Morphology control of sulfonated poly(ether ketone ketone) poly(ether imide) blends and their use in proton-exchange membranes

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Abstract
Polymer blends based on sulfonated poly(ether ketone ketone) (SPEKK) as the proton-conducting component and poly(ether imide) (PEI) as the second component were considered for proton-exchange membranes (PEMs). The PEI was added to improve the mechanical stability and lower the water swelling in the fuel cell environment. Membranes were cast from solution using N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc). The ternary, polymer/polymer/solvent, phase diagram was determined to provide guidance on how to control the morphology during solvent casting of blend membranes.

For blends of SPEKK (ion-exchange capacity = 2 mequiv/g) with PEI as the minority component, the morphology consisted of dispersed particles of \( \sim 0.5–6 \mu m \). Larger particles were achieved by increasing the PEI content and/or lowering the casting temperature. High-temperature annealing after solution casting did not affect the morphology of blend membranes, due to the low mobility and compatibility of the two polymers.

The possible use of SPEKK/PEI blends in PEMs is discussed in terms of existing theories of ion transport in polymers.

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Keywords: Poly(ether ketone ketone); Poly(ether imide); Polymer blend; Proton-exchange membrane

1. Introduction

The design of proton-exchange membrane (PEM) materials for fuel cells is an especially challenging task. A PEM serves as a solid electrolyte with high proton conductivity, and it also acts as a separator between the anode (hydrogen or methanol) and cathode (oxygen/air) compartments. The separation of the electronic and ionic part is crucial for the fuel cell operation. A certain amount of water is also required to ensure high proton mobility in the acidic PEM materials. High-temperature operation (80–120 °C) improves performance and reduces contamination of the catalysts. Thus, PEM materials need to be stable at high-temperature, high-humidity and in oxidative environments.

Perfluorinated polymer electrolyte membranes such as Nafion® have historically been the principal choice for PEMs. The hydrophobic, fluorocarbon backbone ensures mechanical and chemical integrity, while the sulfonated perfluoroether side-chains provide high proton conductivity when hydrated [1]. Those materials, however, are expensive, have relatively poor resistance to methanol transport, which is important in a direct methanol fuel cell, and have poor mechanical properties when highly swollen by water. Largely motivated by the cost penalty for the fluoropolymers, researchers are actively considering polymer electrolytes based on hydrocarbon polymers [2,3].

Blending polymers is a widely used approach for obtaining materials with certain targeted properties. Each component of the blend can be chosen to fulfill a different requirement. Blends of polymer electrolytes with non-conductive engineering thermoplastics have the potential for developing new materials for application as PEMs for fuel...
Sulfonation of PEKK was performed in a 5% (w/v) mixture of 53/47 (v/v) concentrated sulfuric acid to fuming sulfuric acid [16]. The resulting sulfonated polymer, SPEKK, was precipitated by drop-wise addition of the solution into six volumes of rapidly stirred de-ionized ice water. The SPEKK was filtered, washed repeatedly with de-ionized water to remove excess acid and dried at 60 °C overnight and then under vacuum at 120 °C for 3 days. The sulfonation level was determined by titration [4]. The SPEKK nomenclature used in this paper is SPEKKx, where x is the ion-exchange capacity (IEC), which is expressed as the concentration of sulfonate groups in equivalents per mass. Unless stated otherwise, SPEKK based on PEKK with a T/I ratio of 8/2 was used in this work.

Membranes of SPEKK/PEI blends were prepared by casting 5% (w/v) solutions in N-methyl-2-pyrrolidone (NMP) or dimethylacetamide (DMAc) onto glass plates. The solution volume and the area of the glass plate were fixed. The solvent was allowed to evaporate for about 1 day at 60 °C, after which the films were dried at 120 °C under vacuum for 3 days. The residual solvent present after this procedure as obtained from thermogravimetric analysis was in the range of 3-6 wt% for both casting solvents. Higher PEI loadings resulted in higher residual solvent levels (e.g. 6 wt% for a 20/80 SPEKK/PEI blend) indicative of strong polyimide-solvent interactions. Immersion of SPEKK/PEI membranes in hot water is an effective method to leach out residual solvent. However, due to the limited mechanical integrity of these membranes (see Section 3) this procedure was ruled out in this work.

2.2. Blend characterization

The blend morphology was studied with a Philips 420 transmission electron microscope (80 kV) and a Topometrix Explorer atomic force microscope (AFM). The sample preparation for both techniques consisted of embedding membranes in an Epon™, Araldite™ embedding mixture, followed by ultra-microtomy with a diamond knife to obtain thin sections. Sections were placed on copper grids for the TEM specimens and on pre-cleaned glass cover slips for AFM. The TEM specimens were treated with a 1 M Pb(NO₃)₂ aqueous solution, which preferentially stains the SPEKK phase. In the case of the AFM samples, the sections were floated on water and drying them on glass resulted in shrinkage of the swollen ionomer phase. This produced an SPEKK phase that was lower in topography than the PEI. A Philips ESEM 2020 scanning electron microscope (30 kV) was used to image the blend morphology of cryogenic fractured membranes. Particle size histograms were obtained from image analysis of the micrographs. A normal distribution was used to obtain an estimate of the numerical average and standard deviation. In case of elliptically shaped particles, caused by compression during sectioning, the equivalent diameter was calculated.

The thermal properties of membranes were measured using a TA Instruments Q100 differential scanning calorimeter (DSC) for phase separation analysis and a TA Instruments Q2000 PerkinElmer instrument for crystallinity determination. The membranes were scanned at a heating rate of 10 °C/min from room temperature to 200 °C in a nitrogen atmosphere. The melting point (Tm) and crystallinity (Xc) were calculated from the DSC thermograms.

The thermal stability of the membranes was determined by thermogravimetric analysis (TGA) using a TGA Q500 PerkinElmer instrument. The samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The mass loss (wt%) was determined as a function of temperature.

The mechanical properties of the membranes were measured using a Universal Testing Machine (UTM) according to the standard procedure for dynamic mechanical analysis (DMA). The samples were conditioned at 40 °C and 95% relative humidity for 24 hours prior to testing. The tensile strength (TS), Young’s modulus (YM), and elongation at break (EAB) were determined from the stress-strain curves obtained at a crosshead speed of 5 mm/min.

The proton conductivity of the membranes was measured using a 4-probe conductivity meter (Gibson 4377) at 80 °C. The membranes were conditioned at 80 °C and 95% relative humidity for 24 hours prior to testing. The proton conductivity (σ) was calculated from the resistance (R) of the membrane using the equation σ = 1/R × L/A, where L is the thickness of the membrane and A is the area of the membrane.

The water uptake (WU) of the membranes was measured by immersing the membranes in de-ionized water at room temperature for 24 hours. The membranes were then dried at 80 °C for 24 hours and the dry weight (w) and wet weight (w′) were determined using a microbalance. The water uptake was calculated using the equation WU (%) = (w′ - w)/w × 100.

The diffusion coefficient (D) of water in the membranes was determined using the Fickian diffusion model. The membranes were conditioned at 80 °C and 95% relative humidity for 24 hours prior to testing. The membranes were immersed in de-ionized water at room temperature and the change in weight was monitored as a function of time. The diffusion coefficient was calculated from the slope of the logarithm of the weight change vs. time using the equation D = k/L², where k is the slope of the curve and L is the thickness of the membrane.

The swelling behavior of the membranes was studied using the equilibrium swelling ratio (ESR). The membranes were immersed in de-ionized water at room temperature for 24 hours and then dried at 80 °C for 24 hours. The dry weight (w) and wet weight (w′) were determined using a microbalance. The equilibrium swelling ratio was calculated using the equation ESR (%) = (w′ - w)/w × 100.

The stability of the membranes was determined by accelerated aging tests. The membranes were conditioned at 80 °C and 95% relative humidity for 24 hours prior to testing. The membranes were then exposed to an accelerated aging environment of 80 °C and 100% relative humidity for 24 hours. The thermal stability of the membranes was measured using a TGA Q500 PerkinElmer instrument. The samples were heated from room temperature to 600 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. The mass loss (wt%) was determined as a function of temperature.

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calorimeter (DSC). A Solartron SI 1260 frequency response analyzer combined with a Solartron SI 1287 potentiostat was used to measure the proton conductivity of hydrated membranes. Turbidity measurements on ternary solutions were obtained by evaporating the solvent at 60 °C. Solutions with increasing polymer concentrations (as the solvent evaporated) were allowed to equilibrate at 25 °C for about 1 h. When a cloudy mixture was obtained, a small amount of solvent was re-added to obtain a better estimate of the cloud point.

3. Results and discussion

3.1. Sulfonated PEKK membranes

Thermogravimetric analysis indicated that PEI was thermally stable up to 460 °C, but desulfonation of SPEKK occurred at ca. 260 °C [4]. The glass transition (Tg) of the PEKK increased from 160 without sulfonation to 215 °C for SPEKK2.6. This increase, which is found in other sulfonated polymers, is attributed to a reduction of chain mobility due to hydrogen bonding between sulfonic acid groups. Water significantly plasticized SPEKK. For example, when equilibrated at 98% relative humidity (R.H.), the Tg of SPEKK2.0 decreased from 200 to 60 °C. The water content of that membrane at 25 °C corresponded to a hydration number, n(H2O)/n(SO3H), of 10; a melting enthalpy observed by DSC accounted only for seven water molecules/SO3H indicating that three molecules/SO3H were strongly bound to the sulfonic acid groups. A detailed analysis of the effect of water content on the Tg of SPEKK was discussed elsewhere [6]. This result agrees with similar data obtained for NafionTM and sulfonated poly(arylene ether sulfone) [17]. With regard to a PEM candidate, the large Tg decrease of SPEKK due to water is of concern, because the mechanical properties of a PEM usually deteriorate above the Tg of the hydrated membrane [18,19].

The room-temperature proton conductivity of hydrated SPEKK membranes increased exponentially with sulfonation level [4]. Logically, this is due to the increase in the concentration of sulfonic acid sites, which form the locus for proton transport, and the increase in water uptake, which facilitates proton mobility in the membrane [20]. SPEKK2.0 had a conductivity of σ = 0.08 S/cm at 25 °C and 98% R.H., which is comparable to NafionTM 112 (IEC = 0.9 mequiv/g). The hydration number for the SPEKK2.0 membrane at 98% R.H. was 10, which is comparable to the value of 12 reported for NafionTM [21]. Although the fuel cell performance (voltage versus current) of SPEKK in a membrane electrode assembly was similar to NafionTM, [2] SPEKK’s with IEC ~2.0 mequiv/g swelled excessively (e.g. SPEKK1.9 swelled 50% in water at 60 °C) and when the IEC > 2.0 mequiv/g, membrane materials dissolved partly in water (SPEKK2.4 dissolved in water at 80 °C). Obviously, excessive swelling and/or dissolution compromise the long-term durability of the membrane.

3.2. Ternary (SPEKK/PEI/solvent) phase diagrams

Knowledge of the phase diagram is important for optimizing and controlling the evolution of the blend morphology during solution casting. Ternary phase diagrams were obtained by measuring cloud points of ternary mixtures of the polymers and NMP during solvent evaporation, see Fig. 1. NMP is a better solvent for SPEKK2.0 than for PEI, and no cloud point was detected for a binary SPEKK2.0/NMP mixture. At the cloud point, a transparent mixture could be obtained by increasing the temperature, which indicates that these ternary solutions exhibited upper critical solution temperature behavior. Fig. 1 shows that a small amount of PEI in an SPEKK2.0/PEI/NMP mixture results in phase separation during the course of solvent evaporation. When the ratio of SPEKK2.0 to PEI was 50/50, phase separation occurred at the highest solvent concentration.

Fig. 2 shows that the solubility of 50/50 mixtures of SPEKK and PEI in NMP decreased substantially as the sulfonate concentration increased, which can be the result of stronger ion-dipole interactions in the ionomer or a decreasing compatibility between SPEKK and PEI. Evidence of the latter effect will be provided later in the paper. There was also a strong isomer effect in the solubility behavior. SPEKK prepared from PEKK with I/I = 8/2 was soluble in NMP and DMAc only at higher sulfonation levels (IEC > 1.6 mequiv/g), while the SPEKKs based on I/I = 6/4 were soluble for sulfonation levels as low as 0.8 mequiv/g [4]. Those results are most likely due to the greater persistence of crystallinity in the stiffer PEKK I/I = 8/2 isomer after sulfonation.

![Fig. 1. Ternary phase diagram of SPEKK2.0/PEI/NMP at 25 °C: transparent solutions (O), cloudy solutions (▲), dashed line is drawn to separate the miscible from the immiscible region.](image-url)
also on the kinetics of phase separation. Both the thermodynamics and kinetics are dependent on a variety of material and processing parameters, including the solvent used, the T/I ratio of the PEKK, the sulfonation level, the blend composition, the casting temperature and the rate of solvent removal.

Fig. 1 indicates that for the SPEKK/PEI blends, phase separation occurs at relatively low polymer concentrations. One or both co-existing phases freeze when their $T_g$s approach the casting temperature. From that point on, further morphology development is diffusion-limited. Table 1 lists the $T_g$s measured by DSC for various polymer concentrations of solutions of a 50/50 (w/w) blend of SPEKK2.0 and PEI in NMP. According to those results, if one casts a 5% (w/v) solution of 50/50 SPEKK2.0/PEI from NMP at 60 $^\circ$C, which was a typical casting temperature used to produce these blend membranes, the $T_g$ of one of the phases exceeds the casting temperature in the range of 32–40 wt% polymer. Fig. 1 indicates that phase separation occurs below 20 wt% polymer for this ternary blend, so there is little kinetic barrier to the achievement of an equilibrium morphology during the early stages of phase separation during solution casting under those conditions.

### Table 1

<table>
<thead>
<tr>
<th>Polymer concentration (w/v, %)</th>
<th>$T_g$ of phase 1 ($^\circ$C)</th>
<th>$T_g$ of phase 2 ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>$&lt; -60^\circ$</td>
<td>19</td>
</tr>
<tr>
<td>21</td>
<td>$&lt; -80^\circ$</td>
<td>59</td>
</tr>
<tr>
<td>32</td>
<td>$-75^\circ$</td>
<td>88</td>
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<tr>
<td>40</td>
<td>$-7^\circ$</td>
<td>88</td>
</tr>
<tr>
<td>93</td>
<td>177$^\circ$</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>214$^\circ$</td>
<td></td>
</tr>
</tbody>
</table>

The samples were prepared by evaporating solvent from a 5% (w/v) solution at 60 $^\circ$C.

* No $T_g$ detectable within the DSC temperature range.

* Overlapping $T_g$s cannot be resolved.

### 3.3. Blend morphology

Fig. 3 shows the morphology of an 85/15 (w/w) blend of SPEKK2.0 with PEI cast from a 5% (w/v) NMP solution at 60 $^\circ$C. As predicted from the ternary phase diagram in Fig. 1, a
heterogeneous morphology is formed during solution casting. Three microscopic techniques were used to characterize this morphology. SEM was conducted on freeze-fractured samples and showed a dispersed-phase morphology of spherical submicron particles. A similar morphology was previously reported for SPEEK/PEI blends [8]. However, these micrographs depend on the quality of the fracture and are difficult to obtain for higher PEI contents. Therefore, TEM and AFM of microtomed sections were primarily used to characterize the membrane morphologies. Note that the particles imaged by TEM and AFM appear elliptical due to the compression caused by the sectioning procedure. The preferentially stained SPEKK-rich phase (see Section 2), constitutes the dark regions in Fig. 3. In case of AFM, the ionomer phase corresponds to areas that are lower in topography (darker regions in Fig. 3). In case of AFM, the ionomer phase stained SPEKK-rich phase (see Section 2), constitutes the dark regions in Fig. 3. Histograms of particle sizes (not shown) were obtained from image analysis of the micrographs, and for each microscopy technique, the diameter of the dispersed particles averaged ∼0.55 μm.

Another indication of a phase-separated morphology in a polymer blend is the observation of two glass transitions. Because the T_g's of SPEKK and PEI are close, DSC was unable to distinguish two co-existing phases in the cast films. Only a single, though broad, composition-dependent T_g was detected by DSC, which in the absence of the microscopy observations might lead one erroneously to conclude a single-phase morphology. A similar discrepancy between the observations of an apparent single T_g by DSC and two phases by microscopy (Fig. 3) has resulted in conflicting conclusions concerning the phase behavior of SPEEK/PEI blends [7–12].

A second method used to resolve the two phases by thermal analysis was to neutralize the SPEKK phase to its Na-salt by immersing the SPEKK/PEI membranes in aqueous sodium chloride solutions. The stronger intermolecular ionic interactions present in the salt form of SPEKK results in a considerable T_g increase [4], thus effectively separating the T_g's of the SPEKK and PEI-rich phases. Microscopic analysis confirmed that the blend morphology was unaffected by this "Na-staining" procedure. The DSC thermograms of the neutralized cast SPEKK/PEI blend films in Fig. 4 show two T_g's close to those of the pure constituents, which indicates phase-separation of pure or nearly pure ionomer and PEI phases. That result agrees with the phase diagram in Fig. 1, which indicates that two nearly pure phases should form due to the early phase separation from solution. Increasing the PEI content from 2.5 to 25 wt% in SPEKK2.0/PEI membranes cast from NMP at 60°C resulted in larger particle sizes, see Fig. 5. According to the ternary phase diagram in Fig. 1, increasing the PEI content in that range also increased the concentration of solvent remaining at the cloud point. As a result, the T_g of the mixture was lower at this point and the phase-separated morphology, i.e., the particle growth, could evolve for a longer time during solvent evaporation until diffusion limitations froze in the morphology. For PEI contents greater than 25 wt%, and especially 50 wt%, the SPEKK2.0/PEI blends exhibited a grossly macroscopic phase-separated morphology, as shown in Fig. 6A and B. The 50/50 composition corresponds to the cloud point in Fig. 1 with the highest solvent concentration. The presence of micrometer-sized particles within the grossly phase-separated structure (Fig. 6A and B) also indicates that macroscopic phase separation might be followed by secondary phase separation resulting in inclusions of micrometer-sized particles.

For comparison, the same 50/50 SPEKK2.0/PEI blend used to prepare the samples for the micrographs in Fig. 6A and B were precipitated from sulfuric acid in de-ionized water and the resulting morphology is shown in Fig. 6C. In this case, a homogeneous morphology was frozen-in upon precipitation. This again underlines the importance of understanding the interplay between the thermodynamics and kinetics of phase separation during the solution casting procedure.
Fig. 6. AFM micrographs of SPEKK2.0/PEI 50/50: cast from a 5% (w/v) NMP solution at 60 °C (A) and (B), and precipitated from sulfuric acid in de-ionized water (C); micrograph (B) indicates the epoxy resin used in the embedding procedure surrounding the PEM.

The $T_g$‘s of the coexisting phases were found to be within 5 °C of the pure components ($T_g^{(PEI)} = 220$ °C and $T_g^{(NaSPEKK2.0)} = 364$ °C). This again indicates that during solution casting a PEI/NMP and a SPEKK/NMP phase are quickly formed during drying after the onset of phase separation.

3.4. Effect of sulfonation on phase separation of SPEKK/PEI/solvent mixtures

PEKK is partially miscible with some polyimides and exhibits an upper critical solution temperature (UCST) above 400 °C [13]. Miscibility has been attributed to the similarity in the molecular structure of the two polymers. No specific interactions have been identified for this polymer pair. In general, the compatibility of poly(aryl ether ketone)s with polyimide increases as the ketone content increases, which may be a consequence of a closer match of the rigidities of the two polymers [13]. Sulfonation of the PEKK could affect miscibility with PEI in several ways: (1) changes in the rigidity of the chain and the dissimilarity of the ionomer structure with the polyimide might decrease miscibility, (2) intramolecular associations of the sulfonate groups within the ionomer might also decrease miscibility with the polyimide, but (3) any intermolecular associations between the sulfonic acid and imide groups, e.g. hydrogen bonding interactions [10] or electron donor–acceptor complexes [11,12], should improve miscibility.

The effect of sulfonating the PEKK polymer backbone on the phase behavior of 50/50 blends of SPEKK and PEI is shown in Fig. 7. For the lowest sulfonation level used, IEC = 0.8 mequiv/g (which corresponds to 26 mol.% of SO$_3$H groups per repeat unit), the blend was miscible in the amorphous phase. Phase separation occurred, however, when higher sulfonate concentrations were used. The SPEKK/PEI miscibility decreased with increasing SO$_3$H content, which is responsible for the phase separation that occurred at lower solvent concentration in the ternary (polymer/polymer/solvent) mixtures described in Fig. 2. One explanation for this behavior is the strong intramolecular hydrogen bonding interactions that are expected to dominate within the SPEKK phase. It is also worth noting that X-ray diffraction studies showed that PEKK crystallinity only persisted in the SPEKK0.8 ionomer. Beyond IEC = 1.1 mequiv/g amorphous SPEKK polymers were found. Sulfonation therefore disrupts the PEKK chain packing and the ability of SPEKK to pack well with PEI.

Infrared spectroscopy (not shown) failed to identify any perturbations of the S=O vibrations of the aromatic sulfonic acid groups in the spectral region of 900–1100 cm$^{-1}$ for solution-cast SPEKK/PEI membranes. Any specific interactions between the SPEKK and PEI would most surely involve the sulfonic acid groups, and the lack of any effect of PEI on the S=O vibrations strongly suggests the absence of such interactions. That result is also consistent with the reduced miscibility of the SPEKK and PEI with increasing
sulfonation, since a specific intermolecular interaction would be expected to improve miscibility. The determination of the binary phase behavior of polymer blends using samples cast from solution (i.e., ternary mixtures) is never totally unambiguous. This is because of complexities such as miscibility gaps that may occur in the ternary phase diagram and the kinetic influences of freezing in a non-equilibrium morphology below a glass transition temperature of one or more of the phases that may occur in the ternary mixture. The problem of unequivocally identifying the phase behavior of the SPEKK/PEI blends is also exacerbated by the high transition temperatures and high melt viscosities of the two polymers, which makes melt mixing samples difficult, and the limited stability, e.g. desulfonation of the ionomer, at the high-temperatures that are needed for melt processing.

An alternative approach that was attempted to determine miscibility of the SPEEK and PEI was to cast individual thin films of the two polymers, thoroughly dry them, and then bring the films into contact above the glass transition temperature(s) of at least one of the components. Accordingly, stacked films of SPEKK2.7 and PEI were annealed at 200 and 220 °C for 2 h under moderate pressure. The annealing temperature was chosen to be slightly above the Tg of at least one of the components (e.g. Tg (SPEKK2.7) ∼ 200 °C) but below the desulfonation temperature of SPEKK (250 °C). The stacked films annealed at 200 and 220 °C delaminated easily and TEM micrographs revealed sharp interfaces in cross-sectional views on a scale of 500 nm. The lack of adhesion indicated that interfacial mixing did not occur under those conditions. A more diffuse interface was observed after annealing at 240 °C, but considerable desulfonation of SPEKK also appeared to occur after 2 h, which complicated the interpretation of the experiment. It seems safe to conclude that any miscibility between SPEKK2.7 and PEI within this temperature range was likely to have been very low, at best.

3.5. Morphology control

Two approaches can be used to tune the phase morphology of SPEKK/PEI polymer blends. First, the sample can be annealed at an elevated temperature following constant-temperature film casting. In case of an LCST-type phase diagram, for example, this will coarsen the morphology, while refinement and eventually homogenization of the morphology might be expected for an UCST-type behavior. A second approach is to impose a temperature history on the ternary mixture during casting, so that the morphology is altered prior to complete solvent removal. The choice of the solvent is obviously important for that approach, since it will influence not only the thermodynamics of the ternary solution, but also the solvent evaporation rate.

High-temperature annealing of cast SPEKK/PEI blends had no noticeable effect on the film morphology, which may be due to the low molecular mobility in the melt and poor miscibility of the polymer pair. Also, since some desulfonation did occur during high-temperature annealing, this procedure is not considered to be conducive for preparing a quality composite PEM, since desulfonation decreases the proton conductivity and results in embrittlement of the membrane.

The second morphology control approach is illustrated by the effect of casting temperature on droplet size as shown in Fig. 8 for 85/15 SPEKK2.0/PEI blends (see also Fig. 3). Increasing the casting temperature seems to produce smaller particles, probably the combined result of postponed phase separation due to the UCST behavior of the ternary blend and
faster solvent evaporation resulting in a frozen-in morphology. Enhanced inter-diffusion between the coexisting phases at the cloud point, expected at higher temperatures, did not appear to be a determining factor.

SPEKK1.2 was used to study the effect of casting solvent and temperature for 50/50 blends with PEI. That ionomer formed a blend with PEI that is on the border (see Fig. 7) between macroscopically phase-separated (IEC > 1.5 mequiv/g) and homogeneous (IEC = 0.8 mequiv/g) and was, therefore, thought to be the best candidate for morphological design experiments. The evaporation rate was varied by using DMAc (b.p. = 165 °C) or NMP (b.p. = 202 °C) as the casting solvent; the cloud points for both ternary solutions using these solvents were comparable (Fig. 2). A comparison of Fig. 7 (1.2) and Fig. 9(A) indicates that a finer phase-separated morphology was produced when the faster evaporating DMAc was used at the same casting temperature. This confirms that the phase separation process was arrested during casting due to mobility restrictions, which is consistent with the data shown in Table 1. Increasing the casting temperature from 60 to 120 °C produced a more homogeneous blend, presumably by suppressing the onset of the frozen-in morphology. There is even a suggestion of co-continuous morphology for the sample cast at 120 °C.

3.6. PEI as a candidate for reinforcing SPEEK proton-exchange membranes

Composite SPEEK membranes with an optimum proton conductivity and mechanical integrity in the fuel cell environment are sought. As noted earlier, one promising strategy is to achieve a co-continuous morphology with a high-performance blend. For the SPEEK/PEI systems studied here, that required a blend composition close to 50/50. This was only achievable by using a moderately sulfonated ionomer, such as SPEKK1.2 (see Fig. 9), since casting membranes with higher IEC’s resulted in macroscopically phase-separated morphologies that cannot be easily controlled by changing either the casting temperature or the casting solvent (see Fig. 6A and B). However, the low proton conductivities characteristic for the lower IEC SPEEK’s (∼10⁻² S/cm at 25 °C and 98% R.H. [4]) are not competitive with current state-of-the-art membranes or PEM fuel cell targets.

Some reinforcement of the ionomer may be expected, however, by using PEI as a minority component in the form of a dispersed droplet morphology. Therefore, a system of an ionomer with higher proton conductivity (SPEKK2.0) in combination with PEI as the minority component was selected for evaluation as a composite PEM membrane. The effects of PEI content on conductivity and water uptake are shown in Fig. 10A. The addition of the non-conductive polymer reduced the water swelling of these PEMs, but at the expense of a drop in conductivity. On the basis of lowering the water content and improving mechanical properties, but still retaining adequate conductivity, PEI contents between 10 and 20 wt% appear to be optimal. An increase in casting temperature decreases the particle size (see Fig. 8), which will increase the interface fraction. In case of strong interfacial mixing or SPEEK/PEI entanglement, a decrease in membrane swelling is expected. In contrast, a change in casting temperature does not significantly affect the water content (Fig. 10B). This indicates the absence of interfacial mixing, also concluded from the DSC analysis in Fig. 4 (50/50 cast).

Fig. 10. Proton conductivity at 25°C and 98% R.H. (○/H17033) and mass fraction of water in SPEKK2.0/PEI blends (©): (A) effect of PEI composition (wt%) and (B) effect of casting temperature for 15 wt% PEI. The blend membranes were cast at 60°C from 5% (w/v) NMP solutions.

Moreover, no effect of casting temperature or particle size on conductivity was found (Fig. 10B), which opposes the assumption made for SPEEK/PEI blends that the interface would enhance proton conductivity [8].

SPEKK2.0/PEI blends with PEI contents ranging from 10 to 20 wt% were tested in a membrane electrode assembly (MEA) at 80°C and 75% R.H. Under those conditions, the membranes prematurely failed by rupture adjacent to the gasket, which was a consequence of excessive swelling of the membranes. Some effort was made to assess the performance of SPEKK/PEI blends in a direct methanol fuel cell. However, the preferential swelling of SPEKK in methanol combined with the poor interfacial SPEKK/PEI adhesion makes these PEMs poor candidates.

Our current research focuses on the design of SPEKK-based blends using alternatives to PEI that restrict the high swelling of the blend without significantly diminishing the conductivity.

4. Conclusions

Poly(ether imide) can be used to improve the mechanical stability of proton-exchange membranes (PEM) based on sulfonated poly(ether ketone) (SPEKK). Two strategies can be used for controlling the blend morphology to achieve a compromise between PEM durability and proton conductivity: (1) varying the solvent-casting procedure and (2) high-temperature annealing of cast membranes.

High-temperature annealing is only possible above the glass transition region of the blends (>200°C) and below the desulfonation temperature of SPEKK (>250°C). With this strategy, however, no morphological changes occurred for the SPEKK/PEI blends, due to the low mobility of both components at these temperatures. Moreover, the absence of interfacial mixing indicated a low miscibility of these components.

Ternary SPEKK/PEI/solvent phase diagrams pointed out that phase separation occurred earlier during casting, i.e., for higher amounts of solvent, when the PEI content was increased. For SPEKK/PEI ratios from 97.5/2.5 to 75/25 and high SPEKK sulfonation levels, e.g., IEC of 2 mequiv/g, dispersed droplet morphologies were formed, with particle sizes increasing with PEI content. In that range the proton-conducting polymer constituted the matrix of the blend film. Increasing the casting temperature resulted in a decrease in particle size, which was attributed to a postponed phase separation (UCST behavior) combined with faster solvent evaporation, resulting in a frozen-in morphology.

PEKK and PEI were miscible, and miscibility was retained with SPEKK having an IEC of 0.8 mequiv/g. Increasing the sulfonation level beyond 0.8 mequiv/g reduced the miscibility, and when equal amounts of SPEKK2.0 and PEI were used, macroscopically phase-separated blends were obtained. The tendency for extensive phase separation can be understood from the early phase separation occurring in the ternary phase diagram for the SPEKK2.0/PEI 50/50 blend. When intermediate sulfonation levels were used, control of the blend morphology was obtained by changing the casting temperature and solvent.

Membrane integrity can be improved by adding PEI as the minority component, albeit with a decrease in proton conductivity. Improvements were, however, moderate due to poor SPEKK/PEI interfacial mixing. Moreover, proton conductivity was not enhanced at the interface, probably due to the absence of specific intermolecular interactions. The more promising spinodal-like morphology, where the interconnected SPEKK phase optimizes proton conductivity and PEI assures membrane integrity, was achieved for 50/50 blends of SPEKK1.2 and PEI, but those blends had limited practical use due to the low proton conductivity of the parent SPEKK.

Controlling the morphology of PEM blends during solution casting is currently being explored for other polymer blends based on SPEKK with special attention to the development of co-continuous morphologies.

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References


