

## CHAPTER IV

### SULFONATED POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) COMPOSITE MEMBRANE FILLED BY ZEOLITE WITH LOW METHANOL PERMEABILITY

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#### **Abstract**

Composite membranes were fabricated as a proton exchange membrane (PEM) for direct methanol fuel cell (DMFC). Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membrane was prepared by solvent casting. SPPO was subsequently mixed with various contents of zeolite Y to fabricate the composite membranes. The properties of the pristine and composite membranes were characterized by Fourier Transform Infrared spectroscopy (FTIR), Thermogravimetry analysis (TGA), LCR meter, and Gas Chromatography (GC) techniques. The effects of degree of sulfonation and zeolite Y contents were systematically varied to tailor the PEM properties (proton conductivity, methanol permeability, membrane selectivity) in DMFC application. A SPPO/zeolite Y composite membrane at 31% degree of sulfonation with 0.1 %v/v of zeolite Y filling exhibits the highest membrane selectivity, defined as the ratio of proton conductivity to methanol permeability, of  $6.02 \times 10^4$  S.s/cm<sup>3</sup>, which is 1.43 times higher than the membrane selectivity of Nafion 117 which is  $4.20 \times 10^4$  S.s/cm<sup>3</sup>.

**Keywords:** Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide); Composite membrane; Direct methanol fuel cell; Proton conductivity; Methanol permeability

## ***1. Introduction***

Direct methanol fuel cells (DMFC) have recently received considerable attention, as methanol is relatively easy to handle and does not require a fuel reformer [1, 2]. DMFC are promising energy conversion devices for mobile and portable electronic applications such as laptops, cellular phones, and digital cameras [3, 4].

A key component in DMFC is the proton exchange membrane (PEM). The main purpose of PEM is to conduct the protons generated from methanol at the anode side to the cathode side of DMFC [5-8]. A good PEM for DMFC should have high proton conductivity and low methanol permeability [9, 10]. One of the weaknesses of DMFC has been the significant methanol crossover from the anode to the cathode side, due to high methanol permeability of the electrolyte membrane. This phenomenon does not only cause the loss of reactant fuel, but also impair the cathode catalyst, and leads to a decrease of overall fuel cell performance [11-14]. Nafion, produced by Dupont, is commonly used as the PEM in DMFC owing to its good chemical and mechanical stabilities, and high proton conductivity [2, 15]. However, the Nafion still has some drawbacks, such as high methanol permeability, high cost, and low conductivity at low humidity or high temperature operating conditions [16, 17].

Recently, various types of sulfonated polymers were used as proton exchange membranes in DMFC applications: sulfonated polyether ether ketone [4, 17], sulfonated polysulfone [18, 19], sulfonated polybenzimidazoles [20], sulfonated polyimide [14] have been developed as a candidate materials for DMFC.

In this work, sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes were prepared at various degrees of sulfonation. Then, SPPO composite membranes were fabricated via the incorporation of zeolite Y. The effect of the degree of sulfonation on the membrane properties was investigated and shall be reported and compared with those of Nafion 117.

## **2. Experimental**

### **2.1 Materials**

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO; Aldrich) was used as the starting polymer. Zeolite Y (Zeolyst, CBV400, Si/Al = 5.1, H<sup>+</sup>) was used as the filler. Concentrated sulfuric acid (Univar, 98%) was used in the sulfonation process. Chloroform (RCI Labscan, 99.8%) and dimethylacetamide (RCI Labscan, 99.9%) were used as solvents. Hydrochloric acid (HCl; Univar, 37%) was used to protonate the prepared membranes. Sodium chloride (Lab-Scan, 99.0%) and sodium hydroxide (NaOH; Univar, pellets, purity 97%) were used to determine the ion exchange capacity and the degree of sulfonation. Methanol (MeOH; Lab-Scan, 99.9%) and ethanol (EtOH; Lab-Scan, 99.9%) were used for measuring the methanol permeability.

### **2.2 Preparation of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO)**

5 g of PPO were dissolved in 50 ml of chloroform and vigorously stirred at room temperature for 30 min. Then, concentrated sulfuric acid was added dropwise to the solution under vigorous stirring at room temperature. The polymer solution was poured into an ice-cold water bath. Then, the precipitated polymer was filtered and washed with DI water until the pH became neutral. The polymer was dried at 100 °C for 24 h. The obtained product is the sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) powder [21, 22].

### **2.3 Preparation of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes**

SPPO was dissolved in dimethylacetamide (DMA) at 80 °C. The viscous solution was casted on a clean glass plate, dried at room temperature for 24 h, and at 70 °C for 8 h, and then dried overnight at 120 °C [21, 22].

### **2.4 Preparation of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) composite membranes**

SPPO was dissolved in dimethylacetamide (DMA) and stirred at 80 °C. Zeolite Y was added into the SPPO solution at 80 °C and ultra-sonicated for 30 min.

The mixture was stirred at 80 °C for 8 h. The viscous solution was casted on a clean glass plate, dried at room temperature for 24 h, and at 70 °C for 8 h, and then at 120 °C overnight [21, 22].

## **2.5 Characterization and Testing**

### **2.5.1 FTIR spectroscopy**

FTIR spectroscopy (Thermo Nicolet, Nexus 670) was used to study the chemical structures of PPO and SPPO. The spectrometer was operated in the transmittance mode in the wave number range 4000-400cm<sup>-1</sup>. Optical grade KBr was used as the background material. PPO and SPPO were mixed with KBr before the measurement [23].

### **2.5.2 Thermogravimetric analysis (TGA)**

Thermogravimetric analysis (TGA, Thermo, TGA 50) was used to determine the thermal stability of PPO and SPPO. The membranes were dried in vacuum for 24 h to remove any moisture. The experiment was carried out by placing a membrane sample of 4-20 mg weight into a platinum pan. The sample pan was heated under nitrogen atmosphere from 30 to 800 °C with a heating rate of 10 °C/min, and the weight changes were recorded [3].

### **2.5.3 Degree of Sulfonation (DS)**

Degree of sulfonation is defined as the number of sulfonic groups per repeating unit in a polymer chain. The polymer membranes were acidified by 2 M HCl solution at room temperature for 24 h. Then the membranes were dried at 60 °C for 24 h. After that the membranes were placed in a 1 NaCl solution for 24 h. Then, the solution was titrated with 0.01 M NaOH by using phenolphthalein as an indicator. Degree of sulfonation was calculated by the following equation:

$$DS = \frac{(V_{\text{NaOH}} \times M_{\text{NaOH}})/1000}{\text{Mole of polymer membrane}} \times 100 \quad (1)$$

where DS is the degree of sulfonation (%),  $V_{\text{NaOH}}$  is the volume of NaOH consumed (ml), and  $M_{\text{NaOH}}$  is the molarity of NaOH [24, 25].

#### 2.5.4 Ion Exchange Capacity (IEC)

Ion exchange capacities (IECs) of the SPPO membranes were measured by a titration. The membranes were cut into small pieces. Then the membranes were immersed into 1 M NaCl solution for 24 h. The solution was titrated with 0.01 M NaOH solution. Phenolphthalein was used as an indicator. Ion exchange capacity was calculated from following equation:

$$\text{IEC} = \frac{\text{Consumed NaOH} \times \text{molarity NaOH}}{W_{\text{dry}}} \quad (2)$$

where IEC is the ion exchange capacity (meq/g),  $V_{\text{NaOH}}$  refers to the volume of sodium hydroxide solution,  $C_{\text{NaOH}}$  refers to the concentration of sodium hydroxide solution [24, 26].

#### 2.5.5 Water Uptake

The SPPO membranes were dried in an oven at 100 °C for 24 h, weighed, and placed into distilled water overnight at room temperature. After that, the membranes were taken out, and quickly wiped with a tissue paper. The membranes were weighted again. The water uptake of SPPO membrane was calculated from following equation:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  refer to the weights of the wet and dry samples, respectively [24-26].

#### 2.5.6 Proton Conductivity

The proton conductivities of the SPPO and the composite membranes were measured by using an Agilent E4980A LCR meter. The fully hydrated membrane was cut into  $0.5 \times 0.5$  cm pieces and coated with silver. The coated membrane was measured at a constant voltage of 1 V in the frequency range of 20 Hz – 2 MHz. The conductivity was calculated from the impedance as follow:

$$\sigma = \frac{d}{R \times A} \quad (4)$$

where  $\sigma$  is the proton conductivity (S/cm),  $d$  is the thickness of the membrane,  $A$  is the area of the interface of membrane in contact with the electrodes, and  $R$  refers to the measured resistance of the membrane – derived from the low frequency semicircle on the complex impedance plane with the  $Z'$  axis [27, 28].

#### 2.5.7 Methanol Permeability

The methanol permeability of SPPO and the composite membranes was determined by a liquid permeation cell where the concentrations of methanol that permeated the cell at 60 °C were measured. The liquid permeation cell was composed of two compartments. The two compartments were separated by a membrane sample. The methanol concentrations were determined by using gas chromatography. The methanol permeability was calculated from the following equation:

$$P = \frac{k_B V_B L}{A(C_A - C_B)} \quad (5)$$

where  $P$  is the methanol permeability ( $\text{cm}^2/\text{s}$ ),  $C_A$  is the methanol concentration in compartment A,  $C_B$  is the methanol concentration in compartment B,  $k_B$  is the methanol concentration permeate per time of permeate,  $V_B$  is the solution volume of the permeate,  $L$  is the thickness of the membrane,  $A$  is the effective area of membrane [25, 29].

### **2.5.8 Membrane selectivity**

The membrane selectivity, which is defined as the ratio of proton conductivity to methanol permeability, is used to determine the potential performance of DMFC membranes. Membranes which have high selectivity parameters are providing good performance for DMFC applications. The membrane selectivity values of SPPO and the composite membranes were compared with those of Nafion 117 [21, 22].

### **2.5.9 Mechanical properties**

The tensile strength of SPPO and the composite membranes were determined by using a Universal Testing Machine (Lloyd, model SMT2-500N) for characterization of the mechanical properties. The samples were cut into size 1 cm × 5 cm. The samples were immersed in de-ionized water for 24 h before testing and using a speed of 10 mm/min [24, 28].

## **3. Results and Discussion**

### **3.1 FTIR spectroscopy**

The FTIR spectra of PPO and SPPO are shown in comparison in figure 2, indicating characteristic bands of the sulfonic groups ( $-\text{SO}_3\text{H}$ ) on the polymer chains after sulfonation. Some peaks such as 3500 and 669  $\text{cm}^{-1}$  appear after the sulfonation, the characteristic transmittance peaks at 1060 and 1100-1300  $\text{cm}^{-1}$  in SPPO indicate the S=O bonds, and the peak at 1060  $\text{cm}^{-1}$  corresponds to the symmetric stretching band of the aromatic  $-\text{SO}_3\text{H}$  group, and the peak at 669  $\text{cm}^{-1}$  is due to the C-S stretching vibration. The broad band in the SPPO samples at around 3500  $\text{cm}^{-1}$  can be assigned to the O-H vibration. The results confirm that sulfonic groups have been introduced successfully into the polymer backbone [3, 21].

### **3.2 Thermogravimetric analysis**

To evaluate the thermal stability of the membranes at elevated temperatures, thermogravimetric analysis was performed. Figure 3 shows the results for PPO and SPPO. PPO begins to lose weight at 480 °C, owing to the degradation of the polymer chain. Three main weight loss stages can be seen for SPPO. The first weight loss is

located at 50-100 °C, which is related to the desorption of moisture bonded to the hydrophilic sulfonic groups ( $-\text{SO}_3\text{H}$ ). The second stage weight loss starts at 200-260 °C, which could be caused by the decomposition of the sulfonic groups. And the final weight loss is close to 420-480 °C, which is due to the polymer main chain degradation. Overall, the prepared SPPO possessed fairly good thermal stability [3, 30].

### ***3.3 Degree of Sulfonation (DS) and Ion Exchange Capacity (IEC)***

The degree of sulfonation (DS) and the ion exchange capacity (IEC) of SPPO membranes are shown in figure 4. With increasing DS, i.e. presence of more sulfonic groups in polymer chain, the IEC increased. The DS and IEC of SPPO are in the range of 18 – 31%, and 1.18 – 1.74 meq/g, respectively. The SPPO membrane with the highest DS shows the highest IEC value which is 1.91 times higher than that of Nafion 117, which is 0.91 meq/g [14]. Based on these results, the SPPO membrane at the highest DS (DS = 31 %) was selected to fabricate the composite membrane with zeolite Y at various contents (0.1, 0.5, 1, and 2 %v/v).

### ***3.4 Water uptake***

Water uptake is an important property for a proton exchange membrane because the water uptake can be related to the proton conductivity of membrane. The water uptakes of the composite membranes are shown in table 1. The water uptake (%) increases with increasing DS because of the higher hydrophilicity of sulfonic groups. The water uptake of SPPO membrane is in range of 10.32 – 14.62%. These values are lower than that of Nafion 117 (34.21%) [14]. In our study, the water uptakes of composite membranes are in range of 9.13 – 13.01%, and decrease with increasing zeolite Y content. The addition of zeolite particles, which are less hydrophilic than the polymer matrix, induces the rigidity of polymer chains [13, 21].

### ***3.5 Proton conductivity***

Table 1 shows the proton conductivity of composite membranes as a function of zeolite content at room temperature. The conductivity of composite membranes decreases with increasing zeolite Y content, in the range of  $7.34 \times 10^{-3}$  to  $4.54 \times 10^{-3}$

S/cm. These proton conductivity values are significantly lower than that of Nafion 117, which is  $1.00 \times 10^{-1}$  S/cm [14]. The proton conductivity is a water assisted phenomena and adsorbed water is an important factor in proton conduction inside the proton exchange membrane [31, 32]. The water uptake of the composite membranes decreased with increasing zeolite Y content and this affected the proton conductivity of the composite membranes.

### **3.6 Methanol permeability**

To assess methanol crossover, the permeation values of methanol through the membranes were measured. The concentrations of methanol passing through the membrane are shown as a function of time in figure 6. The methanol permeability values of composite membranes were measured as a function of zeolite content, and compared with that of the Nafion 117. In this study, a higher content of zeolite Y in composite membrane exhibits lower methanol permeability than a composite membrane with lower content of zeolite Y, as shown in table 1. The methanol permeability values of the composite membranes are in the range of  $1.01 \times 10^{-7}$  to  $1.22 \times 10^{-7}$  cm<sup>2</sup>/s. By an order of magnitude lower than that of Nafion 117 which is  $2.38 \times 10^{-6}$  cm<sup>2</sup>/s [14]. Methanol permeates through the hydrophilic water channel consisting of the sulfonic groups inside the membrane [27]. The presence of zeolite introduces tortuous pathways for methanol to diffuse resulting in some restriction of the channels for methanol molecules to pass through [13, 21, 33]. The low methanol permeability may also be caused by the higher stiffness of the composite membranes consisting of zeolite particles.

Auimviriyavat *et al.*, (2011) [34] studied composite membranes consisting of sulfonated Poly(ether ether ketone); (S-PEEK) and the Ferrierite zeolite. The methanol permeabilities at 50 °C of the composite membranes with DS of 53 % and 5, 10, 20 %v/v of Ferrierite zeolite were  $5.52 \times 10^{-6}$ ,  $9.62 \times 10^{-6}$ , and  $1.43 \times 10^{-5}$  cm<sup>2</sup>/s, respectively. Thus, all of composite membranes in this study have lower methanol permeability than those of Auimviriyavat's composite membranes.

### **3.7 Membrane selectivity**

The membrane selectivities of the composite membranes were measured to evaluate the PEM performance in DMFC application and are shown in table 1. A higher membrane selectivity value leads to better membrane performance. The membrane selectivity of the composite membrane is higher than pristine SPPO and Nafion 117 membrane thanks to the much lower methanol permeability as shown in table 4.1. The highest membrane selectivity is  $6.02 \times 10^4$  S.s/cm<sup>3</sup>. This membrane selectivity parameter for the Nafion 117 is  $4.20 \times 10^4$  S.s/cm<sup>3</sup> [14]. So, the zeolite Y composite SPPO membrane with 31% degree of sulfonation and 0.1 %v/v of zeolite Y filling has approximately 1.43 times greater membrane selectivity than Nafion 117.

### ***3.8 Mechanical property***

The mechanical properties of the composite membrane were measured by using a Universal Testing Machine (Lloyd, model SMT2-500N) as shown in Table 2. The composite membranes have the tensile strength, the Young's modulus, and elongation at break values of 12.58 to 42.64 MPa, 1251 to 1793 MPa, and 1.31 to 6.10%, respectively. The tensile strength, the Young's modulus, and elongation at break of Nafion 117 are 28.40 MPa, 1000 MPa, and 329.90%, respectively [35]. The tensile strength of composite membranes decreases with increasing zeolite content. But, the stiffness of composite membranes increases with increasing zeolite content. Nevertheless, Nafion 117 exhibits the highest elongation at break, showing it is the most flexible membrane available.

### ***4. Conclusions***

The composite membranes were prepared by incorporation of SPPO and zeolite Y to form a proton exchange membrane (PEM) for Direct Methanol Fuel cell (DMFC). In the first step, SPPO was prepared with different degrees of sulfonation. The properties of the SPPO membranes depend on DS; a higher DS value tends to increase water uptake and IEC. Subsequently, the SPPO membrane at the highest DS was selected to fabricate the composite membrane with zeolite Y at different contents (0.1, 0.5, 1, and 2 %v/v). The composite membranes reveal the highest proton conductivity value of  $7.34 \times 10^{-3}$  S/cm, and the lowest methanol permeability

value of  $1.01 \times 10^{-7}$  cm<sup>2</sup>/s. The membrane selectivity of the SPPO/zeolite Y composite membrane is comparable to that of Nafion 117 membrane in term of membrane selectivity. A SPPO/zeolite Y composite membrane with 0.1 %v/v of zeolite Y shows the highest membrane selectivity of  $6.02 \times 10^4$  S.s/cm<sup>3</sup>, which is higher than that of Nafion 117 of  $4.20 \times 10^4$  S.s/cm<sup>3</sup>. Hence, this work demonstrates the potential of these composites to serve as PEM with smaller methanol permeability for DMFC.

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### Table Captions

**Table 1** The water uptake proton conductivity, methanol permeability and membrane selectivity of SPPO/zeolite Y composite membrane at various zeolite contents

**Table 2** The mechanical properties of SPPO/zeolite Y composite membrane at various zeolite contents

### Figure Captions

**Figure 1** The scheme of sulfonation of poly(2,6-dimethyl-1,4-phenylene oxide).

**Figure 2** The FTIR spectra of poly(2,6-dimethyl-1,4-phenylene oxide); (PPO) and sulfonated of poly(2,6-dimethyl-1,4-phenylene oxide); (SPPO).

**Figure 3** The TGA curves of poly(2,6-dimethyl-1,4-phenylene oxide); (PPO) and sulfonated of poly(2,6-dimethyl-1,4-phenylene oxide); (SPPO).

**Figure 4** Ion exchange capacity and water uptake of SPPO membranes as functions of degree of sulfonation.

**Figure 5** The comparison of methanol permeability of composite membranes with different zeolite contents.

## Tables

**Table 1** The water uptake, proton conductivity, methanol permeability and membrane selectivity of SPPO/zeolite Y composite membrane at various zeolite contents

Composite membranes (%v/v)	Water uptake (%)	Proton Conductivity, $\sigma$ (S/cm)	Methanol permeability, $P$ ( $\text{cm}^2/\text{s}$ )	Membrane selectivity ( $\text{S.s}/\text{cm}^3$ )
SPPO, DS = 31	$14.62 \pm 1.09$	$1.00 \times 10^{-2} \pm 1.63 \times 10^{-4}$	$2.14 \times 10^{-7}$	$4.67 \times 10^4$
CM 0.1 %	$13.01 \pm 0.78$	$7.34 \times 10^{-3} \pm 5.26 \times 10^{-4}$	$1.22 \times 10^{-7}$	$6.02 \times 10^4$
CM 0.5 %	$11.80 \pm 0.48$	$5.80 \times 10^{-3} \pm 1.56 \times 10^{-4}$	$1.09 \times 10^{-7}$	$5.32 \times 10^4$
CM 1 %	$9.39 \pm 0.27$	$5.59 \times 10^{-3} \pm 6.58 \times 10^{-5}$	$1.04 \times 10^{-7}$	$5.38 \times 10^4$
CM 2 %	$9.13 \pm 0.34$	$4.54 \times 10^{-3} \pm 1.12 \times 10^{-5}$	$1.01 \times 10^{-7}$	$4.50 \times 10^4$
Nafion 117 <sup>a</sup>	34.21	$1.00 \times 10^{-1}$	$2.38 \times 10^{-6}$	$4.20 \times 10^4$

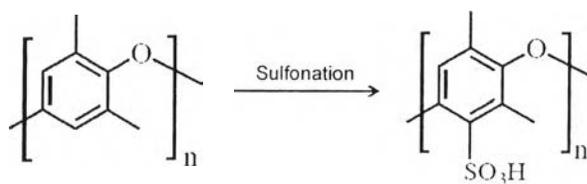
<sup>a</sup> Woo et al.<sup>14</sup>

**Table 2** The mechanical properties of SPPO/zeolite Y composite membrane at various zeolite contents

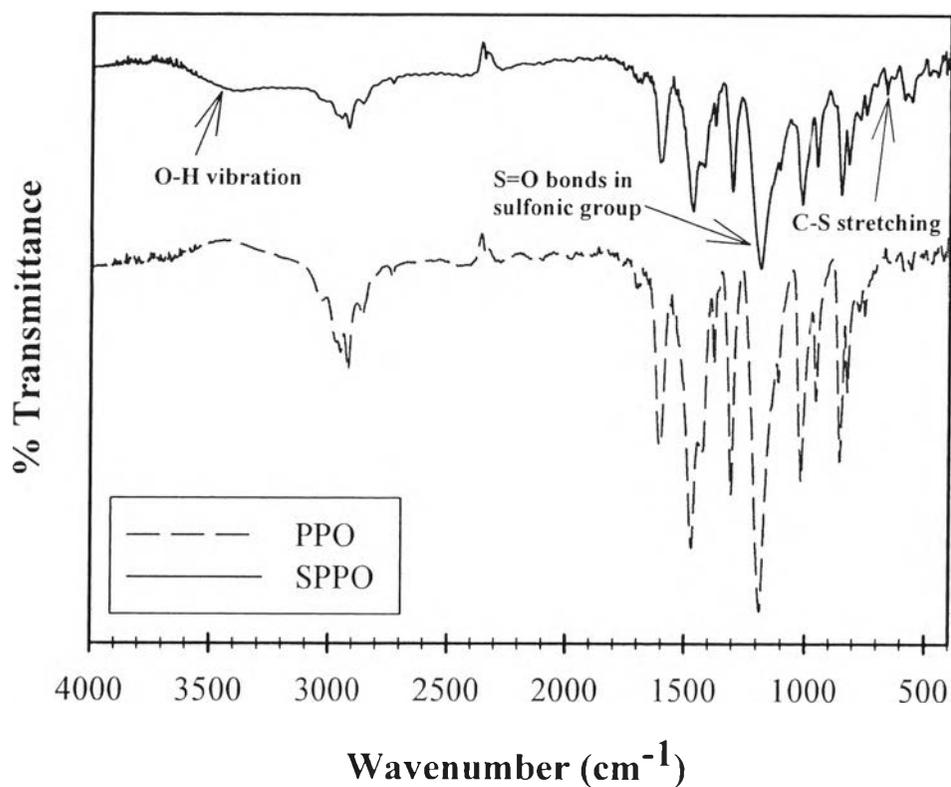
Composite membranes (%v/v)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	Stiffness (N/m)
SPPO, DS = 31	$51.78 \pm 7.8$	$1506 \pm 206$	$6.81 \pm 1.57$	$34228 \pm 3531$
CM 0.1 %	$42.64 \pm 4.3$	$1251 \pm 177$	$6.10 \pm 0.60$	$56533 \pm 3327$
CM 0.5 %	$36.69 \pm 0.5$	$1364 \pm 77$	$5.11 \pm 0.57$	$64034 \pm 3586$
CM 1 %	$28.65 \pm 5.3$	$1664 \pm 86$	$3.00 \pm 0.62$	$89435 \pm 8946$
CM 2 %	$12.58 \pm 3.6$	$1793 \pm 604$	$1.31 \pm 0.01$	$116707 \pm 23457$
Nafion 117 <sup>a</sup>	28.40	1000	329.20	-

<sup>a</sup> Liu et al.<sup>35</sup>

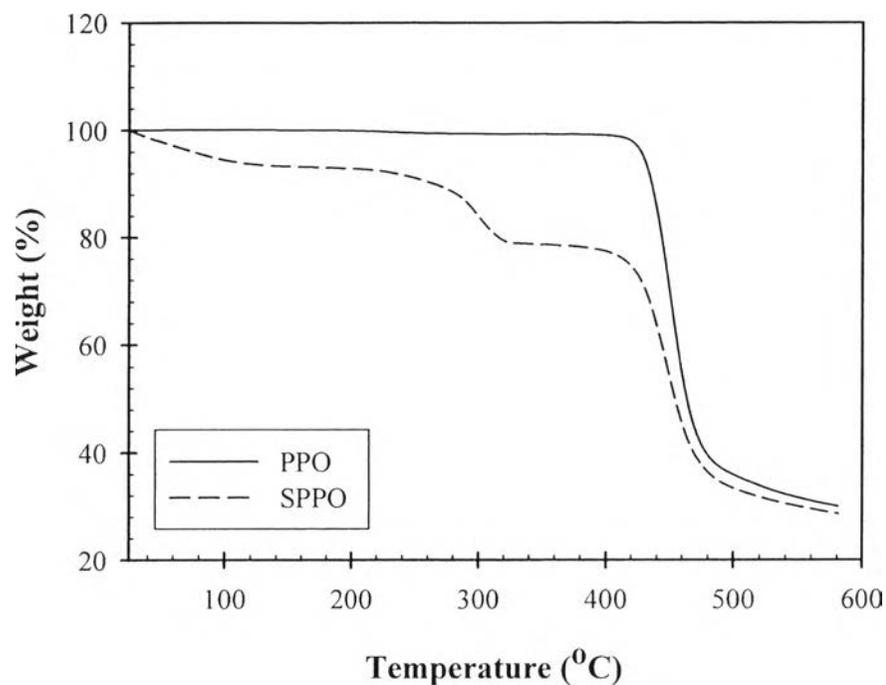
## Figures



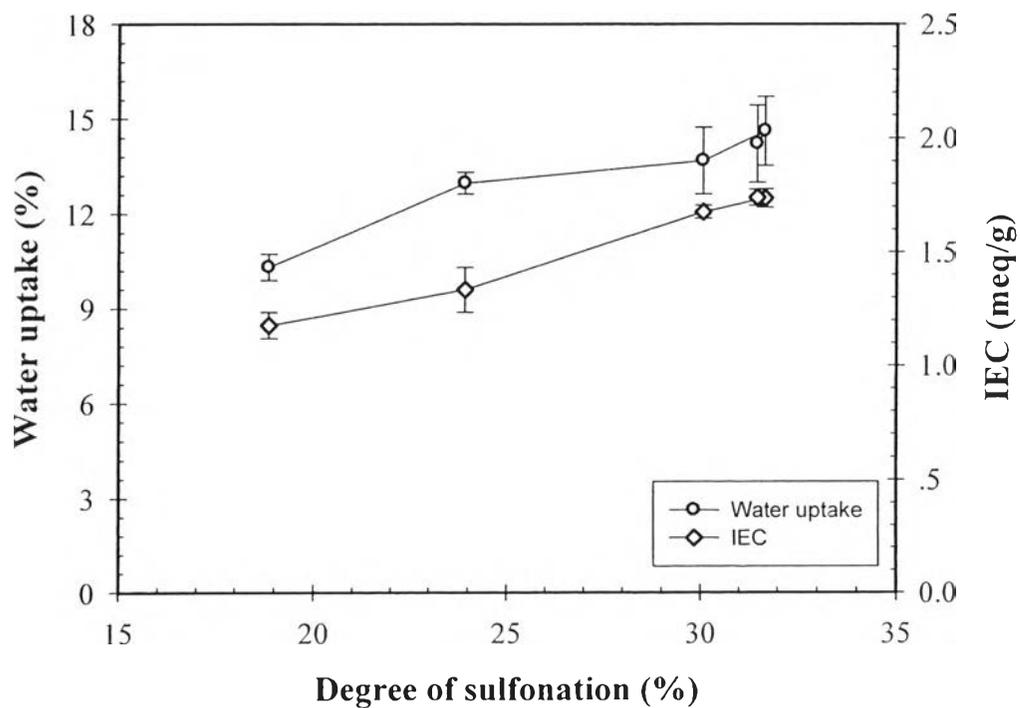
**Figure 1** The scheme of sulfonation of poly(2,6-dimethyl-1,4-phenylene oxide).



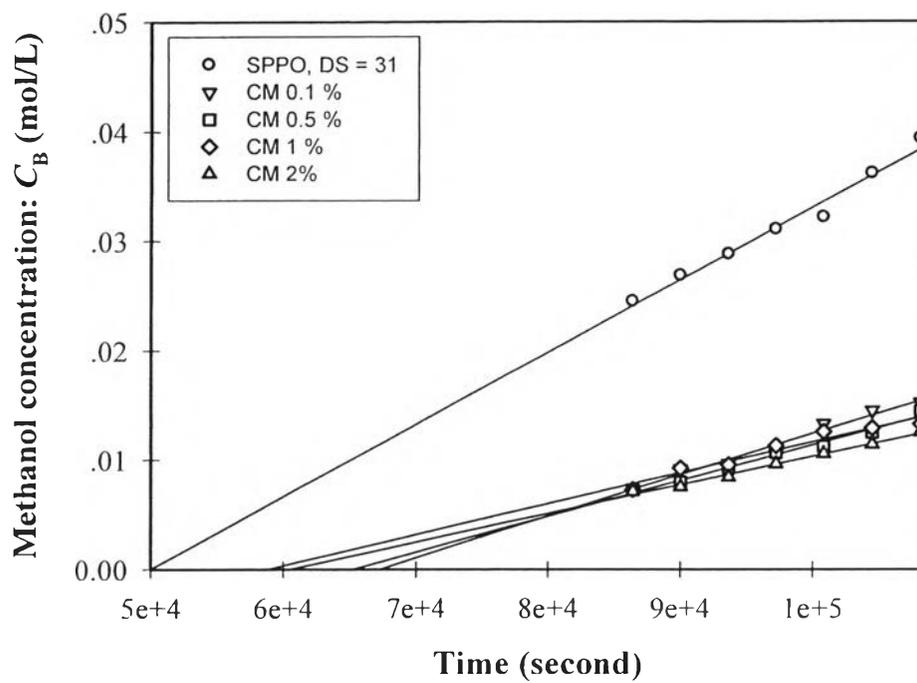
**Figure 2** The FTIR spectra of poly(2,6-dimethyl-1,4-phenylene oxide); (PPO) and sulfonated of poly(2,6-dimethyl-1,4-phenylene oxide); (SPPO).



**Figure 3** The TGA curves of poly(2,6-dimethyl-1,4-phenylene oxide); (PPO) and sulfonated of poly(2,6-dimethyl-1,4-phenylene oxide); (SPPO).



**Figure 4** Ion exchange capacity and water uptake of SPPO membranes as functions of degree of sulfonation.



**Figure 5** The comparison of methanol permeability of composite membranes with different zeolite contents.