The effect of acid-base interaction on the thermal and transport properties of poly(etheretherketone) based composite membranes

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Abstract−Binary composite membranes were prepared by the solution casting method from sulfonated poly(etheretherketone) (SPEEK) and organic additives such as hydroxyquinolinesulfonicacid (HQS), 4-tertiary butylpyridine (TBP), imidazole and succinimide. Ternary composite membranes were prepared from SPEEK, inorganic phosphotungstic acid (PWA) and the same organic additives. The acid base interaction characteristics of the composite membranes were not observed by ATR-FTIR analysis. TGA results showed that the thermal stability of the composite membranes was enhanced in the temperature range up to about 400 °C by the addition of the organic additives. The acid-base interaction between SPEEK and the organic additives of HQS, TBP and imidazole decreased the water uptake, methanol permeability and proton conductivity of the binary and ternary composite membranes. However, the addition of succinimide did not decrease the water uptake, proton conductivity and methanol permeability of the composite membranes. The composite membranes containing succinimide made little acid-base interaction but made hydrogen bonding with SPEEK. The hydrogen bonding proved to be weaker than the acid-base interaction. The selectivity of the composite membranes increased by the addition of PWA, and the selectivities of the composite membranes containing succinimide were higher than those of the other composite membranes.

Key words: Poly(etheretherketone), Composite Membrane, Acid-base Interaction, PWA

INTRODUCTION

The United Nations Framework Convention on climate change has been held every year to prevent global warming. It was requested in the latest convention that all advanced and developing countries should reduce carbon emissions gradually. Fossil fuels can never be major energy sources in the next decades. They will be replaced by clean energies such as hydrogen and solar energy, which do not produce carbon dioxide in the process of energy conversion. Solid electrolytes such as polymer electrolyte membranes have been given much attention due to their possible applications in fuel cells, chemical sensors, dye sensitized solar cells and batteries [1-3].

Perfluorinated polymers, such as Nafion, have been widely used as polymer electrolyte membranes due to their combined chemical, electrochemical, and mechanical stabilities with high proton conductivity at ambient temperature [4]. However, high methanol permeability and greatly reduced proton conductivity above 80 °C have limited their wide uses and applications. A considerable effort has been taken to develop new membrane materials to replace Nafion. Sulfonated derivatives of non-fluorinated aromatic polymers such as poly(etheretherketone) (PEEK) [5-8], polysulfone (PSF) [9,10], and polyimide (PI) [11,12] have been investigated. The non-fluorinated polymers have generally lower proton conductivity than Nafion. Thus, high degree of sulfonation (DS) is necessary to maximize the proton conductivity. However, high DS accompanies the swelling of the polymer membrane, which reduces the mechanical strength

of the membrane. Different strategies have been used to enhance the mechanical strength of the membrane. One of the attempts was making composite mem- branes using inorganic materials such as SiO_2, TiO_2, ZiO_2 and montmorillonite (MMT). The addition of the inorganic materials led to enhancement in thermal and mechanical properties but reduction in proton conductivity [13,14]. Incorporation of polymers with inorganic heteropolyacid (HPA) has also drawn attention because HPA's such as phosphotungstic acid (PWA) and silicotungstic acid (SiWA) are known to have the highest ion conductivity among inorganic compounds. It has been reported that the composite membranes of poly(aryleneethersulfone) with HPA reduced water uptake and meth- anol permeability but increased
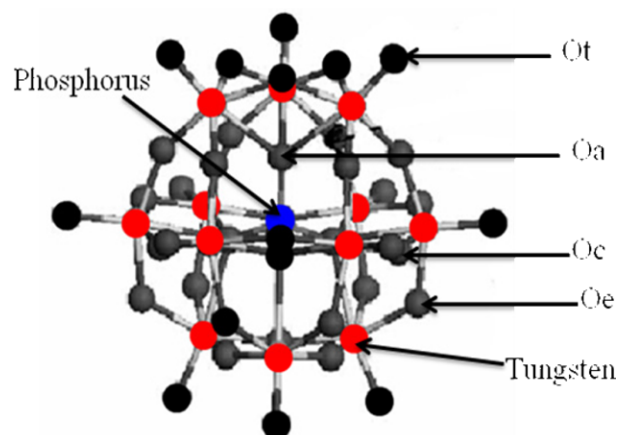

Fig. 1. The primary structure of PWA (called Keggin unit).

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proton conductivity [15]. The chemical structure of PWA is shown in Fig. 1. In another attempt, the membrane has been cross-linked to enhance mechanical strength of the membrane. Kerres et al. [16] prepared crosslinked SPEEK membranes and improved their mechanical strength. However, tough covalent crosslinking often brings about impractically brittle membranes. In contrast, crosslinking of acidic polymers by blending with basic (aminated) polymers, in which acid base interaction took place, did not greatly affect membrane flexibility, and reduced the swelling of the membrane [17].

Ionic (bonding) interaction can take place in acid-base composite materials (which is called acid-base interaction). There are two types of ionic interactions: electrostatic interaction and hydrogen bridging interaction. In acid-base composites, positive charges are developed in basic components due to protonation by acidic components, and negative charges are developed in acidic components. Then an electrostatic interaction takes place between the oppositely charged ions. And, at the same time, the hydrogen atom of the basic component forms hydrogen bridging with the acidic component (hydrogen bonding bridges the two opposite ions of basic and acidic components, so it is called hydrogen bridging). The intensity of ionic interaction depends upon the acidity and basicity of the composite materials. When the acidity and basicity both are high, strong ionic interaction takes place. When the acidity and basicity both are low, the ionic interaction becomes weak. The acidity and basicity are determined by the pK values of the acid and base. pK is defined as the negative logarithm of the dissociation constant (K) of the acid and base. Strong acids and strong bases have high dissociation constants, hence small pK values. Weak acids and weak bases have low dissociation constants, hence large pK values. For example, strong acids such as H_2SO_4 and HCl have pK_a values of -9 and -7, respectively, while pK_a values of weak acids such as CH_3COOH and H_2CO_3 are $+4.8$ and $+6.5$. pK_b values of strong bases such as LiOH and NaOH are $+0.2$ and -0.8 while pK_b values of weak bases such as NH_3 and CH_3NH_2 are $+4.75$ and $+3.4$, respectively, (subscript 'a' refers to acid and subscript 'b' refers to base). Fig. 2 shows an example of ionic interaction in SPEEK/polybenzimidazole (PBI) composite membrane. Benzimidazole in PBI units (basic component) is protonated by sulfonic acid group in SPEEK units (acidic component). Positive charge is developed in the nitrogen atom of PBI and negative charge is developed in the oxygen atom of sulfonic acid group in SPEEK. Then electrostatic interaction takes place between the oppositely charged ions and, at the same time, hydrogen
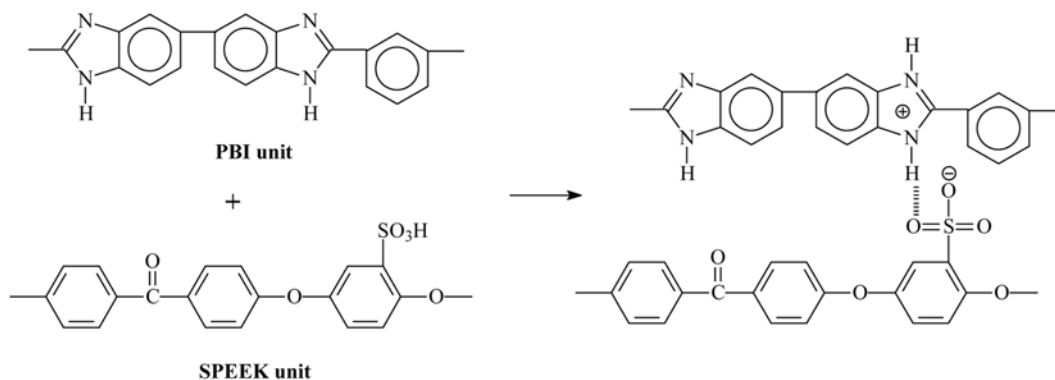
Table 1. Boiling point, K and pK values of the materials used

Materials	Boiling point	K_a	pK_a	pK_b
SPEEK	-	-	-1	-
HQS	-	7.73×10^{-05}	-	+10
TBP	197 °C	5.62×10^{-06}	-	+8.8
Imidazole	257 °C	1.1×10^{-07}	-	+7.05
Succinimide	290 °C	2.5×10^{-10}	+9.5	-
PWA	-	-	~ -8	-

Where subscripts a and b refer to acid and base, respectively

attached to PBI forms hydrogen bridging with the oxygen of sulfonic acid group [18]. However ionically cross-linked membranes prepared from acidic and basic polymers can suffer from microscopic phase separation due to the incompatibility between the two polymers [19].

In this work, SPEEK-based composite membranes were prepared with the organic additives of HQS, TBP, imidazole, succinimide, and inorganic PWA. The physical properties of the additives are shown in Table 1. The composite membranes were prepared by the solution casting method and acid-base interaction was induced between SPEEK and the organic additives. Fourier transform infrared spectroscopy and thermal analysis were performed to investigate the chemical structure and thermal stability of the composite membranes. It was also investigated how the acid-base interaction affected thermal and transport properties such as water uptake, proton conductivity and methanol permeability.

EXPERIMENTAL

1. Materials

PEEK (450PF, M_w: 38,300) was purchased from Victrex. Sulfuric acid (98%), Dimethyl-sulfoxide (DMSO, 99.5%), and methanol (99.5%) were purchased from Dae-Jung Chemical. HQS ($C_9H_7NO_4S \cdot xH_2O$, 99%), TBP ($C_9H_{13}N$, 99%), imidazole ($C_3H_4N_2$, 99%), succinimide ($C_4H_5NO_2$, 99%) and PWA ($H_3PW_{12}O_{40} \cdot xH_2O$, 99%) were purchased from Aldrich. PEEK and PWA were dried at 80 °C in a vacuum oven for 12 hours before use, and the other chemicals were used as received.

2. Sulfonation of PEEK

Sulfonation of PEEK was performed using the same method as

Fig. 2. The schematic representation of acid base interaction between SPEEK and PBI.

suggested by Zaidi [20]. First, PEEK powders were dried at 80 °C for 12 hours under vacuum. Thereafter 5 g of dried PEEK was dissolved in 250 ml sulfuric acid solution and sulfonation reaction was done at room temperature for certain hours. Degree of sulfonation (DS) was controlled by the reaction time. Then the polymer solution was precipitated using ice water, the polymer suspension was filtered, and washed with de-ionized water several times until the pH of the solution became neutral. Then the polymer was dried at room temperature for 12 hours under vacuum followed by drying at 80 °C for another 12 hours. DS was determined by titration method: 1.5 grams of SPEEK was dissolved in 50 ml 0.5 M NaOH and kept 24 hours with stirring. The solution was back titrated with 0.5 M HCl using phenolphthalein as an indicator.

3. Preparation of Composite Membranes

Composite membranes were prepared by the solution casting method. 10 wt% of SPEEK solution was prepared by dissolving into DMSO solution and kept stirring overnight. 10 wt% solutions of the additives HQS, TBP, imidazole and succinimide were prepared separately by dissolving into DMSO. Then, a certain amount of each additive solution was mixed separately with the solution of SPEEK for 12 hours. The mixed solutions were cast in the glass plates at 60 °C, dried initially at 60 °C for 24 hours in a vacuum oven, and the oven temperature was increased up to 150 °C at the rate of 5 °C/hr. Finally, the composite membranes were dried at 150 °C for another 48 hours. In the case of ternary composite membranes, 10 wt% solutions of each SPEEK, PWA and additives were prepared separately by dissolving into DMSO. Then the desired amount of PWA solution and additives solution were mixed first, and mixed with SPEEK solution. The mixture solutions were cast on the glass plate and dried as mentioned above.

4. Characterization

4-1. Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Infrared spectra were recorded on an Equinox55 (Bruker Optik GMBH) FTIR spectroscope equipped with ATR, with a resolution of 2 cm^{-1} in the range of 4,000-400 cm^{-1}. The thickness of the FTIR samples ranged 0.005-0.01 mm.

4-2. Thermogravimetric Analysis (TGA)

The thermal analysis of the composite membranes was carried out using a thermogravimetric analyzer (SDT 2960, TA Instruments). Approximately 10 mg of the membrane sample was heated from 25 °C to 700 °C with a heating rate of 10 °C/min under nitrogen atmosphere, and the weight loss of the sample was recorded.

4-3. Water Uptake

The water uptake was determined by the weight difference between the fully hydrated membrane and the dried membrane. The membrane sample was equilibrated in water at 50 °C for 24 hours, removed from the water, quickly wiped using a dry tissue, and weighed immediately to determine its wet weight (W_{wet}). The dry weight of the sample (W_{dry}) was determined after drying the water soaked sample at 100 °C in a vacuum oven. The water uptake was calculated using the following equation:

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

4-4. Proton Conductivity

Proton Conductivity was measured using a fuel cell test station

(P & P Energy Tech). The conductivity cell was composed of four platinum wire electrodes separated by 1cm each other. The surface of the electrodes was kept clean to avoid any contact resistance during measurements. Before measurement, the membrane sample (3 cm× 1 cm) was soaked in de-ionized water for 24 hours and placed in the conductivity cell. Then a Teflon plate was placed over the sample, and screwed tightly to make good contact between the electrodes and the sample. The AC impedance spectrum of the membranes was recorded from 2 MHz to 42 Hz with amplitude of 1 V using the LCR tester (HIOKI 3532-50). The resistance associated with the membrane conductivity was determined from the high frequency intercept of the impedance in the real axis. The conductivity was calculated using the equation:

$$\sigma = \frac{L}{rA} \tag{2}$$

Where σ, L, r, and A denote the membrane conductivity, thickness of the membrane, resistance of the membrane, and cross-sectional area of the membrane perpendicular to current flow, respectively.

4-5. Methanol Permeability

The methanol permeability of composite membranes was determined using a home-made diffusion cell. The membrane sample, which had a cross sectional area of 7.065 cm^2, was equilibrated in water for 24 hours prior to measurement. Then the sample was attached between the feed and permeate side compartments of the cell. The permeate side compartment (40 cm^3) was initially filled with de-ionized water, and the feed side compartment was filled with 2 M methanol solution. The diffusion cell was maintained in constant temperature bath at 30 °C, and both compartments of the cell were kept stirring during measurement. The concentration difference between the feed and permeate compartments leads to methanol flux across the membrane. Methanol concentration in the permeate side was measured using gas chromatography (680D, TCD detector equipped with Porapak Q column, Young-In Instruments). Methanol permeability was determined from the slope of the plot of methanol concentration in the permeate compartment versus time. Assuming pseudo steady state, the methanol concentration in the permeate side is given by the equation:

$$c_2(t) = \frac{A}{v_2} \frac{DK}{L} c_1(t - t_0) \tag{3}$$

Where, A is the membrane area, L the membrane thickness, D the diffusion coefficient, K the partition coefficient, t the time, and c_1 and c_2 are the methanol concentrations in the feed and permeate side, respectively. The product of DK becomes permeability coefficient (P):

$$P = \frac{1}{A} \frac{c_2(t)}{c_1(t - t_0)} V_2 L \tag{4}$$

RESULTS AND DISCUSSION

1. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Fig. 3 shows the ATR-FTIR spectra of PEEK, SPPEK and SPEEK-based composite membranes. FT-IR spectra of PEEK and SPEEK are compared in Fig. 3(a). SPEEK with 80 (%) DS was used here,
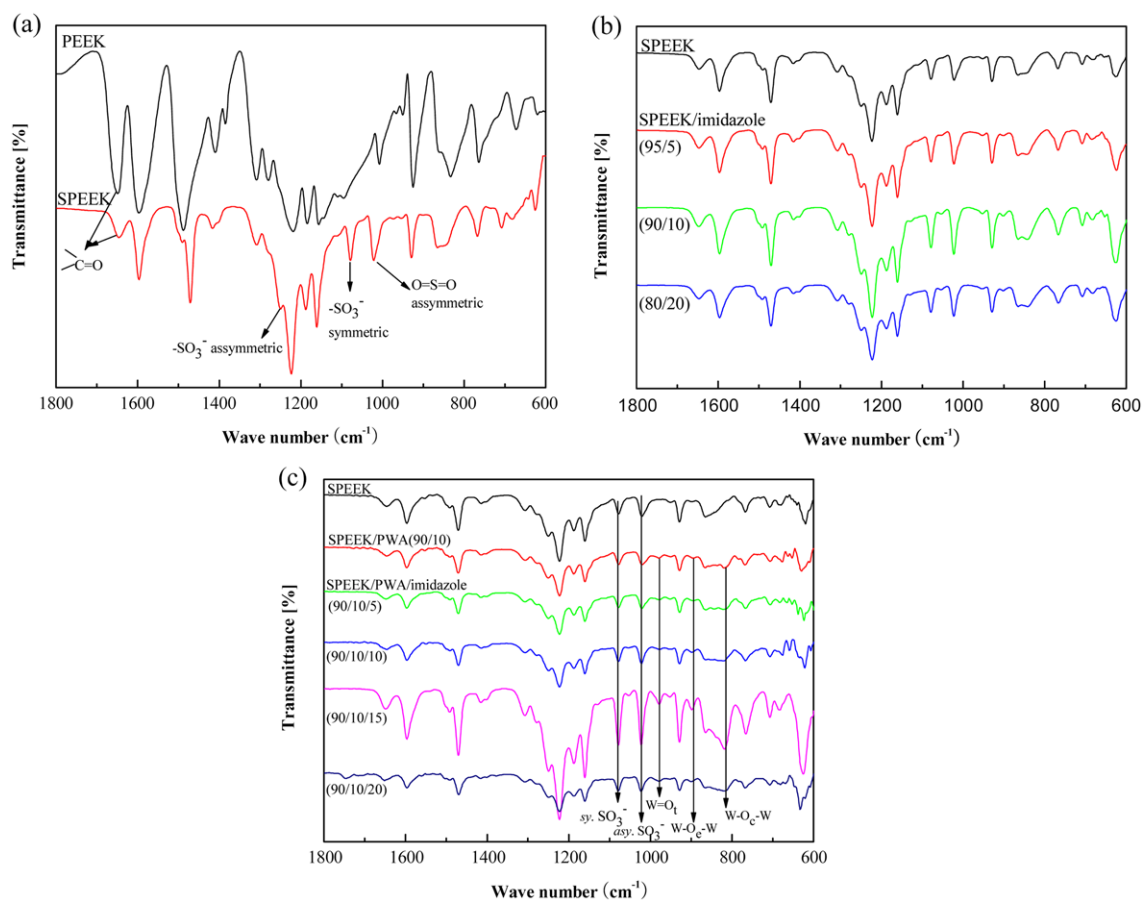
Fig. 3. ATR-FTIR spectra of (a) PEEK and SPEEK; (b) SPEEK and SPEEK/imidazole; (c) SPEEK, SPEEK/PWA and SPEEK/PWA/ imidazole composite membranes.

and all of the composite membranes used SPEEK with 80 (%) DS in this paper. In Fig. 3(a), the aromatic C-C peak at 1,489 cm^{-1} for PEEK split into 1,492 and 1,471 cm^{-1} for SPEEK because of the introduction of sulfonic acid group upon sulfonation. A new absorption peak at 1,080 cm^{-1} in SPEEK was assigned to sulfur-oxygen symmetric vibration of O=S=O, and the peaks at 1,255 and 1,020 cm^{-1} were assigned to the asymmetric vibration of sulfonic acid group in SPEEK [21]. ATR-FTIR spectra of SPEEK/imidazole composite membranes are shown in Fig. 3(b). In the figure, neither new peak nor progressive shifting was observed for all the SPEEK/imidazole composite membranes. Similar results were observed for SPEEK/HQS, SPEEK/TBP and SPEEK/succinimide composite

membranes (the FT-IR spectra are not shown here). There have been contradictory arguments. Fu et al. [22] have not shown any shifting in the FT-IR peak of the sulfonic acid group due to acid-base interaction in SPEEK/PSF (bearing benzimidazole side groups) blend membranes, while Wu et al. [23] have shown a small shift in the FT-IR peak due to acid-base interaction in SPEEK/polyvinylpyrrolidine composite membranes.

FT-IR spectra of SPEEK/PWA/imidazole ternary composite membranes are shown in Fig. 3(c). FT-IR peak assignments of pure PWA, SPEEK and composite membranes with different imidazole concentrations are shown in Table 2. In the table, the characteristic peaks of pure PWA related P-O$_a$, W=O$_t$, W-O$_e$-W and W-O$_c$-W groups

Table 2. The FT-IR peak assignments of PWA, SPEEK and SPEEK/PWA/imidazole composite membranes

Membrane (mass ratio)	Wave number (cm^{-1})				
	-SO$_3^-$	P-O$_a$	W=O$_t$	W-O$_e$-W	W-O$_c$-W
Pure PWA	-	1078	983	887	804
SPEEK/PWA (90/10)	1020	1078	979	896	820
SPEEK/PWA/imidazole (90/10/5)	1021	1078	978	896	822
SPEEK/PWA/imidazole (90/10/10)	1022	1078	977	899	822
SPEEK/PWA/imidazole (90/10/20)	1023	1079	979	900	818

Note: P-O$_a$: central tetrahedral of Keggin unit, W=O$_t$: terminal oxygen of Keggin unit, W-O$_e$-W: edge-shared octahedral of keggin unit, and W-O$_c$-W: corner-shared octahedral Keggin unit
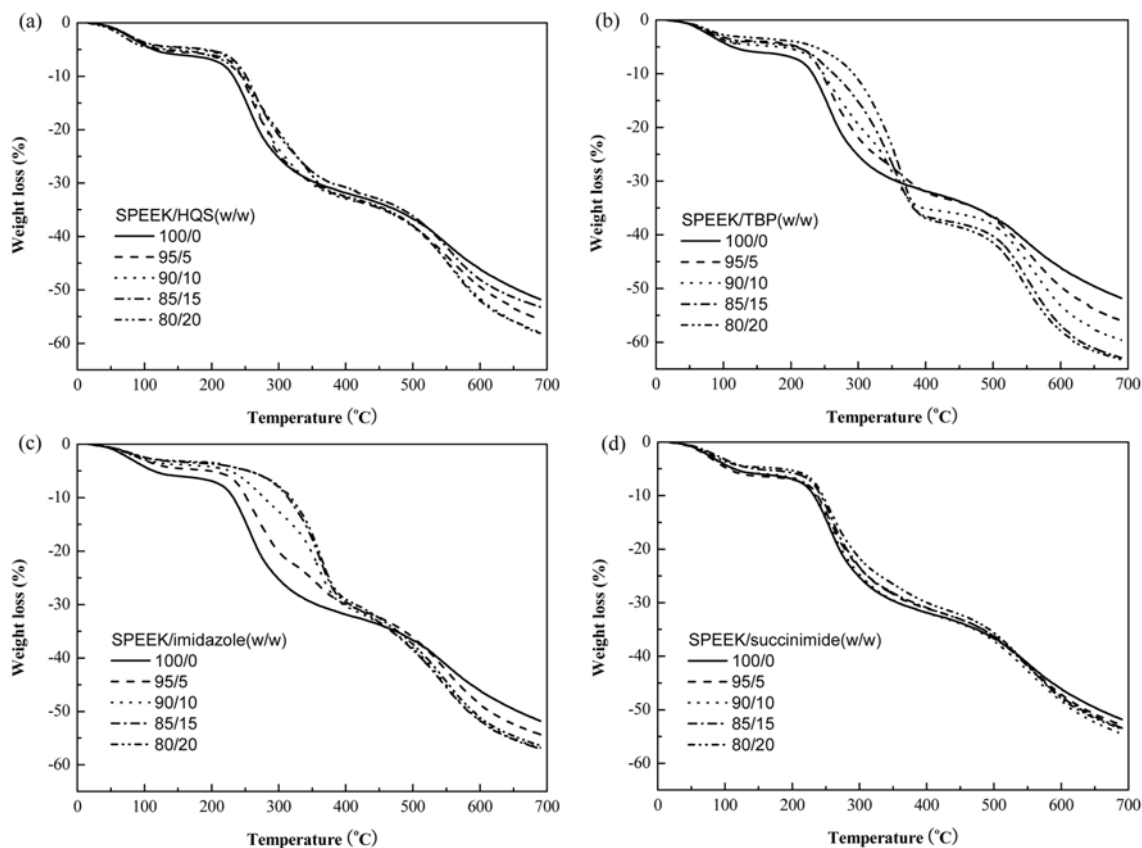
Fig. 4. The TGA curves of (a) SPEEK/HQS; (b) SPEEK/TBP; (c) SPEEK/imidazole; (d) SPEEK/succinimide composite membranes.

appeared at 1,078 cm^{-1}, 983 cm^{-1}, 887 cm^{-1} and 804 cm^{-1}, respectively. The characteristics peaks of W-O$_e$-W and W-O$_c$-W group in PWA shifted from 887 to 896 and 804 to 820 cm^{-1}, respectively, for SPEEK/PWA composite membranes. The result suggests that the bridging oxygen (edge-shared and corner-shared oxygens) of PWA make hydrogen bondings with the sulfonic acid group of SPEEK as reported by Kim et al. [15]. However, the addition of imidazole showed no further shifting of the characteristic peaks as shown in Table 2. FT-IR spectra of the ternary composite membranes containing the other additives HQS, TBP and succinimide showed similar behaviors (FT-IR spectra are not shown). The effect of acid-base interaction will be discussed later in detail.

2. TGA

The thermal resistance of composite membranes was evaluated by TGA. TGA curves of the composite membranes of SPEEK with the additives of HQS, TBP, imidazole and succinimide are shown in Fig. 4(a)-Fig. 4(d). Excluding the initial small weight loss which can be attributed to the absorbed moisture, there are two major weight losses in all of the TGA curves. The first major loss, which occurs in the temperature range between 250 °C and 400 °C, is due to the desulfonation of sulfonic acid groups in SPEEK. The second major loss, which occurs in the range between 450 °C and 650 °C, is due to the thermal decomposition of polymer chains as reported by Xing et al. [8]. In Fig. 4, the weight losses due to desulfonation were greatly decreased as additive concentrations increased for SPEEK/imidazole and SPEEK/TBP composite membranes. The weight losses due to desulfonation decreased in the order SPEEK/imidazole>SPEEK/

TBP>SPEEK/HQS>SPEEK/succinimide. The pK$_b$ values of imidazole and TBP are smaller than that of HQS as shown in Table 1. The smaller the pK$_b$, the higher the basicity. Hence imidazole and TPB would make stronger acid-base interactions with SPEEK, leading to higher thermal resistances. Fig. 5 shows the acid-base interaction scheme between SPEEK and each additive except succinimide. For example, acid-base interaction between imidazole and SPEEK is shown in Fig. 5(c). On protonation of imidazole by the sulfonic acid group of SPEEK, a positive charge is developed in the nitrogen atom of imidazole and a negative charge is developed in the oxygen atom of the sulfonic acid group. Electrostatic interaction between oppositely charged ions takes place. Also, hydrogen bridging interaction between the hydrogen atom of imidazole and the oxygen atom of sulfonic acid group can occur.

It is noted in Fig. 4(c) that the desulfonation temperature shifted to the right as imidazole concentration increased up to 15%, and remained almost the same with further increasing imidazole concentration. 13.4 wt% of imidazole is required for 1 : 1 molar interaction between the sulfonic acid group of SPEEK and imidazole as shown in Table 3. No more ionic interaction seems to take place over the imidazole concentration because all of the sulfonic acid groups have been consumed with 13.4 wt% of imidazole. Thus, no change in weight loss due to desulfonation was observed beyond 15% of imidazole. In Fig. 4, weight losses due to thermal decomposition above 400 °C increased with increasing additive concentrations. It would be suggested that the interactions between the sulfonic acid groups of SPEEK and additives were broken at the high
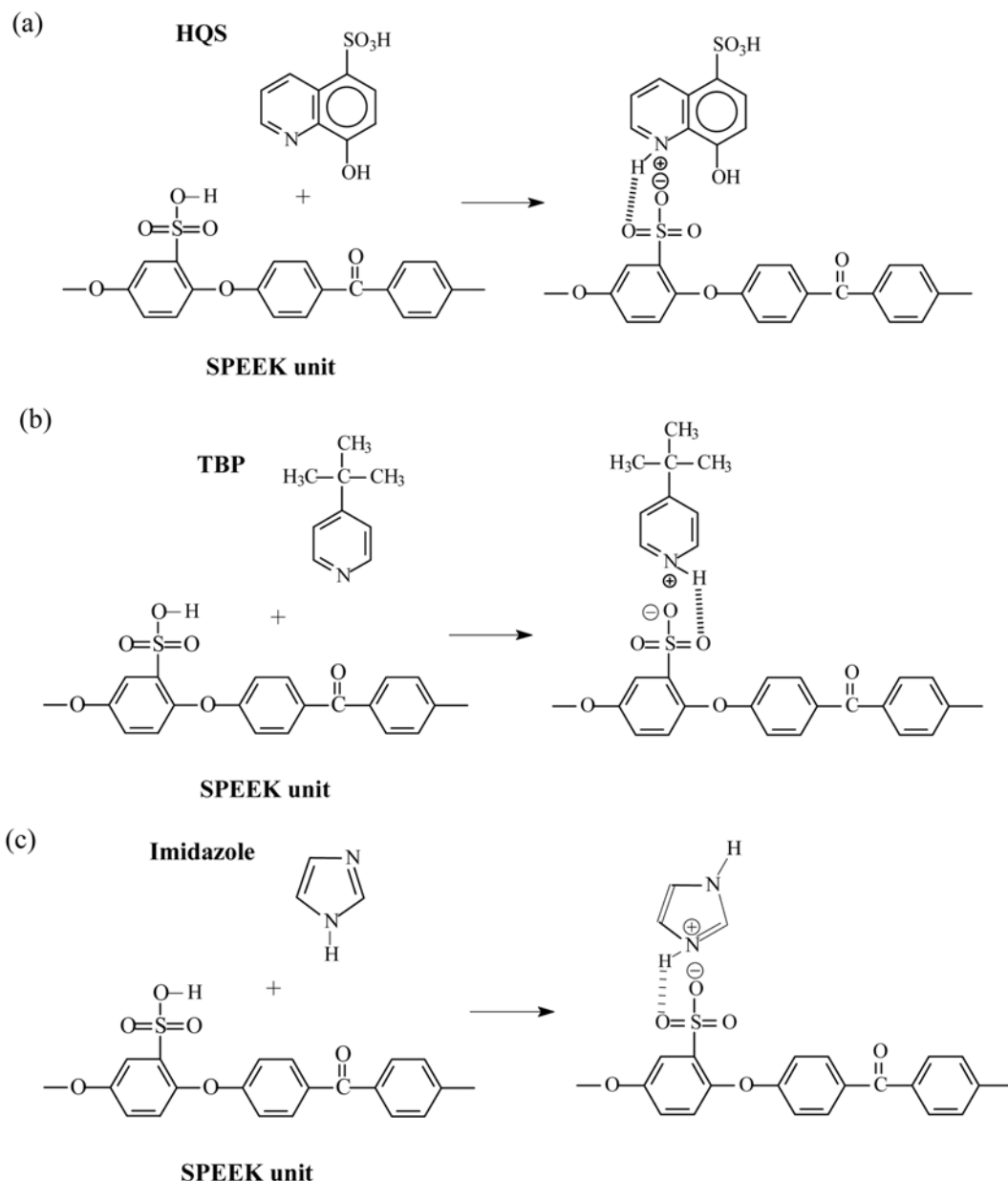
Fig. 5. The schematic representation of acid base interactions between (a) SPEEK and HQS; (b) SPEEK and TBP; (c) SPEEK and imidazole.

Table 3. Molar and mass ratios of the additive for 1 : 1 molar interaction with the sulfonic acid group of SPEEK

Additives	Molecular weight	Molar ratio (additive/SPEEK)	Mass ratio (additive/SPEEK)
HQS	225.23	0.510	0.338
TBP	135.21	0.308	0.265
Imidazole	68.08	0.153	0.134
Succinimide	99.09	0.225	0.184

temperature and the organic additives became thermally decomposed faster than the polymer main chains, resulting in greater weight losses. It is interesting that the thermal decomposition began at lower tem-

perature (around 350 °C) for TBP-containing composite membranes as shown in Fig. 4(b) and Fig. 6(c). TBP seems to be decomposed at lower temperature compared to the other additives because TBP has the lowest boiling point as shown in Table 1.

The TGA curves of SPEEK and SPEEK/PWA composite membrane are shown in Fig. 6(a). The weight loss of SPEEK/PWA composite membranes decreased as PWA concentration increased. The addition of inorganic PWA to SPEEK would improve the thermal stability of the composite membranes especially at high temperatures. The TGA curves of SPEEK/PWA/ additive ternary composite membranes containing 10% PWA are shown in Fig. 6(b)-(e). The addition of the additives decreased the weight losses due to desulfonation for all the ternary composite membranes. The weight loss behaviors due to thermal decomposition were different depend-
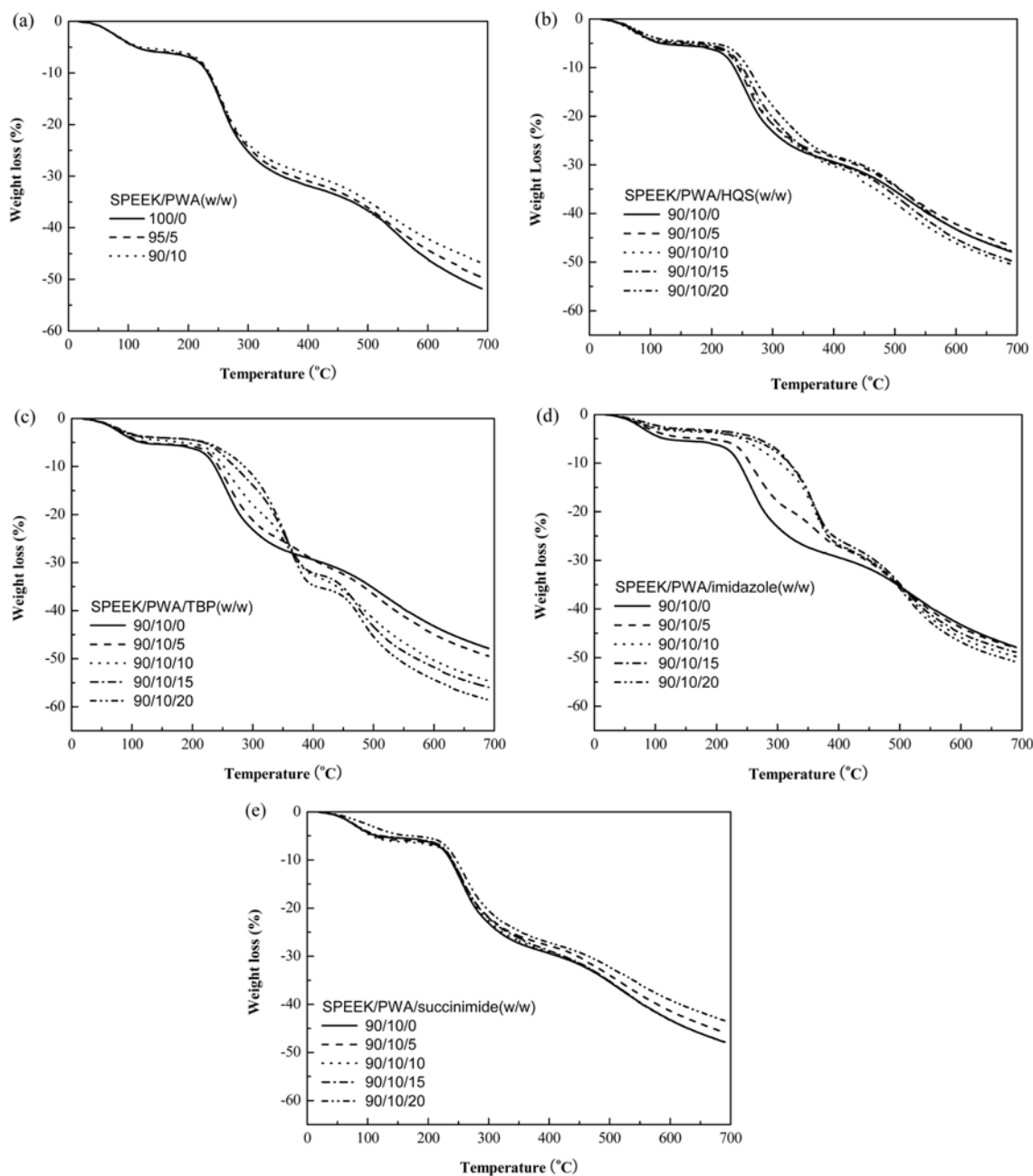
Fig. 6. The TGA curves of (a) SPEEK/PWA; (b) SPEEK/PWA/HQS; (c) SPEEK/PWA/TBP; (d) SPEEK/PWA/imidazole; (e) SPEEK/PWA/succinimide composite membranes.

ing on the additives in Fig. 6(b)-(e). The addition of the additives HQS, TBP and imidazole increased the decomposition weight losses. However, the weight loss due to thermal decomposition decreased as the succinimide concentration increased for SPEEK/PWA/succinimide composite membranes contrary to the other ternary composite membranes. Succinimide is a cyclic organic compound, while the other additives are aromatic organic compounds. Succinimide can undergo ring opening reaction in the presence of nucleophile and get covalently bonded with nucleophile. That is, the high temperature induced the ring opening of succinimide and covalent bonding with SPEEK or PWA, resulting in the greatest thermal stability at high temperatures for SPEEK/PWA/succinimide composite membranes.

3. Water Uptake

The water uptake of membranes has a great influence on the proton conductivity and mechanical strength of the membrane. High water uptake can improve the proton conductivity by generating hydrophilic domains through which proton propagates. However, excessive water uptake causes excessive swelling of the membrane, hence reducing its mechanical strength [24,25]. The water uptakes of SPEEK/additive composite membranes are shown in Fig. 7(a). The water uptake of SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes decreased significantly, but the water uptake of SPEEK/succinimide composite membranes decreased slightly as additive concentrations increased. The acid-base interac-
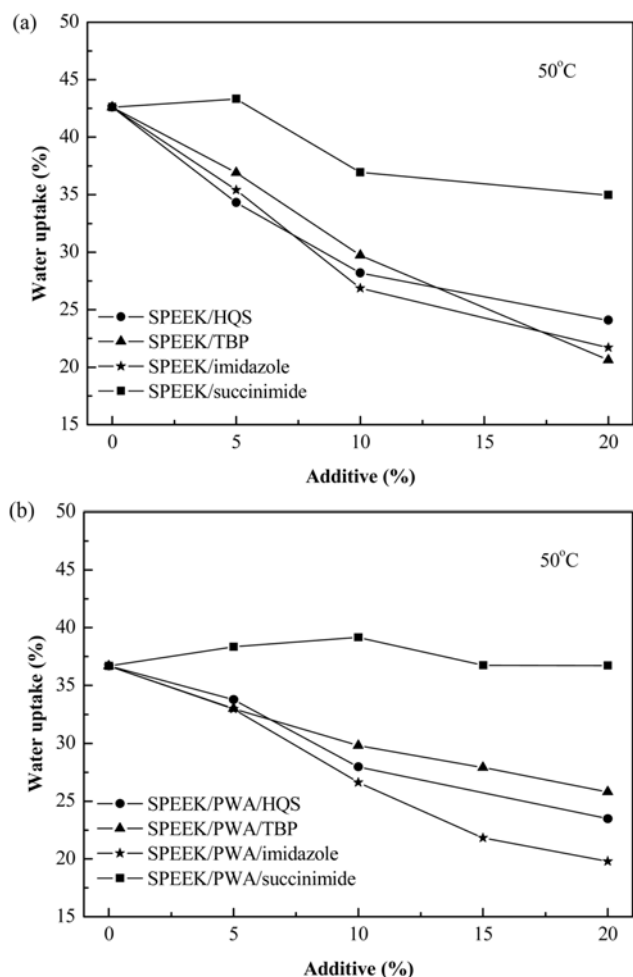
Fig. 7. The water uptakes of (a) SPEEK/additive; (b) SPEEK/PWA/ additive composite membranes.

tion reduced the water uptakes for SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes, since acid-base interaction not only made the composite membranes compact but also reduced the number of free sulfonic acid groups of SPEEK available to form hydrogen bondings with water molecules [26]. Succinimide is a weak acid (pK_a is 9.5 as shown in Table 1) different from the other additives which are all bases. The acid-base interaction does not seem to occur in SPEEK/succinimide composite membranes. Only hydrogen bonding between succinimide and the sulfonic acid group of SPEEK would take place as shown in Fig. 8. In Fig. 8, the hydrogen bonding takes place between the electronegative oxygen or nitrogen atom of succinimide and the hydrogen of sulfonic acid group in SPEEK, and/or between the hydrogen atom of succinimide and the oxygen of sulfonic acid group in SPEEK. The interaction due to the hydrogen bonding appears to be weaker than the acid-base interaction. Hence, sulfonic acid groups can have more chances to take part in another hydrogen bonding with water molecules for the SPEEK/succinimide composite membrane, resulting in higher water uptake as shown in Fig. 7(a). The weak interaction in SPEEK/succinimide composite membrane was also reflected by greater desulfonation weight losses (between 250 °C-400 °C) in TGA results as shown in Fig. 4(d).

In Table 4, the water uptake of SPEEK/PWA composite membranes decreased as PWA concentration increased. The inorganic PWA seems to make the composite membranes denser. The water uptakes of SPEEK/PWA/additive ternary composite membranes are shown in Fig. 7(b). In the figure, the water uptakes decreased as additive concentrations increased except the ternary composite membrane containing succinimide. The water uptake behaviors for the ternary composite membranes were quite similar to those for the corresponding binary composite membranes.

4. Proton Conductivity

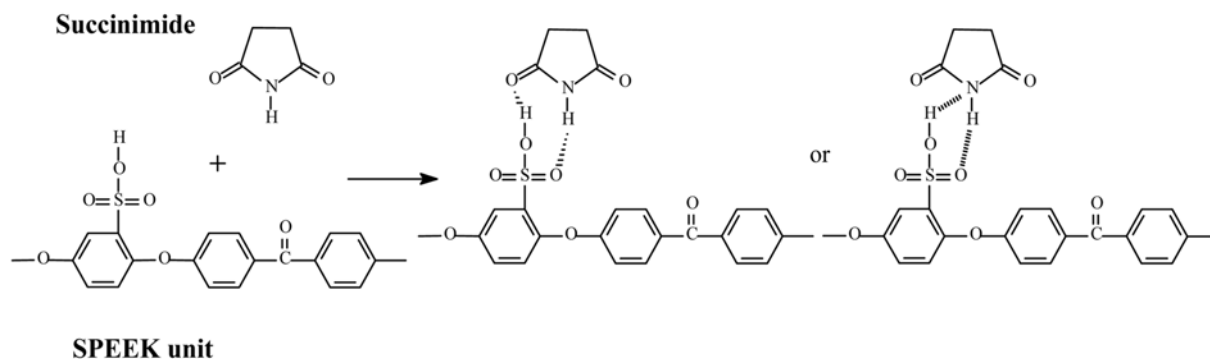The proton conductivities of SPEEK/HQS, SPEEK/TBP, SPEEK/

Fig. 8. The schematic representation of hydrogen bonding between SPEEK and succinimide.

Table 4. The water uptake, proton conductivity and methanol permeability of SPEEK and SPEEK/PWA composite membranes

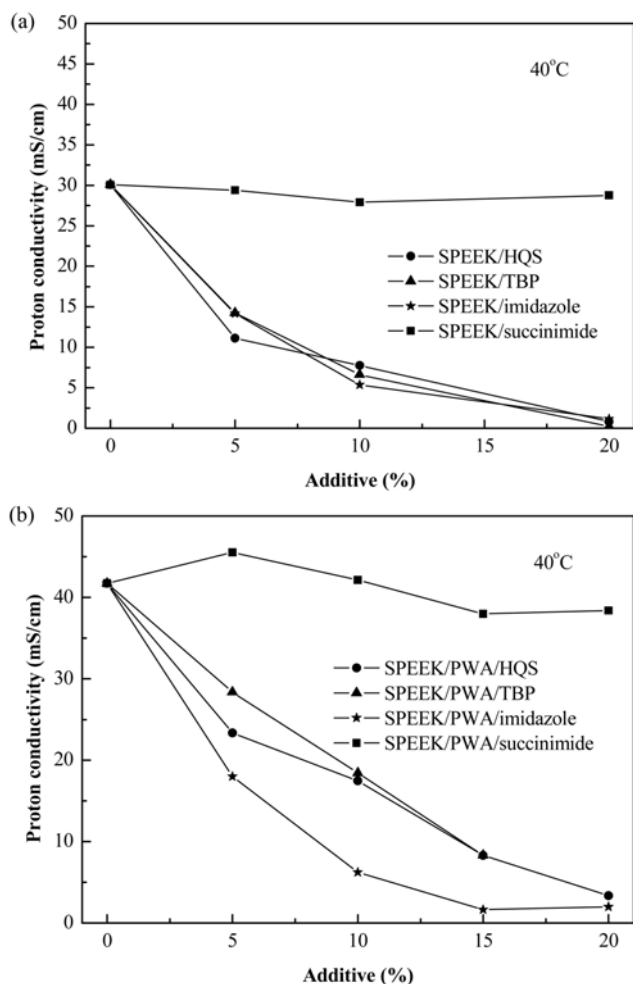| Membrane (mass ratio)	Water uptake (50 °C)	Proton conductivity (mS/cm)		Methanol permeability ($\times 10^{-7}$ cm^2/sec)
		40 °C	60 °C	
SPEEK	42.61	30.09	73.69	4.02
SPEEK/PWA (95/5)	37.5	38.20	76.33	3.62
SPEEK/PWA (90/10)	36.69	41.72	88.23	3.60

Fig. 9. The proton conductivity of (a) SPEEK/additive; (b) SPEEK/
PWA/additive composite membranes.

imidazole and SPEEK/succinimide composite membranes are shown in Fig. 9(a). The proton conductivity for SPEEK/HQS, SPEEK/ TBP and SPEEK/imidazole composite membranes decreased as additive concentrations increased, while the proton conductivity for SPEEK/succinimide composite membrane remained similar to that for pure SPEEK. More compact structures due to the acid-base interactions between SPEEK and the additives reduced the proton conductivity for SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes. As discussed previously, only hydrogen bondings are available for SPEEK/succinimide composite membranes. The weak interaction between SPEEK and succinimide would make protons be viable to take part in conduction and provide less compact space for protons to transport rather easily, resulting in higher proton conductivities. The proton conductivities of the composite membranes in Fig. 9(a) showed a close relationship with the water uptakes of the corresponding composite membranes in Fig. 7(a).

The proton conductivity of SPEEK/PWA composite membranes is shown in Table 4. The proton conductivity increased as PWA concentration increased even though the water uptake for SPEEK/PWA composite membranes decreased. The intrinsic proton conductivity of PWA (>100 mS cm^{-1} at room temperature) [27] would promote the proton conduction for SPEEK/ PWA composite membranes.

Proton conductivities of SPEEK/PWA/additive ternary composite membranes are shown in Fig. 9(b). The proton conductivity behaviors for the ternary composite membranes were similar to those of the corresponding composite membranes without PWA as shown in Fig. 9(a). However, the reduction slopes of the proton conductivities were higher for the ternary composite membranes except the composite membranes containing succinimide than those for the corresponding binary composite membranes. Greater reduction in the proton conductivity with additive concentrations suggests that the organic additives interact not only with SPEEK but also with PWA.

5. Methanol Permeability

The methanol permeability of SPEEK/additive composite membranes is shown in Fig. 10(a). The methanol permeability was measured at 30 °C. In Fig. 10(a), the methanol permeabilities decreased as additive concentrations increased for all the composite membranes except SPEEK/succinimide composite membranes. As explained previously, the acid-base interaction made SPEEK/HQS, SPEEK/ TBP and SPEEK/imidazole composite membranes more dense and compact. The compact structure would prevent methanol molecules from permeating through the membrane, hence lower methanol permeability. The methanol permeabilities showed close relationship with
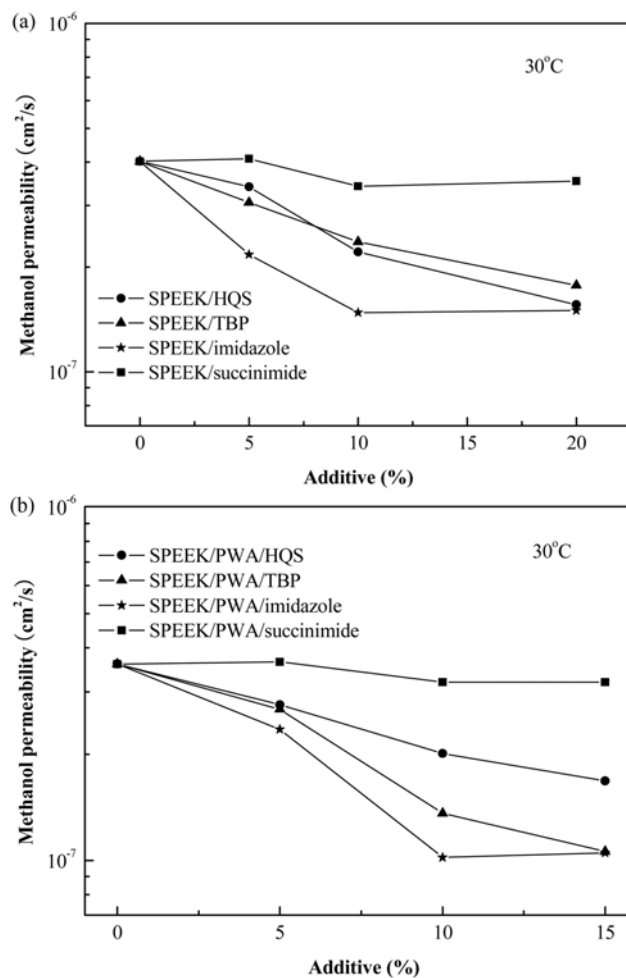

Fig. 10. The methanol permeability of (a) SPEEK/additive; (b) SPEEK/PWA/additive compo-site membranes.

the water uptakes for the corresponding composite membranes in Fig. 7(a). The methanol permeability behavior for SPEEK/succinimide composite membrane in Fig. 10(a) is similar to the proton conductivity behavior for the same composite membrane in Fig. 9(a). Hydrogen bonding between SPEEK and succinimide would not interfere with methanol permeation through the composite membrane.

The methanol permeability of SPEEK/PWA composite membranes decreased as PWA concentration increased as shown in Table 4. In spite of being highly hydrophilic, inclusion of PWA in SPEEK reduced the methanol permeability. The trend is similar to that of the water uptake for the SPEEK/PWA composite membranes in Table 4. The interaction between SPEEK and PWA (as shown in FT-IR spectra of Fig. 3(c) and Table 2) seems to restrict the methanol permeation. The methanol permeability of SPEEK/PWA/additive ternary composite membranes is shown in Fig. 10(b). The methanol permeability behaviors for the ternary composite membranes were similar to those for the corresponding composite membranes without PWA as shown in Fig. 10(a). The interactions between PWA and the organic additives except succinimide were reflected by the higher reduction slopes of the methanol permeabilities with additive concentrations for the ternary composite membranes, of which trend was similar to the case of the proton conductivity in Fig. 9(b).
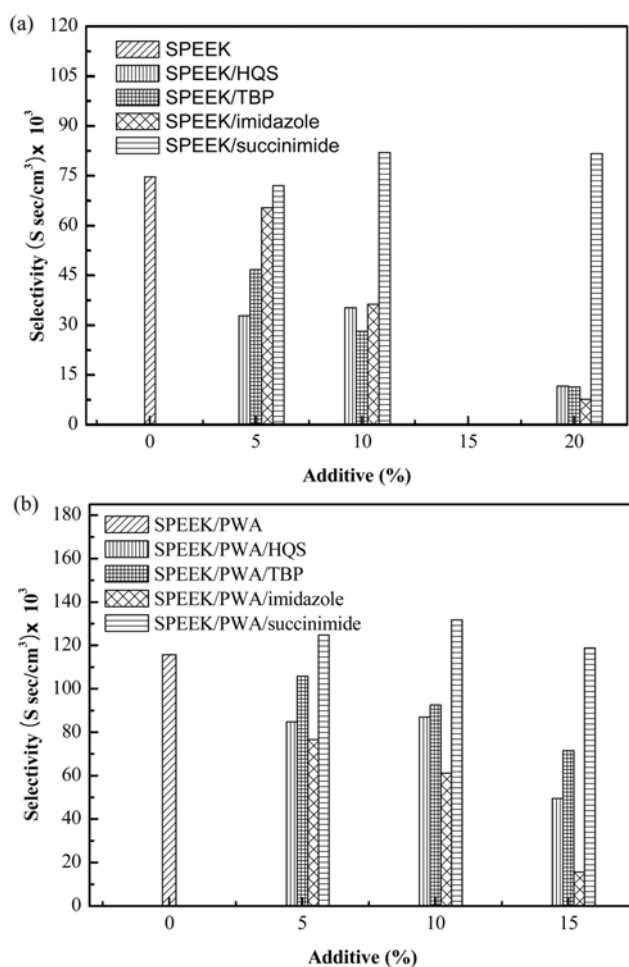

Fig. 11. The selectivity for (a) SPEEK/additive; (b) SPEEK/PWA/ additive composite membranes.

6. Selectivity

The selectivities of SPEEK/additive composite membranes are shown in Fig. 11(a). The selectivity is defined as the ratio of proton conductivity to methanol permeability. The selectivity increased or remained almost the same as additive concentration increased for SPEEK/succinimide composite membranes, but decreased for SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes. The reduction in the selectivities for SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes would be attributed to the acid base interaction and the interaction become stronger as additive concentrations increased. The selectivities of SPEEK/PWA/ additive ternary composite membranes are shown in Fig. 11(b). The selectivities of the ternary composite membranes showed similar behaviors to those of the corresponding binary composite membranes in Fig. 11(a). However, the selectivities for the ternary composite membranes were higher than those of the corresponding binary composite membranes because the addition of PWA increased proton conductivity and decreased methanol permeability.

CONCLUSIONS

Composite membranes were prepared from SPEEK solution with inorganic and organic additives, and their thermal and transport properties were investigated. It was found by TGA measurements that the acid-base interaction improved thermal resistance to the desulfonation of sulfonic acid groups for SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole composite membranes. The addition of PWA enhanced resistance to thermal decomposition for all the composite membranes. The water uptake, methanol permeability and proton conductivity decreased as organic additive concentrations increased for the binary composite membranes of SPEEK/HQS, SPEEK/TBP and SPEEK/imidazole, and for the ternary composite membranes of SPEEK/PWA/HQS, SPEEK/PWA/TBP and SPEEK/PWA/imidazole. SPEEK/succinimide and SPEEK/PWA/succinimide composite membranes showed small or little change with additive concentrations in water uptake, methanol permeability and proton conductivity. The acid-base interaction would not take place in SPEEK/succinimide composite membranes, and only hydrogen bonding between succinimide and the sulfonic acid group occurred. The hydrogen bonding seems to make the composite membranes be less compact than those with acid-base interaction, resulting in small changes in transport properties for the composite membranes containing succinimide. The selectivities of the composite membranes containing succinimide were higher than those of the other composite membranes. The ternary composite membranes containing inorganic PWA showed higher selectivities compared to the corresponding composite membranes without PWA.

The current research would provide significant ideas how to control the properties of polymer electrolyte composite membranes. The results can be applied to proton exchange membrane fuel cells, direct methanol fuel cells, dye sensitized solar cells and other areas to use polymer electrolyte membranes. The acid-base interaction can also be used to enhance the thermal properties of polymers.

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