends in the N−H stretching region.

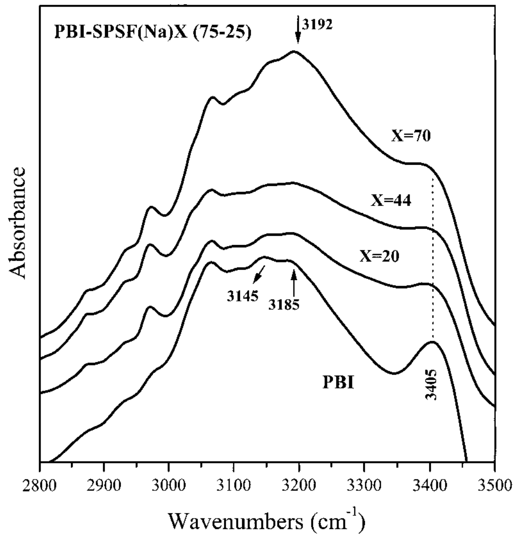

**Figure 9.** FT-IR spectra of PBI−SPSF(Na)*X* 75/25 blends (*X* = 20, 44, 70) in the N−H stretching region.

of lower sulfonation degree, SPSF(Na)44 and SPSF(Na)-20. In Figure 7, with increasing degree of sulfonation, a similar low-frequency shift occurs for the asymmetric stretch of sulfone group at 1321 cm$^{-1}$. All above observations point out the sulfonate−sulfone interaction in highly sulfonated PSF samples.

From the absorption data discussed until now, it is evident that the FTIR spectral regions, which can be sensitive to the occurrence of specific interactions between PBI and SPSF(Na), are those at 2800−3500, 1000−1050, 1100−1200, and 1250−1350 cm$^{-1}$. In the discussion below, we analyze these four regions of the IR spectrum as a function of the blend composition and the sulfonation degree of the sulfonated polysulfone. The various blend and blend compositions investigated are listed in Table 1.

**N−H Stretching Region (2800−3500 cm$^{-1}$).** The high-frequency FT-IR spectra of the PBI−SPSF(Na)20 blends displayed in Figure 3 are composition-dependent. The spectral changes decreasing PBI composition are as follows: (a) the "free" N−H stretching peak at 3405 cm$^{-1}$ broadens, (b) a new peak at around 3194 cm$^{-1}$ becomes predominant, and (c) the N−H stretching envelope at 3145 cm$^{-1}$ shows a decrease in intensity, while the C−H aromatic stretching at 3063 cm$^{-1}$ remains almost insensitive in both frequency and intensity. In the corresponding FTIR spectra of PBI−SPSF(Na)44 blends similar changes were observed, while in those exhibiting even higher degree of sulfonation (PBI−SPSF(Na)70), shown in Figure 8, decreasing PBI, both "free" N−H and self-associated N−H peaks located at around 3405 and 3145 cm$^{-1}$, respectively, are again lowered in intensity while an intense new peak with its maximum weakly composition dependent appears at around 3205 cm$^{-1}$. In the case of the PBI poor blends, not shown here, no structural information in the N−H region occurs anymore. The above-mentioned trends are more clear in Figure 9 where the FTIR spectra of PBI−SPSF(Na)*X* (75−25) blends are presented with regard to the sulfonation degree. The new peak at around 3192 cm$^{-1}$ is increasing with the sulfonation degree, while the "free" N−H peak at 3405 cm$^{-1}$ exhibit a slight red shift. It is obvious that increasing SPSF composition or/and sulfonation degree the interactions of the N−H with other species are predominant and an increase of the sulfonation degree from 44% to 70% results in stronger interactions between the blend components. Consequently, upon blending, sulfonate or/and sulfone groups are most probably involved in specific interactions with N−H. This gives rise to a blue shift of the N−H stretching involving in self-associated hydrogen bonding, from 3145

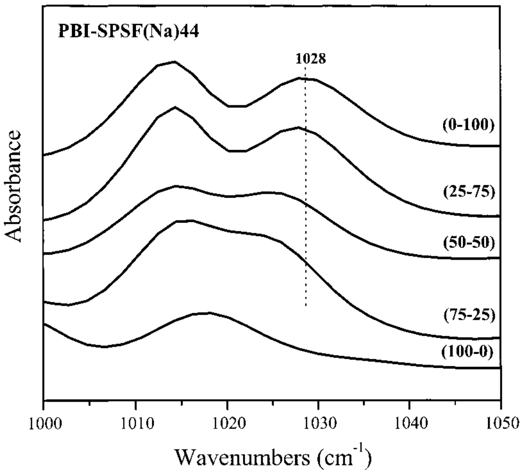

**Figure 10.** FT-IR spectra of PBI–SPSF(Na)44 blends in the sulfonate (SO$_3^-$) stretching region.

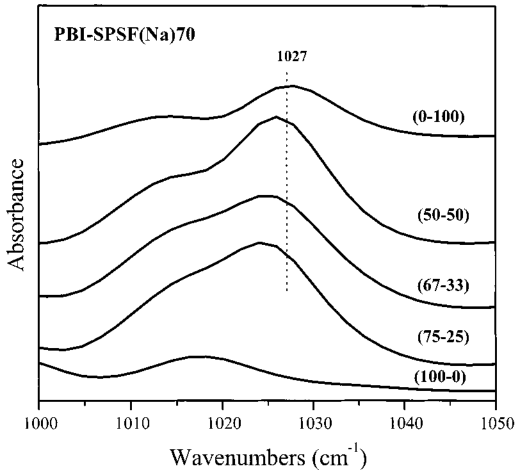

**Figure 11.** FT-IR spectra of PBI–SPSF(Na)70 blends in the sulfonate (SO$_3^-$) stretching region.

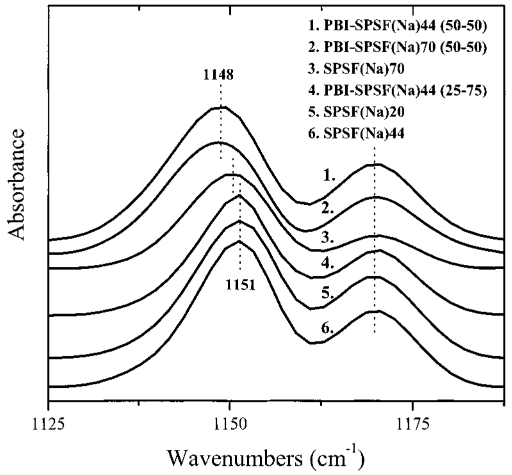

**Figure 12.** FT-IR spectra of PBI–SPSF(Na)$X$ blends ($X$ = 20, 44, 70) in the sulfone stretching region: (1) $X$ = 44, 50/50; (2) $X$ = 70, 50/50; (3) $X$ = 70, 0/100; (4) $X$ = 44, 25/75; (5) $X$ = 20, 0/100; (6) $X$ = 44, 0/100.

to $\sim$3200 cm$^{-1}$, and a red shift in the stretching of "free" N–H bonds to $\sim$3385 cm$^{-1}$. The same behavior has been obtained in blends of PBI with poly(vinyl acetate-*stat*-vinyl alcohol) [PV(Ac/OH)],[24] where the self-association peak at 3145 cm$^{-1}$ was shifted to 3220 cm$^{-1}$ and was assigned as an indication of weakening of the self-associated N–H···N hydrogen bonding, while the "free" N–H peak was shifted to 3350 cm$^{-1}$ and considered as supporting the idea of increased hydrogen bonding in the blends increasing hydroxyl content.

**Symmetric Stretching Region of Sulfonate and Sulfone Groups (1000–1050, 1100–1200, 1250–1350 cm$^{-1}$).** In sulfonated polymers, the symmetric S–O stretching band of the sulfonate anion has been accepted as a band very sensitive to the local environment of the sulfonate anion[5] and has been used to monitor specific interactions in polymeric blends.[37] In PBI–SPSF(Na) system studied here, the peak at $\sim$1028 cm$^{-1}$ assigned to the symmetric stretching mode of the –SO$_3^-$ group is much more pronounced in sulfonated polysulfones with higher degree of sulfonation as already shown in Figures 4 and 5. The influence of the blending on this peak position is shown in Figures 10 and 11 where the FTIR spectra of both PBI–SPSF(Na)44 and PBI–SPSF(Na)70 systems at different blend compositions are displayed. As is easily shown, the peak centered at 1014 cm$^{-1}$ and attributed either to the aryl–ether–aryl symmetric stretch or/and the in-plane vibration of para-substituted benzene ring remains almost unaffected, although it manifests slight changes due to an overlapping with a benzene ring vibration of PBI at 1017 cm$^{-1}$. On the contrary, the peak at $\sim$1028 cm$^{-1}$ in Figure 10 shows a clear shift toward lower wavenumbers. This is expected due to the weakening of the S–O bond caused by the interaction of the sulfonate group or/and Na$^+$ ion with other groups. This displacement is composition dependent apart from the PBI–SPSF(Na)44 25–75 blend composition, which is known from mechanical properties to be phase separated, and this was spectroscopically confirmed since no shift was observed on both sulfonate and sulfone symmetric stretch located at 1028 and 1151 cm$^{-1}$, respectively. The same conclusion comes from Figure 11 as far as the red shift of the peak at 1027 cm$^{-1}$ is concerned, which is directly related to the miscibility behavior of PBI–SPSF(Na)70. But, more and above that, the spectral features shown in Figure 12 in the sulfone symmetric stretching region indicate that S=O stretch is slightly influenced by the high sulfonation degree in SPSF(Na) and at a larger degree by blend miscibility, confirming the involvement of sulfone group in the specific interactions arising by blending. PBI presents no bands in the spectral region shown in Figure 10.

Our attempt to probe similar influence of blend miscibility in the sulfone antisymmetric stretching region at $\sim$1325 cm$^{-1}$ has failed. This is due to the presence in this spectral region (1250–1350 cm$^{-1}$) of the strong enough absorption band of imidazole ring breathing of PBI at $\sim$1286 cm$^{-1}$ that partially overlaps with the relatively weak sulfone band.

**FT-Raman Examination.** In Figure 13, the FT-Raman spectral features observed for PSF and SPSF for different sulfonation degrees are shown in the 700–1200 cm$^{-1}$ region. Upon sulfonation, a new peak attributed to the symmetric –SO$_3^-$ stretch of sulfonate group appears at around 1030 cm$^{-1}$. This vibrational band may be ratioed against internal standards, such as either the 1010 or/and the 793 cm$^{-1}$ bands tentatively attributed to diphenyl ether units' stretch along the main chain and to Ar–S–Ar stretch, respectively. The correlation between the FT-Raman measurements and the sulfonation degree obtained by a direct method such as the NMR spectroscopy is also shown in Figure 13 as an inset. This calibration curve might be used for the

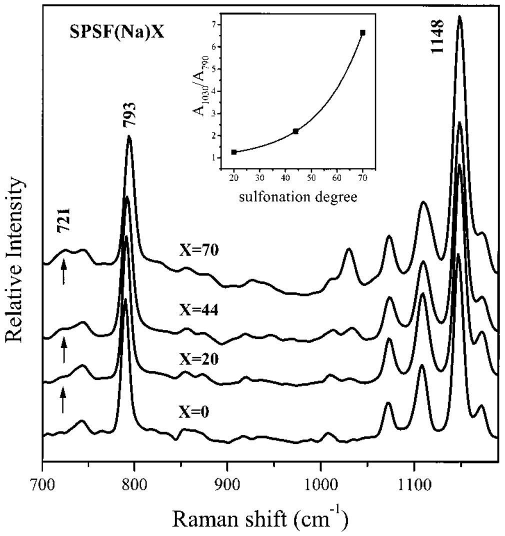

**Figure 13.** FT-Raman spectra of polysulfone (PSF) and sulfonated polysulfones (SPSF(Na)*X*) at various sulfonation degrees ($X = 20, 44, 70$). Inset: correlation of the FT-Raman technique to sulfonation degree obtained by $^1$H NMR.

evaluation of the degree of sulfonation of SPSFs with only one fast Raman measurement. Raman spectroscopy is a rapid, nondestructive method with no need for sample preparation. Another weak Raman band emerges upon sulfonation in the Raman spectra of SPSF specimens, shown in Figure 13, at ~720 cm$^{-1}$ and it is tentatively attributed to $-SO_3^-$ bending.

In the FT-Raman spectra of PBI–SPSF(Na)44 blends at different compositions, not shown here, the symmetric stretching vibrational band of the sulfonate group at 1030 cm$^{-1}$ was very weak to detect any eventual change/shift of its peak maximum with composition that might be attributed to polymer miscibility. Even very careful examination of the spectra in the region of the symmetric stretching vibration of the sulfone group at around 1148 cm$^{-1}$ could not reveal whether this peak is affected or not by mixing. This is due to its partial overlapping with the PBI Raman band, located at 1134 cm$^{-1}$ and tentatively attributed to C–C skeletal stretching, which follows the composition evolution as well.

To perceive any influence on the symmetric stretching vibration of the sulfone group at 1148 cm$^{-1}$ when the sulfonation degree and hence miscibility are increased, the FT-Raman spectra of the blends with 50–50 composition of PBI with polysulfone at various sulfonation degrees as well as with nonsulfonated polysulfone were recorded and depicted in Figure 14. In the same figure the Raman spectra of pure PBI and PSF are shown as well. In the polymer mixtures, the PBI content was kept constant to rule out any influence of the 1134 cm$^{-1}$ peak of PBI on the behavior of the 1148 cm$^{-1}$ band of PSF. All spectra containing PBI were normalized relative to the benzene ring vibration at 998 cm$^{-1}$, which is considered as not influenced by specific interactions. As shown there, a clear differentiation in the Raman spectra of blends with polysulfone or polysulfone with low sulfonation degree and the Raman spectra of blends with high sulfonation degree exists. Increasing the sulfonation degree in PBI–SPSF(Na)*X* (50–50) polymer mixtures from $X = 20$ to 44 and 70, the $SO_2$ symmetric stretch of sulfone group experiences a continuous change either decreasing in intensity and/or exhibiting a red shift. A tentative curve-fitting analysis to testify any new evolving band structure has been also undertaken and presented in Figure 14 as an inset. In the PBI–PSF blend, the complex peak at ~1140 cm$^{-1}$ is composed from the two individual peaks of the pure components, located at ~1134 and 1148 cm$^{-1}$ for PBI and PSF, respectively. This is also more or less the case for the PBI–SPSF(Na)20 blend. A clear difference is observed as the sulfonation degree is increased, which is much more intensive in the PBI–SPSF(Na)70 blend where the curve-fitting procedure suggests the presence of a new peak at ~1141 cm$^{-1}$. This is not considered as doubtless to securely resolve the overlapping components but may probe scattering contributions that might be attributed to polymer miscibility as the sulfonation is increased from 44 to 77%.

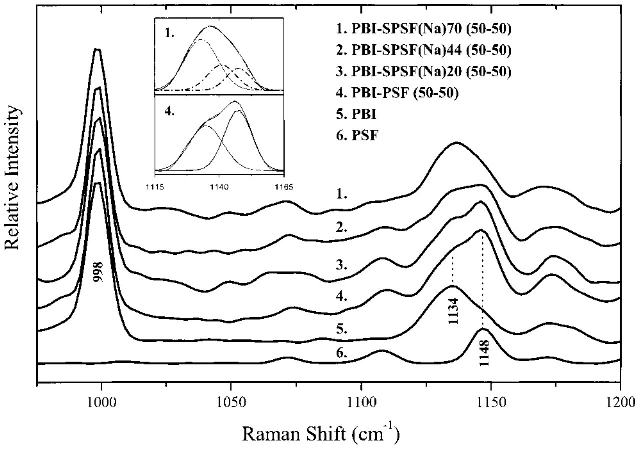

**Figure 14.** FT-Raman spectra of PBI–SPSF(Na)*X* 50/50 blends ($X = 20, 44, 70$): (1) $X = 70$; (2) $X = 44$; (3) $X = 20$; (4) $X = 0$; (5) 100/0, (6) $X = 0$, 0/100. Inset: curve-fitting analysis of the scattering band in the sulfone stretching region for PBI-PSF(Na)*X* 50/50 blend: (1) $X = 70$ and (4) $X = 0$.

The driving force that stimulates miscibility in PBI–SPSF blends is the introduction of Na$^+$–sulfonate groups by sulfonation of PSF. The effect of Na$^+$–sulfonate groups on blend miscibility is most probably accounted for in terms of specific interactions with the “free” or/and self-associated N–H groups of PBI. In blends with a high sulfonation degree (SPSF), even the main chains S=O groups are involved in interactions. This is assisted by the fact that in homogeneous blends the different polar groups are in a close proximity enabling thus interactions which are not observed in phase separated systems. That is how further attractive hydrogen-bonding interactions between other PSF groups such as the S=O of sulfone group with the N–H bonds of PBI might be occurred. This was clearly shown in present work by the FT-Raman spectra.

Taking into account that the corresponding symmetric stretch of sulfone group in FT-IR shows a smaller shift, the observed Raman peak might be accounted for as due not only to interactions involving the main chain sulfone group but also in terms of a further scattering contribution. By increasing sulfonation degree, the blend becomes more homogeneous, as mentioned above, and medium polarity around the sulfone group is changed. Since Raman spectra are sensitive to the medium polarity, such a change is expected to affect the peak maximum.

The above findings show the utility of the Raman spectroscopy in polymer blends not only as a complementary technique to IR, in regards to the specific interactions monitoring, but also to give information,

**Table 3. Vibrational Bands of PBI and SPSF(Na) that Are Involved in Specific Interactions and Induce Miscibility in PBI−SPSF(Na) Blends**

| wavenumber (cm$^{-1}$) | polymer | assignment | vibrational spectroscopic technique |
|---|---|---|---|
| 3405 | PBI | non-hydrogen-bonded "free" N−H stretching | FT-IR |
| 3145 | PBI | hydrogen-bonded self-associated N−H stretching | FT-IR |
| (1325) | SPSF(Na) | antisymmetric stretch of sulfone group | FT-IR |
| 1152 | SPSF(Na) | symmetric stretch of sulfone group | FT-Raman and FT-IR |
| 1028 | SPSF(Na) | symmetric stretch of sulfonate group | FT-IR and (FT-Raman) |

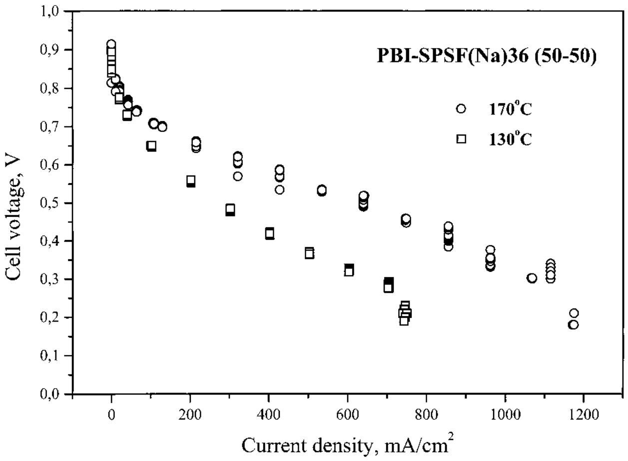

**Figure 15.** Cell voltage versus current density curves of a fuel cell based on the blend membrane electrolyte at 130 and 170 °C. Electrodes with a platinum loading of 0.45 mg/cm$^2$; membrane electrolyte of PBI−SPSF(Na)36 (50−50) doped with 4.5 mol of phosphoric acid per average repeat unit; both oxygen and hydrogen at 1 bar and 200 mL/min flow.

which is directly related to the homogeneity of the blend. Finally, all vibrational bands of PBI and SPSF(Na) that are involved in specific interactions and induce miscibility in PBI−SPSF(Na) blends are given in Table 3.

**Fuel Cell Test.** The conductivity of the blend membranes doped with phosphoric acid has been examined in great detail and will be discussed elsewhere.[39] In all cases, conductivity above $10^{-2}$ S/cm has been obtained. The potential application of these membranes to fuel cells has been demonstrated. The preliminary results are shown in Figure 15.

The noble metal catalyst loading was 0.45 mg/cm$^2$ for both electrodes. The membrane electrolyte was a PBI−SPSF(Na)36 (50−50) blend doped by 4.5 mol of $H_3PO_4$ per average repeat unit of the blend polymer. It should be noted that the fuel cell operates with no humidification for either hydrogen or oxygen. Both gases are under the atmospheric pressure. As seen from the figure, an increase in the operational temperature from 130 to 170 °C significantly improves the cell performance. Further development of the fuel cell technology by optimizing electrodes and membrane electrolytes is under progress.

## Conclusions

New blends of PBI with SPSF(Na) at various sulfonation degrees and compositions have been prepared and studied in regards to their mechanical and spectroscopic properties. Dynamic mechanical analysis has revealed that miscible or partially miscible blends based on the single $T_g$ criterion have been obtained in some cases. This miscibility has been attributed to the presence of specific interactions between the N−H groups of PBI and mainly the sulfonated group of the polysulfone. FT-Raman examination has provided additional information on the homogeneity of the studied blends based on the shift observed in the Raman scattering peak of the main chain sulfone group of the polysulfone, probably due to a local polarity change.

Fuel cell tests have demonstrated the feasibility of the blend polymer electrolyte for an advanced fuel cell, operational at temperatures up to 200 °C.

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