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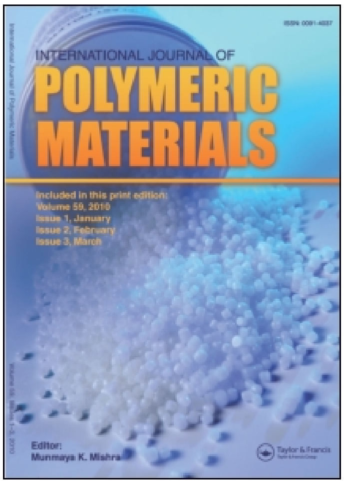

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Blends of Poly(ether imide) and Styrene Sulfonic Acid Based Polymer: Thermal, Mechanical and Ionic Conduction Behavior

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Dense membranes based on poly(ether imide) (PEI) and poly(styrene sulfonic acid-co-maleic acid) (PSSAMA) was obtained by extrusion and compression molding. Blends with different PSSAMA content (1, 3, 5, and 10 wt%) were prepared. Their morphology was investigated by scanning electron microscopy (SEM) and their thermal properties by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic-mechanical analysis (DMA). Two glass transition temperatures (T_g) (100 and 216°C) appeared when high contents of PSSAMA were added to PEI, indicating that the polymers form an immiscible system. TGA curves showed that the first weight loss occurred above 400°C for all blends, indicating a good thermal stability. Water uptake measurements have shown that the membranes presented low swelling when compared with Nafion®. The proton conductivity of the membrane with 10 wt% of PSSAMA obtained bv impedance measurements was $0.006 \times 10^{-2}\, S \cdot cm^{-1}$.

Keywords: blends, ion conductivity, poly(ether imide), poly(styrene sulfonic acid-co-maleic acid)

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INTRODUCTION

Fuel cells (FC) present several interesting characteristics such as low environmental pollution level, high efficiency, and a potential application for automotive industry and portable power systems [1–14]. A proton exchange membrane (PEM) is a solid electrolyte located between the anode (in contact with fuel such as hydrogen or methanol) and cathode (in contact with oxygen/air) compartments of fuel cells.

Perfluorosulfonic acid based membranes such as Nafion® are the reference PEM due to high chemical stability and level of proton conductivity in the high hydrated state [4]. However, Nafion® has some drawbacks: high cost, relatively poor resistance to methanol transport when used in Direct Methanol Fuel Cells (DMFC), low application temperature, poor water retention above 80°C and poor mechanical properties when highly swollen by water [5,6]. Therefore, these peculiarities have stimulated polymer researchers to investigate alternative materials and various sulfonated polymers have been synthesized for fuel cell applications [7–10].

PEM for fuel cell applications have been extensively researched in the last years [5–8]. The development of promising proton conducting membranes is based on physical and chemical changes of polymer materials such as rigidity of the main chain, length of the side chains, equivalent weight of proton donors, and concentration of introduced hydrophilic groups in the membrane [4].

Polymer blends have been used to obtain materials with controlled properties when each component of the blend can be chosen to develop a specific requirement. Thus, ion conducting polymers and engineering thermoplastics could be, in principle, used for designing materials with potential for the mentioned applications.

Poly(ether imide) (PEI) is a high performance amorphous thermoplastic with good thermal stability and remarkable modulus of elasticity and tensile strength [11,12]. It is mainly used in the automotive and electrical/electronics industry. Several kinds of PEI blends have been studied in the last years [13–15], in spite of the difficulty to process this thermoplastic.

Poly(styrene sulfonic acid-co-maleic acid) (PSSAMA) is also a commercial polymer and presents good potential to be used as proton conducting material to be blended with PEI resin. In addition, the maleic acid units have two ion-exchangeable sites each, and exhibit lower capacity of hydration than that of the sulfonic acid group [16–17]. The presence of maleic acid group in the main chain together with poly(styrene sulfonic acid) (PSSA), can increase the membrane charge density and prevent the excessive swelling.

This work reports the morphology as well as thermal, mechanical, and conducting behavior of new membranes based on blends of PEI containing low content of PSSAMA obtained by extrusion.

EXPERIMENTAL

Materials

Commercial poly(ether imide) (PEI) Ultem 1000 purchased from General Electric and poly(styrene sulfonic acid-co-maleic acid) sodium salt (PSSAMA) with styrene/maleic acid molar ratio 3:1 and average M*w* 20,000 supplied by Sigma-Aldrich were used as received. The structures of these polymers are shown in Figure 1. Nafion 117 was supplied by Aldrich.

Membrane Preparation

Initially, PEI was dried in an oven at 150°C for 3 h. The blends were obtained in a conical mini twin extruder (Daca Instruments) at 320°C and 60 rpm. The polymers were blended with different concentration of PSSAMA (1, 3, 5, and 10 wt%) for 5 min using the recycling system of the equipment and after this time, the blends were collected

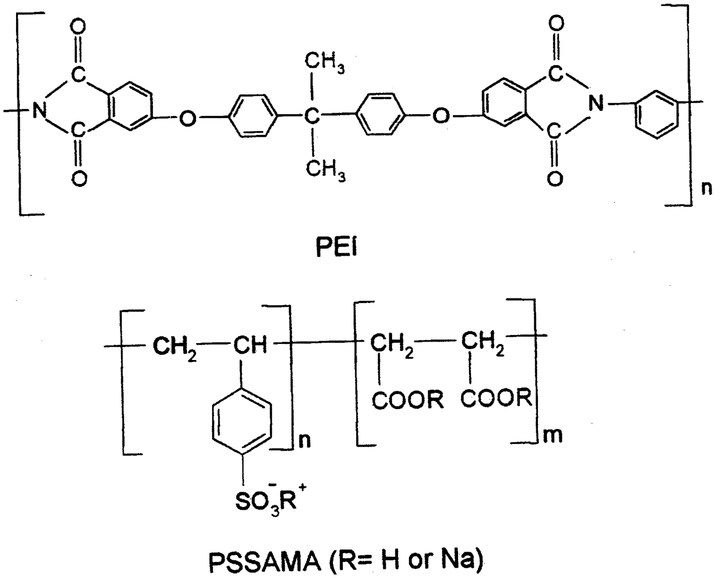

FIGURE 1 Structural formula of PEI and PSSAMA.

and pelletized. The membranes were obtained by compression molding of blend pellets at 270°C and 60 KN for 8 min and cooling slowly to room temperature. All membranes obtained had thickness between 180 and 210 μm, approximately. Then, the membranes were stored for further characterizations.

Thermal Analyses

The calorimetric analysis was performed using a differential scanning calorimeter (DSC) Mettler-Toledo 821e. Each sample (8 mg) was heated from 30°C to 350°C at heating rate of $10^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$ under nitrogen. Then, it was cooled down to 30°C at the same rate. A second heating was carried out in the same conditions of the first one. The glass transition temperature (T_g) was determined from the second heating scan.

The thermal stability of the samples was evaluated in a Mettler-Toledo thermogravimetric analyzer (TGA/SDTA) 85e at 30–600°C and $10^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$ under nitrogen/oxygen atmosphere at a flow rate of $50\,\mathrm{ml} \cdot \mathrm{min}^{-1}$. The degradation temperatures were determined. The initial weight of the samples was approximately 17 mg.

Dynamic-mechanical measurements (DMA) were performed with a Rheometrics solids analyzer RSAII. It was employed to determine the thermal transitions of the membranes. Scans were carried out at heating rate of $5^\circ\mathrm{C} \cdot \mathrm{min}^{-1}$ and frequency of 1 Hz. The loss modulus E' (viscous component) and the storage modulus E'' (elastic component) of the membranes were obtained from the analysis. The T_gs were obtained from the peak of $Tan\,\delta(E''/E')$ versus temperature data.

Scanning Electron Microscopy

Morphological studies were carried out in a scanning electron microscope Jeol JSM-IC 848 with an accelerating voltage of 15 KV. The membrane was cryogenically fractured and the cross-section was coated with gold before the SEM analysis.

Water uptake Measurements

Dried membrane samples were immersed in distilled water at room temperature for 48 h and then taken out to measure the water uptake (WU), which was calculated from Eq. (1).

$$WU = \frac{(W_s - W_d)}{W_d} \times 100 \tag{1}$$

where W_s and W_d are the weights of swollen and dry samples, respectively.

Conductivity Measurements

Proton conductivity of samples was evaluated from membranes resistance measured by a.c. impedance spectroscopy based on Nyquist plots. The Nyquist plot is a graph used in automatic control of a system with feedback. It is represented by a graph in polar coordinates in which the gain and phase of a frequency response are plotted. The plot of these phasor quantities shows the phase as the angle and the magnitude as the distance from the origin. The graph presents an imaginary and a real axis and the related plot is a classic method of assessing stability. The analysis was carried out in the Autolab Potentiostat-Galvaniostat apparatus using a small alternating voltage (10 mV) and varying the frequency of the alternating voltage from 10 Hz to $10'$ Hz. The proton conductivity (σ) was calculated from the impedance data according to Eq. (2)

$$\sigma = \frac{L}{RS} \tag{2}$$

where L and S are the distance between electrodes and the area of the membrane, respectively, at room temperature and 100% RH. R is the resistance value measured. The swollen membrane thickness was used in the calculation of σ.

RESULTS AND DISCUSSION

Morphology

The microstructure of the PEI/PSSAMA membranes was examined by SEM in fractured surfaces obtained after immersing them in liquid nitrogen and manual fracture. Figures 2 and 3 present SEM images for the membranes cross-sections. No difference is clearly seen for the 5 wt% blend when compared to PEI membrane. Nevertheless, different domains suggest a heterogeneous distribution of PSSAMA in the PEI matrix for the 10 wt% blend. This morphology probably occurs due to differences of viscosity and polarity between the two components. PEI has hydrophobic functional groups, whereas the PSSAMA has highly hydrophilic sulfonic acid groups. Due to these structural differences, agglomeration of the more polar dispersed phase may take place in the membranes, particularly with those containing 10 wt% of PSSAMA in the PEI matrix.

Thermal Properties

DSC Analysis

PEI, PSSAMA, and PEI/PSSAMA blends were analyzed by differential scanning calorimetry. The DSC traces are shown in Figure 4.

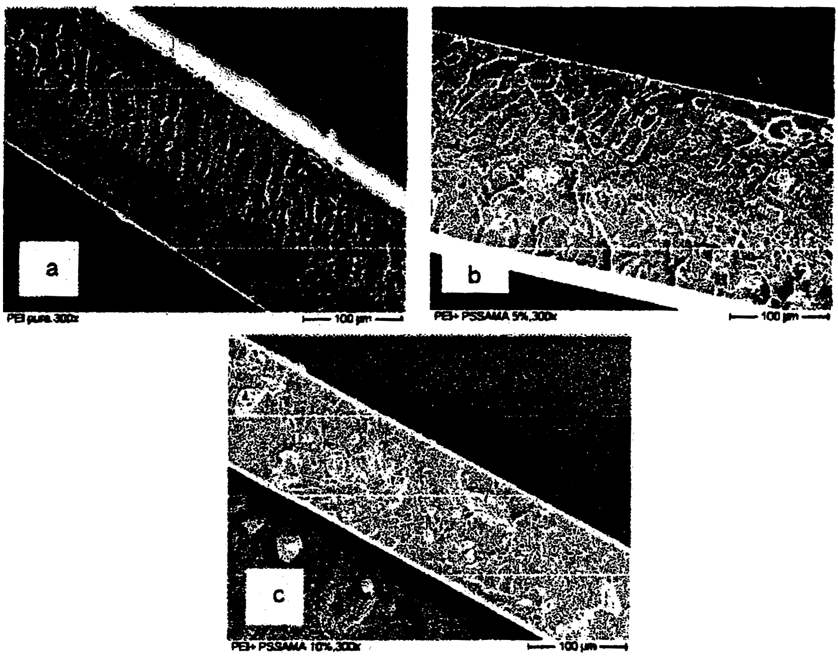

FIGURE 2 SEM microphotographs (300×) of fracture surfaces of: (a) PEI; (b) PEI/PSSAMA 5 wt% blend; and (c) PEI/PSSAMA 10 wt% blend.

PEI and PSSAMA presented only one glass transition temperature (T_g) at 216°C and 105°C, respectively. The blend containing 1 wt% of PSSAMA presented a similar behavior to that of PEI, showing only one T_g at 216°C (Table 1). However, when the amount of PSSAMA increases in the blend, a new T_g can be observed, indicating that a phase separation took place. The DSC trace of the blend with 1 wt% of PSSAMA did not present another T_g simply due to the low amount of the sulfonic acid–based polymer in the PEI matrix.

Figure 4 shows that PEI and the blends presented enthalpic relaxation at T_g in the first and second DSC scans. This behavior was attributed to the cooling condition employed in the membrane preparation and in the DSC analysis.

Thermal Stability

Degradation temperatures of all materials were determined from the onset in the thermograms. The weight lost temperatures (t_i) and the residual mass at 600° were calculated for all samples.

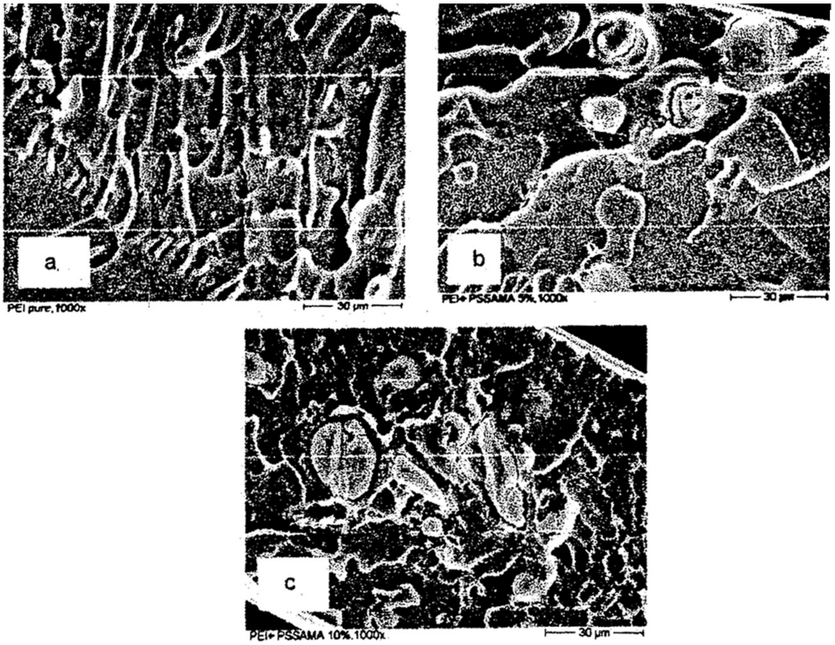

FIGURE 3 SEM microphotographs (1000×) of fracture surfaces of: (a) PEI; (b) PEI/PSSAMA 5 wt% blend; and (c) PEI/PSSAMA 10 wt% blend.

TGA curves of PEI, PSSAMA, and PEI/PSSAMA blends are displayed in Figure 5. PEI and the blends presented high thermal resistance with degradation starting after 400°C for all of them. PEI degradation presented two weight losses at 465 and 537°C, and 27% of residual mass at 600°C. PSSAMA had a different behavior showing five steps of degradation at 95, 170, 317, 420, and 515°C. The first one (95°C) is attributed to elimination of water from the hydrophilic polymer. Sulfonic acid groups were eliminated at 317°C. Nafion® membranes have presented a $-SO_3^-$ lost weight at the same temperature, according to the literature [18]. PEI/PSSAMA blends (1, 3, 5, and 10 wt%) showed degradation behaviour similar to PEI and presented the first weight loss at 454, 436, 423, and 405°C, respectively. PEI matrix is highly hydrophobic and the water weight loss is not present for the pure material and the blends.

TGA curves showed a relatively small decrease in the thermal stability when the PSSAMA content was increased. These PEI/PSSAMA blends presented better thermal resistance than PSSAMA, indicating a delay in the sulfonic acid groups' degradation when they form

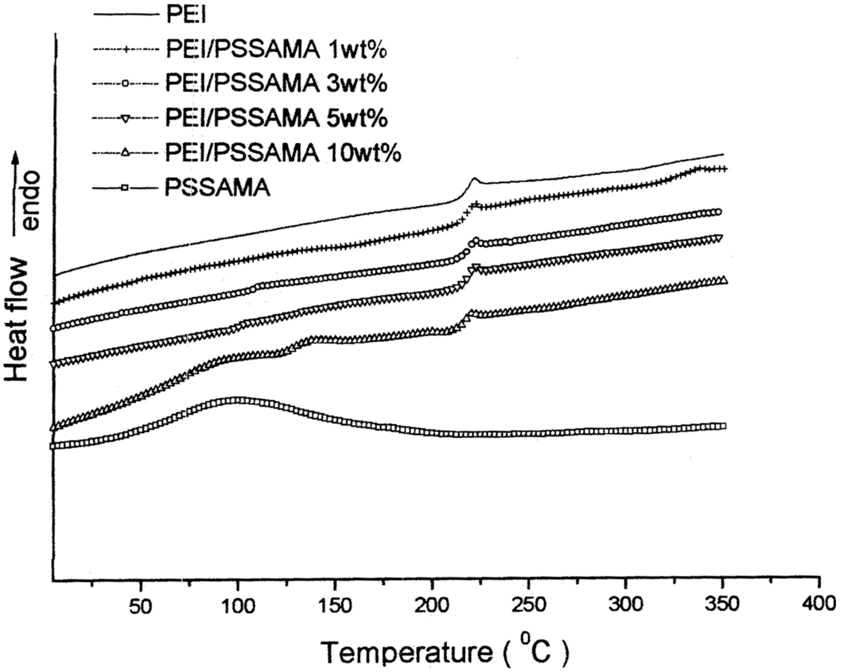

FIGURE 4 DSC traces of PEI, PSSAMA, and PEI/PSSAMA blends.

domains in the PEI matrix. The rise in the degradation onset temperature implied that PEI may increase the thermal endurance of PSSAMA. PEI/PSSAMA 10 wt% blend started to decompose at 405°C, showing a good thermal resistance in spite of the higher content of sulfonic acid groups (Table 2).

TABLE 1 DSC Data of PEI and PEI/PSSAMA Blends

Sample		T_{g1} (°C)	T_{g2} (°C)
PEI		—	216
PEI/PSSAMA	1 wt%	—	216
	3 wt%	108	216
	5 wt%	100	216
	10 wt%	97	216
PSSAMA		105	—

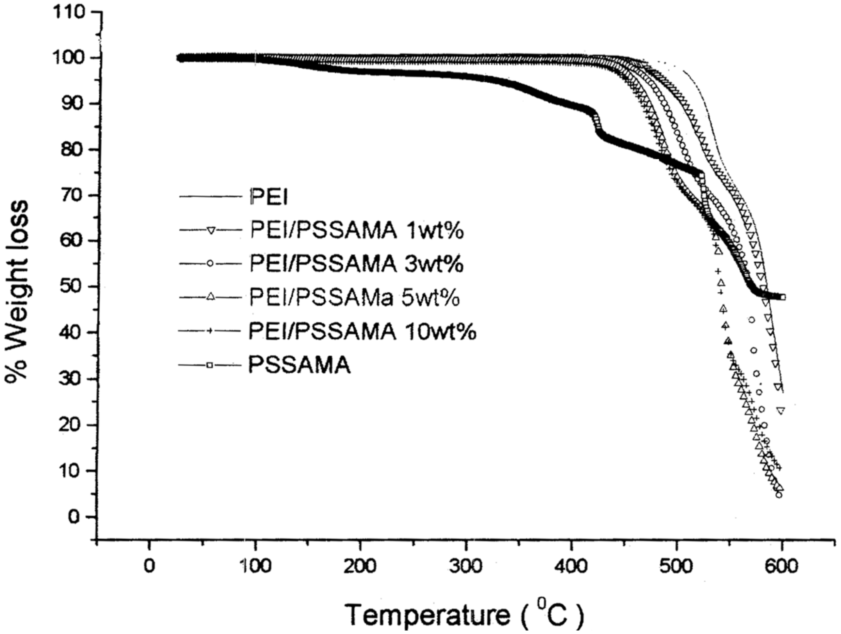

FIGURE 5 TGA curves of PEI and PEI/PSSAMA blends.

DMA Analysis

DMA curves showing the T_g region for PEI and PEI/PSSAMA membranes are presented in Figure 6. For all membranes T_g was obtained from *Tan* δ peak (Table 3). The DMA curves showed a tendency of T_g decreasing when PSSAMA was added to PEI, what could probably be due to an increase of chains mobility caused by a low and partial solubility of the sulfonated polymer in the PEI matrix. The T_g was 224°C for PEI and PEI/PSSAMA 1 wt%, whereas it was 222°C for

TABLE 2 TGA Data of PEI and PEI/PSSAMA Blends

Sample		t_1(°C)	t_2(°C)	t_3(°C)	t_4(°C)	t_5(°C)	Residual mass at 600°C (%)
PEI		465	531	—	—	—	27
PEI/PSSAMA	1 wt%	454	519	—	—	—	19
	3 wt%	436	511	—	—	—	4
	5 wt%	423	496	—	—	—	6
	10 wt%	405	490	—	—	—	10
PSSAMA		95	170	317	420	515	48

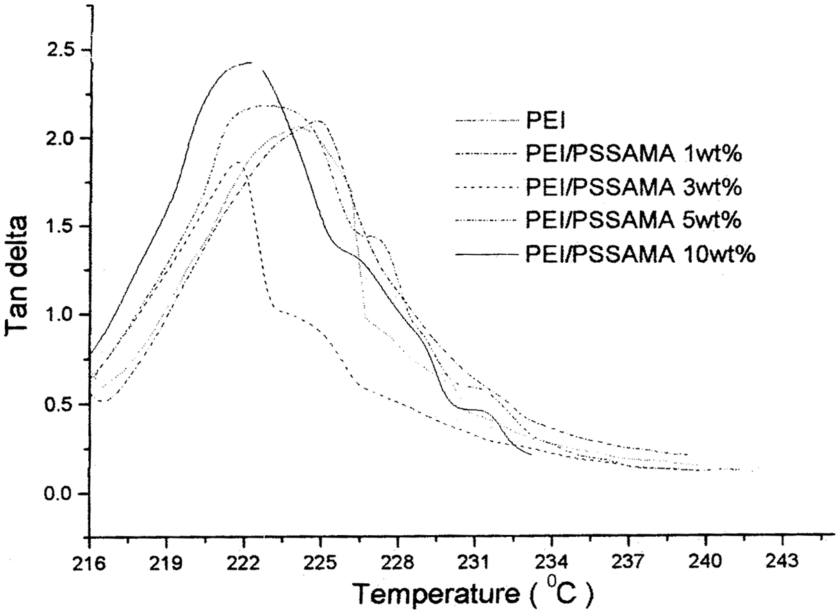

FIGURE 6 *Tan δ* curves of PEI and PEI/PSSAMA blends.

blends containing 3, 5, and 10 wt% of PSSAMA. The storage modulus (E') at 50°C and 100°C was calculated for PEI and PEI/PSSAMA blends. The results showed an increase in E' when low concentration of PSSAMA were used, and a decrease in this modulus in blends with higher contents of the sulfonic acid-containing polymer, mainly at 100°C, due to the proximity to the T_g of PSSAMA. Figure 7 shows the results of E' versus temperature curves at the region of T_g. An significant increase in the E' can be observed for PEI/PSSAMA blends with 1 and 3 wt%, indicating an antiplasticization effect [19]. However, a decrease in this modulus was perceived for blends with 5 and 10 wt% of PSSAMA, indicating that when higher contents of sulfonic

TABLE 3 DMA Data of PEI and PEI/PSSAMA Blends

Sample		T_g (°C)	E'_{50} (10^7 Pa)	E'_{100} (10^7 Pa)
PEI		224	8.2	3.8
PEI/PSSAMA	1 wt%	224	7.4	6.7
	3 wt%	222	3.4	0.6
	5 wt%	222	3.2	0.9
	10 wt%	222	1.5	0.5

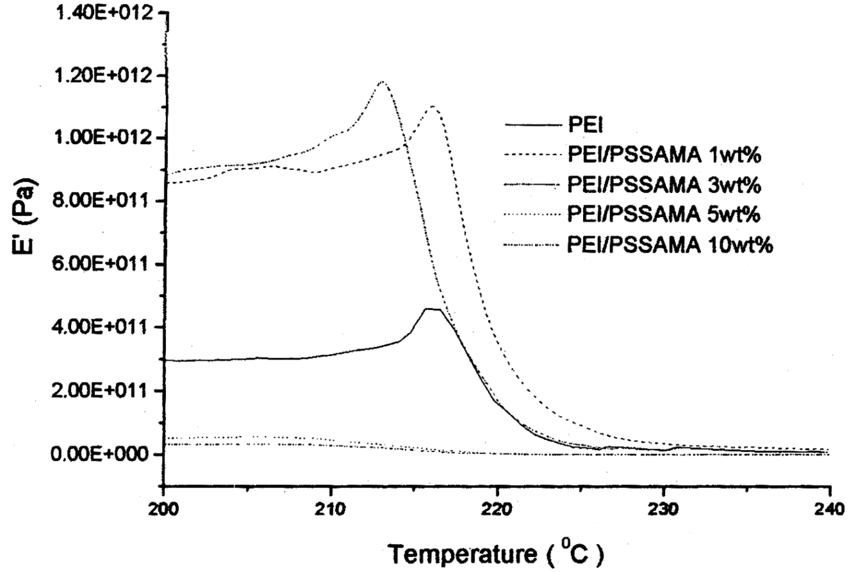

FIGURE 7 Storage modulus (E') for PEI and PEI/PSSAMA blends.

acid polymer are used, this effect is not present. The curves also showed a small and abnormal increase in the modulus just before the drop caused by the glass transition. This behavior could be due to enthalpic relaxation, possibly caused for an increase of chain mobility, allowing certain rearrangement of chains before the glass transition.

Swelling Properties

Water uptake at room temperature as a function of time was evaluated for PEI and PEI/PSSAMA blends and compared with Nafion 117. The polymer and blends were kept in a chamber with distilled water for 48 h and the weight of the membranes before and after swelling was measured (Figure 8). At room temperature, Nafion 117 membrane exhibited initially fast water uptake and reached the equilibrium after approximately 24 h whereas PEI/PSSAMA membranes showed an opposite behavior. For the membranes with lower content of PSSAMA, the water uptake is extremely low (0.4%) due to the hydrophobic characteristic of PEI matrix. However, when the PSSAMA content increases, the swelling of the membrane progressively increases up to 48 h, due to presence of hydrophilic sulfonic groups in the blend, but it is still significantly lower than that observed for Nafion 117, which presents water uptake equal to 16.5% after 48 h.

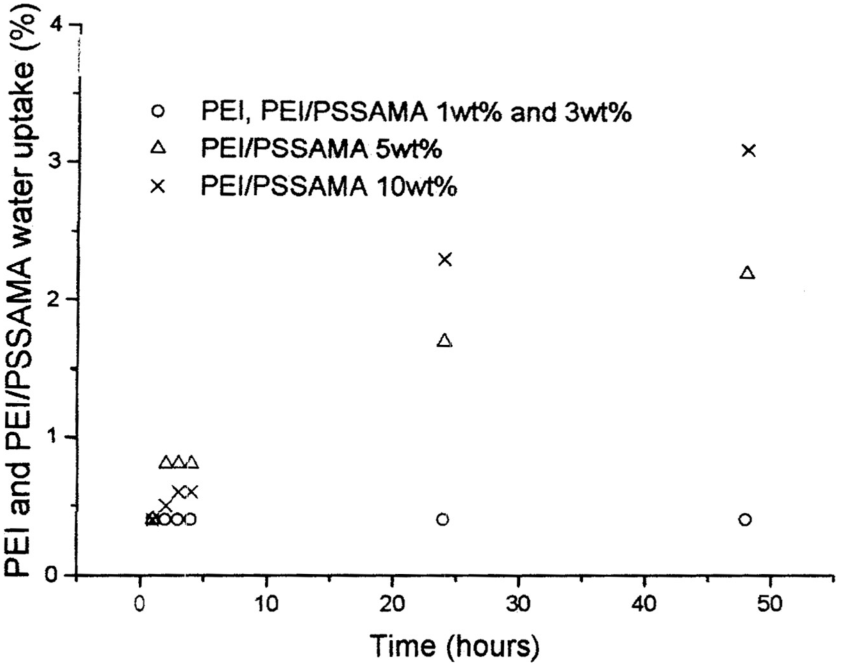

FIGURE 8 Water sorption of PEI, PEI/PSSAMA blends.

Conductivity Measurements

Proton conductivity of the blends were determined at room temperature (100% RH) and compared to Nafion 117 at same condition. PEI/PSSAMA blends with 1, 3, and 5 wt% did not show any proton

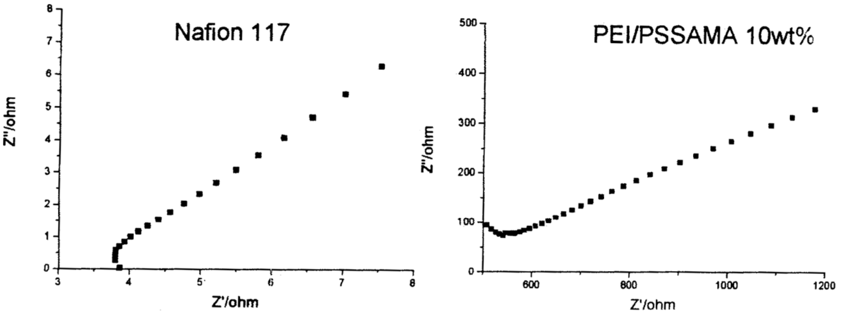

FIGURE 9 Nyquist plots of Nafion 117 and PEI/PSSAMA blend 10 wt% at room temperature.

conductivity, probably due to the low content of sulfonic acid polymer in the PEI matrix. However, the PEI/PSSAMA blend with 10 wt% of PSSAMA dispersed in the polyimide presented conductivity which, still, was lower than that of Nafion 117.

The Nyquist plots of Nafion 117 and PEI/PSSAMA blend containing 10 wt% of PSSAMA are shown in Figure 9. In these plots Z' is the real axis while Z'' is the imaginary axis. Proton conductivity was determined by measuring the membrane resistance by a.c. impedance. PEI/PSSAMA blend present a Nyquist curve significantly different from Nafion 117, suggesting that the mechanism of ion transport is remarkably different.

Table 4 presents the proton conductivity of the blends and Nafion®. Besides the low content of $-SG_3^-$ groups in the PEI/PSSAMA PSSAMA blends, the hydrophobic behavior of PEI matrix seems to suppress the hydration of the material, contributing to the lower proton conductivity.

CONCLUSION

When PEI and PSSAMA were blended by extrusion and the product was compression molded, heterogeneous membranes were obtained. These PEI/PSSAMA membranes are characterized by two glass transition temperatures. When the content of PSSAMA was increased in the PEI matrix, a small decrease in the T_g of PEI was observed. These membranes showed good thermal stability, making possible their application at high temperatures. The domains of PSSAMA dispersed in the PEI matrix were responsible for the proton conductivity of these blends. However, it seems that higher contents of PSSAMA are necessary to increase the capacity of membrane hydration and number of conducting sulfonic acid groups to get ion conductivity close to that of Nafion.

TABLE 4 Proton Conductivity of PEI/PSSAMA Blends and Nafion® at Room Temperature

		Thickness (μm)	Proton conductivity ($\times 10^{-2}\,S{\cdot}cm^{-1}$)
Nafion®		183	0.5
PEI		180	—
PEI/PSSAMA	1 wt%	200	—
	3 wt%	210	—
	5 wt%	190	—
	10 wt%	185	0.006

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