

Proton Exchange Membranes for a Direct Methanol Fuel Cell Based on Sulfonated Styrene-(ethylene-butylene)-Styrene/Polyvinylidene Fluoride Blends

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ABSTRACT: Proton-conducting membranes for a direct methanol fuel cell, based on styrene-(ethylene-butylene)-styrene (SEBS) triblock copolymer blended with polyvinylidene fluoride (PVDF), have been developed. First, the partially sulfonated SEBS with a variety of degrees of substitution was prepared by reacting the SEBS with propionyl sulfate. Then, the sulfonated SEBS was blended with PVDF at various blending ratios and fabricated by using a solution casting technique. The water uptake, proton conductivities, methanol permeabilities, and mechanical properties of the blend membranes were measured by using gravimetry, impedance analysis, gas chromatography, and tensile test, respectively. It was found that water uptake of

the blend membranes increased with the sulfonated SEBS content, at the expense of their methanol resistance. The proton conductivity of the blend membranes, however, did not change linearly with the sulfonated SEBS content. This was related to poor compatibility between the two polymers in the blend membranes. However, by adding 5 wt % of poly(styrene)-*b*-poly(methyl methacrylate) block copolymer, compatibility, proton conductivity, and methanol resistance of the blend membrane increased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 393–399, 2010

Key words: blends; block copolymers; compatibility; membranes

INTRODUCTION

Direct methanol fuel cell (DMFC) is a kind of proton exchange membrane fuel cell (PEMFC), which uses methanol as a fuel to generate electricity without the use of any reforming unit. Currently, Nafion[®], which is a kind of perfluorinated polymer with some sulfonic groups, is commercially available and has been widely used as an electrolyte polymeric membrane in the PEMFC. This is attributed to the fact that Nafion[®] is highly proton-conductive and thermally stable. However, the Nafion membrane also has some disadvantages in relation to DMFC applications. For example, the methanol resistance of the Nafion membrane is not sufficiently high. It was reported that about 40% of the methanol was lost through the process called “methanol crossover.”^{1,2} Beside this, the cost of the commercial Nafion membrane is considerable, and the proton conductivity of

the membrane tends to decrease at operating temperatures above 100°C.³

Consequently, several efforts have been made to develop some new proton-conducting membranes to be used as a replacement for the Nafion membrane in DMFC applications.^{4–12} Our interest in this research area has been involved with the development of DMFC membranes from various types of polymeric systems. This include, sulfonated poly(vinyl alcohol) (PVA) membranes,^{13,14} sulfonated poly(ether etherketone) (PEEK)/polyvinylidene fluoride (PVDF) blend membrane,¹⁵ and sulfonated polystyrene/PVDF blend membranes.¹⁶ The former membrane system based on PVA is interesting with respect to DMFC applications. The proton conductivity of the material can be induced by reacting the polymer with some sulfonating agents, such as sulfosuccinic acid, sulfophthalic acid, and sulfoacetic acid.¹³ Furthermore, the methanol resistance of the sulfonated PVA membrane can be further enhanced by mixing the polymer with some nanoclays, to obtain a form of nanocomposite membrane.¹⁴ However, the stability of the material under actual DMFC operating conditions has yet to be explored and verified. This is partly attributed to the fact that the sulfonated PVA contains some ester bonds within the molecule that are rather sensitive to hydrolysis under warm and acidic conditions.

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Alternatively, membranes based on some styrenic polymers such as PEEK and polystyrene deserve consideration, taking into account the fact that these styrenic polymers can also be sulfonated by reacting with sulfuric acid and/or acyl sulfate. In this case, it is noteworthy that the molecular structures of the sulfonated styrenic polymers will lack any ester bonds, which means that the membranes should be resistant to degradation via hydrolysis. Furthermore, to reduce the methanol crossover in the membrane, the styrenic polymers may be blended with some hydrophobic polymers such as PVDF.

From our previous work,¹⁶ we found that the methanol resistance and tensile properties of the sulfonated polystyrene/PVDF blend membrane (40/60% w/w) improved remarkably after polystyrene-*block*-poly(methyl methacrylate) (PS-*block*-PMMA) block copolymer was added. These changes could be explained in the light of a better compatibility between the two polymers in the blend, provided that the block copolymer served as a compatibilizer. However, some properties of the compatibilized blend membrane have yet to be further improved, including the ductility and flexibility of the membrane.

To obtain a more ductile membrane, the use of styrene-(ethylene-butylene)-styrene (SEBS) triblock copolymer was considered. SEBS is a thermoplastic elastomer, containing some styrene units in the molecules. By carrying out a sulfonation of SEBS followed by blending with PVDF, a flexible proton-conductive membrane with some methanol resistance can be expected. In this regard, compatibility between SEBS and the PVDF becomes an important issue and that should be controlled to afford the blend membrane some useful properties. Mokrini et al.,¹⁷ for example, prepared SEBS/PVDF blend membranes by using an extrusion blending process. It was found that, by adding 1 wt % of the poly(methyl methacrylate-butylacrylate-methyl methacrylate) triblock copolymer as a compatibilizer, the mechanical properties, ion exchange capacity, and proton conductivity of the blend membranes improved.

In this study, rather than preparing the SEBS/PVDF blend membranes via an extrusion process, we examined the properties of the blend membranes prepared and fabricated via solution blending and solution casting processes. Additionally, this study used PS-*block*-PMMA block copolymer as a compatibilizer for the blend system. In our opinion, we believe that the use of this type of block copolymer is suitable, taking into account the fact that styrene repeating units in the partially sulfonated SEBS can be compatible with the polystyrene block of the PS-*block*-PMMA copolymer, whereas the PMMA block is known to be miscible with PVDF. The aim of this

work is to investigate the effects of blending ratios and the use of PS-*block*-PMMA copolymer on the proton conductivity and methanol permeability of the membranes.

EXPERIMENTAL

Materials

Styrene-(ethylene-butylene)-styrene triblock copolymer (G 1652, 30 wt % styrene, $M_w = 125,000$) was supplied by Kraton Polymers LLC. Poly(vinylidene fluoride) ($M_w = 530,000$) was supplied by Fluka. Sulfuric acid (analytical grade from Merck), propionic anhydride (purum grade from Fluka), methanol, and toluene (analytical grade) were obtained from Fisher Chemicals. Dimethyl formamide (analytical grade) was obtained from Univar. All of these chemicals were used as received.

Regarding the chemicals used for the synthesis of PS-*block*-PMMA block copolymer, the styrene was purchased from Dow Chemical, whereas methyl methacrylate and tetraethylthiuram disulfide were purchased from Fisher Chemicals. The monomers were purified by passing through an alumina column before the polymerization to remove an inhibitor. More details concerning the mechanism of the synthesis of the PS-*block*-PMMA block copolymer via a controlled radical polymerization can be found elsewhere.^{16,18}

Preparation of sulfonated SEBS

Sulfonated SEBS was prepared by reacting the SEBS with propionyl sulfate, using the method described in the related literature.¹⁶ First, the propionyl sulfate was prepared by slowly adding 2 mL of sulfuric acid (96 wt %) into the reaction flask containing a solution of propionic anhydride (14 mL) in toluene (17.5 mL), at 10°C under vigorous stirring. Then, the mixture was diluted with toluene to yield 50 mL of the solution. Next, 9 g of the dried SEBS was dissolved in 100 mL of toluene. The solution was heated to 60°C and purged with nitrogen for 15 min. After that, a given amount of the freshly prepared propionyl sulfate was slowly added to the polymer solution and kept stirring for 3 h at 60°C. After carrying out the chemical reaction for the given time, the solution was precipitated in methanol. The precipitated product was refluxed in boiling water for 3 h and this step was repeated two to three times, until the solution was neutral. The precipitated product was further washed twice with ethanol for 2 h. Finally, the precipitated product was dried in a vacuum oven at 70°C for 48 h.

Determination of the degree of sulfonation

Approximately 0.3 g of the sulfonated polymer was dissolved in 30 mL of toluene/methanol mixture (90/10% v/v). The solution was then titrated with 0.1 mol/L of NaOH solution in methanol, using phenolphthalein as an indicator. The degree of sulfonation (DS) was expressed in terms of milliequivalent of sulfonation per 100 g of the sulfonated polymer.

Characterization

Changes in the chemical structure of SEBS both before and after the sulfonation were followed by a Fourier transform infrared spectroscopy (FTIR) technique using a Perkin Elmer (Spectrum One) instrument. The sample was prepared in the form of a solution before casting onto the NaCl window cell. The spectrum was recorded over wave numbers ranging between 4000 and 500 cm^{-1} .

Preparation of the blend membranes

Two separated solutions, one containing sulfonated SEBS in toluene/methanol mixture (90/10% v/v) and another containing PVDF in dimethyl formamide (DMF), were prepared before blending. A suitable quantity of the PVDF solution was added to the sulfonated SEBS solution at the desired blending ratio and then stirred at room temperature for 30 min. The concentration of the total polymers in the solution was kept constant at 5.6% w/v.

The solution was cast onto a clean glass substrate before drying in an oven at 110°C for 1 h. The membrane was peeled off from the substrate and dried in a vacuum oven at 60°C for 24 h to remove any residual solvent. The membrane was kept in deionized water before tests.

Characterization and testing of the blend membranes

Water uptake

The water uptake of the blend membrane was determined by immersing the membrane in deionized water at 25°C for 24 h. The water-swollen membrane was taken out, wiped with tissue paper, and immediately weighed. The water uptake (W) was calculated from the following equation:

$$W (\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100, \quad (1)$$

where W_{dry} and W_{wet} are weights of the dried and the water-swollen membrane, respectively.

Proton conductivity

The method for proton conductivity measurements was based on a four-point probe electrochemical impedance spectroscopy technique. A conductivity cell, which consisted of a Teflon block, a membrane clamp, and four platinum wires, was installed between the anode and cathode plates of the fuel cell hardware. The two fuel-cell plates were used as working and counter electrodes to apply a current to the sample membrane (3 cm \times 3 cm) through the two platinum wires, and the two platinum wires apart were used as reference electrodes. The sample membrane was immersed in the deionized water for 12 h before the measurement. The hydrated membrane was mounted onto the cell, and the AC impedance measurements were carried out over the frequency ranging from 1 Hz to 10 kHz using a Solatron 1260 frequency response analyzer. The proton conductivity (σ) was calculated using the following equation:

$$\sigma = 1/RS, \quad (2)$$

where σ is the proton conductivity (S/cm), R is the measured membrane resistance value, which was determined from the high frequency intercept of the impedance with the real axis using the Zplot/Zview software,^{17,19} S is the cross-sectional area of the membrane (cm^2), and l is the distance between counter electrode and working electrode (cm).

Methanol permeability

The resistances to methanol crossover of the membranes were evaluated by measuring the methanol permeability of the membranes using a diffusion cell and gas chromatography (GC) technique. The membrane was placed between the two compartments in the diffusion cell and then clamped. After that, 20 mL of methanol solution (2M) and 20 mL of deionized water were filled in compartments A and B of the cell, respectively. Both compartments were magnetically stirred at room temperature during the permeation experiments. The concentration of methanol in compartment B was measured as a function of diffusion time by using a GC technique (Shimadzu GC-9A, containing BX-10 column). The injection temperature, the column temperature, and the detection temperature used for the GC experiment were 120, 85, and 150°C, respectively. The area under the methanol peak from each GC chromatogram was used in combination with a calibration curve to determine the methanol concentration. Finally, the methanol permeability was calculated from the slope of the plot between the methanol concentration and diffusion time through the use of the following equation:

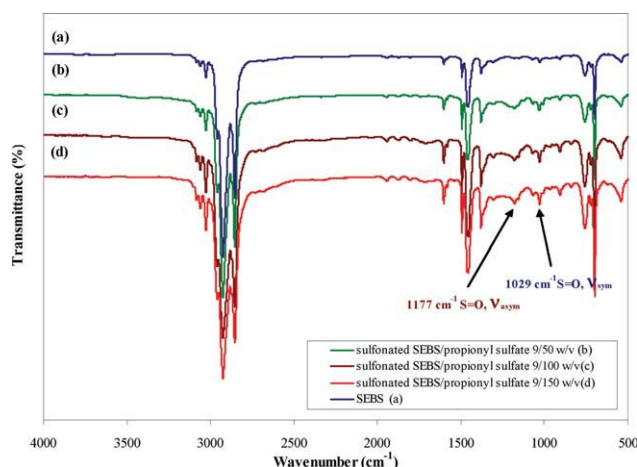


Figure 1 Overlaid FTIR spectra of SEBS and the sulfonated SEBS prepared by using various amounts of propionyl sulfate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$C_B(t) = A(DK)C_A(t - t_0)/VBL, \quad (3)$$

where C_A and C_B are the concentrations of methanol in compartments A and B, and V_A and V_B are the volumes of liquids in compartment A and B, respectively. A and L are the area and thickness of the membrane, and D and K are the methanol diffusivity and partition coefficient, respectively. The product of DK is the membrane permeability.

Tensile test

The mechanical properties of the various membranes were determined from tensile testing. Samples for the tensile test were prepared by cutting the membrane into dumbbell shape specimens in accordance with the ASTM D 882-02. The tensile test was performed using a 5 ton tensiometer, (Universal Tensile Testing Machine, Perkin Elmer) at a crosshead speed of 10 mm/min at room temperature (25°C). At least five specimens were tested for each sample, and the average values of tensile strength and tensile elongation at break were reported.

Scanning electron microscopy

Compatibility and the interfacial region between the sulfonated SEBS and PVDF phase in the blend membrane were examined using a scanning electron microscope (JEOL JSM5800), in conjunction with a secondary electron detector. In this regard, compositional phase contrast between PVDF and sulfonated SEBS needs to be induced. Unfortunately, both polymers lack any heavy atomic element, and there is no selective staining agent available for this blend system. However, attempts have been made to enhance the phase contrast using a solvent etching technique.

In this regard, the SEM specimen was etched by using DMF as a selective solvent to remove the PVDF phase. After that, the specimen was dried to remove some residual solvent before coating with gold using a sputtering machine (SPI-MODULE™ sputter Coater). The SEM experiment was operated at 15 kV accelerating voltage.

RESULTS AND DISCUSSION

Characterization of the sulfonated SEBS

Figure 1 shows the overlaid FTIR spectra of SEBS and the various sulfonated SEBS, obtained by reacting the polymer with different amounts of propionyl sulfate. The FTIR spectra of the sulfonated polymers show some new peaks at 1029 and 1177 cm^{-1} . These were ascribed to the symmetric stretching vibration (S=O) and the asymmetric stretching vibration (S=O) of the SO_3H groups, respectively. The aforementioned results suggest that SEBS has been sulfonated in accordance with the mechanism illustrated in Figure 2.

Regarding the amount of sulfonic acid expressed in terms of the degree of substitution (DS), it was found that the DS values of sulfonated SEBS increased with the propionyl sulfate content. However, as the amount of sulfonating agent used was increased above 50 mL, the modified polymer became insoluble in a nonpolar solvent, such as toluene and thus cannot be further blended or casted into a membrane. This is due to the greater polarity of the sulfonated polymer. Therefore, in this study, the sulfonated SEBS with the DS value of 6.19 wt %, obtained by reacting 9 g of SEBS with 50 mL of propionyl sulfate, was selected for further blending with PVDF.

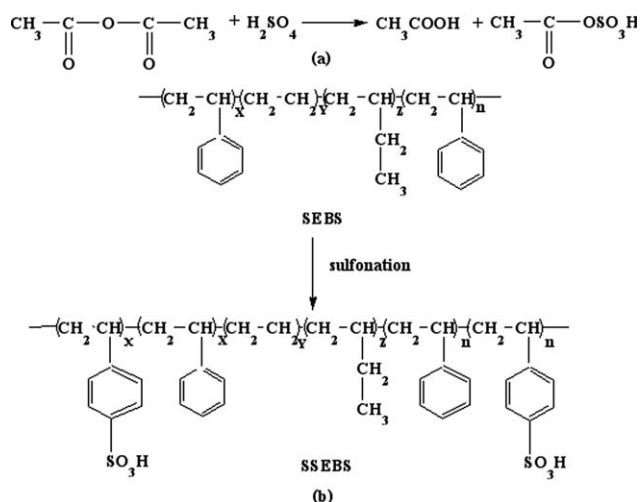


Figure 2 Synthesis of propionyl sulfate and the sulfonation of SEBS.

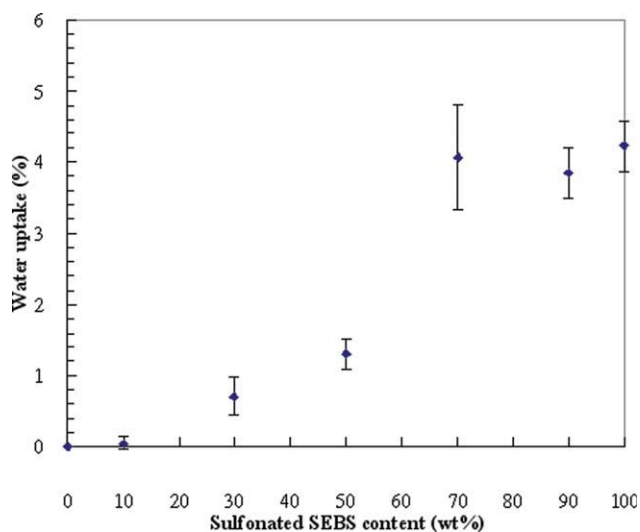


Figure 3 Water uptake values of various membranes.

Properties of the blend membranes

Figure 3 shows the water uptake values of various blend membranes. It can be seen that the water uptake of the pure PVDF membrane is zero. By blending with sulfonated SEBS, the water uptake of the blend membranes increased with the sulfonated polymer content. These values are, however, quite low when compared with those of other blend membrane systems, such as sulfonated PEEK/PVDF¹⁵ and sulfonated polystyrene/PVDF.¹⁶ We believe that this effect can be attributed to the formation of pseudo-crosslinking between SEBS triblock copolymer molecules, limiting the water uptake value. In addition, the ionic interaction between the polymer molecules containing sulfonic acid groups might have come into play and contributed to the low water uptake value.

Noteworthy, as the content of sulfonated SEBS in the blend membranes was increased above 50 wt %, the blend membrane became more incompatible. This is due to the differences in polarity between the two polymers, that is, PVDF is hydrophobic, whereas the sulfonated SEBS is more hydrophilic.

TABLE I
Proton Conductivity and Methanol Permeability of Various Membranes

Membranes	Proton conductivity (10^{-3} S/cm)	Methanol permeability (10^{-7} cm ² /s)
Sulfonated SEBS/PVDF (30/70)	0.03 ± 0.01	0
Sulfonated SEBS/PVDF (50/50)	0.57 ± 0.03	0.014
Sulfonated SEBS/PVDF (70/30)	0.084 ± 0.00	13.4
Sulfonated SEBS/PVDF (90/10)	0.46 ± 0.02	0.167
Sulfonated SEBS/PVDF (100/0)	7.03 ± 0.03	0.183
Nafion 115	9.59 ± 0.12	3.39

Proton conductivity and methanol permeability

Table I compares the proton conductivity of various blend membranes. It is of note that no attempt was made to determine the proton conductivity value of the hydrophobic PVDF membranes, which contain 0 wt % of water uptake. This is because molecules serve as “vehicles” facilitating proton conduction and thus a considerably high water uptake is a prerequisite for a good proton-conducting membrane.

Table I compares the proton conductivity values of various membranes. The proton conductivity of pure sulfonated polymer was about 7.03×10^{-3} S/cm, which is comparable to the Nafion115 membrane (9.59×10^{-3} S/cm) measured using the same apparatus and under the same testing conditions. After the sulfonated SEBS was blended with PVDF, however, the proton conductivity decreased to the lowest value when the blend ratio was 50/50% w/w. This could be ascribed to the fact that the sulfonated groups responsible for the proton exchange process have been decreased. Beyond this blend ratio, the conductivity value increased with the PVDF content. We believed that the above nonlinear trend could be partly attributed to a poor compatibility between the two polymers in the blend membranes, especially, those containing more than 50 wt % of the PVDF. In this regard, the measured conductivity values could be misleading.

Similarly, Table I shows that the methanol permeability values of the various membranes were not linearly related to the blend ratio. Normally, a decrease in methanol permeability of the blend membranes with the hydrophobic PVDF content can be expected. However, this was not true in our case. For example, the methanol permeability of the pure sulfonated SEBS was 0.183×10^{-7} cm²/s, whereas

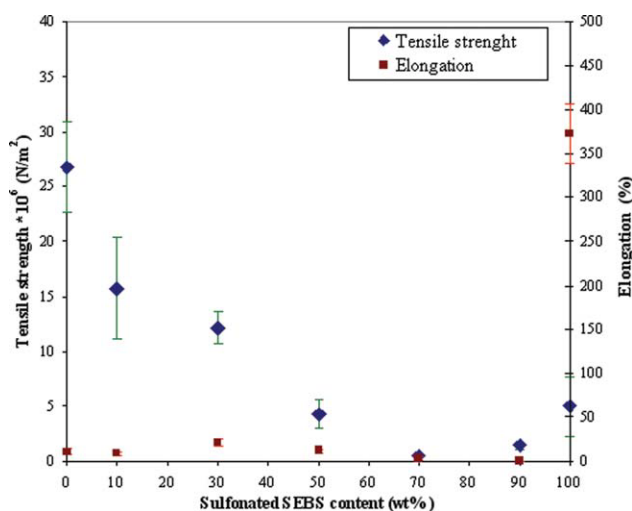


Figure 4 Tensile properties of various membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

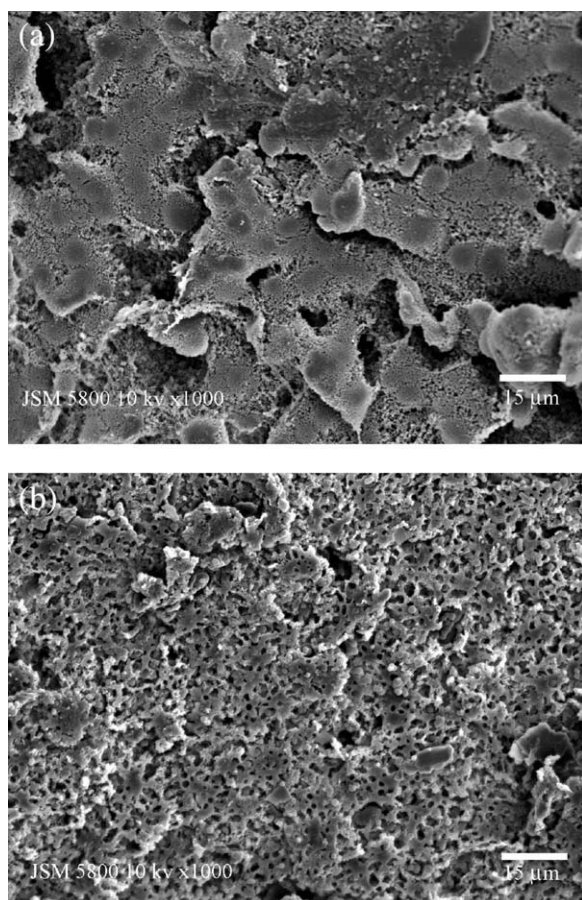


Figure 5 SEM micrographs of SSEBS/PVDF (50 : 50 wt %) blend after PVDF extraction (a) without compatibilizer and (b) with 5% PS-*block*-PMMA.

that of the blend membrane which contained 30 wt % of PVDF was greater. Again, the above effect could be ascribed to the poor compatibility between the two polymers. It could be possible that some of the methanol solution penetrated through the void at the interfacial region in the blend membrane, leading to overestimated values of methanol permeability. Nevertheless, the methanol permeability values of some of the blend membranes are lower than that of the pure sulfonated SEBS membrane.

On the basis of results from proton conductivity and methanol permeability, it might be concluded

that the best membrane for this polymer blend system is that obtained by blending sulfonated SEBS with PVDF at a blending ratio of 50/50% w/w. However, the mechanical properties of the blend membranes have yet to be considered and taken into account.

Mechanical properties and the effect of PS-*block*-PMMA block copolymer

Changes in the mechanical properties of various membranes as a function of sulfonated SEBS content are illustrated in Figure 4. It can be seen that the tensile strength of the semicrystalline PVDF membrane is more than five times greater than that of the sulfonated SEBS membrane. On the other hand, the elongation value of the latter is much better than that of the former. By blending with PVDF, the tensile strength of the membrane decreased with the sulfonated SEBS content. The trend was not in a linear fashion, that is, it seems to deviate from the linear trend or that predicted from a simple mixing rule. This was related to the poor compatibility between the two phases in the blend membranes.

Figure 5 shows the effects of PS-*block*-PMMA block copolymer on the morphology of the selected blend membranes (50/50% w/w of SEBS/PVDF). For the normal blend membrane, a very coarse morphology with irregular and large size domains was observed [Fig. 5(a)]. After adding the block copolymer, the minor phase became finer and the domain size decreased [Fig. 5(b)]. This could be related to a decrease in an interfacial tension between the two polymers caused by an emulsification effect of the block copolymer. Table II shows the effects of the block copolymer on various properties of the blend membranes. The tensile strength of the blend membranes containing 70 wt % of PVDF increased substantially from 0.72 to 4.85 MPa after the block copolymer was added. Similarly, the elongation values of those membranes increased after blending with the copolymer. The aforementioned results suggest that the block copolymer served as an effective compatibilizer, promoting better compatibility between sulfonated SEBS and PVDF in the blend membranes. Finally, as a

TABLE II
Properties of SSEBS/PVDF Blend Membranes (50/50% w/w and 70/30% w/w) Before and After Modified by Block Copolymer

Membranes (wt %) Sulfonated SEBS/PVDF	Water uptake (%)	Proton conductivity $\times 10^{-3}$ (S/cm)	Methanol permeability (cm^2/s) $\times 10^{-7}$	Tensile strength $\times 10^6$ (N/m ²)	Elongation (%)
50/50	1.3 (± 0.21)	0.57 (± 0.03)	0.014	5.45 (± 2.69)	11.63 (± 2.73)
50/50 (with 5 wt % copolymer)	0.60 (± 0.12)	2.19 (± 0.05)	No methanol crossover	5.96 (± 0.79)	60.66 (± 3.04)
70/30	4.07 (± 0.75)	0.084 (± 0.00)	13.4	0.72 (± 0.46)	3.26 (± 1.52)
70/30 (with 5 wt % copolymer)	1.21 (± 0.25)	2.04 (± 0.05)	0.16	4.85 (± 2.51)	19.71 (± 7.48)
Nafion 115	24.3	9.59 (± 0.12)	3.39	43	225

consequence, the proton conductivity and methanol resistance of the blend membranes increased.

CONCLUSIONS

A partially sulfonated SEBS was successfully prepared by using propionyl sulfate as a sulfonating agent. The sulfonated polymer with a degree of substitution of 6.19 wt % was blended with PVDF at a variety of blending ratio. The best membrane provided the highest proton conductivity and the lower methanol permeability is that obtained by blending the two polymers at 50/50% w/w. Compatibility between the two polymeric phases in the blend membrane can be further improved by adding 5 wt % of PS-*block*-PMMA block copolymer as a compatibilizer. Consequently, mechanical properties, proton conductivity, and methanol resistance of the blend membrane improved remarkably.

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