

Sulfonated Poly(ether ether ketone)/Epoxy/Phenol Novolac Blend Proton-Exchange Membranes with Low Methanol Permeability

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Received 27 January 2008; accepted 24 August 2008

DOI 10.1002/app.29150

Published online 22 October 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A crosslinked epoxy [4,4'-diglycidyl-(3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP)], cured by phenol novolac (PN), was introduced into a sulfonated poly(ether ether ketone) (SPEEK) membrane (ion-exchange capacity = 2.0 mequiv/g) with a casting-solution, evaporation, and heating crosslinking method to improve the mechanical properties, dimensional stability, water retention, and methanol resistance. By Fourier transform infrared analysis, the interactions between the sulfonic acid groups and hydroxyl groups in the blend membranes were confirmed. The microstructure and morphology of the blend membranes were investigated with atomic force microscopy. As expected, the blend membranes showed excellent mechanical properties, good thermal properties (thermal stability above 200°C), lower swelling ratios

(1.4% at 25°C and 7.0% at 80°C), higher water retention (water diffusion coefficient = 9.8×10^{-6} cm²/s), and a lower methanol permeability coefficient (3.6×10^{-8} cm²/s) than the pristine SPEEK membrane. Although the proton conductivity of the blend membranes decreased, a higher selectivity (ratio of the proton conductivity to the methanol permeability) was obtained than that of the pristine SPEEK membrane. The results showed that the SPEEK/TMBP/PN blend membranes could have potential use as proton-exchange membranes in direct methanol fuel cells. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1335–1343, 2009

Key words: blends; electrochemistry; polyelectrolytes; resins

INTRODUCTION

Direct methanol fuel cells (DMFCs) with methanol as a fuel have attracted extensive interest for electric vehicles, portable devices, and transportation applications.^{1,2} As the most critical component of DMFCs, the proton-exchange membrane (PEM), which provides an ionic path for protons and hinders the transfer of the fuel from the anode side to the cathode side in a fuel cell, has attracted interest in commercial, academic, and governmental institutions. Thus, a PEM must have acceptable cost, good chemical stability and mechanical strength, high proton conductivity, and low methanol permeability.³

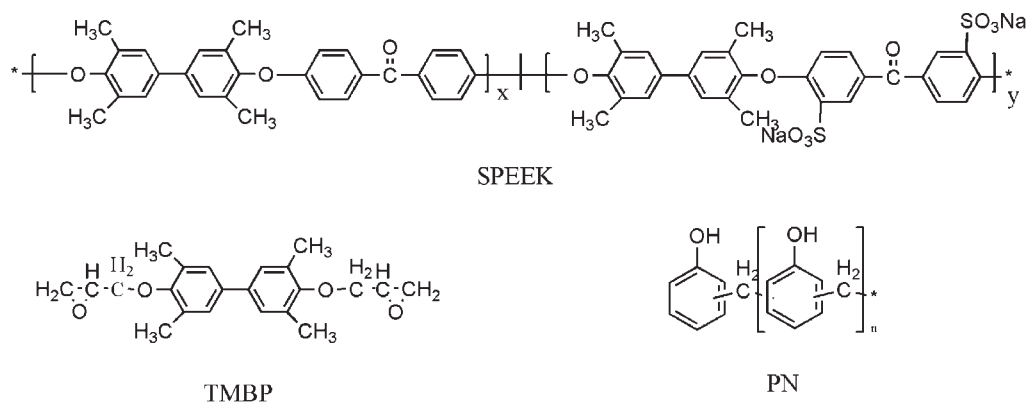
Conventional perfluorosulfonic polymers (e.g., Nafion from Dupont), with excellent chemical and

physical stability as well as high proton conductivity, are used for practical DMFC applications. However, several drawbacks, such as poor proton conductivity at low humidity and high temperatures (>80°C), high cost, and low methanol resistance, limit their DMFC applications.^{4–7} Therefore, alternative membranes with acceptable costs and low methanol permeability to replace perfluorinated membranes have been researched by many experts. For instance, many fluorine-free polymers with sulfonic acid groups on highly stable aromatic polymers such as poly(ether ether ketone)s,^{8,9} poly(aryl ether sulfone)s,^{10–13} poly(phenylene sulfide),^{14,15} and polyimides^{16–19} have been investigated in recent years.

Sulfonated poly(ether ether ketone)s (SPEEKs), because of their excellent chemical and thermal stability, good mechanical properties, low methanol permeability, and low cost, have been intensively studied. However, SPEEK membranes with a high ion-exchange capacity (IEC) have a high swelling ratio even dissolved in water and low mechanical properties and methanol resistance at high relative

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Contract grant sponsor: China High-Tech Development 863 Program; contract grant number: 2007AA03Z218.



Scheme 1 Chemical structures of SPEEK, TMBP, and PN.

humidity.^{9,20} Blending SPEEKs with a polymer is one of the approaches to solve these problems and has been widely reported.^{21–24} Ren et al.²³ and Mena and Mulder²⁵ used poly(ether sulfone) and poly(vinylidene fluoride), respectively, to modify SPEEK to improve the methanol permeability of the membranes in DMFCs. Kerres et al.²⁶ prepared acid–base polymer blend membranes based on sulfonated polymers as acid compounds and polymers with amine or imine groups as basic compounds. The formation of hydrogen bonds between the sulfonic acid groups and amine groups leads to the compatibility of the blend polymers. This favors swelling reduction, an improvement of the mechanical properties, and a further reduction of the methanol permeability of the membranes. Our group²⁷ reported the modification of polymers containing hydroxyl groups into SPEEK, and the interaction between sulfonic acid groups and hydroxyl groups resulted in the reduction of swelling, an improvement of the mechanical properties, and a further decrease in the methanol crossover of the membranes. In our previous study,²⁸ SPEEK/epoxy resin composite membranes composed of a proton-conducting component (SPEEK) and a methanol-barrier component [a cross-linked epoxy resin based on 4,4'-diglycidyl-(3,3',5,5'-tetramethylbiphenyl) epoxy resin (TMBP) and polyamine] were prepared by *in situ* polymerization. As expected, the mechanical properties and methanol resistance of SPEEK were drastically improved with the introduction of the crosslinked epoxy resin.

With these approaches in mind, we studied the properties of SPEEK blended with an epoxy and phenol novolac (PN). Here, PN with aromatic structures was used as a curing agent for the rigid-rod epoxy resin (TMBP). It is well known that the reaction between the epoxy ring and hydroxyl in PN forms lots of hydroxyl groups.²⁹ The hydroxyl groups were proposed to interact with sulfonic acid groups of SPEEK, resulting in changes in the properties of the membranes. Blend membranes based on

SPEEK, TMBP, and PN were prepared by *in situ* polymerization for the purpose of improving the methanol permeability, swelling stability, and mechanical properties and retaining the thermal stability. The proton conductivity and selectivity of the blend membranes were measured and are discussed here in detail.

EXPERIMENTAL

Materials

SPEEK polymers were prepared by direct aromatic nucleophilic substitution polymerization and were reported in our previous work.⁹ The epoxy monomer (TMBP) with an epoxy equivalent of 177 was synthesized.³⁰ PN as a curing agent for epoxy was supplied by Wuxi Resin Plants (Wuxi, China). Phosphorus triphenyl (PPh₃) as an accelerant for the reaction between TMBP and PN was purchased from Zhejiang Dongyang Reagent Co., Ltd. (Zhejiang, China). The chemical structures of SPEEK, TMBP, and PN are shown in Scheme 1.

Preparation of the blend membranes

The blend membranes were prepared by a casting-solution, evaporation, and heating crosslinking method. First, the SPEEK sample was dissolved in *N*-methylpyrrolidone (NMP) at room temperature to prepare a 10 wt % solution. Certain amounts of TMBP, PN, and PPh₃ (TMBP/PN = 3/2 w/w, PPh₃ = 5 wt % of TMBP) were added to the aforementioned SPEEK solution, and they were stirred for about 2 h to form a wholly transparent solution and then cast onto a glass plate. The membranes (50–150 μm) were dried at 75°C for 24 h to remove NMP and then heated at 150°C for 1 h to retain the reaction between TMBP and PN. Each membrane was peeled off from the glass plate by immersion in deionized water. The membranes in an acidic form

were obtained by immersion into a 2M HCl solution for 24 h, and then the membranes were washed with deionized water until the pH reached 6–7. In the following sections, blend membranes with different weight percentages of TMBP and PN are defined as SPEEK/TMBP/PN-*X*, where *X* represents the weight percentages of TMBP and PN in the blend membranes.

Fourier transform infrared (FTIR)

FTIR spectra of the blend membranes were recorded on powder samples dispersed in dry KBr in the form of disks after heating under infrared light for at least 10 min with a Bruker (Ettlingen, Germany) Vector 22 spectrometer at a resolution of 4 cm⁻¹/min from 4000 to 400 cm⁻¹.

Morphology of the membranes

Atomic force microscopy (AFM) was performed with a Shimadzu (Tokyo, Japan) SPM-9500 JZ scanning probe microscope in the tapping mode. A silicon microcantilever (spring constant = 2 N/m, resonance frequency ~ 70 kHz; Olympus Co., Tokyo, Japan) with an etched conical tip (radius of curvature ~ 40 nm as characterized by scanning over a very sharp needle array; NT-MDT, Moscow, Russia) was used for the scan. The scan rate ranged from 1.0 to 2.0 Hz to optimize the image quality. Each scan line contained 256 pixels, and an entire image was composed of 256 scan lines. The SPEEK/TMBP/PN blend membranes were obtained through the spin coating of a solution of SPEEK in an acidic form, TMBP, and PN in 0.05 g/mL NMP onto a freshly cleaned silicon wafer at 2000 rpm for 30 s at room temperature, and it was heated at 150°C for 1 h.

Mechanical properties

The mechanical properties of the fully hydrated samples (15 mm × 4 mm) were measured with a Shimadzu AG-I 1KN apparatus at the test speed of 5 mm/min. For each test reported, at least three samples were taken, and the average value was calculated.

Differential scanning calorimetry (DSC)

A Mettler (Mettler-Toledo Group, Zurich, Switzerland) 821^e model differential scanning calorimeter was used to determine the glass-transition temperature (*T_g*) values of the SPEEK and SPEEK/TMBP/PN blend membranes in the acidic form. The samples were heated from 25 to 350°C at a heating rate of 20°C/min under N₂ at a flow of 200 mL/min.

Thermogravimetric analysis (TGA)

TGA was performed on a Pyris thermogravimetric analysis system (PerkinElmer, Waltham, MA) to study the thermal stability behaviors of the SPEEK and SPEEK/TMBP/PN blend membranes in the acidic form. Approximately 5–10-mg samples of the membranes were heated to 150°C and kept at this temperature for 20 min to remove any residual water or solvent and were then cooled to 80°C and reheated to 700°C at a heating rate of 10°C/min in N₂.

IEC

The titration method was used to determine the IEC values of the membranes as follows. The membranes in the acidic form were converted to the sodium form by immersion in 1M NaCl solutions for 24 h to exchange the H⁺ ions for Na⁺ ions. Phenolphthalein was used as an indicator. The exchanged H⁺ ions within the solutions were titrated with 0.005M NaOH solutions. The IEC values of the membranes were calculated from the titration data with the following formula:

$$\text{IEC} = \frac{\text{Consumed NaOH (mL)} \times \text{Molarity of NaOH}}{\text{Weight of the dried membrane}} \text{mequiv/g} \quad (1)$$

Water uptake and swelling ratio

The water uptake and swelling ratio at various temperatures were determined by the weight and length differences between the fully hydrated membranes and dried membranes, respectively. The membranes were first equilibrated in water at the evaluated temperature for about 12 h and then removed from the water quickly; the extra water on the membrane surface was dry-wiped, and the membranes were immediately measured to determine the wet mass (*W_{wet}*) and length (*L_{wet}*). The dried weight (*W_{dry}*) and length (*L_{dry}*) of the membranes were determined through the drying of the membranes at 100°C for 24 h. The water uptake was defined as follows:

$$\text{water uptake(\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

The swelling ratio was calculated with the following equation:

$$\text{Swelling ratio(\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

Water desorption measurement

The water desorption measurement was tested with a Pyris 1 thermogravimetric analyzer (PerkinElmer).

The temperature remained at 80°C, and the pressure of the test cell was kept constant. The Pyris 1 thermogravimetric analyzer was used to evaluate the weight changes of the samples with time. The water diffusion coefficient (D) was calculated as follows:

$$\frac{M_t}{M_\infty} = \left(\frac{Dt}{\pi l^2}\right)^{1/2} \quad (4)$$

where M_t/M_∞ is the water desorption and l is the membrane thickness.

Methanol permeability measurement

Methanol permeability coefficients of membranes were measured with a two-chamber liquid permeability cell. This cell consisted of two reservoirs, which were separated by a vertical membrane immersed in a 10M methanol solution for 12 h. A 10M methanol solution was placed on one side of the cell, and water was placed on the other side. The magnetic stirrers were used continuously during the measurement. Methanol concentrations in the water cell were periodically estimated with a GC-8A gas chromatograph (Shimadzu). The methanol diffusion coefficient was calculated with the following equation:

$$C_B(t) = \frac{A DK}{V_B L} C_A(t - t_0) \quad (5)$$

where A , L , and V_B are the effective area, the thickness of the membrane, and the volume of the permeated reservoirs, respectively; C_A and C_B are the methanol concentrations in the methanol chamber and water chamber, respectively; and DK is the methanol diffusion coefficient.

Proton conductivity

The proton conductivity was measured by a four-electrode alternating-current impedance method from 0.1 Hz to 100 kHz with a 10-mV alternating-current perturbation and a 0.0-V direct-current rest voltage with a Princeton Applied Research model 273A potentiostat (with a model 5210 frequency response detector from EG&G PARC, Princeton, NJ). The impedance measurements were performed under 100% relative humidity at the desired temperature after the films were full hydrated in water for 24 h.

The proton conductivity [σ (S/cm)] was calculated with the following equation:

$$\sigma = L/RA \quad (6)$$

where L is the distance between the two electrodes, R is the resistance of the membrane, and A is the cross-sectional area of the membrane.

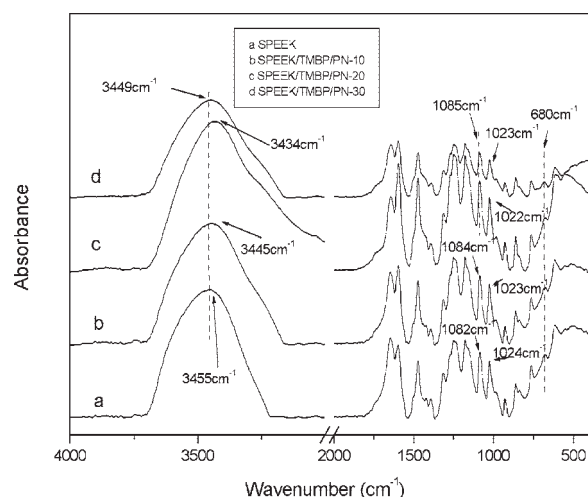


Figure 1 FTIR spectra of SPEEK and SPEEK/TMBP/PN blend membranes.

RESULTS AND DISCUSSION

Characterization

To investigate the structures of the SPEEK and SPEEK/TMBP/PN blend membranes in the acidic form, FTIR spectra were taken (Fig. 1). From Figure 1(a), the sulfonic acid groups in the SPEEK membrane were confirmed with the characterized peaks at 1082, 1024, and 680 cm^{-1} corresponding to the asymmetric and symmetric O=S=O stretching vibrations and the S—OH stretching, respectively. The peak at 3454 cm^{-1} for the pristine SPEEK was attributed to the hydroxyl groups in water and hydronium ions that interacted with the sulfonic acid groups of the polymer at less than 100% relative humidity. The peaks of the asymmetric and symmetric O=S=O stretching vibrations shifted, and the peaks of the hydroxyl groups in the region from 3400 to 3500 cm^{-1} shifted to a lower frequency, as shown in Figure 1(b–d); this might have been induced by the hydrogen bond between sulfonic acid groups of SPEEK and hydroxyl groups formed by the reaction between TMBP and PN.²⁷

Morphology

Representative three-dimensional AFM images were taken to investigate the changes in the morphology of the blend membrane surfaces with the increment of crosslinked TMBP/PN in the SPEEK matrix. The topographic images (Fig. 2) indicated good compatibility of SPEEK with crosslinked TMBP/PN. The pristine SPEEK membrane clearly showed the aggregates characteristic of the supermolecular structure of polyelectrolyte membranes.³¹ The roughness of the pristine SPEEK membrane surface indicated that the height contrast between hydrophilic and

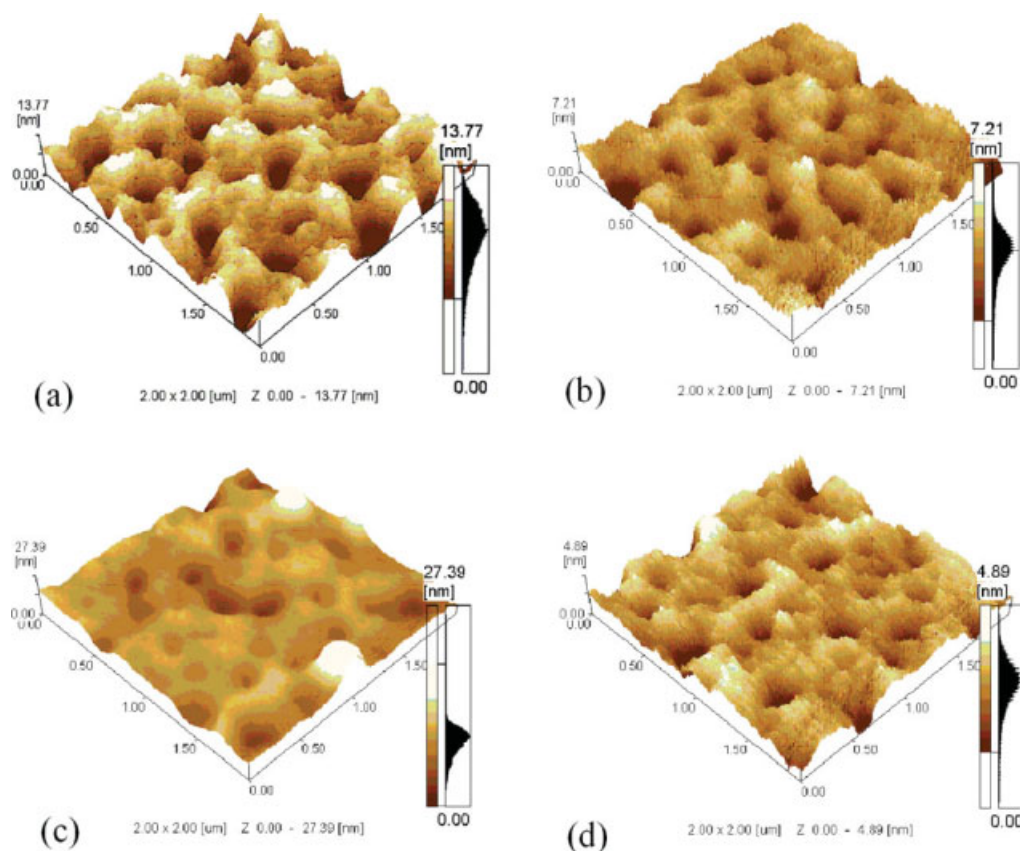


Figure 2 AFM images of SPEEK and SPEEK/TMBP/PN blend membranes: (a) SPEEK, (b) SPEEK/TMBP/PN-10, (c) SPEEK/TMBP/PN-20, and (d) SPEEK/TMBP/PN-30. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

hydrophobic domains was prominent. Comparing the AFM images of different membranes, we found that the morphology of the membrane surfaces changed significantly after casting with TMBP cured with PN. With the increment of the weight ratio of the crosslinked TMBP/PN content, the connectivity and size of the domains showed a decreasing tendency, and the surfaces became gradually smoother because of the formation of hydrogen bonds between the sulfonic acid groups and the hydroxyl groups, as confirmed by FTIR (Fig. 1). The change in the morphology might have led to the changes in the properties, such as the mechanical strength, water uptake, methanol diffusion, and proton conductivity.

Mechanical and thermal properties

A high degree of sulfonic acid groups in a SPEEK membrane results in low mechanical properties at high relative humidity. Good mechanical properties are required for the use of membranes as PEMs in DMFCs. An epoxy cured by curing agents was almost used to improve the mechanical properties of polymers because of the formation of networks between the epoxy and curing agents, which could restrict the molecular segmental motion of the polymer matrix.³² Results for typical mechanical properties of SPEEK and SPEEK/TMBP/PN blend membranes, such as the tensile strength, Young's modulus, and maximum elongation, are listed in Table I. Before the testing,

TABLE I
Properties of SPEEK and SPEEK/TMBP/PN Blend Membranes

| Blend membrane | IEC | Mechanical properties | | | T_g (°C) | T_d (°C) | Methanol permeability coefficient $\times 10^{-8}$ (cm ² /s) | Water diffusion coefficient $\times 10^{-5}$ (cm ² /s) |
|------------------|------|------------------------|------------------------|-----------------------|------------|------------|---|---|
| | | Tensile strength (MPa) | Maximum elongation (%) | Tensile modulus (MPa) | | | | |
| SPEEK | 2.01 | 15.5 \pm 2.8 | 7.2 \pm 0.3 | 386 \pm 78 | 327 | 270 | 118.0 | 8.89 |
| SPEEK/TMBP/PN-10 | 1.60 | 16.6 \pm 5.5 | 6.2 \pm 1.8 | 514 \pm 18 | 275 | 261 | 41.4 | 2.77 |
| SPEEK/TMBP/PN-20 | 1.41 | 32.7 \pm 6.1 | 5.2 \pm 1.4 | 1031 \pm 14 | 270 | 252 | 7.8 | 1.40 |
| SPEEK/TMBP/PN-30 | 1.21 | 24.4 \pm 6.4 | 3.3 \pm 1.8 | 955 \pm 65 | 282 | 257 | 3.6 | 0.98 |

the membranes in the acidic form were immersed in water at room temperature. As expected, Young's moduli of the membranes were improved from 386 MPa for the pristine SPEEK membrane up to 1031 MPa for 20 wt % crosslinked TMBP/PN in the SPEEK matrix. The tensile strength data showed the same trend. However, the maximum elongation of the blend membranes decreased with the introduction of crosslinked TMBP/PN. The restriction of the mobility of SPEEK molecular chains by crosslinked TMBP/PN resulted in an increase in the rigidity and thereby reduced the toughness of the membranes. These data indicated that the modification of crosslinked TMBP/PN in the SPEEK matrix greatly enhanced the rigidity of the mechanical properties of the resulting membranes.

DSC and TGA were performed to evaluate the thermal properties of SPEEK and SPEEK/TMBP/PN blend membranes in the acidic form. The T_g values measured by DSC are listed in Table I. All the DSC curves showed only one thermal transition region. This confirmed the miscibility between SPEEK and crosslinked TMBP/PN, which might be due to the interaction between the sulfonic acid groups of SPEEK and the hydroxyl groups of crosslinked TMBP/PN. The T_g values of the blend membranes were 275, 270, and 282°C with 10, 20, and 30 wt % crosslinked TMBP/PN, respectively, and were lower than that of the pristine SPEEK membranes (327°C).

The thermal stability of all the membranes was studied with TGA and differential thermogravimetry (DTG). Figure 3 shows the TGA and DTG thermograms of the blend membranes from 80 to 700°C in N_2 at a heating rate of 5°C/min in comparison with the pristine SPEEK membrane. All membranes were heated at 150°C for 20 min to remove the water and solvent in the membranes before measurement. All the TGA and DTG curves showed two distinct degradation regions. The extrapolated onset-of-thermal-decomposition temperatures (T_d 's) are listed in Table I. The T_d values decreased from about 270 to 252°C. This was most likely because the methylene in the PN molecule had low thermal stability. Above the T_d values, sharp thermal degradation occurred, which could be attributed to the loosening of sulfonic acid groups in the pristine SPEEK membrane and methylene in crosslinked TMBP/PN. The second degradation region was ascribed to the decomposition of the main links of SPEEK and crosslinked TMBP/PN. Figure 3 shows that all the membranes were stable above 250°C.

The results from DSC and TGA showed that the SPEEK/TMBP/PN blend membranes had excellent thermal properties above 200°C, which could satisfy the requirement of PEMs in DMFCs.

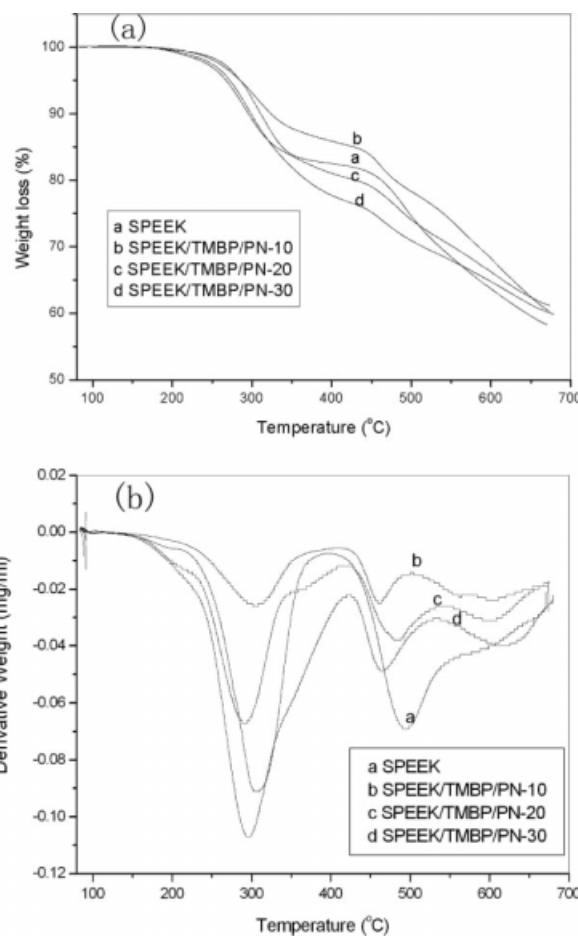


Figure 3 (a) TGA and (b) DTG curves of SPEEK and SPEEK/TMBP/PN blend membranes.

IEC, water uptake, swelling ratio, and water desorption

It has been widely reported in the literature that the IEC, water uptake, swelling ratio, and proton diffusion capability of membranes play important roles in the proton conductivity of sulfonated polymers.³³

The values of IEC, which is defined as the content of sulfonic acid groups in 1 g of a membrane, indicates the concentration of sulfonic acid groups in the membrane, which influences properties such as the water uptake, swelling ratio, and proton conductivity. The experimental IEC values of SPEEK and SPEEK/TMBP/PN blend membranes are listed in Table I. With the increment of crosslinked TMBP/PN, which did not have sulfonic acid groups, IEC sharply decreased from 2.0 to 1.2 mequiv/g. The reduction of IEC might be attributed to the dilution effect of the epoxy polymer cured by PN, which lacked sulfonic acid groups. Additionally, Table I shows that by the addition of only 10 wt % TMBP/PN, the IEC value decreased by 20 wt %. In this respect, it is possible that the reduction of the IEC

value of the membrane can be attributed to the interaction between sulfonic and hydroxyl groups.

Water molecules, forming cationic mixtures such as H_3O^+ and $H_5O_2^+$ in sulfonated polymer membranes, significantly affect the transport of protons in hydrogen-bonded ionic channels in water. Thus, a certain amount of water residing in the hydrophilic domains can facilitate the transport of protons; however, excessive water uptake will result in hindrance of the motion of protons, mechanical frailty, low dimensional stability, and high methanol permeability of membranes, all of which will lead to poor performance, especially in DMFC applications. Therefore, maintaining an appropriate amount of water in sulfonated polymers is indispensable to retaining superior proton conductivity, so it is very important to research the water uptake of membranes for PEM applications. Here, the water uptake was measured by the mass change in the membrane before and after full hydration. The temperature dependence of the water uptake of the SPEEK and SPEEK/TMBP/PN blend membranes is shown in Figure 4. It can be mostly concluded that the amount of water uptake in the sulfonated polymers strongly depended on the microstructure of the polymers, the number of sulfonic acid groups, and the IEC values. It is well known that a cured epoxy resin with a high crosslink density is hydrophobic. The incorporation of crosslinked TMBP/PN into the hydrophilic SPEEK matrix resulted in a reduction of the number of sulfonic acid groups and an increase in the crosslinking density of cured TMBP/PN, which hindered the absorption of water in the membrane. The interaction between sulfonic acid groups and hydroxyl groups also reduced the free volume for water absorption in the membranes. Thus, the water uptake of the blend membranes sharply decreased with the increasing weight content of crosslinked

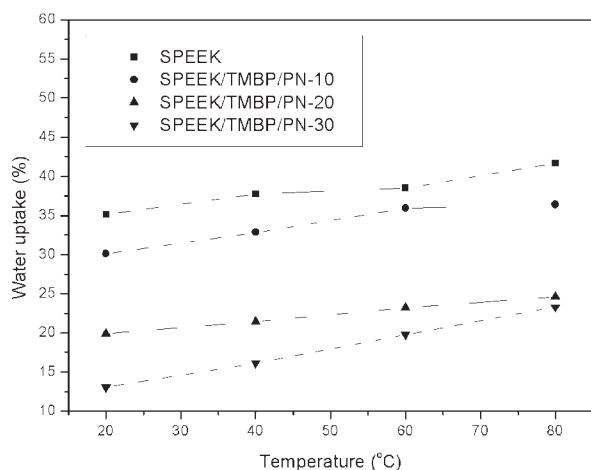


Figure 4 Water uptake of SPEEK and SPEEK/TMBP/PN blend membranes at various temperatures.

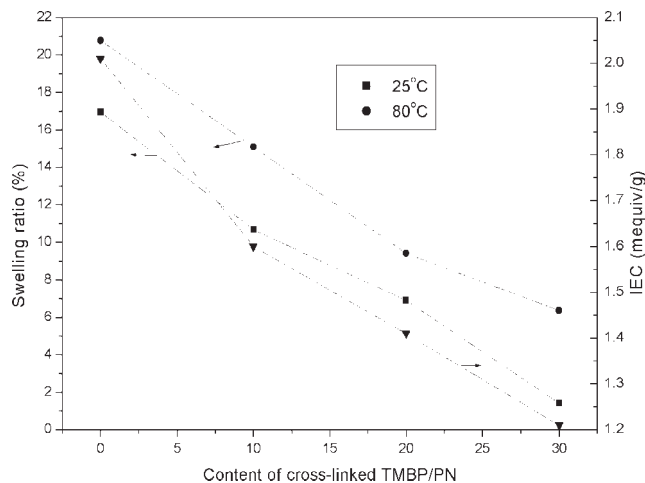


Figure 5 IECs and swelling ratios of SPEEK and SPEEK/TMBP/PN blend membranes.

TMBP/PN, and this was in agreement with the IEC results. With the temperature increasing, the polymer chain mobility and the free volume for water absorption increased, and this resulted in an increase in the water uptake, as shown in Figure 4. The SPEEK membrane with a high degree of sulfonation showed bad dimensional stability; this would limit its usage for PEMs and must be solved. The swelling ratios in the length direction of the membranes at 25 and 80°C were investigated, and the results are shown in Figure 5. The swelling ratio of the pristine SPEEK membranes was as much as 16.8% at 25°C and increased to 20.7% at 80°C. As expected, the swelling ratio drastically decreased to 1.4% at 25°C and 7.0% at 80°C while the concentration of cross-linked TMBP/PN reached up to 30% in the membrane. Thus, the mechanical stability of the blend membranes could be improved by the incorporation of crosslinked TMBP/PN.

Because of the important role of water in PEMs, the diffusion and retention of water by a membrane have significant effects on the proton conductivity, especially at high temperatures and low relative humidity. The speed of water diffusion in membranes may provide information about water retention. Plots of the water desorption versus the half-time ($t^{1/2}$) for Fickian diffusion³⁴ were fitted to be linear and are shown in Figure 6. The water diffusion coefficients of the membranes at 80°C were calculated from the slopes of the lines by eq. (4), and the results are listed in Table I. The water absorption resulted from the hydrophilic domains formed by the ionic clusters of sulfonic acid groups. The introduction of the hydrophobic crosslinked TMBP/PN into the hydrophilic SPEEK matrix hindered the evaporation of water in the membranes. Furthermore, the interaction between sulfonic acid groups and hydroxyl groups, which resulted in more

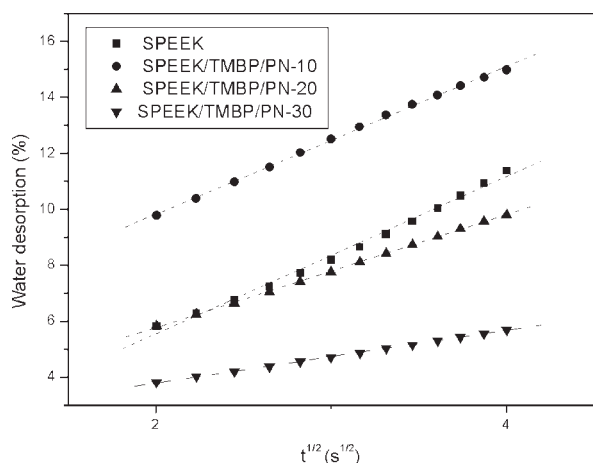


Figure 6 Water desorption of SPEEK and SPEEK/TMBP/PN blend membranes.

compact structures, also limited the speed of evaporation of water. Therefore, the water diffusion coefficients obviously decreased from 8.89×10^{-5} (the pristine SPEEK membrane) to 2.27×10^{-5} cm^2/s (the SPEEK/TMBP/PN-10 blend membranes). The water diffusion coefficients of the blend membranes also decreased from 2.27×10^{-5} to 9.8×10^{-6} cm^2/s when the content of crosslinked TMBP/PN increased from 10 to 30 wt %. The lower water diffusion coefficients meant higher water retention.^{27,28} The results indicated that the water retention of the membranes was drastically improved with the incorporation of the cured epoxy into the SPEEK matrix.

Methanol permeability, proton conductivity, and selectivity

PEMs with low methanol permeability are required to satisfy conventional usage for DMFCs because when methanol diffuses from the anode side to the cathode side of the membrane, the efficiency of a fuel cell is reduced by a loss of fuel, which results into the decrease of the cathode voltage and excess thermal load. The methanol diffusion across the membranes is mainly related to the water uptake and the microstructure of the membranes because the methanol permeability needs connectible channels. The methanol permeability coefficients of SPEEK and their blend membranes were measured under the same conditions and calculated with eq. (5). The relative data are shown in Table I. With the increment of crosslinked TMBP/PN, the methanol permeability coefficients of the membranes drastically decreased. The methanol diffusion coefficient of the pristine SPEEK membrane was 1.18×10^{-6} cm^2/s at room temperature, whereas those of the SPEEK/TMBP/PN blend membranes with 10, 20, or 30 wt % crosslinked TMBP/PN were 4.14×10^{-7} , 7.80×10^{-8} , and 3.63×10^{-8} cm^2/s , respectively.

This phenomenon may be due to the fact that the methanol diffusion channels were hindered by the crosslinked epoxy and the more compact microstructures that were formed by the interaction between sulfonic acid groups and hydroxyl groups. The reduction of the methanol permeability of the membranes was also ascribed to the reduction of water uptake in the membranes.

There are several factors that have an impact on the level of proton conductivity, such as the proton concentration, polymer structure and morphology, proton mobility, and water content.³⁵ The proton conductivities of SPEEK and SPEEK/TMBP/PN blend membranes at 25 and 80°C were measured by a four-electrode alternating-current impedance method in water, and the results are shown in Figure 7. Before the measurements, the membranes were immersed in water for 3 h at the evaluated temperature. The proton conductivities of all membranes were above 0.01 S/cm, and this satisfied the lowest requirement of practical interest for DMFC applications. Regardless of the content of crosslinked TMBP/PN, the proton conductivities increased with the increase in temperature, and this agreed with our previous work.²⁹ However, with the increase in crosslinked TMBP/PN, the proton conductivities of the blend membranes gradually decreased, and this might have been the combined result of the low sulfonic acid concentration (from the values of IEC) and water content, the hindrance of proton mobility from the crosslinked epoxy matrix, and the formation of small proton channels corresponding to the greater compactness of the microstructure formed by the interaction between the sulfonic acid groups and hydroxyl groups.

For practical DMFC usage, PEMs with a good performance of high proton conductivity and low methanol permeability are required. Selectivity, defined

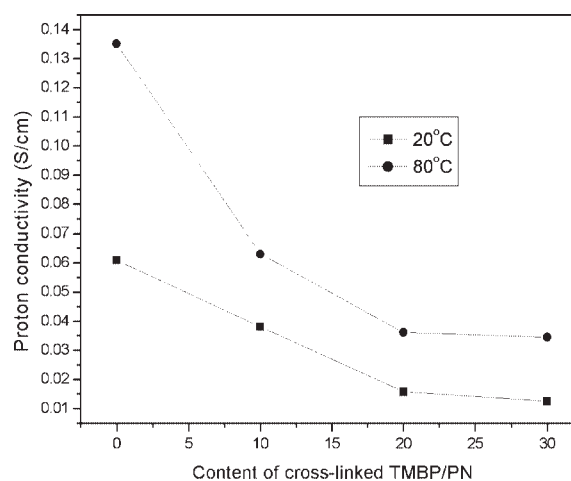


Figure 7 Proton conductivity of SPEEK and SPEEK/TMBP/PN blend membranes.

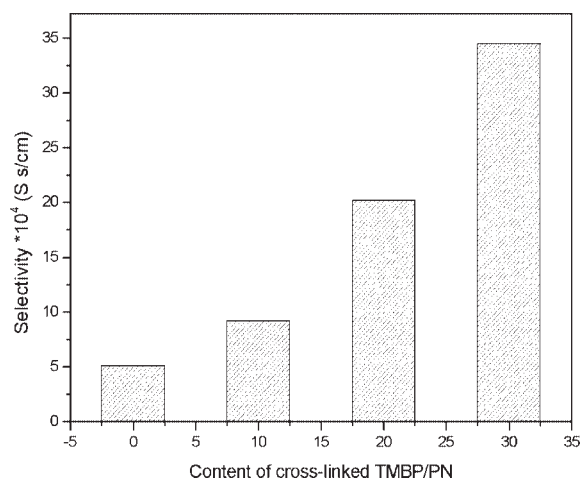


Figure 8 Selectivity of SPEEK and SPEEK/TMBP/PN blend membranes.

as the ratio of proton conductivity to methanol permeability, was used here as a characteristic factor for estimating membrane performance with respect to both proton conductivity and methanol permeability. Figure 8 shows the selectivity of SPEEK and SPEEK/TMBP/PN blend membranes, which is based on the proton conductivity and methanol permeability at room temperature. The values of the selectivity increased with the content of crosslinked TMBP/PN increasing, and this indicated that the incorporation of crosslinked TMBP/PN into the SPEEK matrix resulted in a greater influence on the methanol permeability than the proton conductivity of the membranes. The results show that the SPEEK/TMBP/PN blend membranes have potential as PEMs in DMFCs.

CONCLUSIONS

SPEEK/TMBP/PN blend membranes with different weight percentages of crosslinked TMBP cured by PN were successfully prepared by a casting-solution, evaporation, and heating crosslinking method for the purpose of improving the mechanical properties, dimensional stability, water retention, and methanol resistance. As expected, the mechanical properties at high relative humidity were drastically improved, and the swelling ratios were sharply reduced from 16.8 to 1.4% at 25°C and from 20.7 to 7.0% at 80°C. With the incorporation of crosslinked TMBP/PN, the water diffusion coefficients of the membranes at 80°C significantly decreased from 8.9×10^{-5} to 9.8×10^{-6} cm²/s. Although the proton conductivities of the blend membranes were lower than that of the pristine SPEEK membrane, the methanol permeability coefficients rapidly decreased from 1.18×10^{-6} to 3.63×10^{-8} cm²/s. Higher selectivity was obtained in the blend membrane than in the pristine SPEEK membrane. According to the aforementioned results,

the SPEEK/TMBP/PN blend membranes show good potential for use in DMFCs.

References

- Hampson, N. A.; Wilars, M. J. *J Power Sources* 1979, 4, 191.
- Scott, K.; Taama, W. M.; Argyropoulos, P. *J Power Sources* 1999, 79, 43.
- Kreuer, K. D. *J Membr Sci* 2001, 185, 29.
- Surampudi, S.; Narayanan, S. R.; Vamos, E.; Frank, H.; Halpert, G.; Laconti, A.; Kosek, J.; Surya Prakash, G. K.; Olah, G. A. *J Power Sources* 1994, 47, 377.
- Ren, X.; Springer, T. E.; Gottesfeld, S. *J Electrochem Soc* 2000, 147, 92.
- Gurau, B.; Smotkin, E. S. *J Power Sources* 2002, 112, 339.
- Ren, X.; Springer, T. E.; Gottesfeld, S. *J Electrochem Soc* 2000, 147, 92.
- Yang, B.; Manthiram, A. *Electrochem Solid State A* 2003, 6, 229.
- Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. *J Membr Sci* 2004, 234, 75.
- Notle, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. *J Membr Sci* 1993, 83, 211.
- Meng, Y. Z.; Tjong, S. C.; Hay, A. S.; Wang, S. J. *J Polym Sci Part A: Polym Chem* 2001, 39, 3218.
- Wang, Z.; Li, X. F.; Zhao, C. J.; Ni, H. Z.; Na, H. *J Appl Polym Sci* 2007, 104, 1443.
- Wang, Z.; Li, X. F.; Zhao, C. J.; Ni, H. Z.; Na, H. *J Power Sources* 2006, 160, 969.
- Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. *Macromolecules* 1996, 29, 6969.
- Miyatake, K.; Shoyji, E.; Yamamoto, K.; Tsuchida, E. *Macromolecules* 1997, 30, 2941.
- Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. *J Membr Sci* 1999, 160, 127.
- Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. *Polymer* 2001, 42, 359.
- Fang, J. H.; Guo, X. X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* 2002, 35, 9022.
- Miyatake, K.; Asano, N.; Watanabe, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 3901.
- Xue, S.; Yin, G. P. *Eur Polym J* 2006, 42, 776.
- Manea, C.; Mulder, M. *J Membr Sci* 2002, 206, 443.
- Kerres, J. A. *Fuel Cells* 2005, 5, 230.
- Ren, S. Z.; Sun, G. Q.; Li, C. N.; Wu, Z. M.; Jin, W.; Chen, W. M.; Xin, Q.; Yang, X. F. *Mater Lett* 2006, 60, 44.
- Gohil, G. S.; Nagarale, R. K.; Binsu, V. V.; Shahi, V. K. *J Colloid Interface Sci* 2006, 298, 845.
- Menea, C.; Mulder, M. *J Membr Sci* 2002, 206, 443.
- Kerres, J.; Ullrich, A.; Meier, F.; Haring, T. *Solid State Ionics* 1999, 125, 243.
- Cai, H. L.; Shao, K.; Zhong, S. L.; Zhao, C. J.; Zhang, G.; Li, X. F.; Na, H. *J Membr Sci* 2007, 297, 162.
- Fu, T. Z.; Zhang, G.; Zhong, S. L.; Shao, K.; Zhang, H. Q.; Wang, J.; Na, H. *J Power Sources* 2007, 165, 708.
- Han, S. H.; Kim, W. G.; Yoon, H. G.; Moon, T. J. *J Polym Sci Part A: Polym Chem* 1998, 36, 773.
- Fu, T. Z.; Zhang, G.; Zhong, S. L.; Zhao, C. J.; Shao, K.; Wang, L. F.; Na, H. *J Appl Polym Sci* 2007, 105, 2611.
- Lehmani, A.; Durand-Vidal, S.; Turq, P. *J Appl Polym Sci* 1998, 68, 503.
- Tjong, S. C.; Meng, Y. Z. *J Appl Polym Sci* 1999, 74, 1827.
- Kim, Y. S.; Einsla, B.; Sankir, M.; Harrison, W.; Pivovar, B. S. *Polymer* 2006, 47, 4026.
- Watari, T.; Wang, H. Y.; Kuwahara, K.; Tanaka, K.; Kita, H.; Okamoto, K. *J Membr Sci* 2003, 219, 137.
- Peckham, T. J.; Schmeisser, J.; Rodgers, M.; Holdcroft, S. *J Mater Chem* 2007, 17, 3255.