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Correlating morphology, proton conductivity, and water transport in polyelectrolyte-fluoropolymer blend membranes

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ABSTRACT

Obtaining detailed correlations among multi-scale morphology, ion conduction, and water transport will allow for informed design of novel membrane materials for alternative energy and sustainability applications. We compare morphological and performance features of polyelectrolyte-fluoropolymer blend membranes processed with different degrees of tetrabutylammonium hydroxide (TBA-OH) using the techniques of SEM, elemental analysis, proton conductivity, and water self-diffusion and spin relaxation by NMR. Increased TBA-OH significantly improves membrane phase homogeneity observed by SEM, consistent with observed enhancements in proton conductivity and water diffusion. We further observe drastic changes in local restrictions to water diffusion among the different blend membranes, and use theories of diffusion in porous media to understand improvements in characteristic domain size R_c and tortuosity $\mathfrak{I}$ with phase homogeneity. NMR relaxometry studies yield two-component T_1 values, which further probe structural heterogeneities on smaller (1–10 nm) scales than diffusion experiments (1–10 μm). These multifaceted analyses linking morphology, chemistry, and transport properties provide critical information toward advanced membrane design.

1. Introduction

Generating targeted high performance polymeric materials represents a grand challenge for meeting needs in alternative energy and global sustainability [1–3]. Polymer electrolyte membranes (PEMs) provide a unique medium to selectively transport ions and small polar molecules, therefore manifesting themselves as potential candidates in a variety of applications, from renewable energy materials [1,3–5] to water purification [6,7] to mechanical transducers [8,9]. Typically these ion-containing polymers are composed of a single copolymer, such as a perfluorosulfonic acid, a sulfonated poly (ether ether ketone), a poly(sulfone), or a poly (imide), where balancing all of the needed properties for the membrane by adjusting the composition can be difficult or expensive [1–3,5,10–13]. Over the past decade, great effort has been devoted to improving the performance and efficiency of relevant materials and devices [2,14,15]. Sophisticated synthetic strategies, such as the use of block and graft copolymers, allow for the creation of advanced materials with tailored properties by controlling the membrane morphology in a manner not possible with the use of random copolymers [4,16,17]. Polymer blends present another pathway towards tailoring membrane properties, where two or more components can be fruitfully combined to meet specific membrane requirements [18,19]. Post-synthesis material processing methods such as membrane casting [15], mechanical stretching [11], and electric field application [20] can also have an impact on tuning the membrane's final morphology and structural features, which fundamentally determine water and ion transport [11,20–22]. Thus, systematic investigations on how membrane processing protocols impact transport in polymer membranes will provide instructive guidelines for new material design.

Pulsed-field-gradient (PFG) NMR diffusometry renders its distinctive role in studies of molecular motions by virtue of its chemical (spectral) selectivity as well as its flexible and noninvasive application. This method employs magnetic field gradients (spatially varying magnetic fields) that couple the detected NMR signal with the average displacement of molecules, allowing sensitive determination of the self-diffusion coefficient D for one or more species in a material [23–25]. NMR diffusometry further takes advantage of long-lived spectral coherences to measure molecular diffusion over a broad range of timescales, typically from ~1 ms to 1 s. This can provide useful information on coupling of structural heterogeneity with transport within materials, since molecular diffusants sample the host matrix and their diffusion reflects structural complexity. More specifically, NMR diffusometry offers information over a tunable window of length scale, ranging from ~100 nm to ~10 μm, and when combined with microscopy studies

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can yield pivotal insights regarding morphology, anisotropy and defect or domain structure [22,26–29].

In earlier studies [12,22,26], we have surveyed a range of sulfonated random and block copolymers using multi-modal NMR, and demonstrated that water transport and anisotropy well correlate with morphological variations and structural anisotropy. Here we report detailed experiments and a quantitative analysis based on porous media theories on a series of technologically promising polymer blend membranes with respect to morphology, transport, and anisotropy.

We have systematically examined the use of tetrabutylammonium hydroxide (TBA-OH) in forming homogeneous polymer blends of two immiscible polymers: a fluoropolymer for mechanical strength and chemical stability, and a polyelectrolyte for ion conduction. Blending two readily available polymers yields membranes that show high performance and allow for tuning of properties in an inexpensive material platform. TBA-OH serves to "compatibilize" these two chemically dissimilar polymers, and we will discuss the influence of this additive on membrane morphology and transport. Scanning electron microscopy (SEM), elemental analysis, proton conductivity, and water self-diffusion studies reveal the effects of changes in phase homogeneity on key transport parameters. In addition, we have carried out NMR T_1 and T_2 relaxometry studies that probe structural features at a smaller length scale than diffusion measurements. When combined, these findings highlight the utility of tuning the transport properties of polymer blend PEMs by controlling the morphology and phase homogeneity, and emphasize the power of NMR diffusion and relaxation measurements in correlating transport properties with morphology as well as membrane fabrication.

2. Experimental

2.1. Membrane preparation

Membranes were prepared from a solution blend of polyelectrolyte and PVDF (Kynar[®][1] 2801 from Arkema Inc.). The polyelectrolyte is a random copolymer of vinylbenzyl sulfonic acid and vinylbenzyl alcohol with a M_w of 143 kg/mol and a polydispersity of 3.15. The monomers and polyelectrolyte were synthesized using methods previously described [30]. Molecular weight (M_w) determination was performed using a Waters 2695 Separations Module with a Waters 2414 Refractive Index Detector. Polystyrene sulfonate standards ranging from 1,020,000 g/mol to 697 g/mol were used for M_w calibration. The polyelectrolyte ion exchange capacity (IEC) was 4.3 meq./g (determined by solution ^{1}H NMR in D_2O). The polyelectrolyte was neutralized at three different levels (0, 75, and 95 mol% of the available acid groups) with TBA-OH obtained from Sachem Inc. (99% purity). After the polyelectrolyte was blended with the PVDF and cast into a film, it is re-acidified to obtain the acid form of the final material. The use of the TBA-OH has been shown to promote the miscibility of polyelectrolyte with PVDF [30], and thus we term this to be a compatibilizer. In addition to this system, TBA-OH has been used in the literature to improve the miscibility of blends containing PVDF with poly(2-acrylamido-2-methylpropanesulfonic) acid [31], perfluorosulfonic acid [32] and sulfonated poly(aryl ether sulfone)/poly(ether sulfone) [33].

The polyelectrolyte was blended with PVDF in 1-methyl-2-pyrrolidinone (ACS grade from BDH) to form three 20 wt% solutions, each with its distinct TBA-OH loading. The ratio of PVDF to polyelectrolyte was 65/35 (w/w) to give an IEC value of 1.3, as determined by titration, for all membrane blends. This is just slightly lower than the expected value of IEC$=4.3 \times 0.35 = 1.5$ given by the weight fraction of polyelectrolyte. A blocked isocyanate crosslinker (Trixene[®][2] BI7982 from Baxenden Chemicals Ltd.) was added to the solutions in a hydroxide/isocyanate mole ratio of 0.8:1. An organotin catalyst (Fascat[®] 4202 from Arkema Inc.) was also added to the solution in an amount equal to 0.5 wt% of the solids level. All solutions were blended with a high speed mixer for 2 h and allowed to degas overnight before casting.

The three solutions were then cast into membranes using a Mathis LTE Labdryer. The casting substrate was 2 mil thick aluminum foil with approximate dimensions of 38×30 cm. Approximately 15 g of polymer solution was spread on the foil and drawn down to a wet film thickness of 300 μm using a doctor blade. The films were dried for 6 min at 200 °C in order to completely remove casting solvent while not allowing film decomposition. The thickness of the dried membranes was approximately 25 μm.

The membranes were activated in 3 L of 1 M hydrochloric acid to remove the TBA-OH and obtain the acid form. The acid bath temperature was ramped from ambient to 80 °C at a rate of 40 °C/h and held at 80 °C for 30 min. After removal of the acid, the membranes were washed with 18 MΩ water and subsequently treated with 3 L of 1 M sulfuric acid using the same temperature profile as the hydrochloric acid. The sulfuric acid was then removed and the membranes were washed with 18 MΩ water until the wash water pH was greater than 4. The membranes were labeled A, B, and C, which reflect the different levels of compatiblizer ($A=95\%$, $B=75\%$, and $C=0\%$).

2.2. NMR sample preparation

Membranes were cut into 4.5 mm × 4.5 mm pieces and stacked (6–14 layers) in the same orientation to enhance NMR signal. Membrane stacks were loosely wrapped with poly(tetrafluoroethylene) tape and dried at 70 °C for 12 h in a vacuum oven to obtain their dry weight before soaking in H_2O until saturation. Water uptake (expressed in wt% relative to dry membrane) was determined using the following equation:

$$Water\ uptake = \frac{Mass_{wet} - Mass_{dry}}{Mass_{dry}} \times 100\% \qquad (1)$$

where $Mass_{wet}$ and $Mass_{dry}$ stand for the mass of wet and dry membranes, respectively. Partially swollen membranes were prepared by controlled evaporation of water before sealing with poly(tetrafluoroethylene) tape and LDPE plastic wrap, and the error in water uptake is less than $\pm 2\%$. Membrane stacks were further sealed inside the cavity of a homebuilt poly(tetrafluoroethylene) sample cell [26] with low dead volume ($< 20\%$ of sample volume), which eliminates water content changes (evaporation or absorption) during NMR analyses. Membrane samples were oriented with one in-plane direction (X) along the magnetic field B_0. Diffusion anisotropy was measured by applying pulsed-field gradients along 3 orthogonal membrane axes without repositioning the sample. We use the following axis definitions: X and Y are the in-plane directions and Z is the through-plane direction. An equilibration time of 3 h after sample cell sealing allowed an equilibrated and homogeneous water distribution throughout the partially swollen membranes.

2.3. PFG NMR diffusion and spin relaxation time measurements

^1H_2O self-diffusion measurements were performed using the PGSTE sequence [34] at 25 °C on a Bruker Avance III 9.4 T widebore spectrometer corresponding to a ^{1}H frequency of 400.13 MHz. A