



# Novel acid–base molecule-enhanced blends/copolymers for fuel cell applications

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## ARTICLE INFO

### Article history:

Received 12 December 2008  
 Received in revised form  
 25 December 2008  
 Accepted 30 December 2008  
 Available online 14 January 2009

### Keywords:

Composite membranes  
 Aminated polymer  
 Morphology  
 Fuel cells

## ABSTRACT

A series of acid–base molecule-enhanced composite membranes are successfully prepared. The composite membranes are composed of a sulfonated poly(aryl ether ketone) (6FSPEEK) as an acidic component, and of aminated poly(aryl ether ketone) containing a naphthyl group (AmPEEK-NA) as a basic component. The composite membranes exhibit obviously improved thermal, oxidative and dimensional stability. Especially, these composite membranes possess excellent tensile properties both in the dry and wet state. The proton conductivities of these membranes are higher than  $2.45 \times 10^{-2} \text{ S cm}^{-1}$  at room temperature and higher than  $6.0 \times 10^{-2} \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ . The morphology of the membranes is studied in detail by SEM and AFM. All the data prove that both composite and aminated/sulfonated copolymer membranes may be potential proton exchange membrane for fuel cell applications.

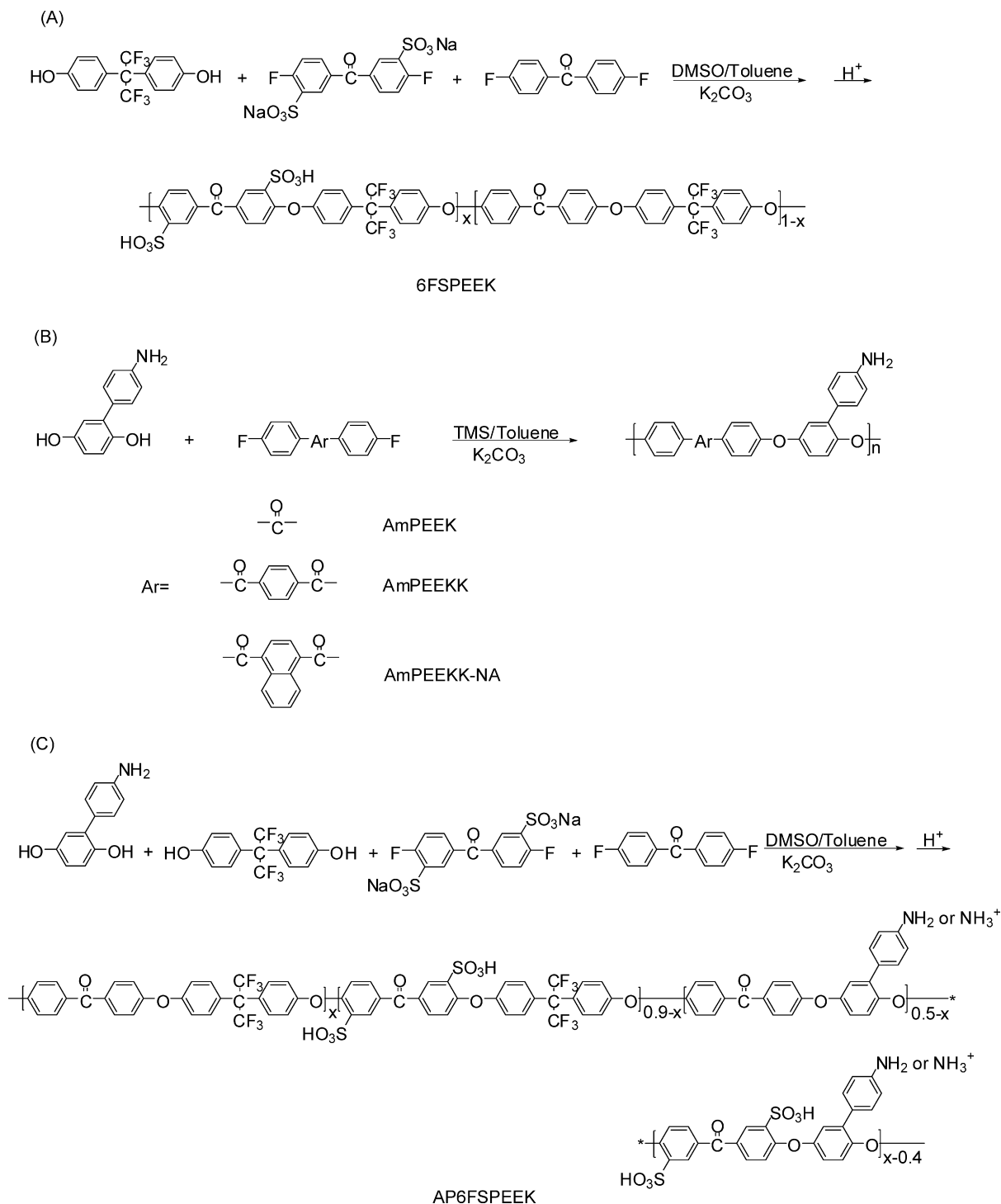
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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs), which operate as energy conversion devices, have the potential to substantially and positively impact many areas, including environment, economy and energy security [1–3]. As one of the key components of PEMFCs, proton exchange membrane (PEM) must suffer from harsh conditions during fuel cell operation. The most commonly used proton exchange membranes are perfluorinated copolymers with pendant sulfonic groups, such as Nafion (Dupont) and Dow membrane (DOW), which combine high conductivity and excellent chemical stability. However, some drawbacks, such as high cost and low operation temperature ( $\leq 80^\circ\text{C}$ ) of perfluorinated polymers limit the large-scale commercialization of PEMFCs [1,3,4]. Therefore, it is significant to develop new kinds of proton exchange membranes with lower cost and considerable performances. Apart from Nafion, new ion conducting polymeric materials have played only a minor role in significantly increasing cell performance. However, new materials that can be used to replace Nafion are now urgently required to afford successful technology commercialization. Therefore, the alternative materials such as sulfonated poly(ether ether ketone)s, poly(arylene ether sulfone)s, poly(phenylene sulfide), polyimides and polybenzimidazoles fall into this category [4–9]. These polymers are satisfied with lower cost as well as higher chemical stability for many applications.

Poly(aryl ether ketone)s (PAEKs) are a class of important high performance aromatic polymers with excellent mechanical strength, and thermooxidative and chemical resistance for advanced materials [10]. Therefore, sulfonated PAEKs have been selected as one of alternative PEM materials [11–13]. However, sulfonated PAEKs with high ion-exchange capacities often have relatively high swelling ratio and low mechanical properties under humid circumstance with increasing temperature [3,11–13], which limit the application for PEMFCs. Cross-linking [14–18] and blending [19–29] are two main routes used to overcome these problems. Although cross-linking is a useful method to decrease the swelling ratio and limit methanol diffusion, it is complicated in post treatment [16]. Compared with cross-linking, blending is lightly easier in post treatment. Blending inorganic materials, such as montmorillonite (MMT) [19],  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$  [20], phosphotungstic acid [21] and heteropolyacids [22], with the membranes is one useful method that can lead to the increase of conductivity, the fall of methanol permeability and the improvement of thermal stability. However, the incorporation of small particles into membranes often leads to the loss of membrane mechanical properties and there is a risk of the escape of the small molecules from the membranes. Introducing the polymeric materials in SPAEK membranes [16,23–27], such as Nafion [23], polyaniline (PANI) [24] and PBI [25], is another important method to improve thermal stability and decrease the methanol permeability without sacrificing mechanical integrity of the membranes. Most recently, Kerres et al. [11] reported an acid–base composite based on SPEEK and N-bases and Han and co-workers [30] reported another acid–base composite based on a sulfonated polyimide and a pyridine-containing polyimide. Hydrogen bonds between the sulfonic acid groups and N-containing groups were believed to

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Scheme 1. Synthesis route of the polymers.

form and these composite membranes showed many attractive properties.

A series of sulfonated fluorinated poly(aryl ether ketone) copolymers (6FSPEEK) have been prepared previously by Guiver et al. [13]. Although these membranes have high proton conductivity, the excess dimensional deformation often existed especially at high level of sulfonic acid content (SC) in hot water. In this study, a novel kind of aminated poly(aryl ether ketone) with naphthene (AmPEEKK-NA) having good mechanical strength, high chemical and thermal stabilities is synthesized as basic component. Blending membranes composed by 6FSPEEK with

AmPEEKK-NA are successfully prepared. The single glass-transition temperature  $T_g$  and the absence of evidence for phase separation in scanning electron microscopy suggest that these systems form so-called 'molecular composites'. As a comparison, a new polymer (copolymer-AP6FSPEEK) containing both amino groups and sulfonic groups has been also prepared (Scheme 1). The polymers used for the preparation of the acid–base blends presented in this study are also shown in Scheme 1. These blends show high proton conductivities and moderate swelling values combined with high thermal stabilities. The study on the relationships of morphology and properties will be useful for further

designing composite membranes systems as proton exchange membranes.

## 2. Experimental

### 2.1. Materials

4,4'-(Hexafluoroisopropylidene)diphenol (6FBPA) was purchased from Aldrich. (4-Amino)phenylhydroquinone (4-AmPHQ) was synthesized in our lab through a two-step coupling-reduction reaction [32]. 1,4-Bi(4-fluorobenzoyl)benzene (BFBB) and 1,4-bis(4-fluorobenzoyl)naphthalene (BFBN) were synthesized in our lab according to a standard procedure. 4,4'-Difluorobenzophenone (DFBP) was purchased from Yianbian Chemical Factory and purified by recrystallization from a mixture of ethanol and deionized water. Sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP) was prepared according to procedure described by Wang et al. [31].  $K_2CO_3$  (Beijing Chemical Reagent) was ground into fine powder and dried at 120 °C for 24 h before polymerization. All the organic solvents were obtained from commercial sources and purified by conventional methods.

### 2.2. Synthesis of polymers

The basic polymer of AmPEEK-NA was prepared through the route shown in Scheme 1. A typical synthesis procedure of AmPEEK-NA as follows: 2.01 g (10.0 mmol) of 4-AmPHQ, 3.72 g (10.0 mmol) of BFBN and 1.45 g (10.5 mmol) of  $K_2CO_3$  were added into three-necked flask with a Dean-Stark trap, condenser, mechanical stirrer and nitrogen inlet and outlet. Sulfolane (23 mL) and toluene (20 mL) were used as solvent and azeotropic reagent. The reaction mixture was refluxed at 140 °C for 4 h to dehydrate the system. After dehydration and removal of toluene, the reaction temperature was increased to 180 °C and held at this temperature for another 8 h. The fiber-like precipitate was filtered off and purified by dialysis.

The acidic polymer (6FSPEEK) and aminated/sulfonated copolymer (AP6FSPEEK) were prepared using the similar procedure and dimethyl sulfoxide (DMSO) was selected as the solvent to replace sulfolane.  $^1H$  NMR spectroscopy was used to confirm the structure of polymers.

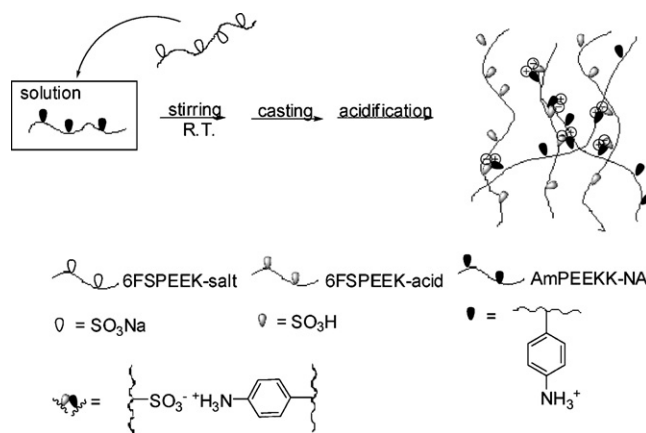
AmPEEK-NA:  $^1H$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 7.83–7.72 (m, 6H), 7.62–7.54 (m, 4H), 7.17–6.91 (m, 9H), 6.47 (d, 2H), 5.23 (s, 2H).

6FSPEEK:  $^1H$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 8.25 (s, 2H), 7.83 (d, 4H), 7.74 (d, 2H), 7.44–7.39 (m, 8H), 7.24 (m, 8H), 7.15 (d, 4H), 7.07 (d, 2H).

AP6FSPEEK:  $^1H$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 8.25 (m, 2H), 7.83 (d, 4H), 7.74 (d, 2H), 7.44–7.39 (m, 7.2H), 7.24–7.15 (m, 11.8H), 7.07 (d, 2H), 7.01–6.53 (m, 0.8H), 5.31 (s, 0.4H).

### 2.3. Membrane preparation

The membranes of pure polymer and 6FSPEEK/AmPEEK-NA composites were prepared by solution casting. And the schematic illustration of composite membranes is shown in Scheme 2. The membranes of pure copolymer in sodium form were obtained by solution casting in N,N-dimethylacetamide (DMAc) (10%, w/v) and then transformed to acid-form by ion exchange in 2 M  $H_2SO_4$  for 24 h. For composite membranes, the sodium-form copolymer and quantitative AmPEEK-NA were dissolving in DMAc (10%, w/v), and the samples with different weight proportion of AmPEEK-NA were named as Composite1 [AmPEEK-NA/6FSPEEK = 0.05/1 (w/w)], Composite2 [AmPEEK-NA/6FSPEEK = 0.1/1 (w/w)], Composite3 [AmPEEK-NA/6FSPEEK = 0.15/1 (w/w)], and Composite4 [AmPEEK-NA/6FSPEEK = 0.2/1 (w/w)], respectively. AmPEEK-NA was first stirred in DMAc for one day at 60 °C, and then 6FSPEEK



Scheme 2. Schematic illustrations for the preparation of composite membranes.

was put into this solution. After stirring for another day at 60 °C, the clear and homogenous solution was cast onto clean glass plate and dried at 60 °C overnight. After drying at 120 °C in vacuum oven for 24 h, the membranes were transformed to acid-form by ion exchange in 2 M  $H_2SO_4$ . The pure and the composite films were about 60–110  $\mu$ m.

## 3. Measurements

### 3.1. Characterization

The viscosities were determined using an Ubbelohde viscometer in thermostatic container with the polymer concentration of 0.5 g dL<sup>-1</sup> in NMP at 25  $\pm$  0.1 °C. FT-IR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer.  $^1H$  NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz for  $^1H$ ) using DMSO- $d_6$  as solvent. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821e instrument at a heating rate of 20 °C min<sup>-1</sup> from 50 to 300 °C under nitrogen. Thermogravimetric analysis (TGA) was employed to assess thermal stability of membranes with a Netzsch Sta 449c thermal analyzer system. Before analysis, the films were dried and kept in the TGA furnace at 150 °C in a nitrogen atmosphere for 15 min. The samples were cooled to 80 °C and then reheated to 700 °C at 10 °C min<sup>-1</sup>, and the temperatures at 5% and 10% weight loss were recorded for each sample.

### 3.2. Water uptake and swelling ratio measurements

A piece of film was vacuum dried at 120 °C to a constant weight, which was recorded as  $W_{dry}$  and then immersed in deionic water at different temperatures. During this period, the wet membrane was quickly weighed several times after removing the surface water with tissue paper until a constant weight was obtained, which was recorded as  $W_{wet}$ . The water uptake was reported using water weight percent of dry membranes as following relation:

$$\text{Water uptake (\%)} = [(W_{wet} - W_{dry})/W_{dry}] \times 100\%$$

The swelling ratio was calculated from the change of film length by

$$\text{Swelling ratio (\%)} = [(L_{wet} - L_{dry})/L_{dry}] \times 100\%$$

where  $L_{wet}$  and  $L_{dry}$  are the lengths of the wet and dry membranes, respectively.

### 3.3. Lambda number

The lambda value ( $\lambda$ ) indicated the number of water molecules absorbed per sulfonic acid groups and could be expressed as:

$$\lambda_w = [(W_{\text{wet}} - W_{\text{dry}})/M_{\text{H}_2\text{O}}]/[\text{IEC} \times W_{\text{dry}}]$$

where  $M_{\text{H}_2\text{O}}$  is the molecular weight of water (18.01 g mol<sup>-1</sup>) and IEC is the ion-exchange capacity of the dry membranes in equivalent per gram. The lambda number like proton conductivity scale with the ion-exchange capacity.

### 3.4. Ion-exchange capacity (IEC) of membranes

The IEC values of pure and composite membranes were determined by classical titration [13,21]. Membrane samples (about 0.06 g) were immersed in 2 M NaCl solution for at least 24 h to liberate the H<sup>+</sup> ions (the H<sup>+</sup> ions in the membranes were replaced by Na<sup>+</sup> ions). The exchanged protons within the solutions were titrated with 4 mM NaOH aqueous solution by using phenolphthalein as an indicator. For each sample, at least three measurements were carried out until the titration reached to a constant value. The IEC value was calculated from the titration result via the following formula:

$$\text{IEC (mequiv./g)} = (\text{consumed ml NaOH} \times \text{molarity NaOH})/W_{\text{dry}}$$

### 3.5. Oxidative and hydrolytic stability

A small piece of the membrane sample was soaked in Fenton's reagent (3% H<sub>2</sub>O<sub>2</sub> containing 2 ppm FeSO<sub>4</sub>) at 80 °C. The oxidative stability was evaluated by recording the time when the membranes disappeared and the retained weights of membranes after treating in Fenton's reagent for 1 h.

### 3.6. Proton conductivity

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&GPARC, Princeton, NJ). The membranes were fixed in a measuring cell which was made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. The specimens were soaked in deionized water for at least 24 h prior to testing. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water, as reported in previous work [33]. The proton conductivity was calculated by the following formula:

$$\sigma = L/RA$$

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

### 3.7. Mechanical properties of membranes

The mechanical properties of both dry and wet membranes were measured at room temperature on SHIMADIU AG-I 1KN at a strain rate of 2 mm min<sup>-1</sup>. The size of samples was 20 mm × 4 mm. The samples in wet state were obtained by immersing them in water for at least 48 h, and the samples in dry state were obtained by putting them in vacuum oven at 120 °C for 24 h.

### 3.8. Morphology

The fractured morphology of the composite membranes was investigated using a scanning electron microscope (Shimadzu

SSX-550 superscan SEM), which was applied to investigate the homogeneity of the phase distribution in the blend of polymers. After dried, the sample was fractured in liquid nitrogen and fresh cross-sectional cryogenic fractures of the composite membranes were vacuum sputtered with a thin layer of Au prior to SEM examination. A SEM apparatus was used with an accelerating voltage of 15 kV. Tapping mode AFM observations which were used to investigate the apparent morphology were performed with a Digital Dimension 3000 Instrument, using micro-fabricated cantilevers with a force constant of approximate 40 N m<sup>-1</sup>. The ratio of amplitudes used in feedback control was adjusted to 0.6 of the free air amplitude for all of the reported images. All samples were measured under relative humidity of 30%.

## 4. Results and discussion

### 4.1. Synthesis of the amine-containing polymers

As an attempt of improving the thermal and oxidative stability, 6FSPEEK and several novel base-N polymers derived from an aminated hydroquinone monomer (4-AmPHQ) were prepared by an aromatic nucleophilic substitution polycondensation, as shown in Scheme 1. The resulting 6FSPEEK and AmPEEK-NA had high viscosities of 1.62 and 0.82 g dL<sup>-1</sup>, respectively, which indicated that both of them possessed high molecular weights. For the comparison with physical blending, we also synthesized a copolymer (some-time was called chemical blending) containing amino and sulfonic groups (AP6SPEEK), which also had high viscosity of 2.47 g dL<sup>-1</sup>. All of them showed good solubility in polar aprotic solvents, such as DMSO, DMAc and N-methyl-pyrrolidone (NMP).

<sup>1</sup>H NMR spectroscopy was used as the principal method for characterization of the polymers. Polymer samples were dissolved in DMSO-*d*<sub>6</sub> for spectroscopic measurements. The sulfonic acid content (SC) of 6FSPEEK polymer calculated from <sup>1</sup>H NMR was 1.57 [13]. All the results of NMR analysis shown in Section 2 were in well agreement with their expected structure.

### 4.2. Preparation of acid–base composites

Generally, the acid–base composite membranes are made via a solution casting approach. Thus, the selection of a good common solvent for both sulfonated polymer and aminated one is especially important. It is well known that the sulfonated 6FSPEEK usually has good solubility in polar solvents, such as DMAc, NMP and DMSO. Therefore, the aminated PAEKs with good solubility in above solvents and similar chemical backbones with 6FSPEEK are preferred in order to prepare acid–base composite membranes. We have synthesized a series of aminated poly(aryl ether ketone)s named as AmPEEK (4-AmPHQ + DFBP), AmPEEKK (4-AmPHQ + DFBB) and AmPEEKK-NA (4-AmPHQ + BFBN), and their structure is shown in Scheme 1.

Unfortunately, AmPEEK and AmPEEKK could not be soluble in common organic solvents due to their intensive molecular interactions and rigid regular backbones. Interestingly, AmPEEKK-NA containing bulky naphthalene linkages showed improved solubility in the polar solvents, and then the uniform composite membranes based on AmPEEKK-NA and 6FSPEEK could be cast by their solution in DMAc.

FT-IR spectra were used to perform on the composite membranes to confirm the structures, as listed in Fig. 1. The peaks at 3462 and 3387 cm<sup>-1</sup> were assigned to the asymmetric and symmetric N–H stretching vibration absorptions of primary amine functionality, but could not be found in composite membranes (Fig. 1(b)). It was attributed to acid–base interaction of sulfonic groups in acid-form and amino groups, and these bands were substituted by the

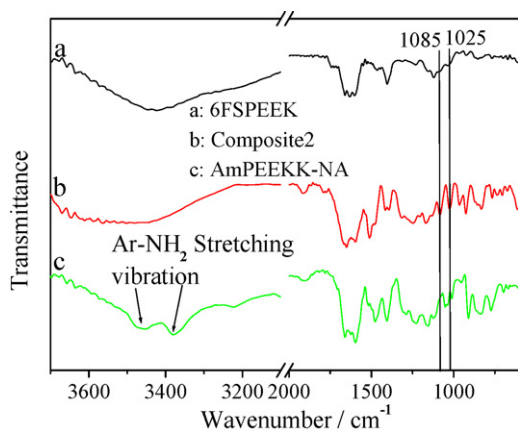


Fig. 1. FT-IR spectra of 6FSPEEK and Composite2 and AmPEEKK-NA membranes.

broad band of the  $\text{N-H}_3^+$  vibration in the  $\text{H}^+$  form of the blend membrane. The characteristic peaks at 1025 and 1085  $\text{cm}^{-1}$  were assigned to stretching of the sulfonic groups, and were not observed in amino component of AmPEEKK-NA (Fig. 1(c)), which exhibited successfully the introduction of sulfonic groups to 6FSPEEK and composite materials.

#### 4.3. Thermal properties of membranes

The thermal properties are one of the important factors on the usage of PEMs.  $T_{gs}$  and  $T_{d5}$  values of sulfonated copolymers and composite materials are listed in Table 1. Their glass-transition temperatures were in the range of 233–262 °C, and the  $T_{gs}$  of composite membranes increased with increasing the content of amino component. It could be attributed to the strong interaction of acid–base between sulfonic groups of acid-form and amino groups. The TGA data and curves of membranes under nitrogen are shown in Table 1 and Fig. 4, respectively. The temperature at 5% weight loss ( $T_{d5\%}$ ) of copolymer and composite membranes were over 340 °C, which exhibited excellent thermal stability for the PEM-FCs. All the TGA curves exhibited two distinct thermal degradation steps. The first weight loss step was at about 260 °C, which associated with the loss of sulfonic groups, whereas the second weight loss observed at about 510 °C was due to main chain degradation. However, AmPEEKK-NA only had one degradation step assigned to the main chain. Moreover, due to the acid–basic interaction between 6FSPEEK and AmPEEKK-NA (Scheme 2), the thermal stability of the composites was improved with the increasing content of AmPEEKK-NA. And also, the  $T_d$  value of AP6FSPEEK was also higher than 6FSPEEK. We could see that acid–base interaction played an important role in improving thermal stabilities of copolymer and composite membranes.

#### 4.4. Water sorption and swelling ratio of membranes

The water uptake of membranes has a great influence on the proton conductivity and mechanical property. Higher water uptake

Table 1  
Thermal properties of copolymers and composites.

Polymer	$T_{g(\text{acid})}$ (°C)	$T_{d(5\%)}$ (°C)	$T_{d(10\%)}$ (°C)
6FSPEEK	233	345	373
Composite1	242	352	385
Composite2	247	353	388
Composite3	251	361	393
Composite4	262	363	394
AP6FSPEEK	251	361	390

Table 2  
Water uptake and swelling ratio of membranes.

Polymer	Temperature (°C)					
	20		80		100	
	WU (%)	SR (%)	WU (%)	SR (%)	WU (%)	SR (%)
6FSPEEK	21.4	9.5	41.5	17.4	107.2	36.1
Composite1	17.8	8.6	33.7	13.6	53.5	21.7
Composite2	15.2	7.5	30.5	11.6	51.5	19.6
Composite3	14.2	4.4	26.9	9.5	33.3	10.5
Composite4	13.1	1.7	25.4	6.6	28.4	7.2
AP6FSPEEK	20.2	9.4	36.5	16.2	69.3	27.7

WU (%): water uptake (%); SR (%): swelling ratio (%).

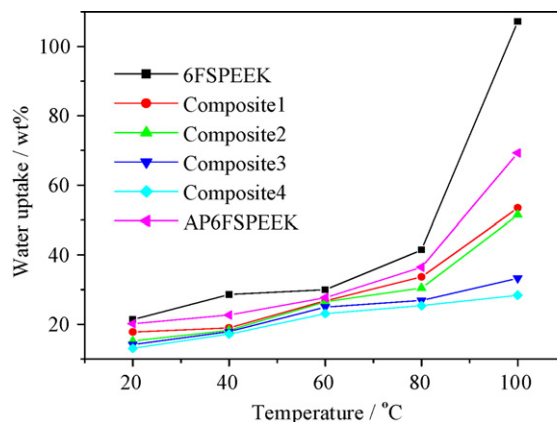


Fig. 2. Water uptake of membranes at different temperatures.

could improve proton conductivity, however, too much water would result in the excess swelling of the membranes and further losing its mechanical property [3,12,15,27]. So the suitable water molecules around the sulfonic acid groups were necessary to maintain the high proton conductivity and good dimensional stability of the PEMs [14]. The water uptake and swelling ratio of the membranes were determined by measuring the changes in the weight and length of hydrated and dehydrated films at desired temperature (Table 2 and Figs. 2 and 3). The small content of rod basic component was expected to act as molecular fiber and supporting framework in molecular composites, and the rigid framework and molecular interaction between sulfonic groups and amino groups were also respected to restrict the movement of the segments and lower the swelling in water. Fig. 2 illustrates the water uptake of pure and composite membranes. Composite membranes showed lower water uptake than 6FSPEEK at the same temper-

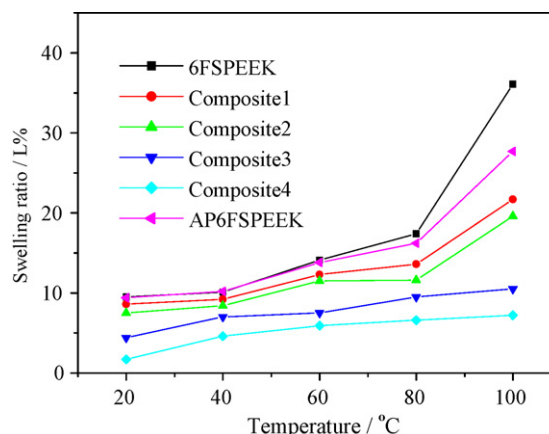


Fig. 3. Swelling ratio of membranes at different temperatures.

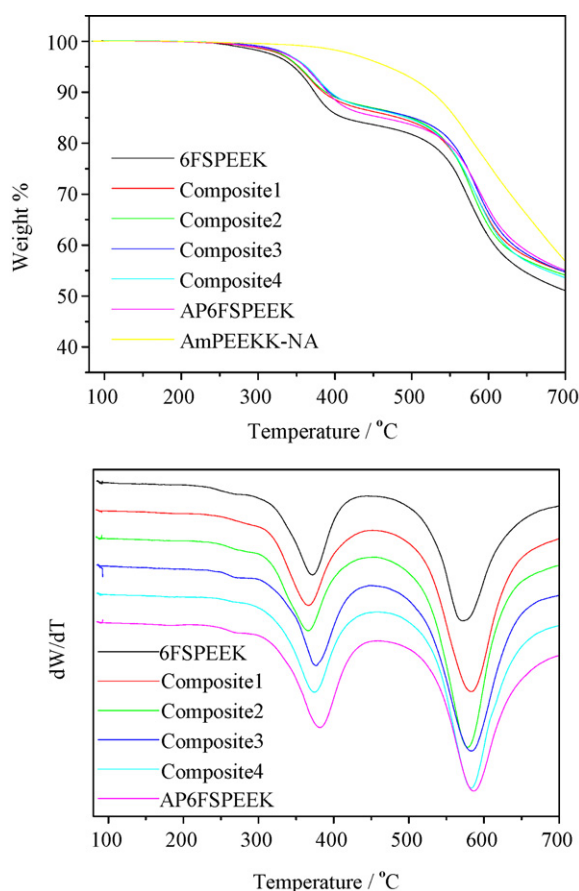


Fig. 4. TGA and derivative curves of membranes.

ature, and a decreasing tendency with the increasing content of AmPEEKK-NA was observed also. Meanwhile, the water uptake of aminated/sulfonated copolymer-AP6FSPEEK was similar to that of 6FSPEEK below 80 °C, but was markedly lower than 6FSPEEK at 100 °C. From Fig. 3, it could be observed that the swelling ratio also decreased with increasing the content of AmPEEKK-NA, and the values of the composite membranes were even lower than Nafion 117 [34]. For example, although the less than 5 wt% of AmPEEKK-NA was incorporated into 6FSPEEK, Composite1 had much lower swelling ratio (13.6% at 80 °C and 21.7% at 100 °C, respectively) in comparison with pure 6FSPEEK (17.4% at 80 °C and 36.1% at 100 °C, respectively). For Composite4, only 7.2% of swelling ratio at 100 °C was observed. Despite high aminated component within the membrane, the dimensional stability of the aminated/sulfonated copolymer membranes-AP6FSPEEK prepared by a chemical blending had no remarkable improvement (Fig. 3).

#### 4.5. Oxidative stability and mechanical property of membranes

Oxidative stability of pure and composite membranes was examined by observing their dissolving behaviors in Fenton's reagent at 80 °C (Table 3). The weight of 6FSPEEK was retained about 74% after treatment in Fenton's reagent at 80 °C for 1 h, and was dissolved within 3 h. However, the composite membranes enhanced through the interactions of molecular chains exhibited excellent oxidative stability. The weight of composites was retained above 90% after treatment in Fenton's reagent at 80 °C for 1 h, and the composite membranes started to dissolve after 6 h, which suggested their excellent thermo-oxidative resistance.

Mechanical properties are one of the necessary demands for PEMs, and the data of all blends in both anhydrous and hydrous states are shown in Table 4. The rigid rod basic component of

**Table 3**  
Properties of copolymers and composites.

Polymer	IEC <sup>a</sup>	IEC <sup>b</sup>	X <sup>c</sup>	$\lambda_{w(R.T.)}$	Oxidative stability	
					RW (%) <sup>d</sup>	t (h) <sup>e</sup>
6FSPEEK	1.68	1.57	0.00	7.56	74	3
Composite1	1.60	1.41	0.06	7.01	>90	>6
Composite2	1.51	1.27	0.11	6.64	>90	>6
Composite3	1.43	1.20	0.17	6.57	>90	>6
Composite4	1.34	1.12	0.22	6.49	>90	>6
AP6FSPEEK	1.72	1.65	0.10	6.79	>90	4

<sup>a</sup> Theoretical value (mmol g<sup>-1</sup>).

<sup>b</sup> Experimental value (mmol g<sup>-1</sup>).

<sup>c</sup> Theoretical content of amino (mol/mol SO<sub>3</sub>H).

<sup>d</sup> Retained weights of membranes after treating in Fenton's reagent for 1 h.

<sup>e</sup> The dissolved time of polymer membranes.

molecular composite showed supporting the 'crosslinking' effects, and all the composite membranes exhibited excellent mechanical properties. The samples in the dry state had tensile strength of 34.4–43.8 MPa, which appeared at the point of break, and Young's moduli of 1.05–1.57 GPa, which were higher than the wet state of 33.7–41.5 MPa and 0.50–0.69 GPa, respectively. Moreover, both of them were obviously higher than Nafion 117 of 22.7 MPa and 0.046 GPa at the same testing condition in our lab. While the elongation at break of dry state was up to 74.2–129.2%, which was closed to wet state of 112.2–135.9% (Table 4). When the content of AmPEEKK-NA reached 10–20%, the elongation at break of dry state was all higher than 100% (Fig. 5), which displayed excellent mechanical property. It might be attributed to the homogeneous distributing framework of AmPEEKK-NA in Composite2, 3 and 4, which led to proper acid–basic interaction. It was noted that with increasing the content of AmPEEKK-NA, the elongation at break was also elevated. The mechanical properties both in dry state and wet state undoubtedly suggested these composite membranes were flexible and strong materials.

#### 4.6. Ion-exchange capacity and proton conductivity of pure and composite membranes

Table 3 shows the theoretical and experimental IEC values, theoretical amino content, lambda number ( $Q_w$ ) of pure and composites membranes. The experimental IEC values were basically consistent with theoretical values.

Proton conductivities of the acid-form membranes were measured at 100% RH in air. The proton conductivities of the membranes were estimated using impedance diagrams. The results at differ-

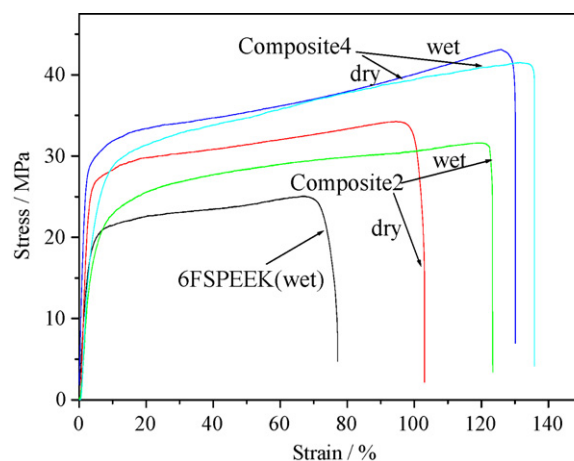
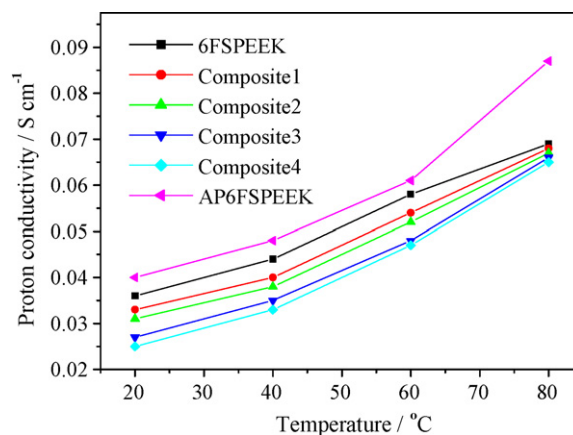


Fig. 5. Stress versus strain curves for hydrated 6FSPEEK, hydrated and dehydrated Composite2, 4 at room temperature.

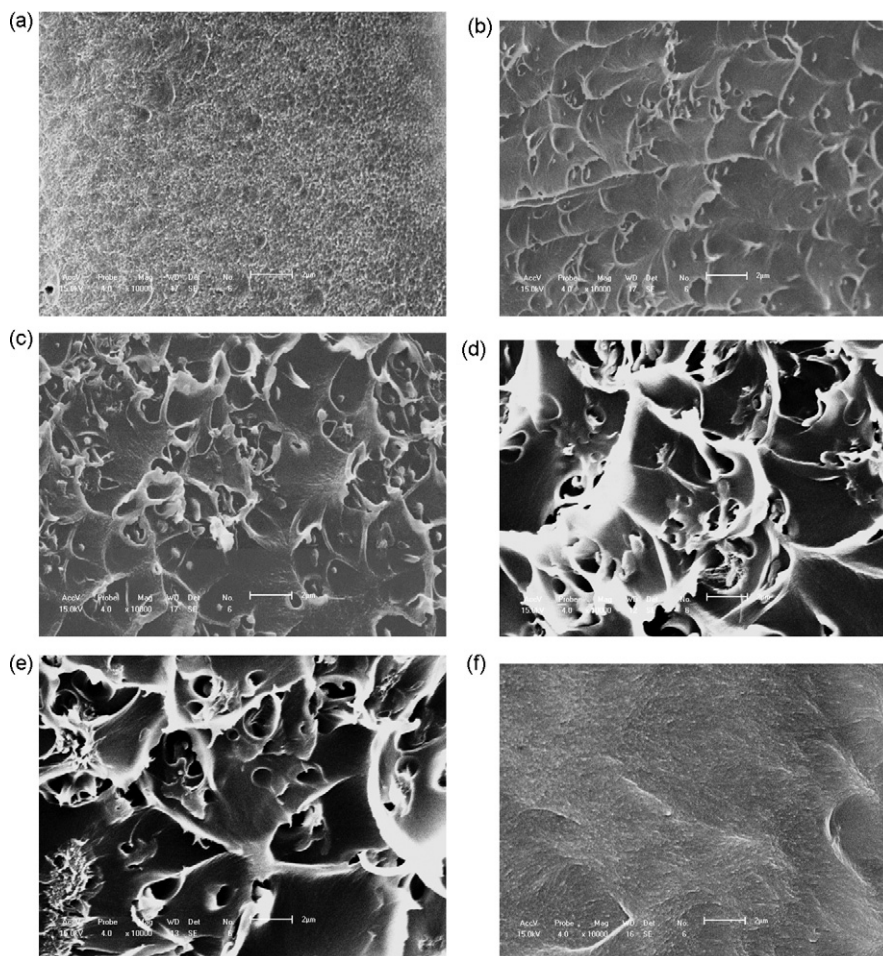
**Table 4**  
Mechanical properties of membranes.

Membranes	Tensile strength (MPa)		Maximum elongation (%)		Tensile modulus (GPa)	
	Dry	Wet	Dry	Wet	Dry	Wet
6FSPEEK	29.6	26.2	59.9	74.8	0.97	0.37
Composite1	34.4	33.7	74.2	112.2	1.05	0.50
Composite2	36.6	35.9	107.2	128.0	1.14	0.51
Composite3	39.3	37.3	119.1	127.2	1.33	0.58
Composite4	43.8	41.5	129.2	135.9	1.57	0.69
AP6FSPEEK	29.2	25.2	40.3	41.8	1.03	0.53

ent temperatures were presented in Fig. 6. The figure showed that the conductivities of all the samples increased with temperature, and decreased with the increasing the content of AmPEEK-NA. However, the proton conductivity of all the membranes was higher than  $0.025 \text{ S cm}^{-1}$  at room temperature, and even reached up to  $\sim 0.065 \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ . At low temperature the proton conductivity decreased obviously with the increasing content of AmPEEK-NA, while they were similar at  $80^\circ\text{C}$ . It might be because that the interaction between basic-N and sulfonic acid was weakened and proton transferred more easily between protonic basic-N and sulfonic acid at high temperature. In addition, the aminated/sulfonated copolymer-AP6FSPEEK having the same sulfonic content with 6FSPEEK showed obviously high proton conductivity of  $0.087 \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ , which was closed to Nafion 117 and higher than 6FSPEEK. The high proton conductivity at  $80^\circ\text{C}$  might be relative to its microstructure and proper water absorption capability.



**Fig. 6.** The proton conductivity of membranes.



**Fig. 7.** The SEM photographs of membranes. (a) SPEEK, (b) Composite1, (c) Composite2, (d) Composite3, (e) Composite4 and (f) AP6FSPEEK. Scale bar:  $2 \mu\text{m}$ .

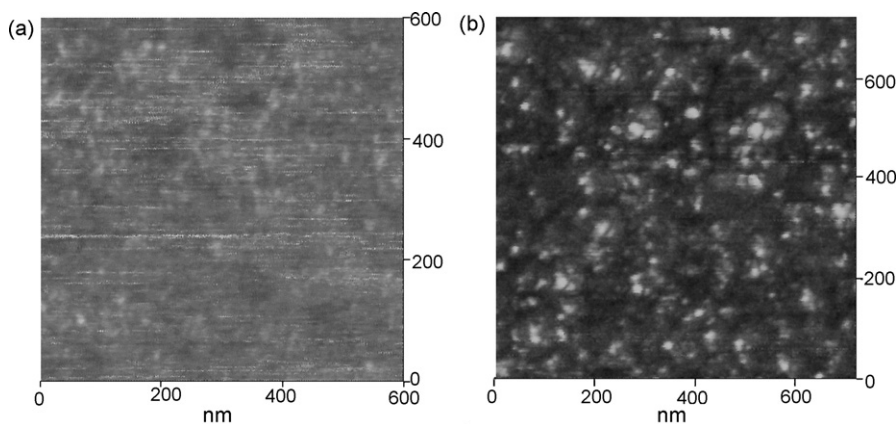


Fig. 8. The AFM phase images of membranes: (a) 6FSPEEK and (b) Composite3.

#### 4.7. Morphology of the membranes

The microstructures could influence the properties of membranes, and the SEM and AFM were the characteristic means of morphology. The internal morphology of the membranes was studied by SEM, as shown in Fig. 7. All of them were fractured in liquid nitrogen. Compared with Fig. 7(f), Fig. 7(a) shows evident microphase separation, which might be attributed to hydrogen bond interaction in AP6FSPEEK and the formation of compact microstructure. However, the composite membranes (Fig. 7(b)–(e)) illustrate very different morphology compared with pure membranes. With the addition of AmPEEK-NA, the particles and tearing belt appeared due to the introduction of rigid AmPEEK-NA. When the weight percent of rigid basic component was lower than 5%, the rod molecule could not be continuous distribution and they illustrated particles in the fractured face. Whereas the weight percent of rigid basic component was higher than 10%, the rod molecule formed continuous framework, and thus the strength and toughness of composite membranes increased. As a result, the fracture of composite membranes was more difficult than others. All of these phenomena were agreed with the results of tensile testing. Fig. 8 is the AFM photographs of the pure and Composite3 membranes, the dark regions in the images were assigned to a soft structure, corresponding to the hydrophilic sulfonic groups containing water. The connectivity and domain size varied depending on the content of AmPEEK-NA. The both membranes showed microphase separation [14,27], and the composite membrane had more obvious phase separation than pure membrane. The domains assigned to the hydrophilic ionic cluster of pure membrane were small in size (10–20 nm), however, the size of hydrophilic domains of composite membranes became more obvious (30–50 nm). This obvious microphase separation might be helpful for the protons to transport.

## 5. Conclusion

Several new base-N polymer and a new aminated/sulfonated copolymer were synthesized. A series of acid–base composite membranes were prepared by solution casting. They all were well agreed with the initial intention to improve mechanical properties, thermal stabilities and reduce excess swelling while maintained high proton conductivity values. Because of the distribution and framework of AmPEEK-NA in 6FSPEEK matrix, microphase separation in composite membrane became more obvious, which allowed the proton conductivities of composite membranes to be close to 6FSPEEK. The proton conductivity of the membranes was higher than  $0.025 \text{ S cm}^{-1}$  at room temperature. Especially, AP6FSPEEK copolymer had high proton conductivity of  $0.087 \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ .

Because of the good performance of these composite membranes, they will be good potential PEMs for fuel cell applications.

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