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Novel Polymer Electrolyte Membranes Based on Semi-Interpenetrating Blends of Poly(vinyl alcohol) and Sulfonated Poly(ether ether ketone)

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ABSTRACT: In this work, the properties of novel ionic polymer blends of crosslinked and sulfonated poly(vinyl alcohol) (PVA) and sulfonated poly(ether ether ketone) (SPEEK) are investigated. Crosslinking and sulfonation of PVA were carried out using sulfosuccinic acid (SSA) in the presence of dispersed SPEEK to obtain semi-interpenetrating network blends. PVA–SSA/SPEEK blend membranes of different compositions were studied for their ion-exchange capacity, proton conductivity, water uptake, and thermal and mechanical properties. The hydrated blend membranes show good proton conductivities in the range of 10^{-3} to 10^{-2} S/cm. When compared with pure component membranes, the PVA–SSA/SPEEK blend membranes also exhibit improvement in tensile strength, tensile modulus, and delay in the onset of thermal and chemical degradation. Semi-interpenetrating nature of the blends is established from morphology and dynamic mechanical analysis. Morphology of the membranes was studied using scanning electron microscopy after selective chemical treatment. The dynamic mechanical properties of the membranes are examined to understand the miscibility characteristics of the blends. The relative proportions of PVA and SPEEK and the degree of crosslinking of PVA–SSA are important factors in determining the optimum properties for the blend. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: ionic polymer blends; crosslinking; proton exchange membrane; semi-interpenetrating network

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INTRODUCTION

The proton-conducting membrane is a vital component of any polymer electrolyte membrane fuel cells (PEMFCs) to attain high power densities.[1–3] The requirements of fuel cell membranes are high proton conductivity, low reactant permeability, good mechanical and thermal stability, and low cost. Membrane materials being investigated for PEMFC can be generally classified as fluorinated polymers, partially fluorinated polymers, nonfluorinated or hydrocarbon polymers, and acid–base blends.[4] Nafion®, a perfluorinated sulfonated ionomer, shows high proton conductivity (~ 0.1 S/cm), good mechanical properties, and thermal stability.[2,3] However, some limitations of Nafion are its poor barrier properties, dimensional stability, and poor performance at temperatures higher than 80°C.[2–6]

Alternative membranes based on poly(vinyl alcohol) (PVA) show good proton conductivity with low methanol permeability.[1] Introduction of negatively charged ion groups in PVA can be achieved by chemical modification through crosslinking using sulfosuccinic acid (SSA).[1,6] The proton conductivity and methanol permeability of PVA–SSA membranes are in the range of 10^{-3} to 10^{-2} S/cm and 10^{-7} to 10^{-6} cm^2/s, respectively.[1] Strategies to obtain membranes with better thermal and mechanical stability from PVA include the addition of particles such as silica and titania.[7,8] PVA along with heteropoly acids have been shown to lead to good proton conductivity.[9]

For the higher operating temperatures of PEMFCs, some of the most promising materials for membranes are based on high-performance aromatic polymers such as polyimides, poly(ether ether ketone), poly(arylene ether sulfone), and polybenzimidazole.[10,11] Sulfonated poly(ether ether ketones) (SPEEK), obtained by the functionalization of PEEK using sulfuric acid, has T_g above 150°C.[12–14] SPEEK blended (and entrapped in) with phenol formaldehyde resin has less water uptake and good mechanical properties.[15] SPEEK membrane has also been modified by blending with uncrosslinked PVA to reduce the methanol permeability.[16]

Other approaches toward developing superior polymer electrolytes use polymers in several modified forms.[17] Such modifications include forming interpenetrating and semi-interpenetrating networks (IPNs and semi-IPNs).[18,19] IPNs and semi-IPNs are combinations of two polymers in network form, in which one polymer is synthesized and/or crosslinked in the presence of the other. In case of IPNs, both the polymers are crosslinked. On the other hand, in semi-IPNs, one of the polymers is crosslinked. This technique may result in a material distinct from a blend of two polymers. Weeks et al.[20] have studied PVA/H_3PO_4/PMMA ionic IPN system. PVA/H_3PO_4 forms an IPN, and the mechanical stability is provided by the network of PMMA. Another example is the semi-IPN based on PVA–SSA and poly(styrene sulfonic acid-*co*-maleic acid) as a proton source.[21] Recently, for membranes more closely related to this work, it was shown that the semi-IPNs of Nafion and fluorine-containing polyimide show high proton conductivities with superior mechanical and thermal properties.[19]

In this work, we report the development and characterization of novel ionic polymer blend membranes based on PVA–SSA and SPEEK. PVA was crosslinked with SSA in the presence of SPEEK to form semi-IPN. The characteristics of blend membranes are described in terms of proton conductivity, ion-exchange capacity (IEC), water sorption, and mechanical and thermal characteristics at different compositions. The blend morphology is examined to understand the semi-IPN nature and its relation to the observed properties.

EXPERIMENTAL

Materials

PVA with a weight–average molecular weight (M_w) of 125,000 and a degree of hydrolysis of 88% was purchased from SD Fine Chemicals Limited (Mumbai, India). PEEK with an average molecular weight of 45,000 was purchased from Victrex (UK). SSA (70 wt % solution in water) used as a crosslinking agent was obtained from Aldrich Chemical (Milwaukee, WI). Sulfuric acid (98 wt %) was obtained from RFCL Limited (New Delhi, India), and *N*-methyl-2-pyrrolidone (NMP) was obtained from Sisco Research Laboratories (India). All the polymers and chemicals were used as received.

Membrane Preparation

PVA solution (10% w/w) was prepared by dissolving required amount of PVA in water at 90°C for 6 h.[7] Simultaneous sulfonation and crosslinking of PVA were carried out by the addition of SSA. SSA was added to the PVA solution at room temperature and stirred for 24 h. The homogenous solution thus obtained was poured into Petri dishes and allowed to dry at 60°C in an air oven for 24 h. To complete the crosslinking, these membranes were heated for 1 h at 120°C in an air oven. For the membranes reported in this work, 20 wt % of SSA (with respect to PVA) was used.

The required amount of dried PEEK particles were dispersed in sulfuric acid, and SPEEK was obtained in powder form.[10] SPEEK particles, thus obtained, yield a clear dispersion in water. Various SPEEK particles, when dispersed in water, would swell to differing degrees and would form entangled particulates. Although macroscopically homogeneous membranes are formed from this water dispersion, the films are very brittle. On the other hand, SPEEK particles are completely soluble in NMP, and SPEEK membranes, thus formed, are macroscopically homogeneous as well as ductile films. This behavior of SPEEK particles in water is important while considering the blend preparation and the resulting morphology. In this work, SPEEK membranes were prepared from NMP solution, whereas blend membranes were prepared from water-based systems. The number of ionic groups in a SPEEK molecule is characterized by the degree of sulfonation, which is the fraction of the number of repeating units with suflonate groups and the total number of repeating units. At lower degree of sulfonation, SPEEK is sparingly soluble in water, and at higher degree of sulfonation, it is completely soluble in water. Therefore, 0.7 was chosen as the degree of sulfonation of SPEEK for preparing the blends.

PVA/SPEEK blend membranes were prepared by adding required amounts of PVA and SPEEK in water at 70°C. For example, for the preparation of 30/70 blend, 30 wt % of PVA and 70 wt % of SPEEK were dissolved in water. After preparing the PVA/SPEEK mixture, 20% of SSA (with respect to the weight of PVA) was added to crosslink the PVA in the presence of SPEEK. The solutions were then poured into Petri dishes and dried (8 h at 40°C, 8 h at 60°C, 8 h at 80°C, and 48 h at 100°C for the gradual removal of solvent and to avoid air bubble formation). SPEEK membranes were prepared by dissolving dried SPEEK (10 wt %) in NMP and casting.[12] All the membranes were stored in distilled water before testing. The thickness of all the membranes prepared was in the range of 150–200 μm.

Different batches of membranes were prepared, and each membrane was also characterized multiple times. Unless otherwise stated, error bars given with the results imply errors due to measurements on different batches of membranes.

IEC and Water Uptake

The membranes were immersed in 0.5*M* of HCl (for protonation) for a day. This was followed by immersion in 2*M* of NaCl for a day. The membrane was removed from the solution, and then, the solution was titrated with 0.1*M* of NaOH to determine the molar proton content.[22] After determining the dry weight of the membranes (drying condition: 60°C for 2 h for PVA–SSA and blend membranes; 100°C for 2 h for SPEEK membrane), the IEC was calculated as the ratio of proton content and dry weight. As mentioned earlier, the degree of sulfonation gives the fraction of repeating units of polymer chain with $-SO_3H$ group. This can be estimated from IEC based on the weights of repeating units of PEEK and SPEEK.[22] The degree of sulfonation for the SPEEK used in this work is 0.70 ± 0.02.

The water uptake of membranes was determined by immersing circular-shaped samples (diameter: 30 mm) in distilled water at 25°C for 24 h. The samples were taken out (the surface water was removed carefully using tissue paper) and weighed immediately on a microbalance. The equilibrium water uptake (W) of the membrane is given by the following equation:

$$W = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}}, \tag{1}$$

where W_{dry} and W_{wet} are the weights of dry and wet (or hydrated) membranes. The variation in water uptake values with repeated trials was in the range of ±5%.

Proton Conductivity

Proton conductivity of the membranes was obtained from impedance measurements using an impedance analyzer in combination with an electrochemical interface (GILL ACM Instrument) in the frequency range 1–300 kHz using circular films (diameter: 10 mm).

The proton conductivity of the membrane (S/cm) is given by the following equation:

$$\sigma = \frac{l}{\mathrm{RS}}, \tag{2}$$

where R is the bulk resistance or ohmic resistance of the membrane sample, l is the thickness (cm), and S is the cross-sectional area of the sample (cm^2). Proton conductivities of the membranes were measured under ambient conditions, wet or hydrated state (membranes after swelling in water), at varying relative humidity (50–95% relative humidity) at 30°C, and at different temperatures (40–70°C) with 95% relative humidity. Techlab humidity chamber with Eurotherm 2604 controller was used for controlling temperature and humidity during the conductivity measurement.

Thermal Analysis

Thermal analysis of the polymer membranes was performed using a thermogravimetric analyzer (Netzsch Thermal Analyzer) from 30 to 500°C at a heating rate of 10°C/min under air atmosphere.

Mechanical Properties

The mechanical properties of the membranes were determined using a Universal Testing Machine (Zwick Roel 1464). Samples were prepared according to ASTM D-882-01 for mechanical testing of thin polymer films. Tests were performed in the tensile mode at 25°C, 55% of relative humidity, and at a crosshead speed of 10 mm/min. For each test result reported, measurements were made on at least three samples.

Dynamic Mechanical Analysis

The membranes were characterized for the miscibility and interaction of the blend components with water using dynamic mechanical analysis (DMA; TA Instruments DMA Q800). Rectangular membrane samples ($25 \times 6 \times 0.2$ mm^3) were subjected to oscillatory sinusoidal tensile deformation at 1 Hz with 4 μm amplitude and a preload of 0.05 N. The storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were measured from 25 to 300°C at a heating rate of 2°C/min. Dynamic mechanical behavior of dry (for 2 h at 80°C) and hydrated membranes (24 h in distilled water) was examined.

Surface Morphology

Morphology of the membranes was studied using high-resolution scanning electron microscope (FEI Quanta 200). Energy-dispersive X-ray spectroscopy (EDS) was used to obtain estimates of qualitative distribution of different elements. Peak strengths of carbon (C), oxygen (O), and sulfur (S) were determined in terms of weight percent.

Before examination using SEM, the membranes were subjected to selective treatment with NMP and Fenton's reagent.[23] SPEEK dissolves in NMP, whereas PVA–SSA is not be affected by NMP; however, SPEEK and PVA–SSA are both affected by Fenton's reagent, with SPEEK being more susceptible.

Membranes were dipped in NMP for a period of 30 min. Excess NMP, from the membrane surface, was removed before taking the SEM images. Fenton's reagent was prepared by dissolving $\mathrm{Fe(NH_4)_2(SO_4)_2}$ (4 ppm) in 3% aqueous $\mathrm{H_2O_2}$ solution. Before the treatment, the membranes were dried in a vacuum oven at 60°C for 12 h. Dry membranes were weighed and kept in Fenton's reagent at 70°C for a period of 1 h. The membranes were then taken out, washed, and kept in distilled water to prevent further degradation. Treated membranes were dried at 60°C for 12 h before microscopic examination.

RESULTS AND DISCUSSION

IEC and Water Uptake

The IEC of pure components and blends is shown in Figure 1. IEC is a measure of the sulfonic acid groups present in the membrane. Because of the higher degree of sulfonation used in this work, SPEEK has higher IEC.[11] The IEC and the degree of sulfonation of PVA and SPEEK are in good agreement with the reported values.[7,11,12]

As PVA–SSA and SPEEK are individually sulfonated, IEC of a blend is expected to be equal to the sum of the IEC of the individual constituents. However, as can be observed from Figure 1, the IEC of the blends are lower than those expected from the additive combination of IEC of the pure components. In other words, the effective IEC that could be achieved by blending the two polymers is lower than expected. This may be due to the lower sulfonation and crosslinking of PVA in the presence of SPEEK, which may be hindering the PVA–SSA reaction. The distribution of SPEEK molecules in the crosslinked network of PVA–SSA is further discussed in the "Mechanical Properties" section. The incorporation of the sulfonic acid groups was less than expected by 25, 24, and 13% in PVA–SSA/SPEEK (70/30), (50/50), and (30/70) blends, respectively. The ratio of the effective SSA content per unit weight of the blend membrane and SSA content of the PVA–SSA membrane (equivalent to the likely number of crosslinks per unit weight of the membrane) was 0.53, 0.38, and 0.20, respectively. PVA–SSA networks in the blend membranes are therefore not the same as that in pure PVA–SSA. This characteristic of the PVA–SSA networks is an important consideration in understanding various properties of the blend membranes, which is discussed hereafter. The distribution of SPEEK in PVA–SSA appears to be in the form of a semi-IPN. This is explored further with discussion of other properties and microscopic examination.

The effect of PVA content on the equilibrium water uptake of different blend membranes is shown in Figure 2. PVA–SSA membrane shows higher uptake (56%) in comparison with other membranes. Water uptake is higher for PVA/SPEEK (30/70) and (50/50) blends, although less than that for PVA–SSA membrane. This is due to lower number of crosslinks of PVA networks in these membranes. On the other hand, the water uptake of PVA/SPEEK (70/30) and (60/40) membranes is much lower. With the increase in crosslinking and with the presence

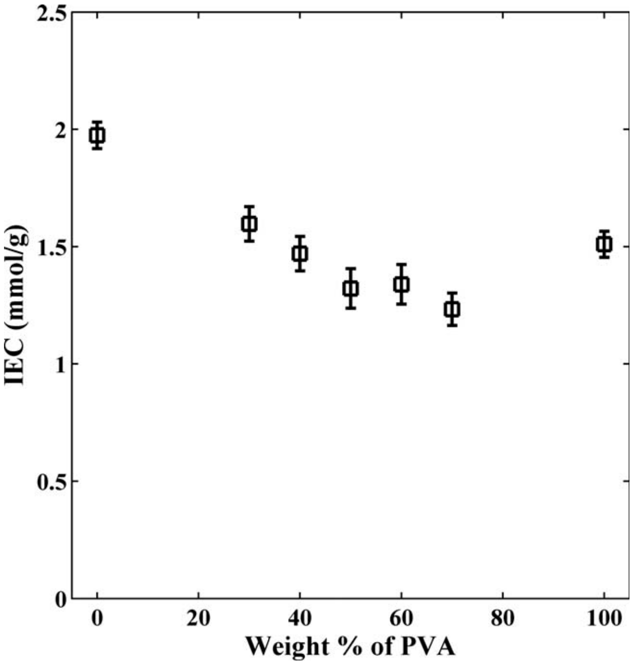

Figure 1. Ion-exchange capacity (IEC) of PVA–SSA/SPEEK membranes as a function of PVA–SSA component.

of SPEEK, the membranes are expected to swell less, limiting the amount of water that can be absorbed.[18] This nonmonotonic variation in water uptake with SPEEK content alludes to differing nature of crosslinking and component distribution in the blend membranes.

Proton Conductivity

Figure 3 shows the proton conductivity of the hydrated membranes as a function of PVA content. Under hydrated condition, the membranes show very high proton conductivity in comparison with that under ambient condition. The variation of conductivity for all the membranes is within one order of magnitude and in the range 10^{-3} to 10^{-2} S/cm. Proton conductivity of 0.07 S/cm was observed in the case of PVA–SSA/SPEEK (70/30) blend membranes, which is 70% of the conductivity of Nafion.

Proton conductivity of PVA–SSA[1,5–8] and SPEEK[10–12] are comparable with the literature. The effect of the nature of nanoscopic/microscopic molecular assemblies on ionomer proton conductivity has been investigated using various tools such as scattering techniques.[24] The SPEEK morphology is relatively well understood. It is known that hydrophobic (backbone) and hydrophilic (ionic groups) regions are dispersed in SPEEK, with the hydrophilic domains being connected by hydrophilic channels.

Several mechanisms such as bulk and structural diffusion (hopping) and surface diffusion are responsible for the overall proton conduction. PVA–SSA with the hydrophilic backbone and the ionic (crosslinking) groups is likely to have a morphology very different from that of SPEEK. In the fully hydrated PVA–SSA membranes, water is held between the swollen networks of the crosslinked PVA–SSA network and the proton–water–sulfonate groups may be contributing to the observed higher conductivity. The conductivity pathways in PVA–SSA are likely to be similar to the case of hydrogels, as opposed to "the islands/channels" of Nafion or SPEEK. The nature of conductive pathways in the semi-IPN of PVA–SSA and SPEEK is likely to be combinations of the two systems. However, more investigations are needed to establish conductivity mechanisms in such blend systems. It should be noted that PVA–SSA/SPEEK (70/30) blend membrane shows better proton conductivity in comparison with all the other membranes, although the water uptake for this membrane is the lowest among the blend membranes.

The effect of relative humidity on the proton conductivity for all the membranes is shown in Figure 4. At different humidities, proton conductivities are in the range of 10^{-7} to 10^{-3} S/cm. As expected, conductivity increases with the increase in relative humidity for all the membranes. It is interesting to note that the blend membranes show higher conductivities than either of the pure components under humidified conditions. Therefore, the blend membranes are expected to show much less susceptibility to drier operating conditions.

Proton conductivity was also measured as a function of temperature (25–70°C). The variation of conductivity can be effectively described by Arrhenius dependence for pure as well as blend membranes investigated in this work. The activation energy is less for blend membranes (3–8 kJ/mol) when compared with that for PVA–SSA and SPEEK membranes (8–15 kJ/mol). These values are comparable with those reported earlier.[4,7,25] It is noteworthy that activation energies of PVA–SSA and the blend membranes are lower than that of Nafion. Such low values of

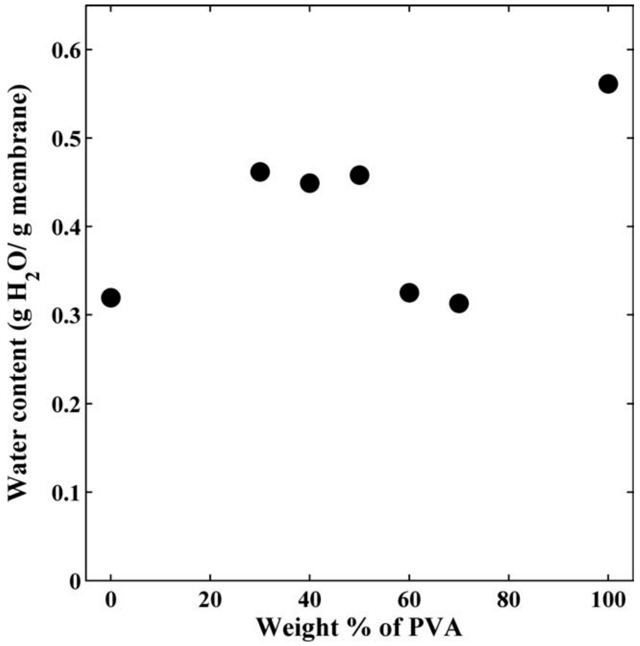

Figure 2. Equilibrium water uptake in PVA–SSA/SPEEK blend membranes (error is less than ±5%, and the error bars are smaller than the symbol size).

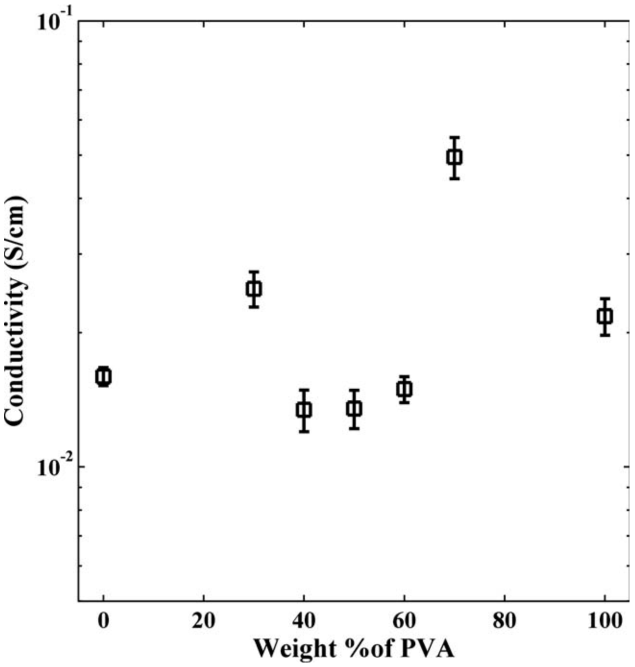

Figure 3. Proton conductivity of hydrated PVA–SSA/SPEEK blend membranes.

activation energies have been reported earlier, especially for PVA-based membranes. This is most possibly due to the effect of swelling, as it leads to a change in the effective IEC of the membrane. However, the prevalence of this effect for PVA-based membranes needs to be investigated further.

Thermal Stability

Thermal stability, as measured by percent weight loss, of various membranes is shown in Figure 5. The percent weight loss is much higher for PVA–SSA membranes in comparison with other membranes. SPEEK membranes show less weight loss up to 300°C. It is known that SPEEK has high thermal stability in comparison with that of PVA–SSA.[7,12] Three consecutive weight-loss steps can be observed for all the membranes. These can be attributed to weight losses due to thermal solvation (∼ 100°C), thermal desulfonation (250–400°C), and finally, thermal oxidation of the polymer (>450°C), respectively.[6] PVA–SSA has major weight loss in the first step due to its larger water content.

It is interesting to observe that PVA/SPEEK blend membranes show gradual, slow weight loss, and better thermal stability than PVA–SSA and SPEEK membranes. Blending seems to have a synergistic effect on the thermal stability. It has been reported that IPN membranes have higher thermal and mechanical stability.[16] The presence of SPEEK and the crosslinking of the PVA with SSA in the blend, forming a semi-IPN, seems to lead to higher thermal stability. As in the case of water uptake and proton conductivity, PVA–SSA/SPEEK (70/30) blend membrane shows higher thermal stability, that is, very low weight loss even at higher temperature in comparison with other blend membranes.

Mechanical Properties

Load–deflection behavior of various membranes under ambient conditions is shown in Figure 6. PVA–SSA membrane and SPEEK membrane show similar tensile strength, as can be seen in the Figure 6. SPEEK membranes display a ductile behavior characterized by a yield point followed by neck formation and large deformation.[25] It can be observed that the tensile strength of (70/30) blend is higher than either PVA–SSA or SPEEK. On the other hand, the tensile strength of (50/50) and (30/70) blends are lower than the pure components. The tensile moduli for various membranes are shown in Figure 7. Moduli of all the blend membranes are higher than that of the pure component membranes.

For a crosslinked polymer, modulus increases and elongation at break decreases with increasing crosslinker concentration or crosslink density. It is worth noting that mechanical properties of PVA–SSA membranes do not follow this usual trend. Because of the ionic groups and their concentration (which also increases with crosslinking density), water uptake also becomes an important factor in these systems. For the PVA–SSA system, the elongation at break is the highest for membranes with 20% SSA (when compared with 10 or 30%). In the blend membranes, PVA–SSA network along with SPEEK distribution would determine the overall behavior, and therefore, results presented in Figures 6 and 7 would have to be analyzed in this context. In the hydrated state, the modulus and tensile strength of SPEEK are higher than all the other membranes. The swelling stresses, along with the heterogeneities and the plasticizing effect of water, seem to lead to poorer mechanical properties for the hydrated blend membranes.

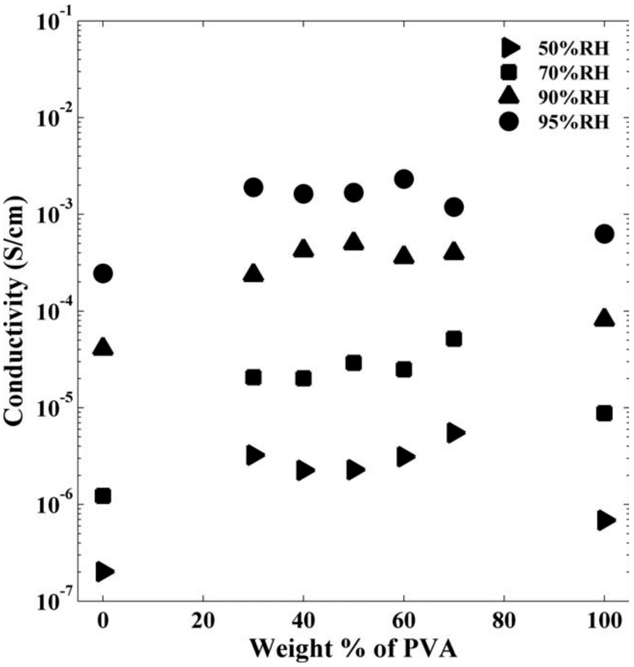

Figure 4. Effect of relative humidity on proton conductivity for PVA–SSA, SPEEK, and PVA–SSA/SPEEK blend membranes (error bars were less than ±5% and smaller than the symbol size).

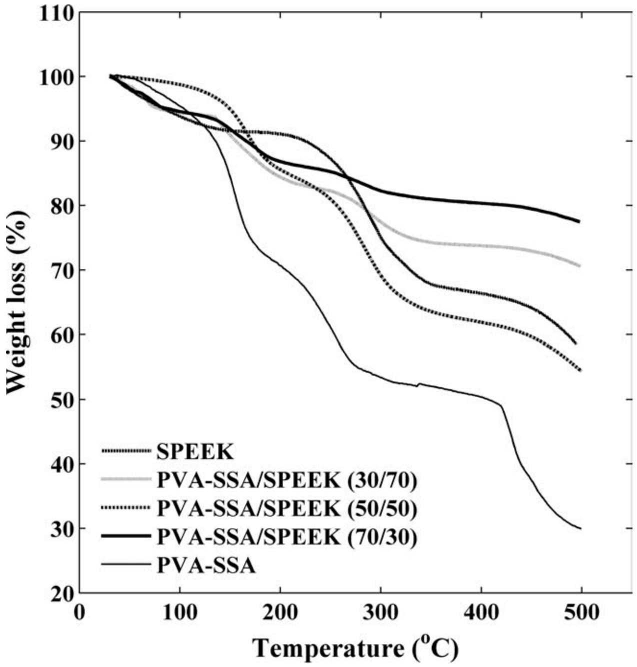

Figure 5. Weight loss in PVA–SSA, SPEEK, and PVA–SSA/SPEEK blend membranes.

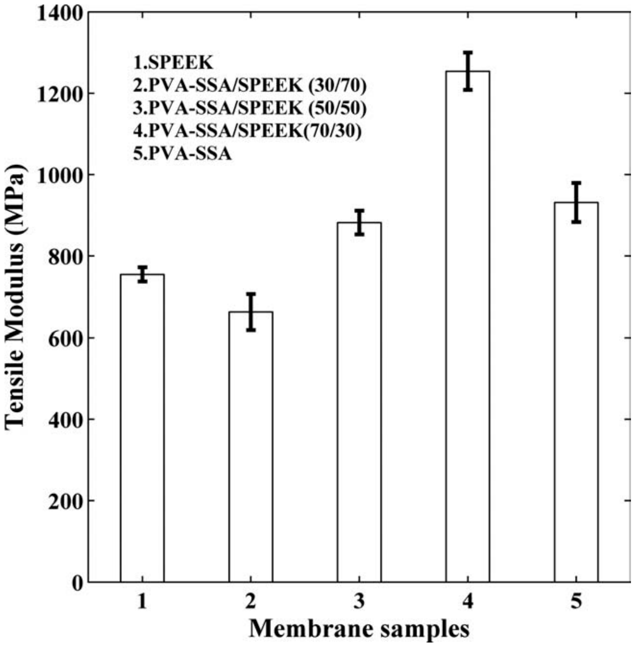

Figure 7. Tensile modulus of PVA–SSA/SPEEK membranes.

The results so far demonstrate that the properties of PVA–SSA/SPEEK blends vary nonmonotonically with the blend ratio. Additionally, considering the overall performance, properties are better for the blends than either of the pure components. In addition to the crosslinking in the networks, the interactions among ionic polymer chains are expected to be the determining factors for this behavior. The results presented in sections below highlight the interdependent nature of various factors in these blend membranes. It would be interesting to examine model material systems in which degree of crosslinking and amount of ionic groups could be varied independently.

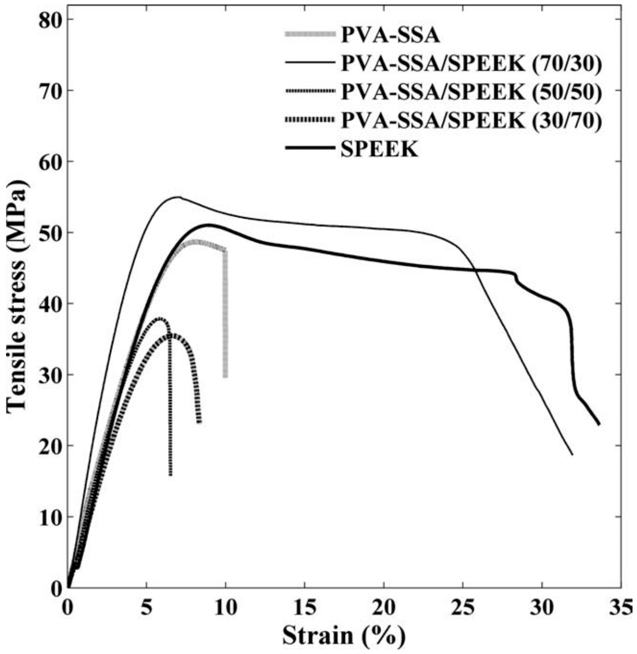

Figure 6. Tensile load–deflection behavior of PVA–SSA/SPEEK membrane.

Optimum properties were observed for PVA–SSA/SPEEK (70/30) membrane. This blend seems to have the appropriate amount of crosslinking and blend ratio to exhibit higher strength as well as modulus, without too low elongation at break. This blend also exhibited the highest proton conductivity, the lowest water uptake, and the highest thermal stability. As mentioned earlier, the overall number of crosslinking in the PVA–SSA/SPEEK (70/30) membrane is higher than that of the other blend membranes. However, further investigations about the distribution of SPEEK chains and their interactions with the PVA–SSA network are required to provide microscopic/molecular insights into the behavior reported here. To arrive at a broad understanding, some results from DMA and microscopy are presented in the following sections. These results are used to provide a qualitative description of the miscibility and morphology of different blend membranes.

Dynamic Mechanical Analysis

Initially, dynamical mechanical behavior of PVA and PVA–SSA is presented to highlight influence of the ionic crosslinker. E' and tan δ for dry PVA and dry PVA–SSA membranes are shown in Figure 8. As expected, PVA membrane shows a decrease in E' and a peak in tan δ at the glass transition (at 73.9°C). However, a significant effect of the crosslinker can be observed in the dynamic mechanical behavior of PVA–SSA membrane. At low temperatures ($<60°$C), the E' values of PVA–SSA are lower than PVA. As the temperature is increased, E' decreases less gradually for PVA–SSA due to the crosslinked nature. Correspondingly, broadening and shifting of the tan δ peak are also observed.

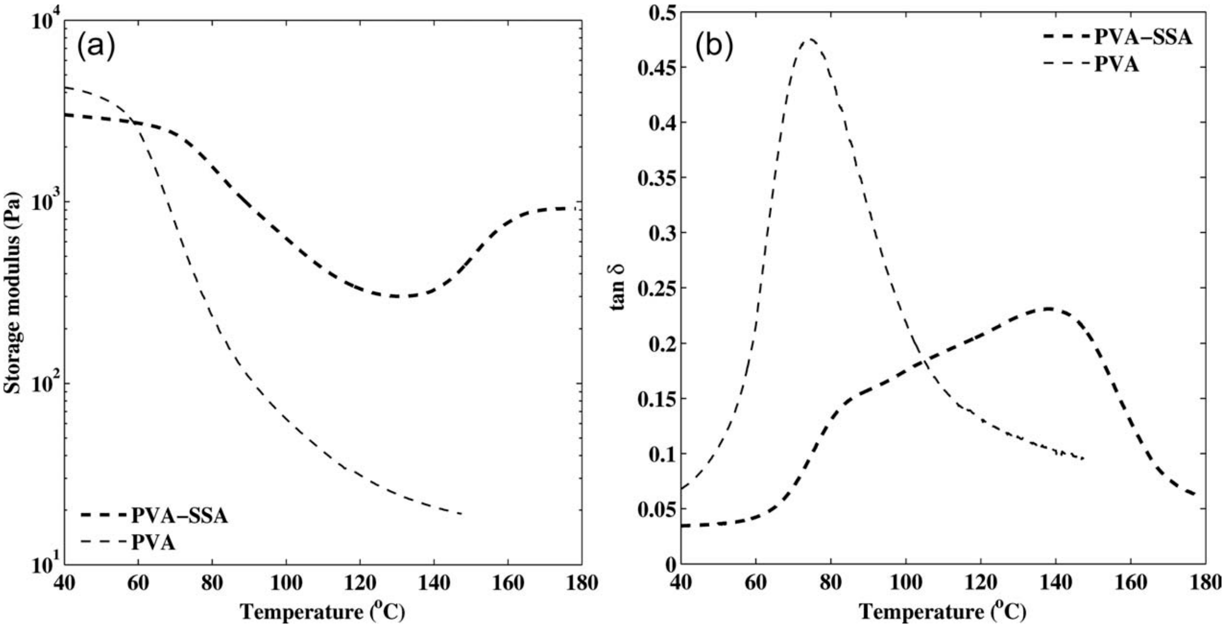

Figure 8. Effect of crosslinking with SSA on the dynamic mechanical behavior of PVA membranes: (a) E' and (b) tan δ.

Because of crosslinking, the glass transition shifts to a higher temperature, and the storage modulus is higher for PVA–SSA at higher temperatures. At temperatures higher than 130°C, after the decrease in E' between 80 and 130°C, E'' increases as a function of temperature, indicating residual crosslinking reactions. As PVA–SSA membranes were crosslinked at 120°C, residual crosslinking takes place when membranes are subjected to higher temperatures.

The dynamic mechanical behavior of the dry, pure components and blends, membranes as a function of temperature is shown in Figure 9(a,b). SPEEK shows a glass transition at 161.5°C, with a drastic decrease in E' and corresponding sharp peak in tan δ. As observed in the case of PVA–SSA membrane, E' decreases for all the blend membranes in the temperature range of 80–130°C. This decrease in E', which is due to glass transition in PVA–SSA network, is gradual for blends when compared with that for PVA–SSA. The presence of SPEEK is responsible for this behavior, as higher SPEEK content leads to more gradual decrease in the E'. At temperatures higher than 130°C, increase in E' is less pronounced in blend membranes when compared with the increase observed in the case of PVA–SSA membrane. The sharp decrease in the E' due to the glass

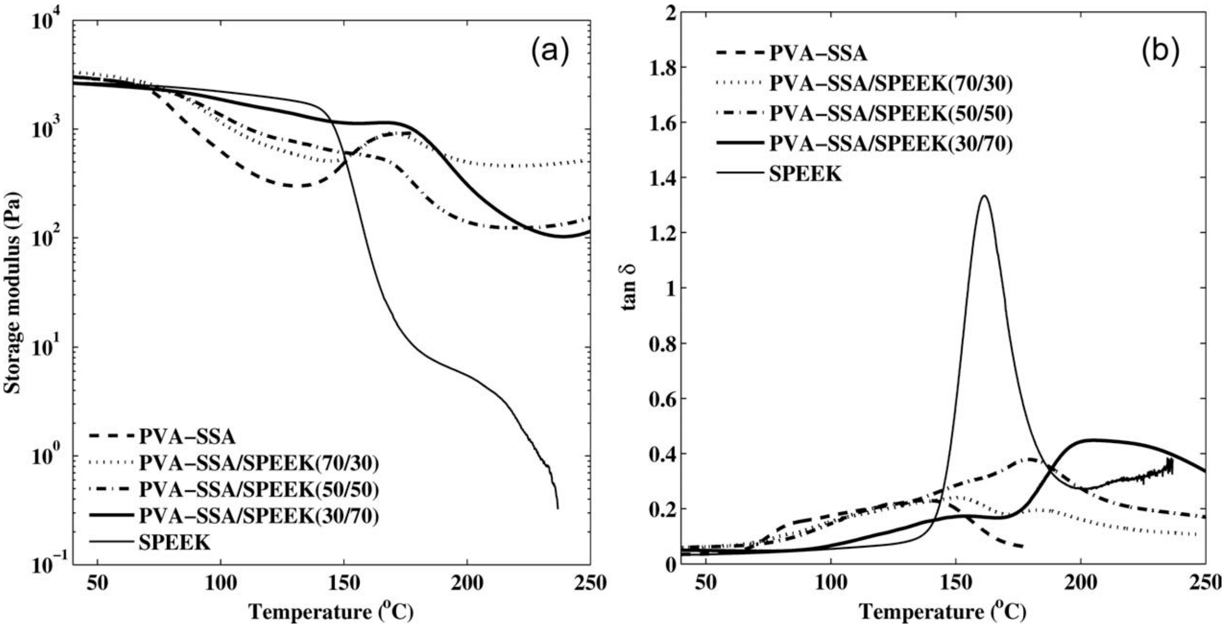

Figure 9. Dynamic mechanical behavior of dry pure component and blend membranes: (a) E' and (b) tan δ.

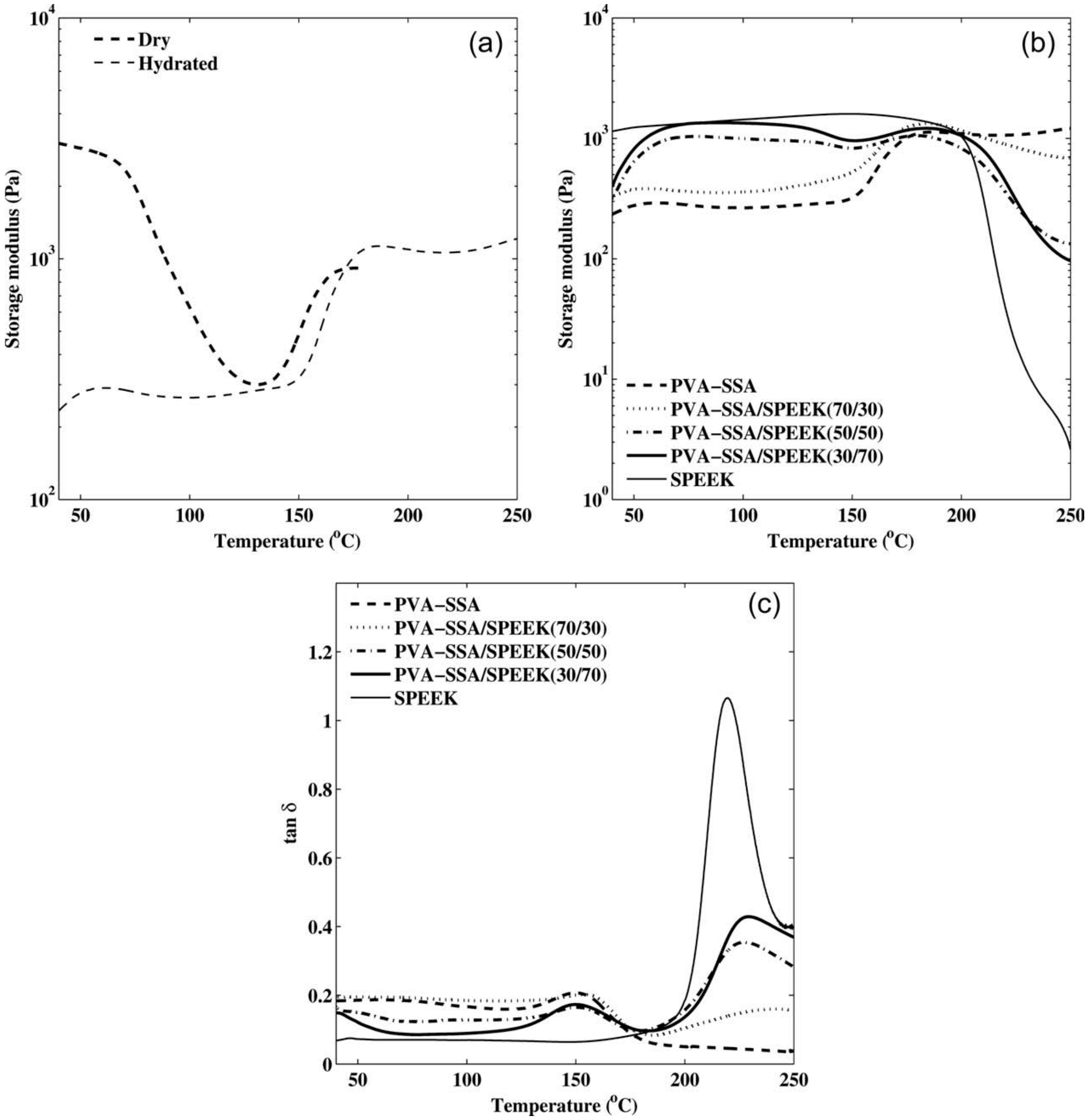

Figure 10. Dynamic mechanical behavior of hydrated membranes: (a) storage modulus for dry and hydrated PVA–SSA membranes; (b) storage modulus for hydrated pure component and blend membranes; and (c) tan δ for hydrated pure component and blend membranes.

transition of SPEEK is not observed in the blend membranes; there is only an order of magnitude decrease in E' for the blend membranes, as opposed to 3–4 orders of magnitude decrease for SPEEK. Strong influence of the PVA–SSA network and the residual crosslinking, even at high SPEEK content of 70%, is evident in these results.

Corresponding tan δ for the pure components and the blends are shown in Figure 9(b). In the case of PVA–SSA/SPEEK blends, the peaks are broader and are observed at different temperatures than for the pure components. It is also interesting to note that the tan δ peak corresponding to the SPEEK phase (in the blend membranes) shifts to higher temperatures when compared with pure SPEEK. As the peaks corresponding to the PVA–SSA and SPEEK phases are less prominent and have become broad in the blends, the existence of an IPN with some distributed regions of SPEEK and/or PVA–SSA can be surmised. The interpenetrating and the distributed nature of PVA–SSA/SPEEK blends were further explored using SEM, and these results are discussed in the next section.

The tensile modulus and the strength of hydrated ionic membranes are known to be significantly lower when compared with their dry counterparts. The dynamic mechanical behavior of hydrated membranes is shown in Figure 10(a–c). In case of PVA–SSA [Figure 10(a)], E' values are significantly lower for the

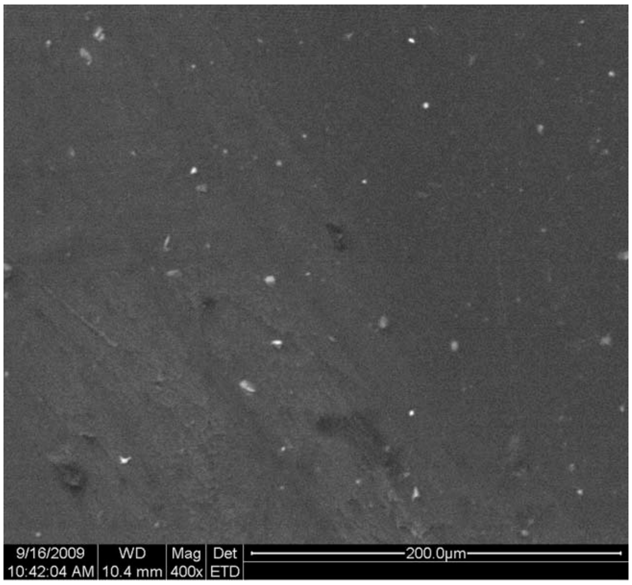

Figure 11. SEM micrographs of SPEEK membranes prepared using SPEEK/water dispersion (×400).

hydrated membranes only at lower temperatures (<120°C). At higher temperatures (>120°C), E' values of dry and hydrated membranes are similar. The decrease in E' associated with the glass transition of PVA–SSA network is absent in the hydrated membrane. However, the increase in E' associated with the residual crosslinking (after 130°C) is similar for both the dry and hydrated membranes.

The storage modulus and the loss tangent variations with temperature for the hydrated, pure components and the blend membranes are shown in Figure 10(b,c). The increase in E', associated with the residual crosslinking, can be observed in the membranes containing PVA–SSA. The decrease in E', associated with the glass transition of SPEEK at temperatures greater than 180°C, is less in the case of the blend membranes. This was observed in case of the dry membranes as well. The comparison of tan δ for dry and wet membranes shows an interesting trend. In the case of hydrated blend membranes, the tan δ peaks are more pronounced and separate unlike in the case of dry blends. This is due to the fact that tan δ peak corresponding to the PVA phase is almost at the same temperature for both the dry and the hydrated membranes. On the other hand, the tan δ peak due to the SPEEK glass transition is at a higher temperature for the hydrated membranes.

The effect of hydration on the T_g of sulfonated polymers has been reported to be due to plasticization and structural contributions (e.g., increased hydrogen bonding and dissociation).[26–30] The effect of water content on the structural changes in Nafion has been documented not only through property variations but also through scattering/molecular simulation studies.[29] The origins of the structural contributions lie in electrostatic interactions among ionic groups in aqueous systems. The unusual variation of T_g of ionic polymers with water content has also been reported through dynamic mechanical and creep studies.[28] Clearly, the results of the current study suggest that the dominating feature of the effect of water in PVA–SSA/SPEEK membranes, at higher temperatures, is due to structural contributions, which leads to an increase in T_g of the hydrated membranes. At low temperatures, plasticizing effect of water is evident due to the lower storage moduli for the hydrated membranes.[28] This is contradictory to earlier observations, where it was reported that, the water acts predominantly as a plasticizing agent in SPEEK and decreases its Tg.[27] As reported in case of Nafion,[26,29] the effect of hydration in the the pure component and the blend membranes is different for different temperature ranges. It should be highlighted that the effect of water is indirect, as hydration and thermal histories could affect the microstructure in different ways. Therefore, behavior at high temperatures in the range of 150–200°C, is not due to the presence or absence of water, but could be due to modification of microstructure due to water. The effect of level of hydration on the structure and T_g in these ionic polymeric systems needs to be explored further.

The hydration of the blend membranes results in better thermomechanical stability of the system indicated by the higher values of storage modulus at high temperatures. Although the dry membranes failed (during DMA) at high temperatures, the wet membranes could withstand high temperatures (during DMA). It may be noted here that the blends show better dynamic mechanical properties than both the pure components in the dry as well as the hydrated states. Single and broad T_g peak is in general considered to be an indication of the miscibility of the blends.[30] This evidence for miscibility can be taken as one of the pointers for semi-IPN nature of the blends. SPEEK molecules are dispersed in the PVA–SSA network. DMA also highlights the nature of water-induced molecular relaxations in these ionic polymeric systems.

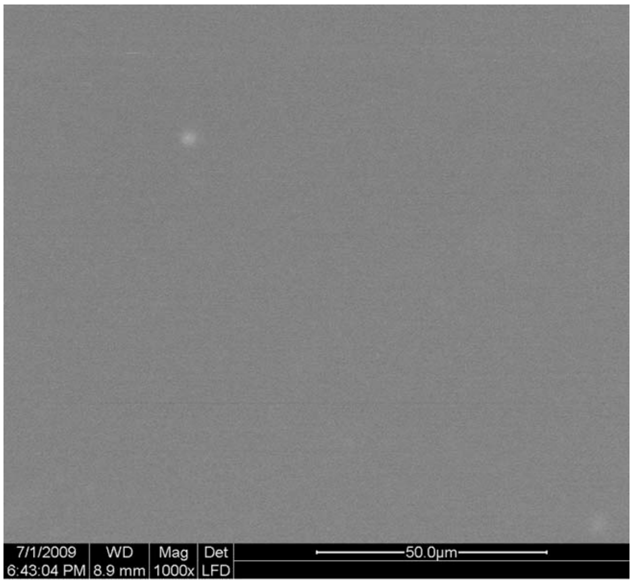

Figure 12. SEM micrograph of PVA–SSA/SPEEK (70/30) membrane showing surface homogeneity due to PVA–SSA crosslinked network (×1000).

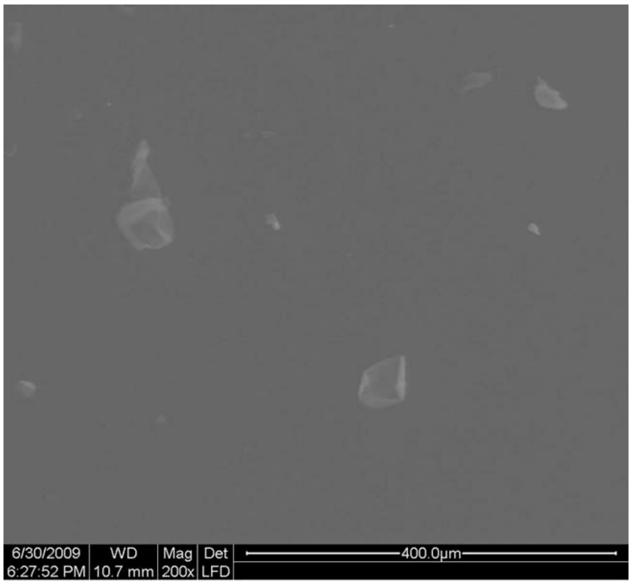

Figure 13. SEM micrograph of PVA–SSA/SPEEK (30/70) membrane after treatment with NMP showing heterogeneous domains due to SPEEK particulates (×200).

The presence of tan δ peak corresponding to T_g of SPEEK in the blend membranes is an indicator of the presence of limited presence of phase-separated SPEEK phase. The SEM results, presented in the section, also confirm this finding.

Blend Morphology and Semi-Interpenetrating Nature

The limited solubility of SPEEK in water can be shown by observing the membranes prepared from SPEEK/water dispersion and SPEEK/NMP solution. From the SEM micrographs shown in Figure 11, distinct identities of several SPEEK particulates are evident in the membrane prepared using water. This heterogeneous SPEEK membrane, as mentioned earlier, was therefore brittle. On the other hand, no such microscopic features were observed with the membrane prepared using NMP.

Although the blend membranes were also prepared with SPEEK water dispersions, distinct SPEEK particulates are not evident [e.g., PVA–SSA/SPEEK (70/30) blend is shown in Figure 12] when surfaces of these membranes are studied. This could be due to the surface homogeneity obtained due to the PVA–SSA crosslinked network. To examine the distribution of SPEEK in the PVA–SSA network, treatment with NMP and with Fenton's reagent was carried out. Among these, NMP is expected to dissolve SPEEK only, whereas Fenton's reagent is expected to oxidize/dissolve SPEEK, PVA, and PVA–SSA crosslinks. After treatment with these solvents for controlled periods, the membrane morphology was studied using SEM.

EDS was used for the qualitative estimation of C, O, and S contents (wt %) of the membranes. For the SPEEK membrane (considering SPEEK molecules only), the weight percent of C, O, and S contents are expected to be 80, 12, and 8, respectively. Similarly, for PVA–SSA (considering PVA–SSA molecules only), C, O, and S are expected to be 58, 38, and 4 wt %, respectively. The range of C, O, and S content for different samples and at different test points varied from 58 to 78%, 15 to 38%, and 2 to 9%, respectively. On a seemingly homogeneous membrane sample, elemental content varied from point to point. This could be due to the experimental limitations as well as due to the nanoscale and microscale heterogeneities. However, for the large observation area, the variation of elemental contents for different membranes showed expected trend. For example, S content was in the following order: SPEEK > PVA–SSA/SPEEK (30/70) > PVA–SSA/SPEEK (50/50) > PVA–SSA/SPEEK (70/30) > PVA–SSA. Therefore, in further discussion, S content is used as a qualitative indicator of the relative distribution of SPEEK in the overall samples.

As expected, SEM micrographs of PVA–SSA before and after NMP treatment indicate that PVA–SSA membranes are not affected by NMP. When the PVA–SSA/SPEEK blend membranes are subjected to NMP treatment, SPEEK is expected to dissolve in NMP. Bright regions, created due to SPEEK/NMP interaction, were observed in the NMP-treated blend membranes. These regions were larger in number for blend membranes with higher SPEEK content. As an example, Figure 13 shows these regions for PVA–SSA/SPEEK (30/70) membrane. The bright (or white) regions, which appear after the exposure to NMP, are similar to those observed on SPEEK membrane prepared from SPEEK/water dispersion (Figure 11). These results, similar to DMA, highlight that the SPEEK particles largely disperse in blend, while some remaining as heterogeneous regions. These heterogeneous regions lead to the bright regions after treatment in the case of SEM and a separate tan δ peak in the case of DMA. Despite the presence of some of these heterogeneous regions, it is surmised that SPEEK molecules do disperse in PVA–SSA network and that blends are largely semi-IPN of SPEEK and PVA–SSA.

After the NMP treatment, PVA–SSA/SPEEK (30/70) blend membrane shows a significant reduction in the sulfur content as given in Table I. This clearly indicates that due to larger SPEEK content, dispersion and interpenetrating distribution of SPEEK molecules in (30/70) blend membrane are not as effective. On the other hand, the PVA–SSA/SPEEK (70/30) blend membrane shows significantly less S reduction after the NMP treatment.

Even though both PVA and SPEEK are individually very susceptible to Fenton's reagent, crosslinked network of PVA–SSA prevents the membrane from dissolving in the Fenton's reagent after 2 h of treatment. PVA–SSA and PVA–SSA/SPEEK

Table I. Percentage Reduction in Sulfur Content of Membranes After Fenton's Reagent and NMP Treatment

Samples	Fenton's test (%)	NMP treatment (%)
PVA-SSA	51.20	1.37
PVA-SSA/SPEEK (70/30)	22.24	5.67
PVA-SSA/SPEEK (50/50)	32.08	4.38
PVA-SSA/SPEEK (30/70)	31.55	28.13

membranes after the treatment with Fenton's reagent are shown in Figure 14. In the micrographs after the treatment, features developed due to treatment are visible in all the membranes. PVA–SSA surface shows smaller (fine blister-like) regions [Figure 14(a)]. PVA–SSA/SPEEK (50/50) blend, on the other hand, shows particulate heterogeneities and larger regions of etching due to the treatment [Figure 14(b)]. Microscopic features of PVA–SSA/SPEEK (70/30) membrane are in between these two extremes [Figure 14(c)]. We can conclude that for this blend, an effective semi-IPN of SPEEK and PVA–SSA is formed. In general, the lack of significant features in the blend membranes, after treatment with NMP and Fenton's reagent, is due to their semi-interpenetrating nature.

After Fenton's test, there is a significant reduction in sulfur content for PVA–SSA membranes in comparison with blend membranes as shown in Table I. The SPEEK membrane dissolves almost instantaneously in Fenton's reagent. Hence, it is interesting to note that the blend membranes are stable in comparison with both pure PVA–SSA and SPEEK membranes. As expected, a reduction in proton conductivity is also observed for all the membranes after Fenton's test due to the loss of sulfonic acid groups from the SPEEK and PVA–SSA. However, reduction in conductivity after Fenton's test is less for the blend membranes, and particularly for the (70/30) blend.

Based on the physicochemical and mechanical characterization in this work, the semi-IPNs of PVA–SSA and SPEEK can be summarized as follows. When SPEEK is mixed with the PVA solution, the SPEEK molecules get dispersed among the PVA molecules. When SSA is added to this blended solution, it crosslinks the PVA network and thereby leads to the entrapping of SPEEK molecules in a network of PVA–SSA. The separation of hydrophilic and hydrophobic domains in SPEEK by itself is well known, and this separation would be influenced due to sulfonic acid groups of PVA–SSA in the blends. The nature of hydrophilic and hydrophobic separation in these blends needs to be investigated further. Nanoscale and microscale heterogeneities in IPN and semi-IPN networks are known to lead to phase domains of size ranging from few nanometers to micrometers.[31] Nonadditivity of properties in IPN and semi-IPN networks are also known.[32] The proton-conducting blend membranes prepared in this work are also examples of such semi-IPNs. These blend membranes combine an ionic polymer SPEEK, which is known to have a nanoscopic heterogeneous phase, with the ionic crosslinked network of PVA–SSA. Because of the complexity of interactions among these ionic polymer systems, further investigations are needed to elucidate structure–property relations in these blend material systems.

CONCLUSIONS

Novel polymer blends based on PVA crosslinked with SSA in the presence of SPEEK were developed and studied. All the blend membranes show proton conductivities in the range of 10^{-3} to 10^{-2} S/cm under fully hydrated condition. PVA–SSA/SPEEK (70/30) blend shows the highest proton conductivity, mechanical strength, and thermal stability with low water

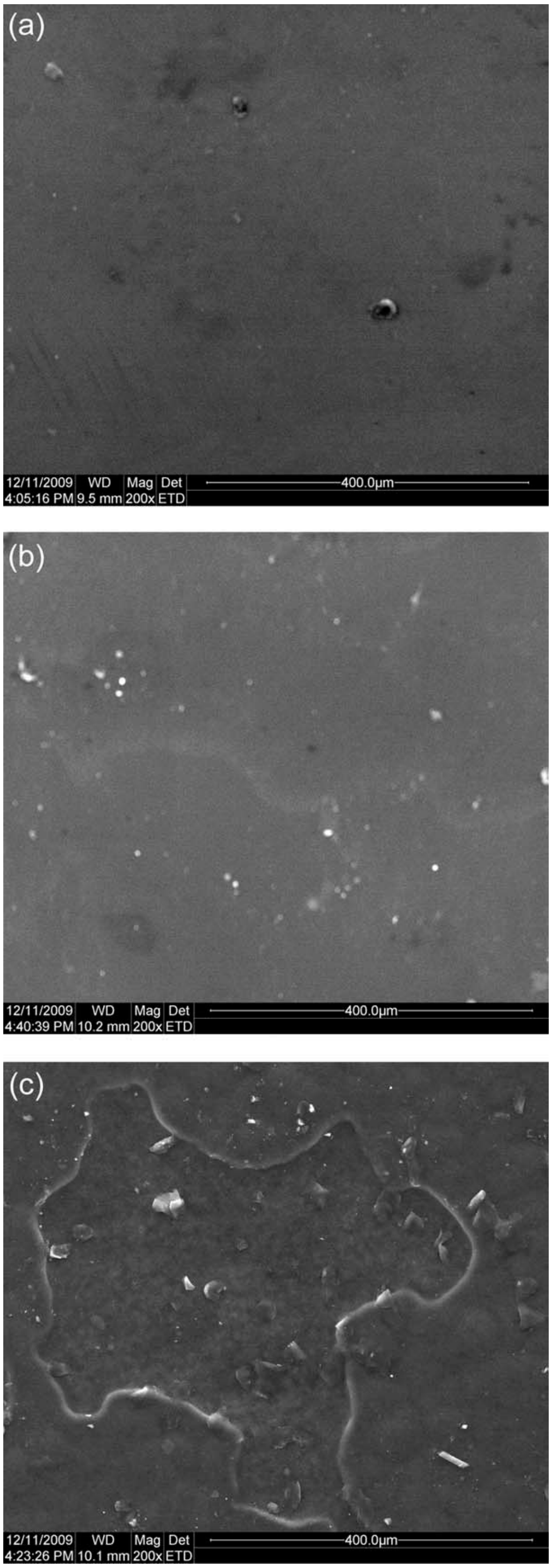

Figure 14. SEM micrographs after Fenton's test: (a) PVA–SSA (×200); (b) PVA–SSA/SPEEK (70/30) (×200); and (c) PVA–SSA/SPEEK (30/70) (×200).

uptake. DMA demonstrated dominant IPN structure of the blends along with the presence of some SPEEK phase separation. Hydration in the pure component as well as in the blend membranes leads to an increase the transition temperature associated with SPEEK glass transition. Uniform surface morphology was observed in all the prepared membranes. After treatment with NMP, SEM studies show the presence of few SPEEK particulates and largely dispersed SPEEK in the PVA–SSA network. Therefore, the blends are shown to be semi-IPNs of SPEEK in PVA–SSA. Blend membranes showed less reduction in weight and conductivity when subjected to the treatment with Fenton's reagent. Overall properties of the blend membranes were better than the pure components, and therefore, it would be interesting to further investigate the morphology and structure–property relations of these ionic polymer systems.

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