



## CHAPTER V

# POLY (ACRYLIC ACID-CO-4VINYLMIDAZOLE)/SULFONATED POLYETHERETHERKETONE (POLY (AA-CO-4VIM)/SPEEK) BLEND MEMBRANES FOR PEM FUEL CELL APPLICATIONS

### 5.1 Abstract

The sulfonated polyether ether ketone (SPEEK) and various types of poly (acrylic acid-co-4-vinylimidazole) were prepared under non-humidified system for fuel cells. The blend membranes showed homogeneous morphologies between SPEEK and copolymers via the hydrogen bond interaction between  $\text{SO}_3\text{H}$  or  $\text{COOH}$  groups and imidazole group observed by SEM and DSC. Thermal stability from TGA curves has been improved in blend membranes compared only with copolymer membrane due to the excellent thermal resistance of SPEEK. However, the mechanical properties of blend membranes without cross-linking process such as tensile strength and elongation percentage were obtained with lower values than SPEEK. IEC and proton conductivity of the blend membranes were increased with increasing with the acrylic acid content. SPEEK/M3 blend membrane exhibited relatively high proton conductivity of  $25 \times 10^{-3}$  S/cm at  $120^\circ\text{C}$  with the lowest activation energy of 5.61 kJ/mol. The lower % swelling ratio of SPEEK blended membranes than SPEEK provided the better dimensional stability for MEA fabrication. The simple fabrication and low cost of the blend membranes have made an attractiveness of these polymer electrolyte membranes to non-humidified fuel cell application.

**Keywords:** Acrylic acid; 4-Vinylimidazole; Sulfonated(polyether ether ketone); Proton conductivity; Polymer electrolyte membrane

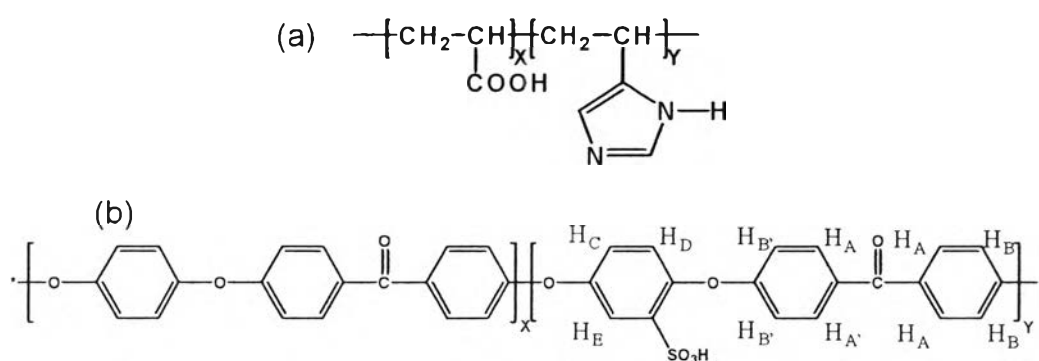
### 5.2 Introduction

In several decades, Nafion<sup>®</sup> has been a commercial polymer membrane for fuel cell (PEMFC) in which the proton conductivity 0.1 S/cm was given via Grotthus mechanism of water molecules [1–2]. Its high chemical and mechanical properties has been achieved much interest for PEMFC, albeit does not retain that proton conductivity value at ~120 °C for the fuel cell engine requirement [3]. In other words, the future trend of fuel cell systems may require operating at higher temperature up to 120 °C without humidification of fuel gas and air, and pressurization [4]. Alternative polymer membranes have been designed for accomplishing high proton conductivity at higher temperature with low relative humidity (RH), including good mechanical properties. With a good candidate for high temperature PEMFC, SPEEK<sup>®</sup> possesses good mechanical properties, high chemical resistance, cheap price and thermal stability [5–8]. Transport properties of SPEEK occurred with narrower channel than that of Nafion<sup>®</sup> due to the less connected hydrophilic channels and to larger separations between less acidic sulfonic acid functional groups. Therefore, at high water content, water permeation and electro-osmotic drag were decreased, yet remaining high proton conductivity [9]. Jung et al. prepared SPEEK/PVdF blend in order to improve dimension stability and compatibility with Nafion<sup>®</sup> binder [10–12]. Novel sulphonated poly (phthalazine ether sulfone)/polyacrylic acid interpenetrating network membranes were demonstrated with the higher proton conductivity  $\sim 1.88 \times 10^{-2}$  S/cm than Nafion<sup>®</sup> [13]. The acid-base polymer blends of sulfonated poly (ether ether ketone) and poly (ether sulfone) have been evaluated. The membranes show excellent thermal stabilities and good proton conductivities [14]. The solid polymer membranes of PVA/PAA/KOH were prepared with ionic conductivity 0.301 S/cm, including excellent thermal and mechanical properties [15]. Another polymer blends of poly (vinyl alcohol)/ poly (styrene sulfonic acid-co-maleic acid) showed the proton conductivity as high as Nafion<sup>®</sup> but the methanol permeability was lower more than one order of magnitude [16].

Various polymer blends based on SPEEK and other polymer blends for DMFC or PEMFC were summarized in Table 5.1 and Table 5.2, respectively. In our previous paper, anhydrous poly (AA-co-4VIm) consists of proton donors and

acceptors which give a useful proton conductivity  $\sim 10^{-2}$  S/cm (see Scheme 5.1). Imidazole group provides the proton hopping process as same as water molecule [35], whereas carboxylic acid group provides a proton source. In this paper, we reported an improvement of proton conductivity by solution blending between poly (AA-co4VIm) and SPEEK under non-humidified system for the PEMFC application.

**Scheme 5.1** Chemical structure of (a) Poly (AA-co-4VIm) and (b) SPEEK.



**Table 5.1** Literature survey on using SPEEK blends for fuel cell applications

Membrane	Proton conductivity	Thermal stability	Reference
1. SPEEK/phenolic resin	0.031-0.06 S/cm @ 25 °C	250 °C	[17]
2. SPEEK/AMPS blend	0.084 S/cm @ 25 °C	287 °C	[18]
3. SPEEK/Poly(amide imide)	0.02 S/cm @ 25 °C	-	[19]
4. SPEEK/Poly(ether sulfone)	0.034 S/cm @ 25 °C	184 °C	[20]
5. SPEEK/Polyaniline	0.009 S/cm @ 25 °C	290 °C	[21,22]
6. SPEEK/Polybenzimidazole	0.046 S/cm @ 25 °C	300 °C	[23]
7. SPEEK/TMBP membranes	0.03 S/cm @ 25 °C	300 °C	[24]
8. SPEEK/Polyacrylonitrile	0.052 S/cm @ 25 °C	-	[25]
9. Methyl substituted SPEEK/Polypyrrole	0.05 S/cm @ 25 °C	300 °C	[26]
10. SPEEK/Poly(ether imide)	$10^{-3}$ S/cm @ 25 °C	-	[27]

AMPS = 2-acrylamido-2-methyl-1-propanesulfonic acid

TMBP = 4, 4'-diglycidyl(3,3',5,5'-tetramethylbiphenyl) epoxy resin

**Table 5.2** Summary of physical modification of the membranes based on polymer blending

Membranes	Comments	Reference
1. Nafion 112/PVA	44% methanol permeation reduction with a slightly increase in resistance R, compared with Nafion.	[28]
2. H <sub>3</sub> PO <sub>4</sub> /Nafion-PBI	55% durability improvement in H <sub>2</sub> /O <sub>2</sub> test system, compared with H <sub>3</sub> PO <sub>4</sub> / PBI.	[29]
3. Nafion/PBI	Methanol crossover reduction 1.2–2.7 times Nafion 117/112 at the same DMFC performance.	[30]
4. Nafion/SPEEK/Nafion membranes	Higher methanol crossover but better conductivity compared with the same thickness of SPEEK membrane.	[31]
5. Nafion/Sulfonated poly(aryl ether ketone)	Better mechanical properties but lower conductivity and methanol permeability, compared with Nafion.	[32]
6. Sulfonated PPO oligomers/Nafion	50% methanol permeation reduction compared with Nafion.	[33]
7. PPO/Poly(styrene- <i>b</i> -vinylbenzylphosphonic acid)	thermal stability up to 350 °C, and conductivity $2.85 \times 10^{-2}$ S/cm at 140 °C (RH = 100%)	[34]

## 5.3 Experimental Section

### 5.3.1 Materials

Urocanic acid and 2, 2'-azobisisobutyronitrile were purchased from Sigma Aldrich (USA.). Methanol, N, N'-dimethylformamide, and acetone were obtained

from Lab-Scan (Ireland). Acrylic acid, hydrochloric acid, and sulfuric acid were purchased from Fluka Chemicals (Buchs, Switzerland). Poly (ether ether ketone) (VESTAKEEP 4000 FP) was obtained from JJ-Degussa Chemicals (Thailand) Ltd. Nafion<sup>®</sup> 117 membrane was purchased from Ion Power, Inc (USA.). All chemicals were AR grade and used without further purification except acrylic acid.

### 5.3.2 Instruments and equipment

Fourier transform infrared (FTIR) spectra were obtained from a Thermo Nicolet Nexus 670 with 32 scans with a resolution of 2 cm<sup>-1</sup>. A frequency of 4000–400 cm<sup>-1</sup> was observed by using deuterated triglycerinesulfate detector (DTGS) with specific detectivity,  $D^*$ , of  $1 \times 10^9 \text{ cm} \cdot \text{Hz}^{1/2} \cdot \text{w}^{-1}$ . Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded using a Varian Mercury-400BB spectrometer. Thermal analysis was investigated by a TGA 2950 Dupont. Samples were heated to 800 °C at a heating rate 10 °C min<sup>-1</sup> under nitrogen or air at a flow rate 20 ml min<sup>-1</sup>. DSC was carried out at the temperature range of 20–300 °C using a DSC 7 (Perkin Elmer) with a heat-cool-heat cycle program and heating rate 10 °C·min<sup>-1</sup>. All data were collected in the second heating cycle in order to obtain reproducible analysis.

### 5.3.3 Procedures

#### 5.3.3.1 Synthesis of copolymers of acrylic acid and 4-vinylimidazole

The copolymerization of acrylic acid and 4-vinylimidazole were reported elsewhere [36]. A series of reactions using various ratios of acrylic acid (AA) and 4-vinylimidazole (VIm) were carried out as follows: 1AA:4VIm (**M1**), 1AA:1VIm (**M2**), 4AA:1VIm (**M3**), and 19AA:1VIm (**M4**) with the found VIm contents at 66.6%, 64.5%, 28.6%, and 4.2%, respectively.

#### 5.3.3.2 Sulfonation of Poly (ether ether ketone)

PEEK powder was dried in vacuum oven at 70 °C for 48 h. Dried poly (ether ether ketone) 12 g was gradually dissolved in 95–97 % concentrated sulfuric acid

600 mL for 48 h at room temperature under vigorous stirring. After the desired time, the polymer solution was precipitated into a large excess of ice-cold water under continuous stirring. The precipitated polymer was filtered and washed several times with de-ionized water until pH = 6. The polymer was dried in vacuum oven at 70 °C for 18 h to obtain SPEEK [3].

#### 5.3.3.3 Membrane preparation

Two separated polymer solutions of 50 wt% SPEEK and 50 wt% copolymers were dissolved in DMF. The polymer blends were mixed and stirred at 60 °C for 24 h to give homogeneous solution. The concentration of polymer blend was kept constantly at 10 %w/v solution. The blend solution of 15 ml was poured onto silanized glass plate and dried at 60 °C overnight. After that, the obtained membrane was dried in vacuum oven at 70 °C for 12 h to remove a residual solvent.

#### 5.3.3.4 Swelling ratio

Membranes are cut with area size of 10 mm × 50 mm and weighed before measurement [37]. After that, the membranes were immersed in distilled water at room temperature for 24 h. The weight and dimensional change of films were measured. Swelling ratio is calculated by using following equation:

$$\text{Swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad ; L = \text{length}$$

#### 5.3.3.5 Ion exchange capacity (IEC)

Ion exchange capacity (IEC) of the membrane is an important factor to indicate the efficiency of proton transferring through the membrane. The membrane is immersed in 1M NaCl for 48 h at ambient temperature. By titration of NaCl solution with 0.01 M NaOH solution using phenolphthalein as indicator, IEC can be varied depending on the number proton exchangeable groups. The volume of NaOH solution titrated is expressed it in term of milliequivalent of exchanged proton per dry polymer weight (meq<sub>H+</sub>/g) (Basile *et al.*, 2006) [38].

$$\text{IEC (mmol/g)} = \frac{\Delta V_{\text{NaOH}} \times C_{\text{NaOH}}}{\text{Sample dry weight}}$$

#### 5.3.3.6 Morphology

Scanning electron microscope (SEM) analysis was used to study the morphology at cross section of the membranes. The pieces of membranes were immersed in liquid nitrogen for 30 s and were frozen. Frozen membranes of various blends were broken for SEM images. The analysis was carried out with a JEOL JSM-5410V SEM.

#### 5.3.3.7 Mechanical strength

Universal testing machine (UTM) of Lloyd instrument, model LRX, was used to measure tensile strength-elongation tests according to the standard method (ASTM D 882). The test specimens were cut into strips 50 mm long and 25 mm wide and the thickness of each strip was approximately 160  $\mu\text{m}$ . The films were then placed between the grips of the testing machine with the grip length of 30 mm. The crosshead speed was set at 500 mm/min. Tensile strength was calculated using the equation

$$\text{Tensile strength} = \frac{\text{maximum load}}{\text{Cross-sectional area}} \quad \text{N/mm}^2$$

#### 5.3.3.8 Proton conductivity measurement

Proton conductivity was measured by impedance spectroscopy with a Zahner IM6 spectrometer. Membranes were sandwiched between gas diffusion electrodes (ELAT containing 1 mg/cm<sup>2</sup> Pt loading) by way of porous stainless steel discs. The conductivity of membranes is carried out as a function of temperature (from 40 to 120 °C) and without humidity in the frequency ranges 1 MHz-10 Hz at the signal amplitude  $\leq 100$  mV. The impedance data was accurate by the contribution of the empty and short-circuited cell. The membrane resistance was extrapolated to the real axis on the high frequency part. The membranes were treated in vacuum oven at 70



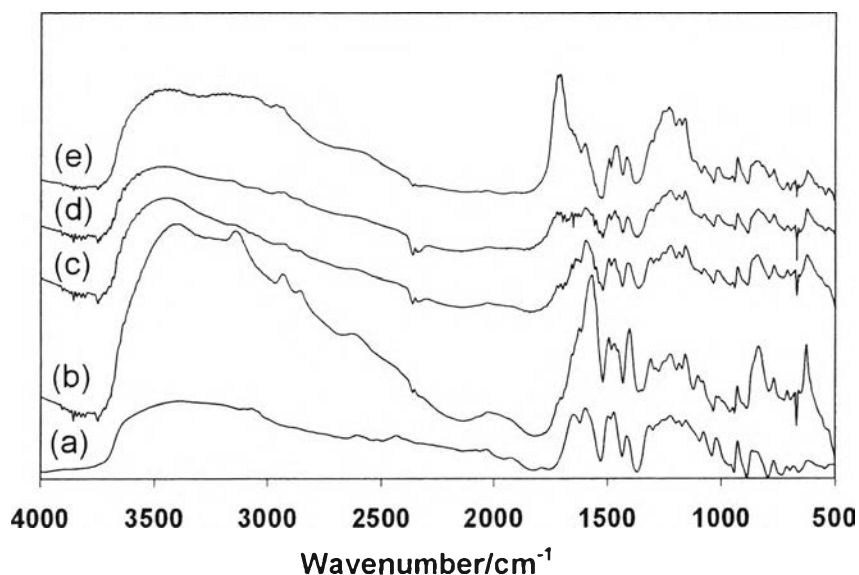
°C for 24 h before measurement. All conductivity measurements were carried out after the conductivity reaching a constant value at least 3 h.

## 5.4 Results and Discussion

### 5.4.1 Characteristics of SPEEK and Poly (AA-co-4VIm)

In order to increase proton conductivity and solubility with organic solvents, direct sulfonation of polyether ether ketone is traditionally used to introduce the charged units into the polymer structure. Consequently, a semicrystalline PEEK is changed to an amorphous form. After sulfonation, hydroxyl group of sulfonic acid was broadly appeared at  $3440\text{ cm}^{-1}$ . In addition, the ortho-substituted benzene and two O=S=O stretching bands can be observed at 1026, 1082, and  $1250\text{ cm}^{-1}$ , respectively. The other characteristic peaks of SPEEK were shown at  $1659\text{ cm}^{-1}$  (C=O),  $1601\text{ cm}^{-1}$  and  $1498\text{ cm}^{-1}$  (=CH), and  $1234\text{ cm}^{-1}$  (C-O-C). The chemical shift from  $^1\text{H-NMR}$  of SPEEK has been determined by the equation below [6]. The proton designation of each position was clarified as follows. The chemical shift at 6.562 and 7.142 ppm belong to singlet ( $\text{H}_E$ ) and doublet ( $\text{H}_B$ ) protons. Moreover, doublet protons of  $\text{H}_D$  and  $\text{H}_{B'}$  were found to be at 7.215 and 7.27 ppm. The peaks at 7.34 and 7.7–7.9 ppm are ascribed to characteristic protons of  $\text{H}_C$  (singlet) and  $\text{H}_{A, A'}$  (multiplet).

$$\frac{n}{(12-2n)} = \frac{A\text{H}_E}{\Sigma A\text{H}_{A,A',B,B',C,D}}$$



**Figure 5.1** FTIR spectra of SPEEK blended with copolymers of acrylic acid and 4-vinylimidazole: (a) SPEEK, (b) SPEEK/M1, (c) SPEEK/M2, (d) SPEEK/M3, and (e) SPEEK/M4.

$^1\text{H-NMR}$  and elemental analysis were used to estimate sulfonation degree of SPEEK as shown in Table 5.3. The sulfonation degree calculated from  $^1\text{H-NMR}$  and elemental analysis were found to be 43% and 47%, respectively. The combination FTIR peaks of blend films (Fig. 1.) were shown both functional groups of SPEEK and Poly (AA-co-4VIm). A peak due to the  $\text{SO}_3\text{H}$  group was occurred at  $1050\text{-}1300\text{ cm}^{-1}$  whereas the broad peak position of the inter- and intra-molecular hydrogen bonding between  $\text{SO}_3\text{H}$  and imidazole rich copolymer were occurred at  $2400\text{-}3600\text{ cm}^{-1}$ .

**Table 5.3** Elemental analysis of SPEEK

EA	SPEEK powder	SPEEK film
C	56.85	57.85
H	4.07	4.45
S	4.62	5.14
DS%	47	53

#### 5.4.2 Swelling ratio and IEC of SPEEK/Poly (AA-co-4VIm) blend

The swelling ratio was used to determine the ability of membrane absorbed water as presented in Table 5.4. Blended membranes exhibit more absorption with higher acrylic acid content. It should be noted that when a swelling ratio of the membrane is high, higher membrane resistance will be obtained, resulting in poorer proton conductivity. Nevertheless, ion exchange capacity values obtained from blended membrane were increased with increasing acrylic acid content.

Ion exchange capacity provides the information about a number of ionizable hydrophilic groups in the membrane matrix, which are responsible for the proton conduction, which might regard to the proton conductivity of the membranes. The IEC values for all SPEEK/Poly (AA-co-4VIm) and Nafion<sup>®</sup> membranes are shown in Table 5.4 ranging from 1.28–1.67 mmol/g. When the acrylic acid content increased, IEC values were increased referring to the density of –SO<sub>3</sub>H and –COOH groups. It can be seen that copolymer blend of SPEEK/M4 which contains highest amount of acrylic acid has the highest swelling ratio, yet compromising with a high IEC value.

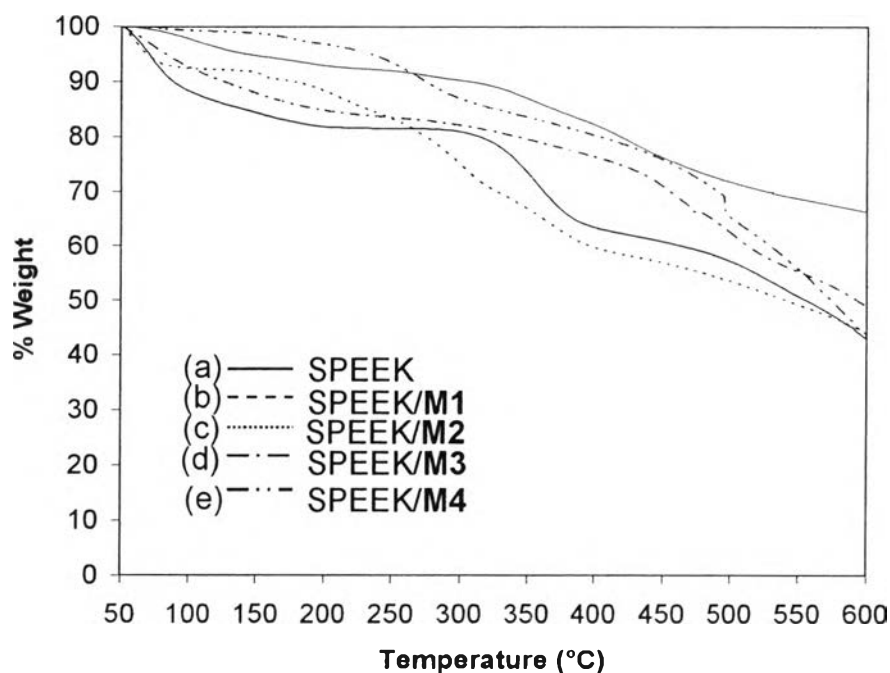
**Table 5.4** Transition temperature, swelling ratio, and IEC of Nafion<sup>®</sup>117 and SPEEK blended with Poly (AA-co-4VIm)

No.	Membrane	Tg (°C)	Tm (°C)	%Swelling ratio	IEC (mmol/g)	E <sub>a</sub> (kJ/mol)
1	Nafion <sup>®</sup> 117	132	N/F	9	0.92	-
2	PEEK	143	343	-	-	-
3	SPEEK53	208.3	343	13	1.82	-
4	SPEEK/M1	193.2	-	6	1.28	10.20
5	SPEEK/M2	167	-	6.6	1.35	9.21
6	SPEEK/M3	142.7	-	8	1.44	5.61
7	SPEEK/M4	162.5	-	9.4	1.67	6.49

#### 5.4.3 Thermal stability of SPEEK/Poly (AA-co-4VIm) blend

Sulfonated polyether ether ketone contains a glass transition temperature of 208.3 °C and a melting temperature of 343 °C [28]. It was found that the only one  $T_g$  can be observed for these blends which imply that the two polymer blends are miscible. The glass transition temperature of SPEEK/copolymer blends are in between  $T_g$  values of SPEEK and copolymer itself. Transition temperature of SPEEK and its blends are summarized in Table 5.4, which show decrease in  $T_g$  with increase in acrylic acid content in the copolymer. However, the glass transition temperature of SPEEK/M4 tends to increase. The reasons are not clear for this increase and more detailed analyses are needed to observe this behavior. In contrast, SPEEK/M1 shows higher  $T_g$  value than M1 which implies that there was a strong acid-base interaction between the acid from COOH and SO<sub>3</sub>H and imidazole of the two polymer blend.

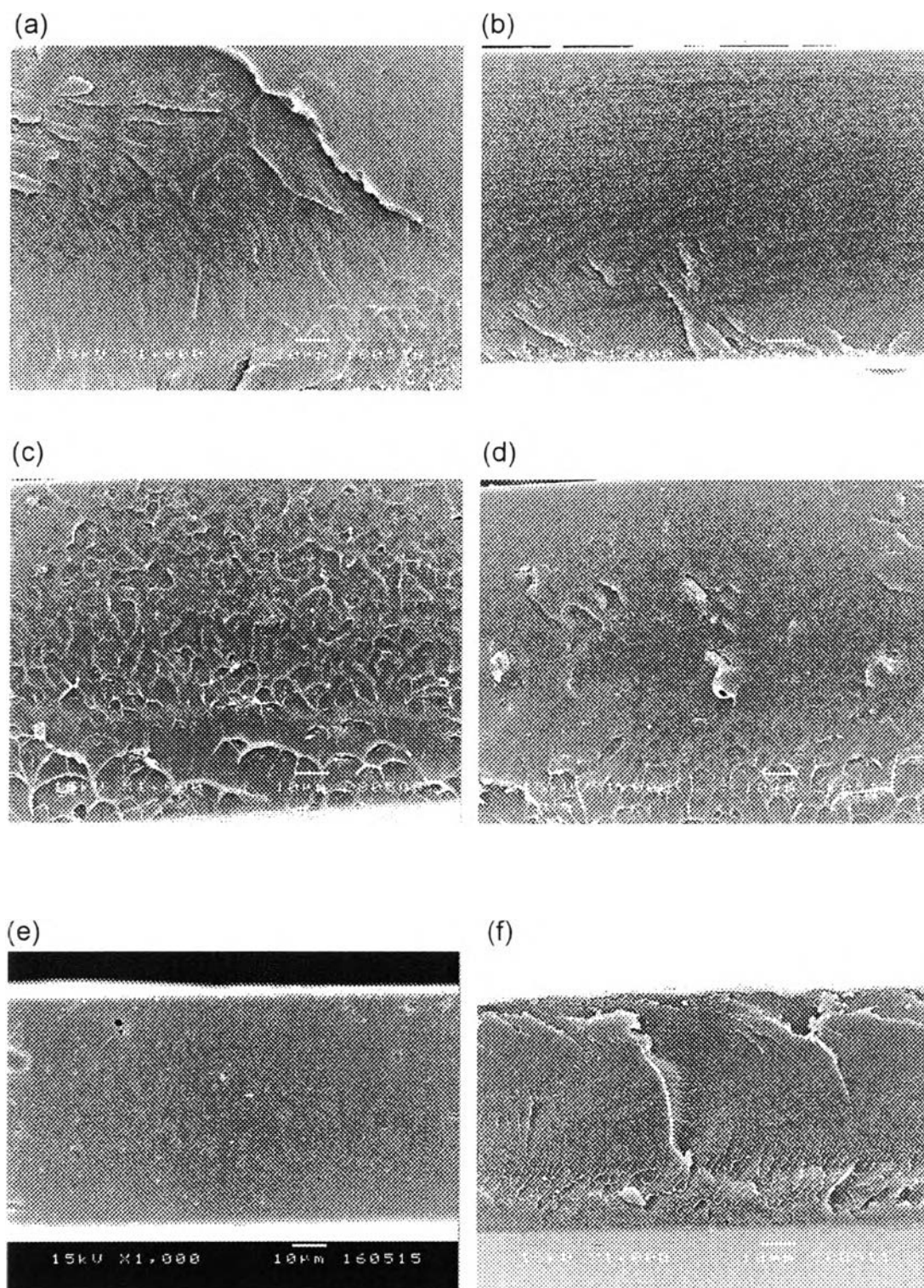
Thermo-stability curves under nitrogen in the SPEEK/Poly (AA-co-4VIm) films are presented in Figure 5.2. The SPEEK film shows a simple thermal degradation curve, where the degradation takes place in two steps at the temperature of 300 and 500 °C. Approximately at the temperature of 300 °C, a step change can be seen in the TGA curve due to the loss of sulfonic acid groups in the material. Then, at the temperature of 500 °C, a thermal loss of material is due to PEEK backbones. Weight loss percentage of blend membranes was lower than that of Poly (AA-co-4VIm) itself in all temperature range. In other words, thermal stability of SPEEK/Poly (AA-co-4VIm) blends has been improved. The increase in thermal stability of the copolymer blends is owing to the specialty thermal stability of SPEEK and the specific interactions between the acidic and basic sides in the blend.



**Figure 5.2** TGA thermograms of SPEEK blended with copolymers of acrylic acid and 4-vinylimidazole under nitrogen: (a) SPEEK, (b) SPEEK/M1, (c) SPEEK/M2, (d) SPEEK/M3, and (e) SPEEK/M4.

#### 5.4.4 Morphology of SPEEK/Poly (AA-co-4VIm) blend

Figure 5.3 shows the SEM photographs of various compositions of SPEEK/Poly (AA-co-4VIm) with cross-sectional images. The cross-sectional morphologies of Nafion<sup>®</sup> and SPEEK membranes were simple and relatively smooth. The morphology of SPEEK/Poly (AA-co-4VIm) films was slightly changed. It was found that the copolymer compositions had a strong effect on the film morphology. The smooth structure was destroyed with the higher ratio of acrylic acid monomer. However, no pore formation was detected in all blended membranes which retain dense structure. The appearance of dense membrane structure can be described by the interaction between the sulfonic acid groups of SPEEK and the imidazole units of Poly (AA-co-4VIm). This might be due to the strong acid-base interaction and no phase separation detected during solvent evaporation. Thus homogeneous and transparent films can be formed.



**Figure 5.3** SEM photographs of cross-sectional SPEEK/Poly (AA-co-4VIm) membranes with different blend compositions: (a) Nafion<sup>®</sup> 117, (b) SPEEK, (c) SPEEK/M1, (d) SPEEK/M2, (e) SPEEK/M3, and (f) SPEEK/M4.

#### 5.4.5 Mechanical properties of SPEEK/Poly (AA-co-4VIm) blend

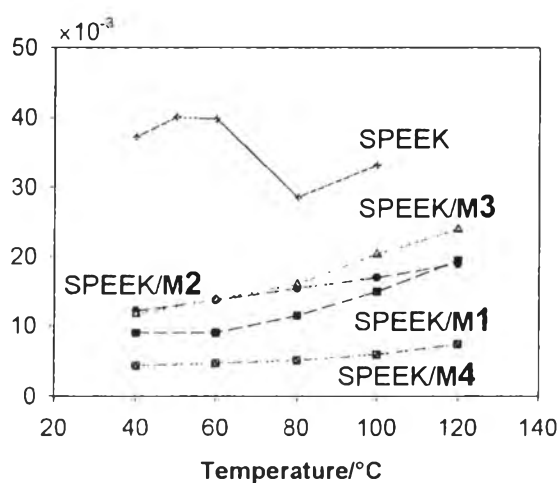
The tensile strength at break of the blend membranes in dry state are given in Table 5.5. From the results, it can illustrate how the various copolymers affect on the tensile strength and elongation at break. Elastic ductile polymer films show two characteristic region of deformation in stress-elongation curves [39]: below yield points, a steep initial slope can be seen in elastic moduli in which the stress increases rapidly with increasing elongation; above yield points, the stress slowly decrease with breaking failure in elongation. An increase in acrylic acid content causes a transition from brittle to ductile behavior. Taking to the consideration, the copolymer blends with ductile property meet the requirements for PEM. By contrast SPEEK with **M2** blends show higher tensile strength values than the other copolymers blended with SPEEK. This indicated that the hydrogen-bonding interactions between sulfonated or carboxylic acid groups and imidazole might play an important role for reinforcement [40].

**Table 5.5** Mechanical properties of Nafion 117, SPEEK, and SPEEK/Poly (AA-co-4VIm) blend membranes

No.	Membrane	Tensile strength (MPa)	Elongation at break (%)
1	Nafion <sup>®</sup> 117	47.34 ± 4.7	186.18 ± 2.5
2	SPEEK	32.4 ± 2.1	44 ± 0.8
3	SPEEK/M1	10.84 ± 4.3	17.35 ± 0.2
4	SPEEK/M2	28.61 ± 3.7	25.40 ± 0.7
5	SPEEK/M3	26.50 ± 4.0	99.66 ± 0.4
6	SPEEK/M4	10.34 ± 6.1	26.92 ± 1.6

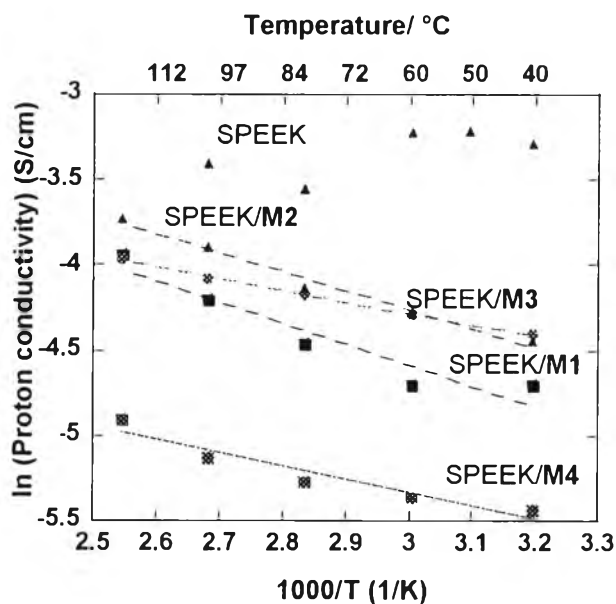
#### 5.4.6 Proton conductivity of SPEEK/Poly (AA-co-4VIm) blend

The proton conductivity measurement is one of important criteria for polymer membrane in fuel cell. Generally, protons can be transferred by hydrogen-bonded ionic channels and with cationic mixtures, such as imidazole with a configuration  $\text{Imi}\cdots\text{ImiH}^+\cdots\text{Imi}$  [41]. Without additional humidification during measurement, membrane conductivity data was presented in Figure 5.4 with that of SPEEK membrane in the range of  $7\text{-}25 \times 10^{-3}$  S/cm. When acrylic acid content in the membrane increased, protons pass through the hydrophilic regions of the membrane. These hydrophilic areas might play an important role to form around the cluster chains leading to strong affinity with water, enhancing easy proton transfer [42].



**Figure 5.4** Proton conductivity of blended membranes between SPEEK and copolymer of acrylic acid and 4-vinylimidazole.





**Figure 5.5** Arrhenius plot of conductivity vs temperature of (---■---) SPEEK/M1, (---▲---) SPEEK/M2, (---●---) SPEEK/M3, and (—■—) SPEEK/M4.

The activation energy ( $E_a$ ), which is the minimum energy required for proton transport, which was obtained from gradients of Arrhenius plot using the following equation:

$$\sigma_{dc} = \sigma_0 \exp(-E_a/RT)$$

The Arrhenius plot for different membranes is presented in Figure 5.5. The activation energy was calculated as shown in Table 5.4, for different Poly (AA-co-4VIm)/SPEEK blend as well as SPEEK.  $E_a$  values of Poly (AA-co-4VIm)/SPEEK were found to be in the range of 5.61–10.20 kJmol<sup>-1</sup>.  $E_a$  values for the copolymer blends become lower by increasing acrylic acid content. Proton conductivity increased with increasing in temperature for all the membranes, owing to high proton donor group. However, SPEEK/M3 provides higher proton conductivity with lowest activation energy than other copolymer blend membrane, this might be due to the optimum content of [imidazole]/[COOH] groups at 0.4. The fact that conductivity decreases with increasing 4-vinylimidazole content in the copolymers can be explained as follows: the number of free SO<sub>3</sub>H and COOH groups decreases by the formation of hydrogen bonding to the imidazole groups, leading to the difficulty in reorientation of imidazole ring during proton transfer process [43].

## 5.5 Conclusion

SPEEK blended with Poly (AA-co4VIm) proton-conducting membranes were prepared in different copolymer contents. High IEC and low %swelling ratio of Poly (AA-co-4VIm)/SPEEK assured good electrochemical properties such as proton transport species and membrane conductivity, which are comparable to the SPEEK membrane under certain cases. The glass transition temperature of the blends show only one  $T_g$  in which the  $T_g$  of the blends are in between SPEEK and copolymer types of **M1-M4**. Thermal and mechanical properties of these copolymer blends revealed adequate thermal and mechanical stabilities, which are crucial requirements for the polymer membrane in Fuel Cell. The SEM morphology of films revealed the smooth and dense structure. This information indicated the good interactions between the acid groups either by  $\text{SO}_3\text{H}$  or  $\text{COOH}$  and the base group. The proton conductivity of all blend membranes was maintained during temperature up to  $120\text{ }^\circ\text{C}$ . The proton conductivity of SPEEK/**M3** gave the highest values at  $25 \times 10^{-3}\text{ S/cm}$  at  $100\text{ }^\circ\text{C}$ , with the lowest in the activation energy  $6.49\text{ kJ/mol}$ . The contents of proton donor and acceptor groups which enhance the proton conductivity value are an important factor for the PEM design. Even though SPEEK/**M4** contains a large amount of proton donor groups but giving higher activation energy, this indicated that not only proton donor group but also proton transfer group are needed to consider for giving good proton conductivity. Therefore, SPEEK/**M3** is promising as an alternative membrane in PEM, due to its satisfactory swelling ratio, activation energy, and proton conductivity.

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