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Processing induced morphological development in hydrated sulfonated poly(arylene ether sulfone) copolymer membranes

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Abstract

The development of morphological solid-state structures in sulfonated poly(arylene ether sulfone) copolymers (acid form) by hydrothermal treatment was investigated by water uptake, dynamic mechanical analysis (DMA), and tapping mode atomic force microscopy (TM-AFM). The water uptake and DMA studies suggested that the materials have three irreversible morphological regimes, whose intervals are controlled by copolymer composition and hydrothermal treatment temperature. Ambient temperature treatment of the membranes afforded a structure denoted as *Regime1*. When the copolymer membranes were exposed to a higher temperature, AFM revealed a morphology (*Regime2*) where the phase contrast and domain connectivity of the hydrophilic phase of the copolymers were greatly increased. A yet higher treatment temperature was defined which yielded a third regime, likely related to viscoelastic relaxations associated with the hydrated glass transition temperature (hydrated T_g). The required temperatures needed to produce transitions from Regime1 to Regime2 or *Regime3* decreased with increasing degree of disulfonation. These temperatures correspond to the percolation and hydrogel temperatures, respectively. Poly(arylene ether sulfone) copolymer membranes with a 40% disulfonation in Regime2 under fully hydrated conditions showed similar proton conductivity ($\sim$0.1 S/cm) to the well-known perfluorinated copolymer Nafion® 1135 but exhibited higher modulus and water uptake. The proton conductivity and storage modulus are discussed in terms of each of the morphological regimes and compared with Nafion 1135. The results are of particular interest for either hydrogen or direct methanol fuel cells where conductivity and membrane permeability are critical issues.

Keywords: Morphology; Proton exchange membrane; Disulfonated polysulfone copolymers

1. Introduction

The electrochemical and mechanical properties of sulfonated copolymers such as Nafion™, sulfonated polyethersulfones, etc. has become increasingly important as their potential application in proton exchange membrane fuel cells (PEMFC) becomes more evident [1,2]. Detailed knowledge of their solid-state structure is essential for the design of advanced fuel cell materials such as proton exchange membranes (PEM) and membrane electrode assemblies (MEA). It is well known that the electrochemical properties of the materials are strongly dependent on the chemical structure of the copolymer as well as the morphology. In particular, the nanophase hydrophilic domain structure of these materials under hydrated conditions plays an important role in protonic and methanol transport. Nevertheless, the literature concerning the morphological structure of these materials under fuel cell operating conditions has been limited because (1) scattering techniques do not easily provide detailed morphological information such as domain connectivity [3], and (2) microscopic techniques are largely unable to mimic the fuel cell environment, i.e. elevated temperature and high humidification. Therefore, indirect methods must be used to investigate the morphological transformations occurring in these membranes under fuel cell-like conditions.

The morphology of the sulfonated copolymers is recognized to be influenced by several factors such as copolymer composition [4], specific interactions between components [5], casting solvent [6,7], membrane formation procedures [8], and hydrothermal history [9–11]. The effect

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of hydrothermal history on certain electrochemical properties has been reported in previous papers [9–11]. Bauer et al. reported that post sulfonated poly(ether ether ketone) (s-PEEK) membranes showed higher proton conductivity when treated in boiling water or acids [9]. Recently, our laboratory reported the effect of the acidification temperature on water uptake and proton conductivity of disulfonated poly(arylene ether sulfone) directly copolymerized copolymers and Nafion® [10]. The fully hydrated sulfonated polyethersulfone membrane treated by boiling in dilute sulfuric acid and then water showed higher proton conductivity, greater water absorption, and less temperature dependence on proton conductivity as compared to membranes acidified at 30 °C. In contrast, the conductivity and water absorption of Nafion was almost invariant with treatment methods. Another effect of hydrothermal treatment on electrochemical properties was reported by Alberti et al. [11]. They measured the proton conductivity of membranes in a sequence of heating-cooling cycles at constant relative humidity. For Nafion, a decrease of the conductivity was observed during the cooling cycle, while the sulfonated poly(ether ether ketone) membranes showed higher conductivity. It was suggested that this effect was probably a result of an irreversible morphological change in the post sulfonated poly(ether ether ketone) membrane.

This paper provides a systematic approach to the relationship between the morphology of the hydrated sulfonated copolymers and their electrochemical properties by defining three different morphological regimes in the fully hydrated sulfonated copolymers. The morphological regime of the hydrated sulfonated copolymer was determined by the observation of water absorption, dynamic mechanical behavior and morphology. Correlations of these regimes with protonic conductivity and modulus are then demonstrated. Commercially available perfluorinated copolymer, Nafion 1135 and directly copolymerized sulfonated poly(arylene ether sulfone) copolymers [12–14] (Fig. 1) were the materials utilized.

2. Experimental

Sulfonated poly(arylene ether sulfone) copolymers (BPSHs) were successfully synthesized via nucleophilic aromatic substitution polycondensation of biphenol, 4,4′-dichlorodiphenylsulfone and 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone. Membranes were prepared by solution casting using dimethylacetamide (10% w/v). Detailed synthetic procedures and characterization of these copolymers were reported previously [10,12,13]. The copolymer membranes in their sodium salt form were converted to the required acid form by immersion in 1.5 M sulfuric acid solution at 30 °C for 24 h, followed by immersion in deionized water for 24 h. This has previously been defined as *Method 1* [10]. The Nafion membrane with an equivalent weight of 1100 (N1135, Du Pont) was acidified with the same procedures as described above. All membranes were stored in deionized water at 30 °C for at least 2 days after acidification. The deionized water was changed every 6 h in an effort to remove all of the residual sulfuric acid in the membrane. Hydrothermal treatments were conducted in deionized water at 30–160 °C in a pressure vessel with a feedback temperature controller (Parr reactor). The acidified samples were treated at specified temperatures and pressures for 24 h, then immersed in deionized water at 30 °C for 24 h before testing.

Percent water absorption of the membranes at 30 °C was determined by the following procedure; the wet membranes were equilibrated at 30 °C for 24 h, removed and blotted to remove surface water droplets, then quickly weighed. The dry weight of membrane was determined by weighing the membranes after vacuum drying at 120 °C for 24 h. The percent water absorption was calculated using the equation, water absorption $(\%) = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100$ where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

Tensile deformation and storage modulus of membranes in liquid water was measured using dynamic mechanical analysis (DMA) (TA Instruments, DMA 2980) in the tensile submersion mode at a frequency of 1 Hz. For temperature scanning, the temperature was increased from 35 to 80 °C at a rate of 0.1 °C/min. Films with dimensions of about $3 \times 10 \times 0.1\ \text{mm}^3$ were subjected to sinusoidal deformation with a 20 μm amplitude.

Tapping mode atomic force microscopy (TM-AFM, Digital Instruments Dimension 3000) was performed with a micro-fabricated cantilever with a force constant of approximately 40 N/m. All treated samples were dried at 30 °C for 12 h under nitrogen and were then allowed to equilibrate by exposure to 50% relative humidity at 30 °C for 2 h before testing. The samples were then imaged immediately at 30 °C under a relative humidity of about 50%. The morphology of the Nafion membrane was investigated by field emission scanning electron microscopy (FE-SEM, Leo 1550 Gemini) using an in-lens detector at 5 kV incident beam voltage. The hydrated sample was dried

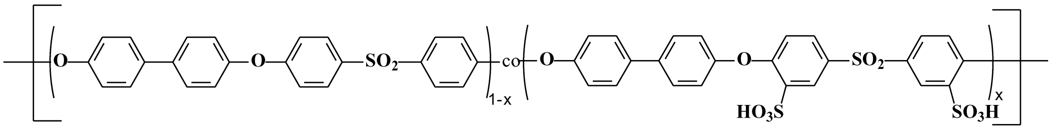

Fig. 1. Chemical structure of direct copolymerized poly(arylene ether sulfone)s (BPSH-XX) (Bi Phenyl Sulfone H form; XX: molar fraction of disulfonic acid unit).

by critical point drying (LADD Research Industries) in liquid carbon dioxide at a critical temperature of 42 °C and a critical pressure of 1300 psi [15]. A dried sample was vacuum sputtered with a 5 nm gold layer before imaging.

Proton conductivity was measured using a Hewlett Packard 4192 Impedance/Gain-Phase Analyzer over the frequency range of 10 Hz–1 MHz. The detailed procedures have been reported previously [10,12,16].

3. Results and discussion

Fig. 2 shows the effect of the hydrothermal treatment temperature on the water absorption of the BPSH copolymer and Nafion at 30 °C. The percent water absorption of the BPSH copolymer had a tendency to increase as a function of the hydrothermal treatment temperature. The water absorption results defined three discernable regimes which are dependent on the treatment temperature. For example, in *Regime1* water absorption only slightly increases with treatment temperature. In *Regime2* water absorption increased steadily with temperature. Finally, *Regime3* showed water absorption that increased rapidly with treatment temperature. The transition temperatures of Regime1/Regime2 and Regime2/Regime3 are marked by the darker and lighter arrows in the figure, respectively, and are summarized in Table 1.

For Nafion 1135, only one transition temperature at around 100 °C was detected, which was assigned to the Regime2/Regime3 transition temperature, primarily by the morphological characteristics (see following section). Apparently, the transitions of Regime1/Regime2 and Regime2/Regime3 were irreversible since the water absorption of the lower regime could not be recovered after the hydrothermal treatment.

The transition behavior was also characterized by DMA. Fig. 3 shows the tensile deformation of the BPSH copolymer under constant force, where the first and second transition temperatures were in the range of 35–70 °C. The transition temperature of BPSH-45 was clearly observed by the slope change of the tensile deformation. The slope of the tensile deformation in the Regime1 was almost constant with temperature but increased in Regime2 as shown in Fig. 3(a). In order to verify the irreversibility of the Regime1 to Regime2 transition, the BPSH-45 copolymer was treated in water at 80 °C for 24 h and then subject to tensile deformation at temperatures. As shown with the dotted line in Fig. 3(a), no transition temperature was observed in the experimental temperature range, unlike the as cast BPSH-45 specimen. This result confirmed that the transition from Regime1 to Regime2 is an irreversible process. Thus, if a copolymer is converted to Regime2 morphology by high temperature treatment, it will not revert to Regime1 morphology after cooling, but rather would require recasting. Another observation is that the increase of tensile deformation of the fully hydrated sample in Regime1 is

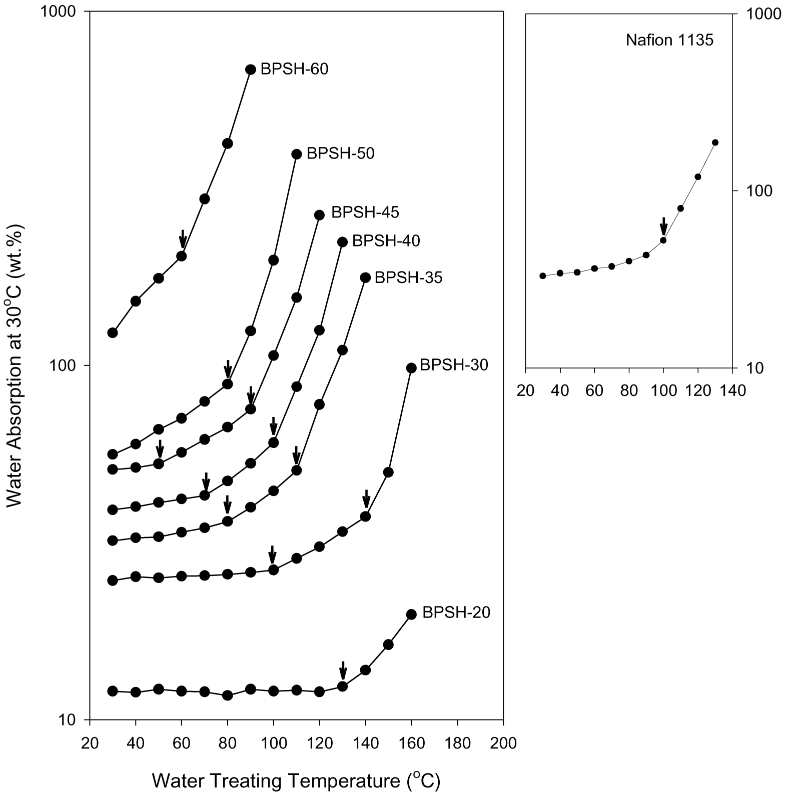

Fig. 2. Water absorption of BPSH copolymers as a function of water treating temperature; the dark and light arrows indicate the Regime1/Regime2 and the Regime2/Regime3 transition temperatures, respectively.

Table 1
Transition temperatures of BPSH and Nafion 1135

Copolymer	Regime1/Regime2 transition temperature, T_p (°C)	Regime2/Regime3 transition temperature, T_{hg} (°C)
BPSH-20	130	ND
BPSH-30	100	140
BPSH-35	80	110
BPSH-40	70	100
BPSH-45	50(53)[a]	90
BPSH-50	30	80
BPSH-60	ND	60(59)[a]
Nafion 1135	ND	100

ND: not detected in the experimental temperature range.

[a] Values in parenthesis was determined by the tensile elongation test (see text).

more significant than that in Regime2. This result suggests that as long as the membrane remains at a temperature below the transition temperature, the dimensional change of the membrane in water under a modest stress is small.

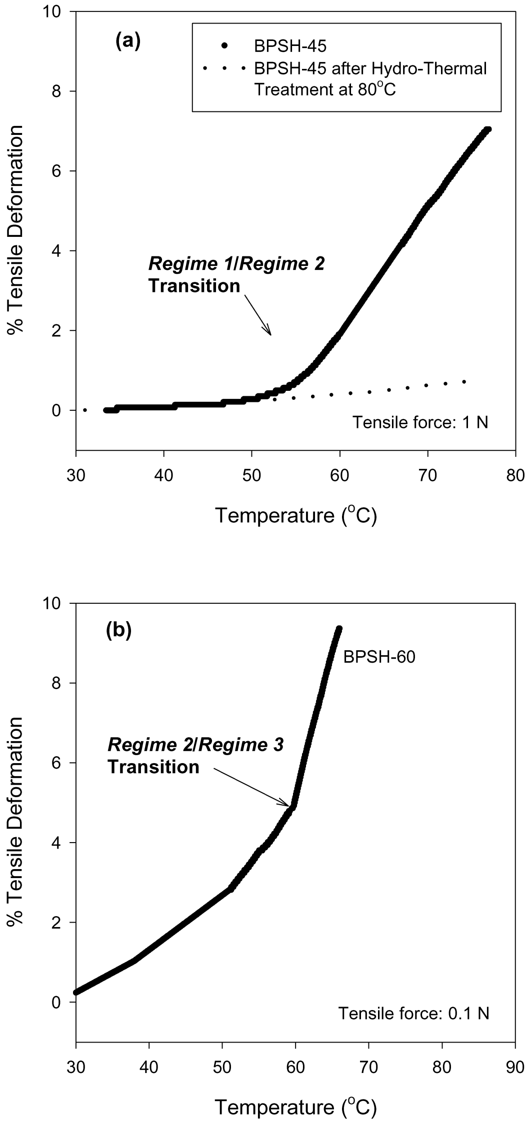

Fig. 3. Tensile deformation of (a) BPSH-45 and (b) BPSH-60.

Fig. 3(b) shows the tensile deformation of BPSH-60, which has a Regime2/Regime3 transition temperature of 60 °C as determined by the water absorption test. Since the mechanical properties of highly swollen BPSH-60 in water were poor, only 0.1 N was applied for the constant force in the tensile test. The tensile deformation trace showed a transition point at around 59 °C, which was in a good agreement with the water absorption test. For Nafion (not shown here for brevity), no transition point during tensile testing was observed across the experimental temperature range, as expected from the water uptake experiment. This physical behavior as a function of hydrothermal treatment temperature is no doubt related to a viscoelastic and/or morphological change within the membranes, since no chemical structural change could be detected [10].

Fig. 4 shows the representative morphology of BPSH-45 in the three different regimes as derived from TM-AFM. All TM-AFM micrographs shown here were taken under partial hydration as described in the experimental section since swelling under full hydration would complicate imaging [18]. The BPSH-45 copolymer in Regime1 suggests that the hydrophilic copolymer chain segments aggregate as isolated domains, i.e. closed structure, although some local connection of hydrophilic domains may still exist as evidenced by the proton exchange membrane's good proton conductivity. On the other hand, the BPSH-45 copolymer in Regime2 showed higher phase contrast and a more connected hydrophilic domain structure, i.e. open structure. Based on this morphological characteristic of Regime1 and Regime2, the Regime1/Regime2 transition temperature can be defined as a percolation temperature, T_p. Recent ^{1}H pulse NMR spectroscopy results also revealed that additional free water exists in Regime2 [19,20]. As for the morphology in Regime3, a somewhat indistinguishable phase structure was observed. Significant phase mixing has likely occurred. Previously, pressure DSC experiments showed that this morphological relaxation occurs near the glass transition temperature of the fully hydrated sample [20]. Therefore, one can conclude that the Regime2/Regime3 transition temperature denoted as the 'hydrogel' temperature, T_{hg}, was closely related to the glass transition temperature of the hydrated sample.

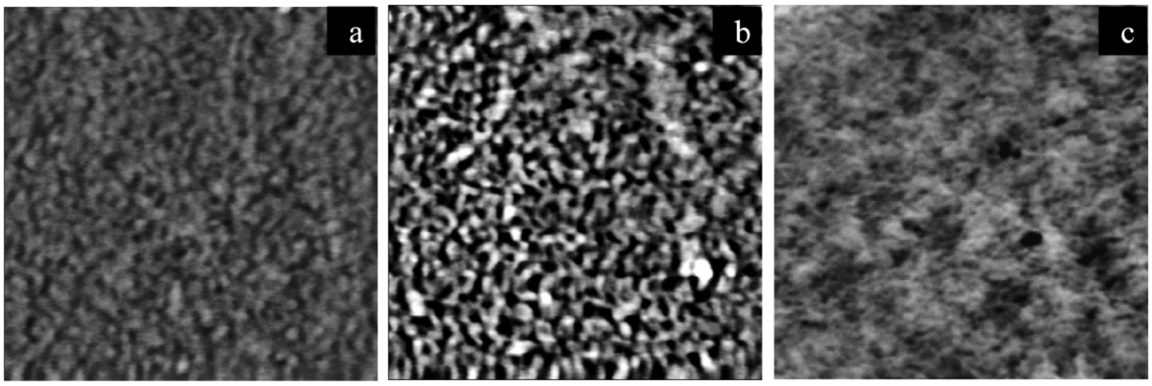

Fig. 4. TM-AFM phase image of BPSH-45 in (a) Regime1, (b) Regime2, and (c) Regime3; Hydro-thermal treatment temperatures of (a), (b), and (c) were 30, 80, and 120 °C, respectively, phase angle: 30° Scan size: 500 nm; darker features represent the hydrophilic phase while lighter features represent the hydrophobic phase [10,12,17].

Nafion is considered to be a well phase-separated system, with a small hydrophilic domain structure. This was supported by FE-SEM results which used a CO_2 critical drying technique [15]. Since the sample is ultimately examined under vacuum in the microscope, complete water removal must be achieved. Normal drying procedures would cause excessive shrinkage of the sample and the ionic domains, which would obviously change the morphology. By using the critical point drying method, the vapor and liquid phases are in equilibrium at the critical point, and there is minimal surface tension. However, there are the strong interactions between Nafion and normal dehydrating fluids such as methanol, ethanol and acetone. In this research, supercritical carbon dioxide was used as the dehydrating fluid to displace the water contained in the ionic domains. It is suggested that after this procedure, the water absorbed in the ionic domains near the surface of the Nafion membrane was displaced by supercritical CO_2 and the hydrated morphology was largely preserved. The change of the sample size during the drying process was undetectable. Fig. 5 shows the morphology of Nafion-1135 after full hydration followed by CO_2 critical drying. It is clearly seen that crack-like hydrophilic domains were connected to form a continuous hydrophilic phase indicative of the Regime2 morphology. This morphology was in good agreement with the multiplet-cluster model [21,22] determined by X-ray scattering, which suggests that multiple clusters of cations and the associated anions from the pendent group of the perfluorinated copolymer are connected to form a continuous phase in a hydrophobic matrix. Similar morphologies for Nafion in Regime2 and the morphological relaxation in Regime3 were also found in TM-AFM micrographs [10,12,17,23]. However, Regime1 morphology, i.e. closed structure, was not observed in the fully hydrated Nafion. This result suggests that the transition temperature, which was determined by water absorption, may be T_{hg}

The proton conductivity of the BPSH copolymer and Nafion at 30 °C water as a function of hydrothermal treatment temperature is presented in Fig. 6. The conductivity behavior of BPSH was strongly dependent on the morphological regime. For example, conductivity in Regime1 slightly increased, but the conductivity significantly increased from the Regime1/Regime2 transition point. Moreover, it continued to further increase in Regime2

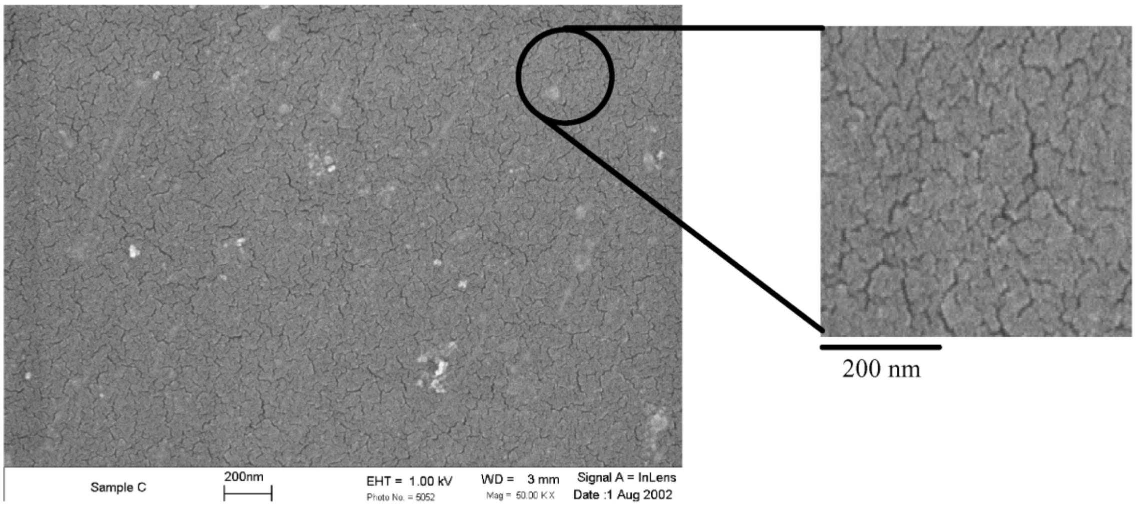

Fig. 5. FE-SEM micrograph of fully hydrated Nafion-1135.

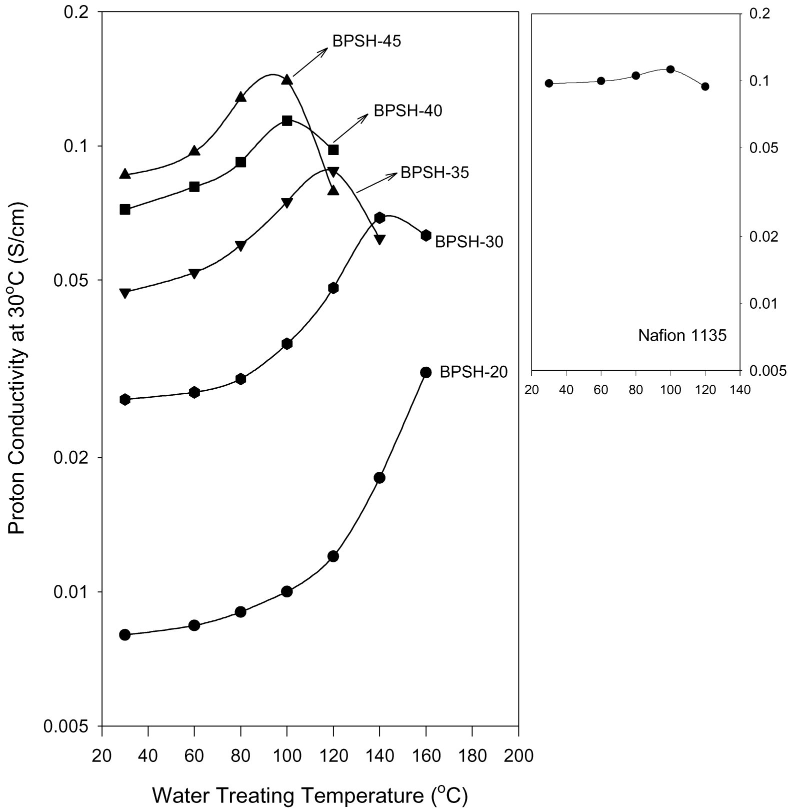

Fig. 6. Proton conductivity of BPSH copolymers and Nafion 1135 at 30 °C as a function of hydro thermal treatment temperature.

with hydrothermal treatment temperature. In contrast the conductivity in Regime3 decreased. The behavior in Regime2 is attributed to the hydrophilic domain structure becoming more continuous, thus allowing increased proton transport. Nafion in Regime2 had relatively little improvement in conductivity with the hydrothermal treatment temperature. The explanation is not clear but it is possibly due to the small amount of a semicrystalline phase which may retard morphological reorganization. The protonic conductivity reduction in Regime3 is related to a morphological relaxation or destruction of the hydrophilic domain structure. The results described in this paper thus explains previous observations [9,10] that the acidification in boiling conditions and/or the boiling water treatment of hydrocarbon based sulfonated copolymers produced higher proton conductivity. This can also explain how the conductivity of usually neat film Nafion PEM decreases above 100 °C even under fully hydrated conditions. Furthermore, it suggests why the conductivity of poly(arylene ether) based sulfonated copolymer with a moderate degree of sulfonation can increase above 100 °C, as observed by Alberti et al. [11]. The concept of a hydrated T_g is thus a key consideration for producing higher temperature (e.g. 120–150 °C) PEM. In addition to the importance of loss of conductivity due to dehydration, the T_g of the polymer matrix when hydrated must also be considered when designing a membrane that is intended to operate above 100 °C.

These results imply two important facts in the practical use of these materials for fuel cell applications. First, proton conductivity of BPSH copolymers can be improved simply by an adequate hydrothermal treatment. For example, proton conductivity of BPSH-30 can be increased from 0.03 to 0.07 S/cm at 30 °C by hydrothermal treatment at 140 °C in water for 24 h. Secondly, the upper limit use temperature of all sulfonated copolymers as proton conductors may be related to the Regime2/Regime3 transition temperature, i.e. glass transition temperature of the fully hydrated copolymer. These results may allow prediction of the upper limit use temperature for PEM (for more details, see Ref. [10]).

Mechanical properties of the membranes are another important issue clearly dependent on morphology. Fig. 7(a) shows the storage modulus of the copolymers at 25 °C in water as a function of hydrothermal treatment temperature. The storage modulus decreased as the degree of disulfonation and the hydrothermal treatment temperature increased. It is noted that a significant decrease in modulus occurred at the T_p and T_{hg} transition temperatures. Modulus data for some of the copolymers in Regime3 was not measurable due to the very low values after treatment. This suggests that any unreinforced copolymer film in Regime3 may not have good enough mechanical properties for practical fuel cell applications.

The correlation between modulus and water uptake for the BPSH materials and Nafion is described in Fig. 7(b). The

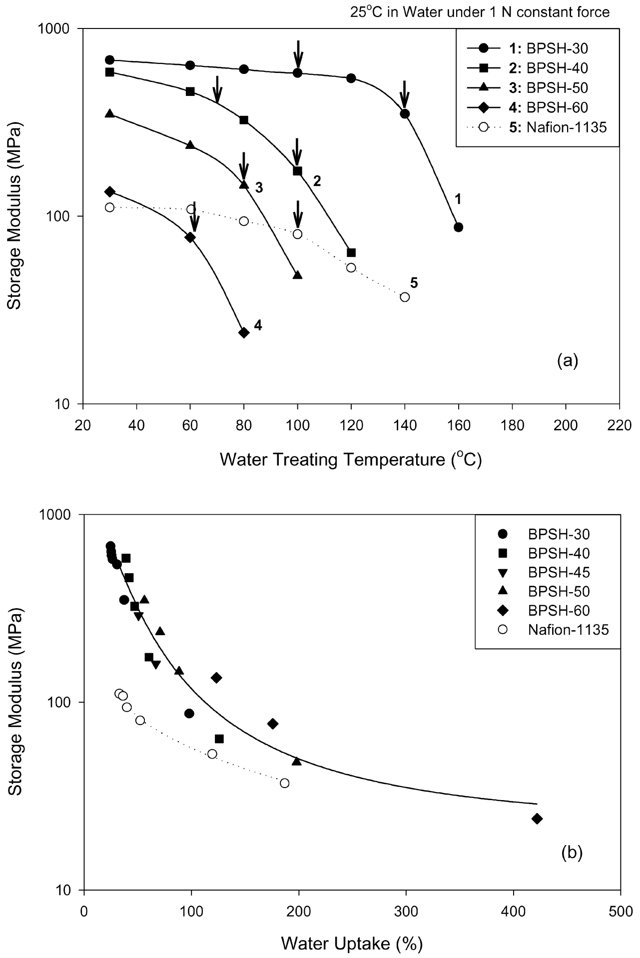

Fig. 7. Storage modulus in water at 25 °C as a function of (a) hydro-thermal treatment temperature and (b) water uptake; dark and light arrows indicate the Regime1/Regime2, and Regime2/Regime3 transition temperatures, respectively, which were determined by water uptake test.

apparent modulus of the BPSH copolymers and Nafion was inversely proportional to the water uptake. It is noted that the storage modulus of BPSH is strongly dependent on the water uptake. The comparison of modulus data between the BPSH system and Nafion indicates that the former has approximately a seven times higher modulus than Nafion when water uptake was less than 30%, but the difference in modulus decreases as a function of increasing water uptake. It is suggested that the higher modulus for the BPSH copolymer after water uptake is a result of the stiffer aromatic backbone structure of the copolymer compared to the flexible perfluorocarbon structure of Nafion. The slow modulus decrease may be related to the semi-crystalline structure in Nafion. These results are consistent with the previous stress–strain data of both systems under dry and wet conditions: The tensile strength and modului of BPSH were generally higher than those of Nafion and decreased with water uptake. Moreover, the elongation at the break beyond the tensile yield of the copolymers increased with water uptake while a nearly constant elongation was observed in Nafion [25,26]. The relatively small elongation change of Nafion under wet conditions might also be due to its semi-crystalline phase.

In summary, this paper demonstrates that sulfonated poly(arylene ether sulfone) copolymer morphology can be defined in terms of three regimes which impart markedly different water uptake, proton conductivity, and mechanical properties. The data may suggest that BPSH-40 in Regime2 structure may be attractive for practical fuel cell applications because the proton conductivity is quite similar to Nafion 1135. However, the selection of degree of disulfonation and regime structure should also be carefully defined by the specific fuel cell application. For example, BPSH-35 in Regime1 may be a promising candidate for direct methanol fuel cell applications because of its low methanol permeability, high dimensional stability, and mechanical integrity.

4. Conclusions

One may conclude that the sulfonated poly(arylene ether sulfone) copolymers have three morphological regimes, which are determined by the copolymer composition and the hydrothermal treatment temperature of the membrane. Regime1 has hydrophilic domains that are isolated (closed structure) and both water uptake and proton conductivity were almost constant with treatment temperature. In Regime2 hydrophilic domains show increased connectivity (open structure) and water uptake and proton conductivity monotonically increased. In Regime3 the hydrophilic/hydrophobic phase domain structure was no longer well defined (morphology changed and viscoelastic relaxation occurred) and water uptake greatly increased while the proton conductivity decreased. The transition temperatures of Regime1/Regime2 and Regime2/Regime3 were also detected by dynamic mechanical measurements and were defined as the percolation temperature, T_p, and the hydrogel temperature, T_{hg}, or hydrated T_g, respectively. The morphological solid-state structure has a highly significant influence upon methanol permeability [24] and other electro-chemical properties of the proton exchange membranes.

Our findings thus highlight the potential of the materials for use as a proton exchange membranes, in terms of both proton conductivity and mechanical behavior. This morphological regime evolution and the associated transition temperatures not only may allow the production of sulfonated copolymer membranes with significantly better proton conductivity (by choosing an appropriate treatment temperature), but also could be used to predict upper limit use temperature for any proton exchange membrane fuel cell in elevated temperature operation. Although, we only applied the hydrothermal treatment to the sulfonated poly(arylene ether sulfone) copolymers, it should be equally applicable to many other amorphous sulfonated copolymer systems.

Acknowledgements

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