Effect of PES on the Morphology and Properties of Proton Conducting Blends with Sulfonated Poly(ether ether ketone)

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ABSTRACT: Development of alternate materials to Nafion, based on ionically conducting polymers and their blends is important for the wider applications of proton exchange membrane fuel cells. In this work, blends of sulfonated poly(ether ether ketone) (SPEEK) with poly(ether sulfone) (PES) are investigated. SPEEK with various ion exchange capacity (IEC) was prepared and blended with PES, which is nonionic and hydrophobic in nature. A comparative study of the water uptake, proton conductivity, and thermo-mechanical characteristics of SPEEK and the blend membranes as a function of the IEC is presented. Addition of PES decreases the water uptake and conductivity of SPEEK. Chemical and thermal stability and mechanical properties of the membrane improve with the addition of PES. The effect of water content on the thermo-mechanical properties of membranes was also studied. The morphology of blend membranes was studied using SEM to understand the microstructure and miscibility of the components. On the basis of the results, a plausible microstructure of the blends is presented, and is shown to be useful in understanding the variation of different properties with blending. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The repeating units of ionic polymers contain varying amount of ionic groups along the backbone. On one hand, there are predominantly hydrophobic polymers with small amounts of ionic groups (<15 mol %), called ionomers. On the other hand, there are polyelectrolytes, with each repeating unit containing an ionic group. Varying the ionic content of the polymers can result in large variations in the microstructure of these materials resulting in significantly different proton and ion transport in them. In ionic polymers with limited number of ionic groups, the incompatibility of the hydrophobic backbone polymer, and ionic groups results in ion-rich aggregates or microphase-separated domains.[1–6] The ionic group aggregation produces changes in the chemical, mechanical, dielectric, and transport properties.[1] Understanding the effect of microstructure of ionic polymers on these properties has been a major challenge for material developers.[2] An important class of ionic polymers, mainly sulfonated polymers, is being investigated as electrolyte material for polymer electrolyte membrane in fuel cells. Currently, commercial perfluorinated membrane materials such as Nafion,[3] which have high chemical stability, long term durability, and excellent proton conductivity at low-operating temperatures find potential applications in fuel cells.[7] However, because of its relatively high cost, poor methanol crossover, low proton conductivity at high operating temperatures, and poor mechanical properties under swollen conditions, development of alternative polymer electrolyte membrane materials to Nafion is necessary.[8]

Alternative materials used for these membranes are based on modification of engineering thermoplastics such as, poly(ether ether ketone) (PEEK),[3,8–10] poly(ether sulfone) (PES),[11] polystyrene,[12] polyimide,[13] polysulfones,[14] and their blends. In these materials, sulfonation is carried out to make them conducting, and therefore the degree of sulfonation (DS) is one of the most important variable in determining the proton conductivity and other properties. Sulfonated poly(ether ether ketone) (SPEEK) is widely considered as a potential alternative because of its low methanol permeability, good thermal stability, and good proton conductivity. SPEEK membranes have been studied for their proton conductivity, at varying temperatures[8,10,15] and humidities.[16] Proton conductivity is strongly influenced by water uptake. For example, it was shown that conductivity increased nonlinear from 1×10^{-2} to 1×10^{-1} S/cm, as the water uptake was increased from 33 to 115%.[17] In addition to the DS,

the solvents used for casting the membranes and the membrane preconditioning were found to affect properties such as the proton conductivity and the water uptake of SPEEK, and the membrane electrode assembly performance due to variations in the microstructure.[18] Studies show that the performance of SPEEK can be improved by adding organic and inorganic dopants,[19] hetero-polyacids,[15] and by blending with polybenzimidazoles,[20] polysulfones,[21] poly(ether sulfone) (PES),[3,9,14,22] polyetherimide,[23] PVA,[24,25] polyacrylonitrile,[26] and poly(vinylpyrrolidone).[27]

The compatibility of SPEEK and PES is expected to be better, as the chemical groups on monomer units of both the ionic and nonionic polymers are identical.[9,28] Hence, favorable penetration and entanglements of polymer chains are expected among these blend components.[29] Therefore, SPEEK has been considered to be miscible with PES in the entire range of the blend composition.[30] However, it has also been shown that PES causes micro domain aggregation of the hydrophilic phase in these blend membranes.[31] Current-voltage curves and chronopotentiometry have also shown some extent of membrane heterogeneity in SPEEK/PES blends.[32]

High glass transition temperature (T_g) and good mechanical properties of PES are expected to improve these properties of SPEEK/PES blends. However, on blending with PES, SPEEK also shows lower water uptake, proton conductivity, and methanol permeability.[9,14,22] The water uptake of SPEEK/PES blends was observed to be lower than the theoretical estimate obtained from rule of mixing.[9] It was argued that the ion transport in these blends is influenced more by the ion exchange capacity (IEC) of the SPEEK base polymer, than by the blend ratio.[9] One of the highlights of the present work is to investigate the relative influence of IEC on the properties of the base polymer and the blends with various blend ratios. The proton conductivity, water uptake, and methanol permeability have been shown to vary from 2 to 34 mS/cm for SPEEK/PES blends of different compositions.[22] SPEEK/PES blends exhibit a single glass transition, and positive deviation when compared to T_g predicted by the rule of mixing.[22] The main objective of this work is to understand the effect of microstructure and morphology on the proton conductivity and the water uptake characteristics in blends of SPEEK with PES. SPEEK with different degrees of sulfonation (DS) were prepared, and their properties are compared with different blend ratios of SPEEK/PES. One of the objectives of this work is to also compare SPEEK and SPEEK/PES blends of similar IEC. The results of water uptake characteristics, proton conductivity, thermo-mechanical properties, and scanning electron microscopy observations are analyzed for SPEEK and SPEEK/PES blends. An attempt is made to arrive at suitable microstructure that explains the observed properties.

EXPERIMENTAL

Materials
Medium grade PEEK powder (450PF) was obtained from Victrex, UK (T_g = 143°C, $\langle Mw \rangle$ = 45 kg/mol). PES was provided by BASF India limited, Mumbai (Ultrason® E6020P, $\langle Mw \rangle$ = 51 kg/mol, M_n/M_w = 3.5). Sulfuric acid (98% pure), HCl and NaCl of analytical grade were obtained from Merck Chemicals, Mumbai. N-Methyl-2-Pyrrolidone (NMP, 99.5% pure) was received from Sisco Research Laboratories Ltd, Mumbai. NaOH pellets obtained from Ranbaxy Fine Chemicals, Mumbai, India. All polymers and chemicals were used as received.

Sulfonation of PEEK
Random sulfonation of PEEK was carried out using sulfuric acid (98% conc).[8–10] PEEK was dissolved in sulfuric acid with constant stirring at 40°C. The reaction time was varied to obtain SPEEK of different DS. To terminate the sulfonation reaction, the solution was decanted into large excess of ice-cold water under continuous mechanical stirring. The SPEEK polymer was then filtrated and washed thoroughly until pH ∼ 6, and dried at 80°C for 24 h. Dried SPEEK was stored in desiccators for further use.

Preparation of the Membranes
Membranes were prepared by stirring and dissolving 10 wt % SPEEK in NMP. The homogeneous solution was cast in Petri dishes and dried in an air oven for 72 h at 60°C and at 100°C for 6 h to obtain membranes of desired thickness. The membranes were further dried in a vacuum oven for 2 days at 100°C to remove traces of NMP. After cooling to room temperature, the membranes were treated with $1M$ H$_2$SO$_4$ solution for 1 day at 25°C and subsequently rinsed with water several times until the washed solution reaches pH of 7. All the membranes were kept in distilled water prior to testing. The thicknesses of the dried SPEEK membranes were 150 ± 10 μm.

SPEEK of IEC 2.22, 1.99, 1.8 meq/g (DS of 83, 71, and 63%, respectively) was blended with PES by preparing individual solutions of 10 wt % each and mixing them by mechanical stirring, in different blend ratios (SPEEK/PES, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 20/80) at 25°C temperature for 24 h. Membranes were characterized for the water uptake, proton conductivity, and the morphology. The solutions were cast to prepare the blend membranes, treated with $1M$ H$_2$SO$_4$, and stored in a desiccator. A Perkin Elmer Spectrum FTIR was used to obtain the infrared spectra of the membranes.

Water Uptake
The water uptake of the 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 blotted dry carefully using tissue paper) and weighed immediately on a microbalance. The equilibrium water uptake (WU in wt %) of the membrane is given by,

$$WU = \frac{w_s - w_d}{w_d} \times 100 \tag{1}$$

where w_s is the weight of the saturated wet membrane and w_d is the weight of the dry membranes.

λ (ratio of the number of moles of water to the number of moles of —SO$_3$H groups) was calculated for the corresponding membranes using the % of water uptake and IEC. λ was calculated using

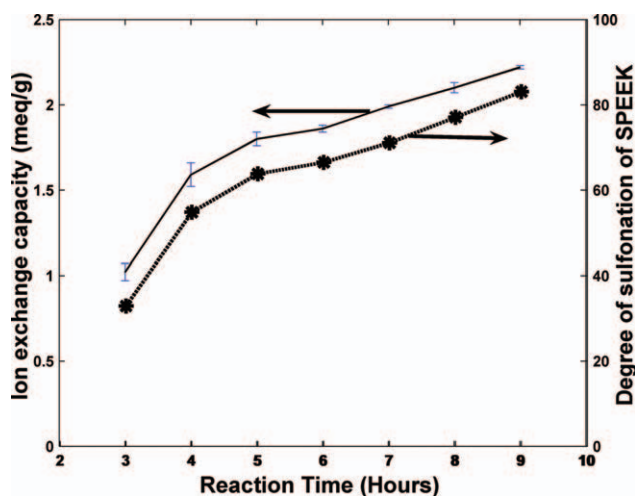$$\lambda = \frac{WU}{M_{H_2O} \times IEC} \times 10 \tag{2}$$

Figure 1. Variation on IEC and DS with sulfonation reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

where M_{H_2O} is the molecular weight of water (18 g mol^{-1}). λ indicates the number of water molecules per sulfonic acid group, and is used to characterize the ionic group/water interactions in a membrane. Nafion of IEC 0.91 has λ of about 19.[17]

IEC and DS

The IEC of the membranes was determined by the titration method. The membranes after treating with $1M$ H_2SO_4 solution as mentioned earlier, was immersed in 2 mol L^{-1} NaCl for 24 h to exchange protons with sodium ions. The exchanged protons within the solutions were titrated with a 0.01 mol L^{-1} NaOH. The IEC value was calculated by using

$$\text{IEC} = \frac{M_{E,NaOH}}{w_d} \qquad (3)$$

where $M_{E,NaOH}$ is the mol equivalent (meq) of NaOH. The DS (in %) was calculated from IEC using

$$DS = \frac{M_p \times IEC}{1 - (IEC \times M_f)} \times 100 \qquad (4)$$

where M_p is the molecular weight of the polymer repeat unit without the functional group, and M_f is the molecular weight of the functional group with the counter ion ($-SO_3Na$).[7]

Proton conductivity

Proton conductivity of the prepared membranes was measured using AC impedance spectroscopy (PARSTAT 2263 Impedance Analyzer) over a frequency range of 10^2–10^6 Hz with voltage amplitude of 50 mV at 24°C. Measurements in the plane of the membrane were made using two-probe electrode method. The conductivity (σ) of the membrane was obtained using

$$\sigma = \frac{L}{\rho \times A} \qquad (5)$$

where ρ is the membrane resistivity, A is the area of crosssection of circular silver electrodes (1.13 cm^2), and L is the thickness of the membrane.

Contact Angle

The contact angles of water on the membranes were measured using Goniometer (GBX Digidrop Contact angle meter). A single drop of the test liquid (drop volume $\sim$ 5 μL) was placed on the membrane using micro liter syringe, which was rinsed with distilled water in advance. The equilibrium contact angles were measured at 30 $\pm$ 2°C and 80 $\pm$ 3% RH. For each membrane, the contact angles were measured six times at different positions on the membrane and the average values are reported. Variation in contact angle was found to be within $\pm$1.5°.

Mechanical Properties

Tensile properties of the membranes were determined using a Universal Testing Machine (Zwick Roel 1464). Samples were prepared according to ASTM standard (D882-01) for the tensile testing. Tests were performed at 25°C and 55% relative humidity and at a crosshead speed of 1 mm/min. For each test result reported, measurements were made on at least three samples.

Miscibility and Morphology

Miscibility of SPEEK/PES blends were studied using a dynamic mechanical analyzer (TA Instruments DMA Q800) in the film tension mode from 25 to 250°C at a heating rate of 2°C/min and 1 Hz frequency.

The morphology of the blends was investigated using high resolution scanning electron microscope (HRSEM) FEI Quanta 200 equipment. To study the morphology, the membranes were subjected to selective etching using Fenton's reagent. SPEEK is known to dissolve in Fenton's reagent,[33] while PES does not. Prior to the treatment, the membranes were dried in a vacuum oven at 60°C for 12 h. Dry membranes were kept in Fenton's reagent at 70°C for a period of 30 min. The membrane surface was blotted dry carefully using tissue paper before taking the SEM images. Treated membranes were dried at 25°C for 12 h before the SEM examination. Fenton's reagent was prepared by dissolving $Fe(NH_4)_2(SO_4)_2$ (4 ppm) in 3% aqueous H_2O_2 solution.
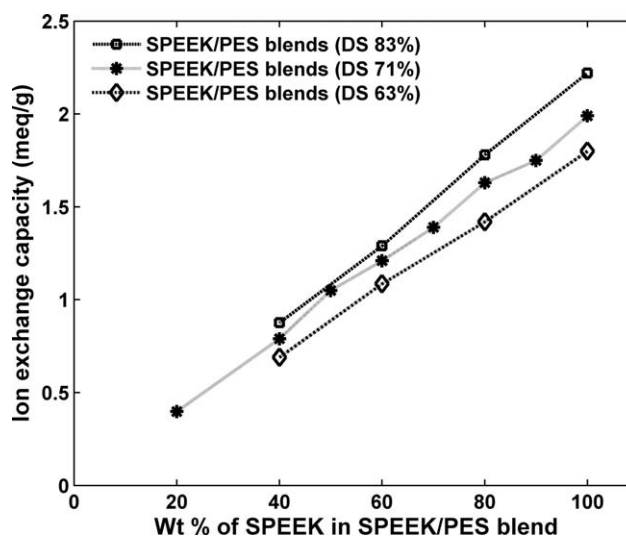

Figure 2. Influence of blend ratio on IEC in different blends.
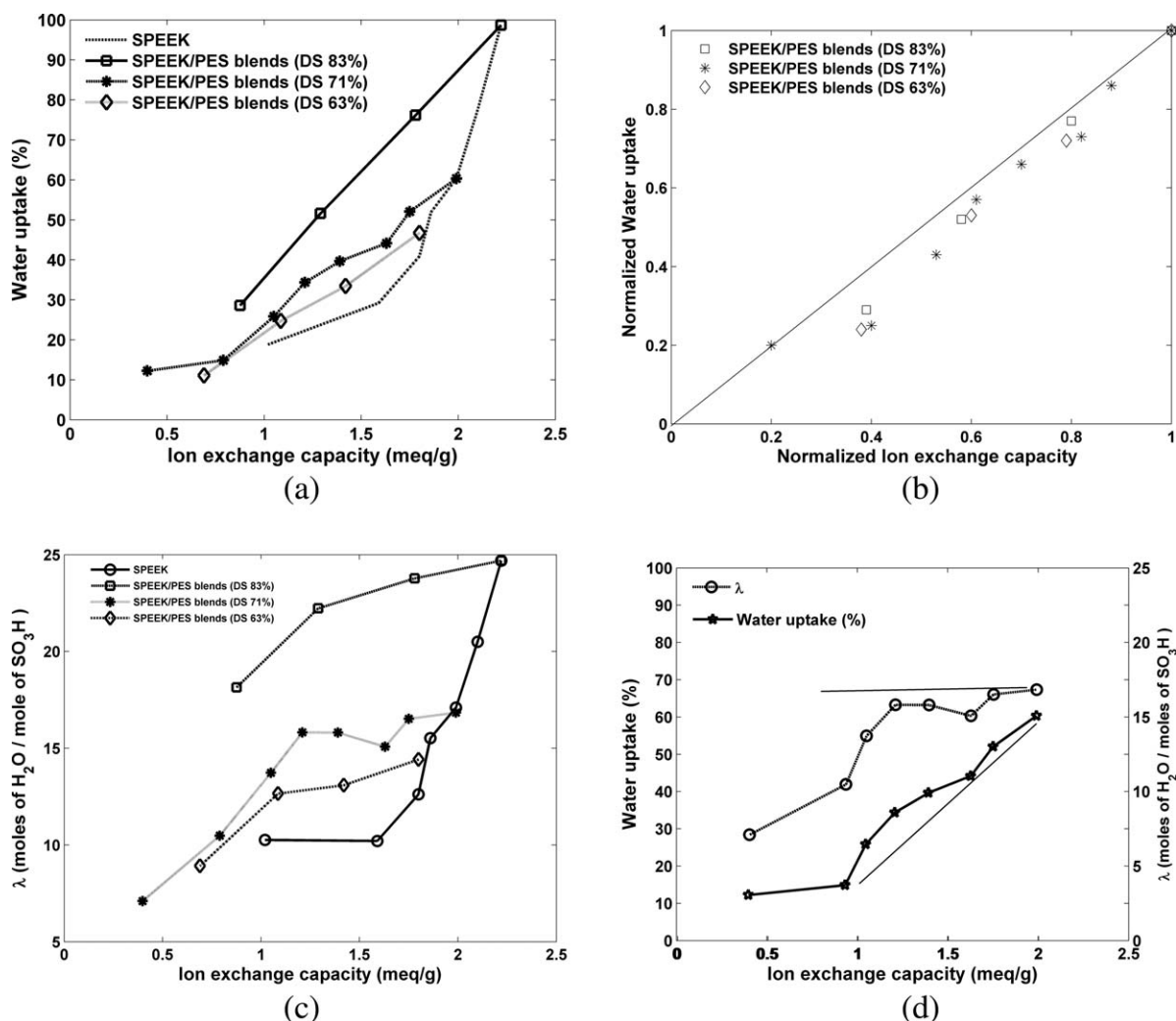
Figure 3. (a) Water uptake of SPEEK and SPEEK/PES blends as a function of IEC. (b) Normalized water uptake of SPEEK/PES blends as a function of IEC. (c) Variation of λ in SPEEK and SPEEK/PES blends. (d) Comparison of water uptake and λ of SPEEK/PES blends (DS 71) as a function of IEC. The straight lines are drawn to highlight the different variation of water uptake and λ.

RESULTS AND DISCUSSION

IEC and Water Uptake

The IEC of the membranes gives an indication of the number of accessible functional groups for proton conductivity.[5] SPEEK with varying IEC were prepared by varying the reaction time of PEEK with sulfuric acid. The IEC and the DS of the prepared SPEEK as a function of the reaction time are shown in Figure 1. The IEC and the DS increase with increase in the reaction time of PEEK. For intermediate reaction times (5–9 h), the DS varies linearly with time. The reaction rate is expected to be slow at low and high reaction times, due to the dissolution of PEEK and due to reaction nearing completion, respectively.[15] Figure 2 shows the variation of IEC of SPEEK/PES blends as a function of SPEEK content, for different DS. The IEC of the blends obey the rule of mixing as only the ionic groups of SPEEK in the blend contribute to the IEC.[9] This is observed for all DS investigated in this work, as shown in Figure 2. However, as discussed further in results, most of the properties deviate from the rule

of mixture highlighting the importance of the morphology of the blends.

Figure 3(a) shows the water uptake as a function of IEC for SPEEK and SPEEK/PES blends. Though the water uptake in the SPEEK increases, it is not a linear function of the IEC.[9] It is interesting to note that for the same IEC values, the water uptake of the blends is higher than that of pure SPEEK. This may be due to the fact that, the sulfonic acid groups are distributed in the blends because of molecular level miscibility and thus organized in a more appropriate manner. Wilhelm et al., found that the water uptake decreases on blending SPEEK with PES.[9] For example, the water uptake decreased from 75% for SPEEK (of DS 70%) to 25% for SPEEK/PES 60/40. It was stated that this may be due to the ionic contribution of SPEEK of high DS in the blend that forms morphology suitable for higher water transport. From this work also, we can state that the PES molecules being hydrophobic, would lead to decrease in accessibility of sulfonated molecules, and therefore
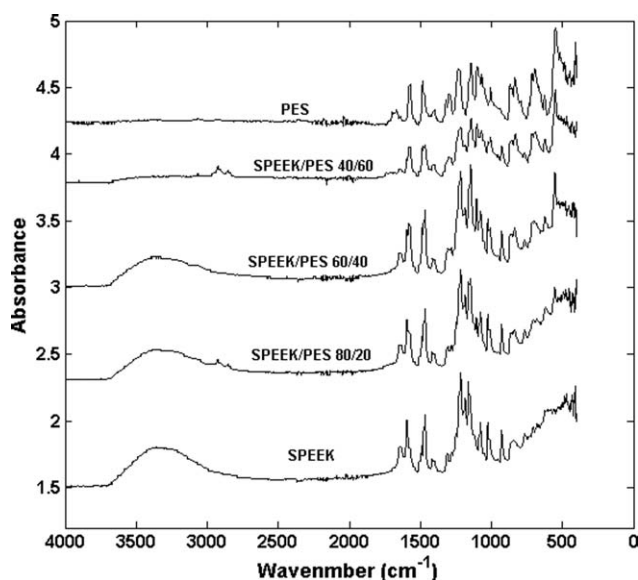
Figure 4. FTIR of SPEEK, PES, and SPEEK/PES blends.

one would expect a decrease in the water uptake. It can also be observed that blends prepared from SPEEK (DS 81%) have higher water uptake; around 50–100% more than the other blends, for different blend ratios. Water uptake decreases drastically from 98 to 29% with the addition of 40% PES (SPEEK DS 71%), shows the advantage of PES in controlling water uptake of blends. Water uptake of Nafion 117 (IEC 0.91 meq/g) is 21%, which is close to the water uptake of SPEEK/PES blends for the same IEC.

With increasing PES content, the IEC of the blends decreases resulting in a decrease in the water uptake of the blends. At IECs lower than 1 (when the PES content is very high), similar amounts of water uptake are observed in SPEEK membranes and in the blend membranes. When the IECs are lower, in blends as well as in SPEEK, the number of sulfonic acid groups is too low for an effective organization of ionic clusters into percolation pathways for ionic transport, as discussed later.

The water uptake is higher in a blend membrane when compared to an SPEEK membrane of the same IEC. This observation, however, does not imply that the addition of PES leads to enhancement in the water uptake of a membrane. To highlight this point, a plot of normalized water uptake with normalized IEC is shown in Figure 3(b). Water uptake and IEC values of blends have been normalized with respect to the water uptake and the IEC of pure SPEEK of respective blends. From the figure, it can be observed that the water uptake is always lower than what is expected from the rule of mixing (diagonal line in the figure) for the blend membranes prepared from SPEEK of a given DS. In summary, when one blend is compared with another prepared with SPEEK of the same DS, water uptake is lower than the mixing rule. However, when a blend is compared with an SPEEK of the same IEC, water uptake is higher.

To examine the implication of these results further, λ (a measure of the number of water molecules per sulfonic acid group)

and its variation with the IEC are shown in Figure 3(c). This variation provides further insights into the microstructure of SPEEK and the blend membranes. Results for SPEEK are described first, followed by results for the blends. λ values for SPEEK remained relatively constant at low IEC values (1 and 1.59 meq/g) but increased above the IEC value of 1.59 meq/g. A constant value of λ, with varying IEC, implies similarity in organization of ionic groups and this is elaborated later in the case of blends also. λ of SPEEK varies between 10 and 24, when the IEC is between 1.59 and 2.22 meq/g. The increase in λ with increasing IEC in the case of SPEEK would be due to the increase in the number of ionic clusters and the resultant increase in water content for given amount of $-SO_3H$ groups.[18] At higher IEC, with a larger number of smaller clusters,[33] the area over which these clusters can associate with water molecules and absorb water is much higher. Therefore, the water uptake is much higher at higher IECs.

The variation in λ with IEC for blend membranes follows a very interesting trend. It appears that at lower PES contents, λ is the same for all the blend membranes and this λ value is the same as that in pure SPEEK membrane. λ remaining constant, with varying IEC, suggests the similarities in the structures of the ionic clusters in SPEEK/PES blends (such as the size and shape of cluster, number of sulfonic acid groups, and their distribution in a cluster, the ratio of ionic groups in clusters to ionic groups not in clusters etc). In Figure 3(d), the water uptake and λ of SPEEK/PES blends (DS-71) are shown together. The λ values of the blend membranes (60–90 wt % of SPEEK content) are almost constant, and are similar to the λ values of corresponding SPEEK. Therefore, it may be stated that the addition of PES does not lead to any significant altering of sulfonic acid clusters (as present in pure SPEEK) in which most of the water is associated with the sulfonic acid groups. Hence, even though IEC is lowered when PES is added, the molecular organization remains similar to that in pure SPEEK. This indicates that PES molecules preferentially reach the hydrophobic regions present in the SPEEK morphology, thereby leaving the ionic clusters
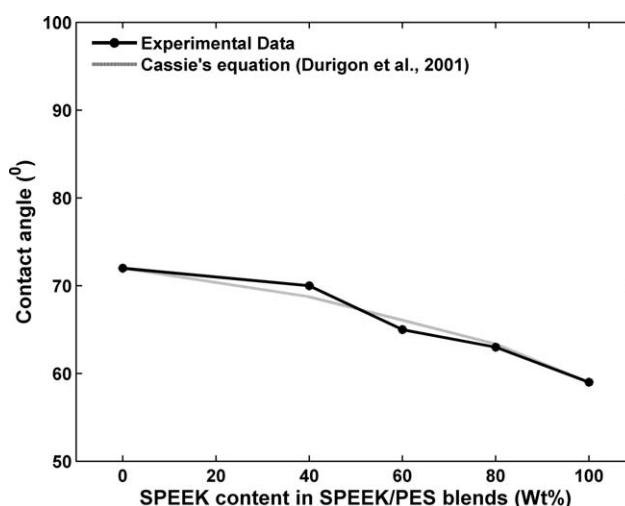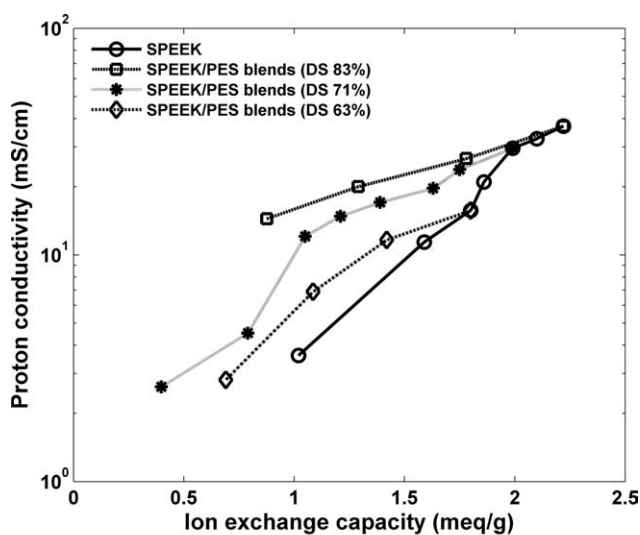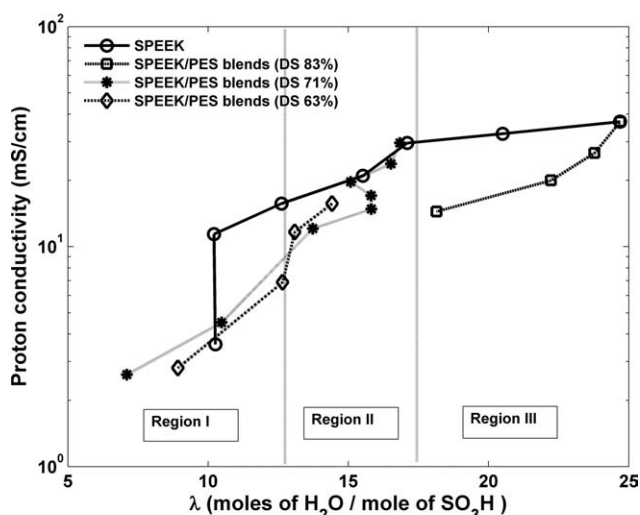

Figure 5. Contact angle of water drop on SPEEK/PES blend surface.

(a)

(b)

Figure 6. (a) Proton Conductivity of SPEEK and SPEEK/PES blends. (b) Variation of proton conductivity with λ for SPEEK and SPEEK/PES blends.

intact. Before describing the influence of blending on the conductivity, FTIR spectra and surface contact angles are discussed.

FTIR spectra of SPEEK and SPEEK/PES blends in the hydrated state are shown in Figure 4. The broad absorption band observed at 3428 cm^{-1} corresponding to —OH group is because of the presence of water in the sample.[7] —OH group peak intensity decreases with increase in PES content and the difference between 60/40 and 40/60 blends is large, as was indicated by λ values as well. Hydration significantly influences the FTIR absorption bands in the case of ionic polymers. No further indications about molecular organizations could be inferred from the FTIR spectra of different blends.

Contact angle is used as a measure of the surface hydrophilicity of the membranes. Figure 5 shows the contact angles of SPEEK, PES, and blend membranes. Contact angles of water on blend
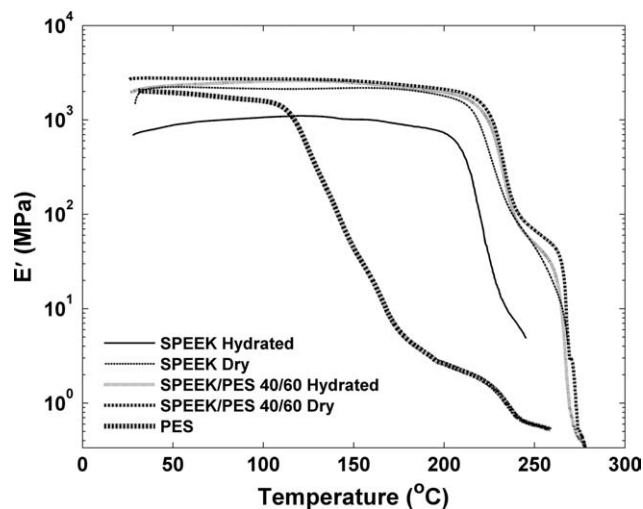

Figure 7. E' as a function of temperature of dry and hydrated SPEEK, SPEEK/PES blends, and PES.

membranes increases with increase in PES content, because of the hydrophobicity of PES. In Figure 5, the contact angles measured for the blends (θ) are compared with Cassie's equation,[34]

$$\cos\theta = f_{SPEEK}\cos\theta_{SPEEK} + f_{PES}\cos\theta_{PES} \qquad (6)$$

where θ_{PES} and θ_{SPEEK} are contact angles measured for PES and SPEEK, respectively. f_{PES} and f_{SPEEK} are area fractions of PES and SPEEK on the surface of the blends ($f_{PES} + f_{SPEEK} = 1$). It can be assumed that the weight fractions of the components are similar to the distributions of these components on the surface. Further, it can be stated that the contact line of the spreading drop would encounter the two components in the same fractions as given by the weight and area fractions. Therefore, weight fractions can be used in eq. (6). As Figure 5 shows, the fit of Cassie's equation is reasonable.
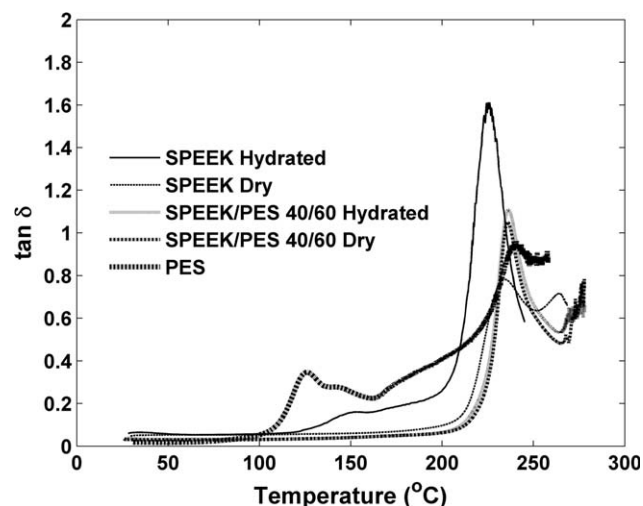

Figure 8. Effect of tan δ as function of temperature of dry and hydrated SPEEK, SPEEK/PES blend, and PES.
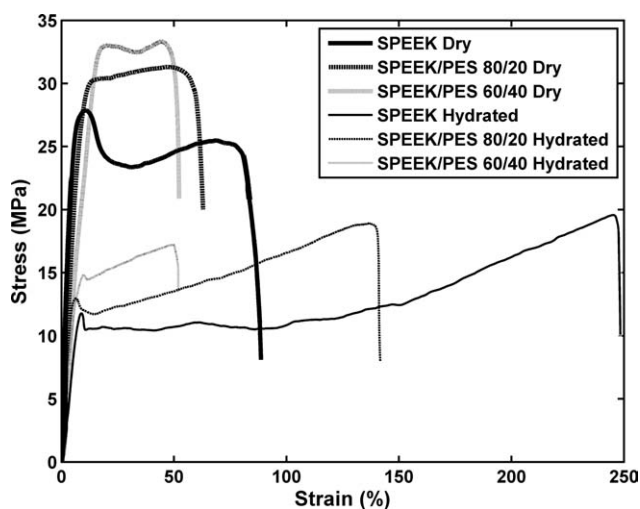
Figure 9. Effect of blending and hydration on the stress–strain behavior of SPEEK and SPEEK/PES blends.

Proton Conductivity

Proton conductivities of hydrated membranes were obtained from AC impedance spectroscopy. The dependence of conductivity on IEC is shown in Figure 6(a). With the increase in IEC, water uptake increases and it facilitates the transport of more protons, thus leading to increase in proton conductivity with IEC.[35] Similar to water uptake, the conductivity of blends is higher than the conductivity of SPEEK of the same IEC. For example, an order of magnitude of variation in conductivity of SPEEK and blends was observed at the IEC value of 1 meq/g. The transport of protons and the amount of water uptake is influenced by similar contributions of the microstructure of the membranes.[35] It is also evident that blends prepared from higher DS show higher conductivity as well as higher water uptake.

Figure 6(b) shows the relationship between proton conductivity and λ. Three regions can be observed in the figure. Proton conductivities are very low for SPEEK and blends in Region I and they increase significantly with an increase in λ. In Region II, proton conductivities are very similar for SPEEK and blends, irrespective of the blend composition and DS of SPEEK. The transition from Region I to II is based on a threshold value of λ, which is required to attain higher levels of conductivity. In Region III, the proton conductivity remains relatively constant even with very significant increase in λ (from 17 to 24). Figure 6(a,b) show that for similar IEC, blends show high proton conductivity but relatively higher λ than pure SPEEK.

Mechanical and Dynamic Mechanical Properties

Since the membranes are very sensitive to hydration, membranes were preconditioned before the mechanical and dynamic mechanical properties were studied. Hydrated condition implies membranes saturated with water, where as dry condition implies membranes dried for 3 h at 80°C prior to the test. Water is known to act as plasticizers in these polymers at low temperatures. Additionally, to understand the effect of temperature and hydration on the viscoelastic properties of sulfonated polymers,

structural changes in the hydrophilic domains should also be considered.[36] The overall performance, therefore, is complex due to the plasticization and structural changes.

Temperature dependence of storage modulus and tan δ of SPEEK, PES and the blend membranes are shown in Figures 7 and 8. Low storage moduli were observed for hydrated membranes at temperatures below 120°C and this behavior is comparable to Nafion.[16] Elastic modulus of hydrated membranes decreases with hydration. Effect of hydration on the variation of elastic modulus is less in the case blend membranes. Storage moduli of SPEEK/PES membranes of different compositions show similar behavior and are close to that of SPEEK membranes. The effect of temperature and hydration on mechanical properties could be due to structural changes in the hydrophilic domains of the SPEEK and blend membranes.[37] The major peak in the tanδ curve in Figure 8 is considered as the glass transition temperature of SPEEK, PES and their blends. Sulfonation of PEEK increases the glass transition temperature of PEEK (T_g) from 143 to 226.1°C because of the incorporation of —SO$_3$H ionic side groups. It is known that the incorporation of ionic groups affects the glass transition temperature, and it increases with increase in ionic content.[38] A small peak indicating a second transition at higher temperature ($>T_g$) is also observed in the case of dry SPEEK, and this is attributed to the relaxation in the ion cluster region.[39] This transition is not observed in the case of hydrated SPEEK indicating rearrangement of the ion groups in the hydrated state. Storage modulus is lower for the hydrated SPEEK membrane throughout the temperature range since water acts as a plasticizer.

Two transitions can be observed in the case of PES, one around 145°C, which corresponds to the glass transition of the material (drop in the storage modulus can be observed at this temperature range) and another small secondary peak around 240°C. The blends of SPEEK and PES show only one transition indicating molecular level mixing in the case of these two polymers. It should be noted that this mixing is along with the underlying clusters because of sulfonic acid groups. However, these clusters are present in the pure SPEEK as well as the blend membranes. Effect of hydration on storage modulus and tanδ is less in the case of blend membranes. In addition, the behavior of the blend membranes (dry and wet conditions) is closer to that of dry SPEEK. Both these are due to the presence of hydrophobic polymer, PES in the blends. Storage modulus and tan δ of SPEEK/PES 40/60 are less affected on the water content.

Table I. Young's Modulus of SPEEK/PES Blends

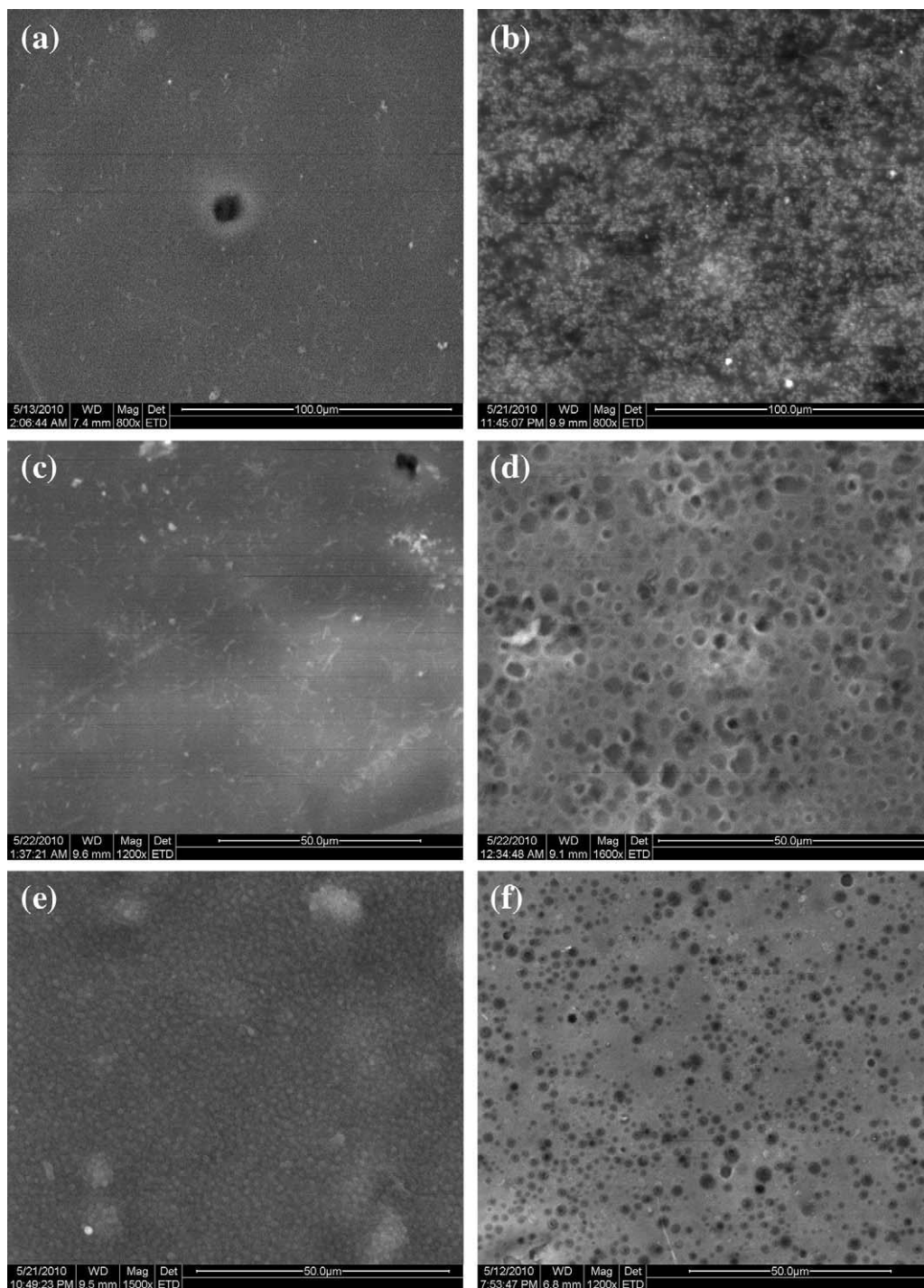| Membranes	Young's modulus (MPa)
SPEEK (Dry)	4.8
SPEEK/PES 80/20 (Dry)	3.6
SPEEK/PES 60/40 (Dry)	2.2
SPEEK (Hydrated)	1.5
SPEEK/PES 80/20 (Hydrated)	2.6
SPEEK/PES 60/40 (Hydrated)	2.4

Figure 10. SEM micrographs of the surface of SPEEK/PES blends after etching with Fenton's reagent: (a, c, e) SPEEK/PES 60/40 (SPEEK DS 63, 71, 83%, respectively) (b, d, e) SPEEK/PES 40/60 (SPEEK DS 63, 71, 83%, respectively).

Stress–strain behavior were studied at 25°C on membranes, which were hydrated as well as on those equilibrated under ambient conditions (55% RH) (Figure 9). SPEEK conditioned at 55% RH shows high yield stress. The elongation at break increases in hydrated SPEEK as well as in the hydrated blends. As was observed in dynamic mechanical analysis, the effect of hydration is less in the case of blends with higher PES content.

Young's moduli were calculated from the slope of the stress–strain curve in the elastic (small strain $\sim$ 5%) region and are given in Table I. The modulus decreased with hydration in the case of SPEEK. However, in the case of blends the tensile moduli changed less for blends with higher PES content.

The mechanical behavior observed from the DMA and the stress–strain response shows the molecular level mixing in
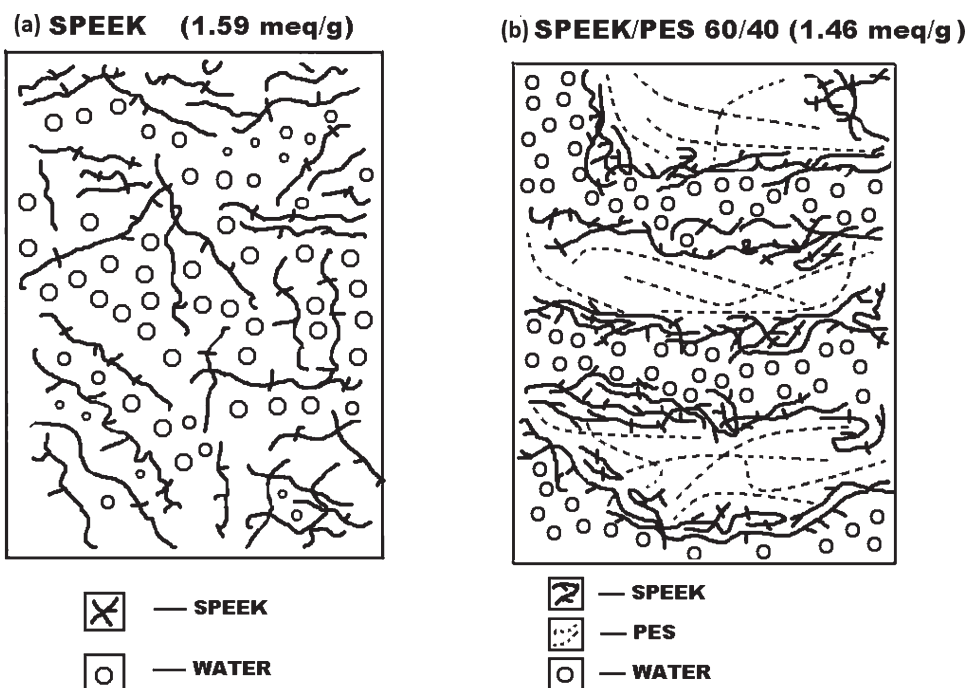
Figure 11. Schematic representation of the effect of PES on morphology of the blend membranes (a) SPEEK (b) SPEEK/PES blend with equivalent IEC as (a).

SPEEK/PES blends, as is evident from the observation of a single glass transition. The other feature of molecular level organization that was observed in case of dynamic mechanical response was the secondary tanδ peak due to ion clusters. The structural features of these blends, which are to do with cluster size, shape and numbers, and their organizations, do not seem to contribute to mechanical response as reported here. However, as was argued earlier, the structural features of ionic clusters and their organization is very important in understanding the variation of water uptake and conductivity in these blend systems. To investigate these features further, surface morphology and conductivity modeling were carried out as described below.

Surface Morphology

HRSEM was used to analyze the surface morphology of the blend membranes after selective etching of one of the phases. SPEEK is soluble in Fenton's reagent, whereas PES is not. Therefore, the morphology of blend membranes was analyzed after etching out the SPEEK using Fenton's reagent. Both SPEEK and SPEEK/PES 80/20 membranes dissolved in Fenton's reagent in less than 30 min, indicating selective susceptibility of SPEEK to Fenton's reagent.

Figure 10 shows the SEM micrographs of membranes prepared from different SPEEK/PES blends and DS. SPEEK/PES 60/40 membranes shown in Figure 10(a,c,e) exhibit a more uniform surface morphology and do not show any specific features because of etching of SPEEK. Therefore, even with 40% PES no phase separation is observed, at the scales observed in SEM. This is irrespective of the different DS of SPEEK. SPEEK/PES 40/60 membranes after etching with Fenton's reagent are shown

in Figures 10 (b,d,f). A comparison of the two sets of SEM micrographs shows the difference in the morphology of SPEEK/PES 60/40 and SPEEK/PES 40/60 blends. SPEEK forms a miscible blend in SPEEK/PES 60/40, whereas the addition of further PES content in SPEEK leads to phase separation as can be observed in SPEEK/PES 40/60 blends. Since, the DMA for these blends showed a single T_g, the observed morphology in SEM is most likely due to the kinetics of dissolution of SPEEK during etching from the blend. Therefore, the phase separated
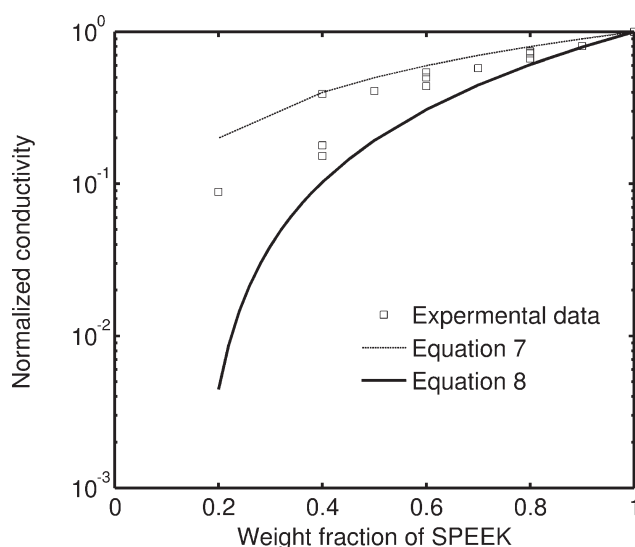

Figure 12. Variation of conductivity with composition for different blends investigated in this work.

morphology is evident only in the case of higher content of PES. The miscibility in the SPEEK/PES 60/40 blend can be correlated to its higher water uptake and proton conductivity in comparison to the SPEEK/PES 40/60 blend. Cocontinuous morphology has been observed earlier by blending SPEKK of two different IECs.[40]

Microstructure of SPEEK and SPEEK/PES Blends

Results presented in this work suggest that blending SPEEK of higher DS with hydrophobic, nonionic polymer-like PES may help to attain similar morphology to that of Nafion. For pure SPEEK, it is known that with higher DS, increase in the number of ionic clusters leading to channel formation.[41] The sulfonic groups of SPEEK in the blend membranes form hydrophilic domains and channels due to larger hydrophobic and hydrophilic difference between the polymer back bone and the ionic side groups. For the blends, it is proposed that the clusters/channels are modified because of the presence of hydrophobic PES. In SPEEK/PES blend membranes, the hydrophobic/hydrophilic difference is intermolecular, where as in Nafion and in SPEEK, the difference is intramolecular.[39] The microstructure formed due to the addition of PES is shown in a schematic representation in Figure 11. It should be noted that the hydrophobic/hydrophilic domain separation in the blend membranes may not be as effective as in the case of Nafion. However, PES does lead to a microstructure that can be more conducting than SPEEK with the same IEC. Proton transport in the polar clusters and interconnecting channels may occur due to the regulated interstitial water, narrow water filled channels, number of $-SO_3H$ groups, the segmental motion of SPEEK backbone, and placement of PES in the blend membrane. Ion transport is controlled by percolation, which depends on the connectivity of ionic clusters/channels. Therefore, it may be concluded that the blend membranes may have more bulkier ionic aggregates and better connected channels because of the presence of SPEEK of high DS [as shown in Figure 11(b)]. For the equivalent IEC pure SPEEK (which would have a lower DS), will is likely to have smaller clusters/channels [as shown in Figure 11(a)].

Microstructural features shown in Figure 11 can also be corroborated by observing the variation of conductivity as a function of blend composition. Figure 12 shows the normalized conductivity (normalized with respect to conductivity of pure SPEEK) as a function of blend composition for all the blends investigated in this work. This variation of the conductivity can be understood by comparing with variation predicted by empirical models. One of the simplest models is based on parallel rule of mixing, which implies an additive contribution from the conductivity of pure components,[41]

$$\sigma_b = w_{SPEEK}\sigma_{SPEEK} + w_{PES}\sigma_{PES} \qquad (7)$$

where σ_{SPEEK} and σ_{PES} are conductivities of SPEEK and PES. The conductivity of blend, with SPEEK and PES weight fractions of w_{SPEEK} and w_{PES}, is σ_b. For cocontinuous morphology, where both the components would form percolating networks, the variation of conductivity can be described by the following equation,[41]

$$
\begin{aligned}
\sigma_b = {} & \left(\frac{w_{SPEEK} - 0.156}{0.844}\right)^{1.833}\sigma_{SPEEK} + \left(\frac{w_{PES} - 0.156}{0.844}\right)^{1.833}\sigma_{PES} \\
& - \left[1 - \left(\frac{w_{SPEEK} - 0.156}{0.844}\right)^{1.833} - \left(\frac{w_{PES} - 0.156}{0.844}\right)^{1.833}\right]^2 \\
& \div \left[\left(1 - \left(\frac{w_{SPEEK} - 0.156}{0.844}\right)^{1.833}\right)\frac{1}{\sigma_{SPEEK}}\right. \\
& \left. + \left(1 - \left(\frac{w_{PES} - 0.156}{0.844}\right)^{1.833}\right)\frac{1}{\sigma_{PES}}\right] \qquad (8)
\end{aligned}
$$

The blend conductivities observed in this work are bounded by the predictions of eqs. (7) and (8), as shown in Figure 12. This again confirms that clusters/channels morphology in blends is less effective than the pure SPEEK, but is more effective than percolating SPEEK. Moreover, when comparing blend of an equivalent IEC with SPEEK, the clusters/channels are better organized in the blend when compared to pure SPEEK.

CONCLUSIONS

SPEEK of varying DS were prepared and blended with PES at different blend ratios. Water uptake and proton conductivity of SPEEK and the blends were studied as function of varying IEC. With increase in IEC, water uptake and proton conductivity increase in SPEEK as well as in the blends. The variation in these properties was examined to understand the underlying morphology of the SPEEK/PES blends. It was shown that at the same IEC, blends have a more suitable microstructure, resulting in higher water uptake and conductivity. Effect of water content on dynamic mechanical analysis and stress–strain behavior of all the membranes was significant and is expected due to sulfonic acid groups. The overall effect of PES was to organize the ionic groups of SPEEK, leading to possibly larger clusters/channels in blends. This leads to better properties for the blend, when compared to pure SPEEK of equivalent IEC.

ACKNOWLEDGMENTS

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