Macromol. Symp. **2005**, 230, 33–38 DOI: 10.1002/masy.200551139

Blends of Sulfonated Polysulfone and Poly(ethylene oxide)-Grafted-Polyethersulfone as Proton Exchange Membranes for Fuel Cell Applications

V. Deimede,[*1,2] *G. Kandilioti,*[2] *J. K. Kallitsis,*[1,2] *V. G. Gregoriou*[2]

Summary: Blends composed of sulfonated polysulfone (SPSF) and poly(ethylene oxide)-grafted-polyethersulfone (PEO-*g*-PES) in different compositions have been prepared and studied in terms of fuel cell relevant parameters like thermal behaviour, water uptake and ionic conductivity. Moreover, spectroscopic characterization (FT-IR) has also been conducted in order to elucidate their miscibility and to investigate the influence of polymer blending on the crystallinity level of the individual components. These blends exhibit very good mechanical properties, a very high water uptake and a high ionic conductivity (4×10^{-3} S/cm) at ambient temperatures and they are amorphous, a property that facilitates their use as polymer electrolytes in fuel cells.

Keywords: blends; fuel cells; infrared spectroscopy; membranes; poly(ethylene oxide)

Introduction

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for vehicular transportation and domestic applications.[1] As one of the key components of the membrane electrode assembly (MEA), proton exchange membranes (PEM) support the catalyst, provide ionic pathways for protons and prevent crossover of gases or fuel. At present, sulfonated perfluoropolymers such as DuPont's Nafion have been almost the only advanced membranes that are used in practical systems due to their high proton conductivity, good mechanical strength, and high thermal and chemical stability. However, there are a few drawbacks including high cost, low conductivity at low humidity or high temperatures as well as high methanol permeability which seriously limit their application. Thus, the development of alternative materials overcoming these problems is strongly desired.

All existing membrane materials for low temperature PEM fuel cells rely on absorbed water and its interaction with acid groups which act as proton exchange sites to facilitate ionic conductivity. Thus, an effective approach is the acid functionalization of wholly aromatic polymers which are thought to be one of the most promising routes to high performance PEMs. Specifically, sulfonated poly(arylene ether) materials such as sulfonated poly(arylene ether ether ketone) (SPEEK),[2] sulfonated poly(arylene ether sulfone)[3] and their derivatives are the focus of many investigations.

An alternative approach for the development of proton conducting materials is the incorporation of hydrophilic poly(ethylene oxide) (PEO) units onto a stiff polymer backbone. PEO-based polymeric electrolytes are still among the most extensively studied polymeric conductors, since their structures are beneficial for supporting fast ion transport.[4] A main drawback is the high crystallinity which limits the high ionic conductivity of PEO-based electrolytes.[5] In order to suppress the crystallinity of

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[1] Department of Chemistry, University of Patras, Patras 26500, Greece

[2] Foundation for Research and Technology-Hellas, Institute of Chemical Engineering and High-Temperature Chemical Processes (FORTH/ICEHT), Patras 26504, Greece

PEO, it is blended with other polymers in which PEO forms the conductive phase and the other component acts as a mechanical support.

In this study sulfonated polysulfone with different sulfonation degrees and PEO-*g*-PES blends with different PEO molecular weights (MW 5000, 2000) are investigated for their potential use as polymer electrolytes in PEM fuel cells.

Experimental

Materials

4-fluorophenyl sulfone (DFDPS), 2,2-bis-(4-hydroxyphenyl)-propane, and decafluorobiphenyl (DFB) were obtained from Aldrich Chemical Co. *N*,*N*-Dimethylformamide (DMF), *N*,*N*-Dimethylacetamide (DMA), toluene, methanol, dichloromethane, chloroform, and diethyl ether were obtained from commercial sources and used as received. Anhydrous potassium carbonate was dried at 60 °C for 10 hours in a vacuum oven. Dihydroxy-PEO 5000 and dihydroxy-PEO 2000 were synthesized as described elsewhere.[6] Sulfonated polysulfone in the sodium salt form (SPSF(Na)) was prepared according to known procedures.[3a,7] The sulfonation degrees determined by ^{1}H-NMR spectroscopy were 55% and 45%.

Synthesis of PEO-grafted -Poly (arylene ether)s

(a) Synthesis of Polymer PEO-g-PES-1

A typical polymerization procedure is as follows; to a 10 ml, three-neck flask equipped with a magnetic stirrer, a Dean-Stark trap and an argon gas inlet, dihydroxy-PEO 5000 (0.4635 g, 0.09 mmol), 4-fluorophenyl sulfone (0.0229 g, 0.09 mmol), potassium carbonate (0.0186 g, 0.13 mmol) in 3 ml DMF and 2.1 ml toluene were added under argon atmosphere. The reaction mixture was heated to 160–170 °C and maintained at this temperature for 20 h. The reaction mixture was diluted with DMF (5 ml) and poured slowly into a large excess of diethyl ether. The precipitated polymer was filtered and washed several times with diethyl ether. The polymer obtained was redissolved in 20 ml chloroform and poured slowly in a large excess of diethyl ether with stirring. The polymer was precipitated out, filtered, washed with diethyl ether and dried at 50 °C under vacuum for 24 h. The molecular weight of the polymer was $M_n = 21.3$, $M_w = 42.6$ Kg/mol determined by GPC measurements.

(b) Synthesis of Polymer PEO-g-PES-2

Polymer **PEO-*g*-PES-2** was synthesized from dihydroxy-PEO 2000 and 4-fluorophenyl sulfone using the same procedure as the synthesis of polymer **PEO-*g*-PES-1**. The molecular weight of the polymer was $M_n = 35$, $M_w = 77$ Kg/mol determined by GPC measurements.

Characterization

^{1}H-NMR spectra were obtained on a Bruker Advance DPX 400 MHz spectrometer. The samples were dissolved either in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (d_6-DMSO).

Gel permeation chromatography (GPC) measurements were carried out using a Polymer Lab chromatographer equipped with two Ultra Styragel columns (10^4, 500 Å), UV detector (254 nm), and $CHCl_3$ as eluent, at 25 °C with a flow rate of 1 ml/min.

Thermal Properties

DMA measurements were conducted using a solid-state analyzer RSA II, Rheometrics Scientific Ltd., at 10 Hz.

SEM Studies

Membrane morphology was studied by Scanning Electron Microscopy (SEM) using a LEO Supra 35VP microscope. Solution cast samples were cryo-fractured in liquid nitrogen. The sample surfaces were coated with a thin layer of gold before examination.

Determination of Water Uptake

Membranes were soaked in distilled water for 24 hours at determined temperatures.

Surface-attached water was quickly removed with tissue paper and the weight of the wet membrane determined. The water uptake content can be calculated by

$$\text{Uptake content }(\%) = \omega_{\text{wet}} - \omega_{\text{dry}}/\omega_{\text{dry}} \times 100\% \qquad (1)$$

where ω_{wet} and ω_{dry} are the masses of wet and dried samples, respectively.

Proton Conductivity Measurements

Conductivity measurements were carried out by the current interruption method using a potentiostat/galvanostat (EG and G model 273) and an oscillator (Hitachi model V-650F).

Membrane Preparation of Polymer Blends ($SPSF(Na)_x$/PEO-g-PES, $x = 45, 55$)

Blends were prepared by dissolving sulfonated polysulfone (SPSF(Na)) and PEO-*g*-PES in DMF (5% w/v) at different ratios. Membranes of the blends were cast by pouring the solution onto a glass plate at 85 °C in an oven for 20 h. Homogeneous, transparent films with good mechanical properties were obtained. To remove any excess of the solvent, the membranes were dried under vacuum at 90 °C for 3 days. The synthesized blends are shown in Tables 1 and 2.

FT-IR Characterization

ATR-FT-IR spectra were collected using a Nicolet 850 FT-IR spectrometer equipped with an MCT/A detector. The experiments were carried out on ZnSe internal reflection elements (80 × 10 × 3 mm, twelve bounces, and an angle of incidence of 45°). Each measurement was the accumulation of 128 scans at 2 cm^{-1} spectral resolution.

Table 1.
Compositions of $SPSF(Na)_{55}$/PEO-*g*-PES-1 blends.

Compositions	
$SPSF(Na)_{55}$	PEO-*g*-PES-1 ($MW_{PEO} = 5000$)
95	5
90	10
85	5

Table 2.
Compositions of $SPSF(Na)_{45}$/PEO-*g*-PES-2 blends.

Compositions	
$SPSF(Na)_{45}$	PEO-*g*-PES-2 ($MW_{PEO} = 2000$)
90	10
80	20
70	30

Results and Discussion

In Figures 1a and b the molecular structures of sulfonated polysulfone (SPSF) and poly(ethylene oxide)-grafted-polyethersulfone (PEO-*g*-PES) which were used to prepare blends with different compositions, are presented.

In Figure 2 a plot of the water uptake level for the different PEO-*g*-PES-2 concentrations is shown. In particular, the 70/30 blend exhibits an order of magnitude

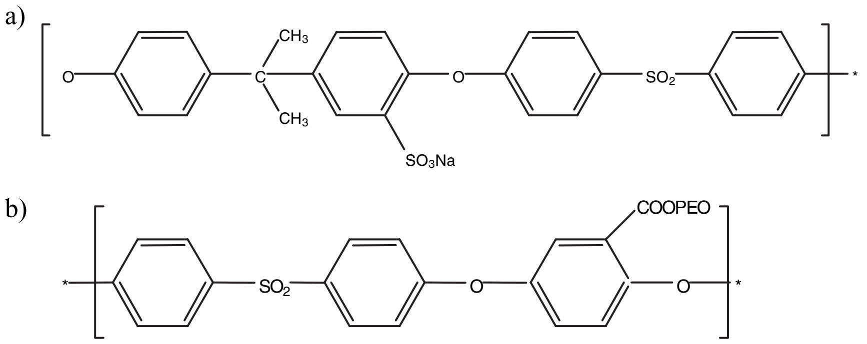

Figure 1.
a) Sulfonated polysulfone (SPSF(Na)), b) PEO-grafted-polyethersulfone (PEO-*g*-PES), $M_{w\ PEO} = 5000$, 2000.

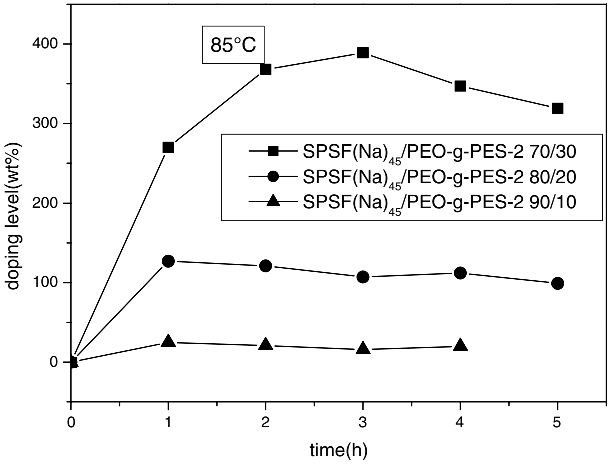

Figure 2.

Water uptake of the blends $SPSF(Na)_{45}$/PEO-*g*-PES-2 in compositions 70/30, 80/20 and 90/10 as a function of time at 85 °C.

increase in the doping level as compared to the 90/10 blend. Therefore, the amount of PEO-*g*-PES, due to the hydrophilicity of PEO, increases the water uptake of the final blend with beneficial consequences for its operation in PEM fuel cells.

In order to investigate the phase behavior of the blends, dynamic mechanical analysis has been performed. The loss (E″) modulus curves of blends $SPSF(Na)_{45}$/PEO-*g*-PES-2 with compositions 90/10 and 80/20 respectively, as a function of temperature are given in Figure 3. Careful examination of the E″-T curve of the blend 90/10 revealed two broad overlapping peaks above 200 °C. One possible explanation for the appearance of more than one peak is due to partial miscibility of the two components of the blend. In particular, the higher temperature peak is associated with the T_g of a rich $SPSF(Na)_{45}$ phase whereas the lower temperature peak is attributed to a phase that has higher PEO-*g*-PES-2 content blended in it. In contrast, in the

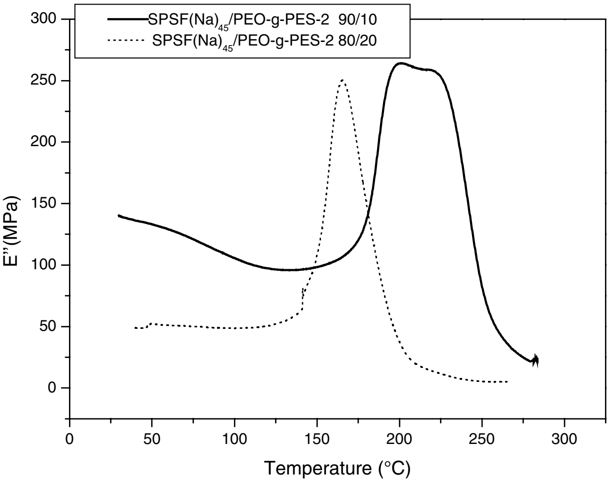

Figure 3.

Temperature dependence loss (E″) modulus of the blend (—) $SPSF(Na)_{45}$/PEO-*g*-PES-2 90/10 and (---)$SPSF(Na)_{45}$/PEO-*g*-PES-2 80/20.

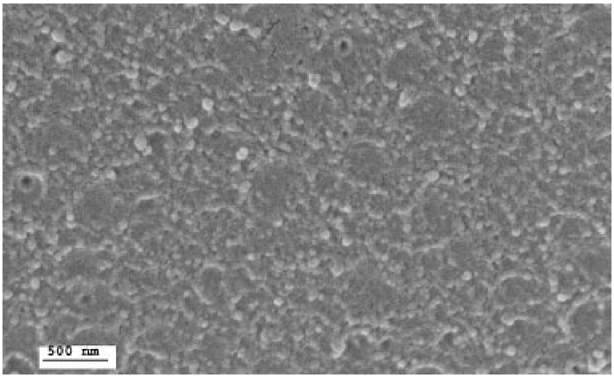

Figure 4.
SEM image of the cryofractured surface of the water immersed blend SPSF(Na)$_{55}$/PEO-*g*-PES-1 90/10.

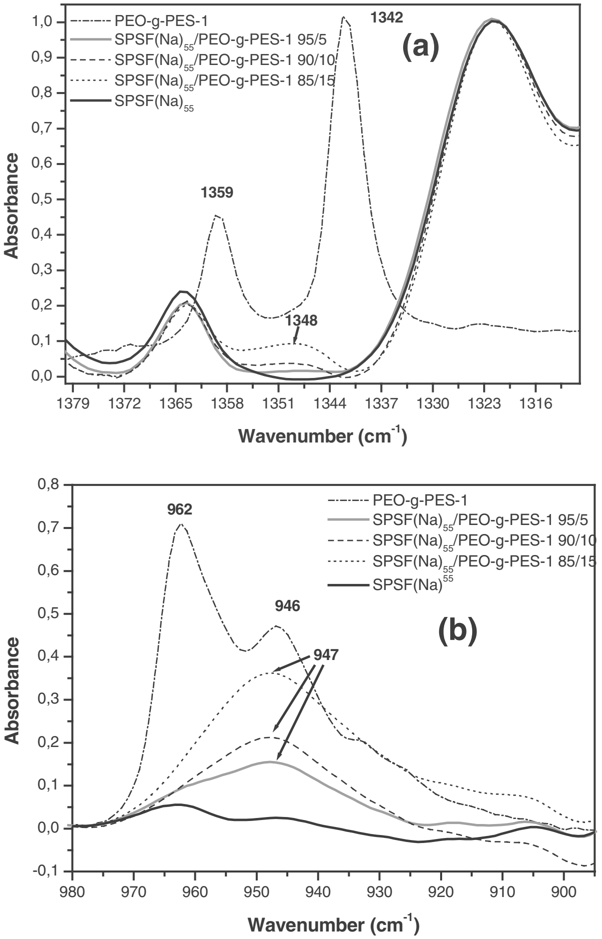

Figure 5.
ATR-FT-IR spectra of the blends SPSF(NA)$_{55}$/PEO-*g*-PES-1 for different compositions in comparison to the spectra of their initial components a) in the spectral region: 1380–1310 cm^{-1}, b) in the spectral region: 980–890 cm^{-1}.

case of blend 80/20 one sharp peak is observed, corresponding to the T_g of the blend and it is shifted to lower temperatures (at 165 °C), an indication that the T_g's of blends $SPSF(Na)_{45}$/PEO-*g*-PES-2 decreased with increasing PEO content.

In Figure 4 the morphology of 90/10 $SPSF(Na)_{55}$/PEO-*g*-PES-1 blend was investigated using scanning electron microscopy (SEM). In this picture, nanophase separation of the hydrophilic and hydrophobic units is observed, which persists even after immersion in water.

In Figures 5a and 5b the infrared spectra of $SPSF(Na)_{55}$/PEO-*g*-PES-1 blends with compositions 95/5, 90/10 and 85/15 are compared. The infrared spectrum of PEO-*g*-PES-1 in Figure 5a exhibits two narrow bands at 1359 and 1342 cm^{-1} which are attributed to the crystalline PEO[8] and have been associated to the CH_2 wagging motion.[9] When PEO-*g*-PES-1 is blended with $SPSF(Na)_{55}$, the doublet is replaced by a broad band at 1348 cm^{-1} which is attributed to the amorphous PEO.

A similar behavior is observed in Figure 5b. Again the spectrum of PEO-*g*-PES-1 exhibits a doublet located at 946 and 962 cm^{-1}. These two bands are associated with the CH_2-rocking vibration of crystalline PEO in a 7_2 helix.[10] Upon blending PEO-*g*-PES-1 with $SPSF(Na)_{55}$ this doublet turns into a singlet at 947 cm^{-1} which is a characteristic band of amorphous PEO.

Conclusions

Blends of sulfonated polysulfone, (SPSF) and poly(ethylene oxide)-grafted-polyethersulfone, (PEO-*g*-PES) were prepared and studied for potential use in PEM fuel cells. Spectroscopic characterization reveals the amorphous nature of the membrane in addition to its good mechanical properties and high ionic conductivity.

Acknowledgements: We thank the European Social Fund (ESF), Operational Program for Educational and Vocational Training II (EPEAEK II), and particularly the program PYTHAGORAS, for funding the above work.

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