

CHAPTER III METHODOLOGY

3.1 Materials and Instruments

3.1.1 Materials

Polysulfone (PSF; Aldrich) and polyvinylidene fluoride (PVDF; Aldrich) were used and fabricated as polymer based membranes. Concentrated sulfuric acid (H_2SO_4 ; Univar, Ar grade) acted as a sulfonating agent was used to introduce sulfonic groups onto the polymer backbones in the sulfonation process. Dichloromethane (DCM; RCI Labscan, Ar grade), N-methyl-2-pyrrolidinone (NMP; RCI Labscan, HPLC grade), and dimethylacetamide (DMAc; RCI Labscan, Ar grade) were used as solvents. Methanol (Univar, Ar grade), sodium hydroxide, sodium chloride, and deionized water were used in the methanol permeation study.

3.1.2 Instruments

A Fourier transform infrared spectrometer (FT-IR; Thermo Nicolet, Nexus 670), with the number of scans of 64, was used to determine functional groups of sulfonated polysulfone (SPSF) and sulfonated poly(vinylidene fluoride)(SPVDF). A thermalgravimetric analyzer (TGA; DuPont, model TGA 2950), with the temperature scan from 50 to 700 °C with a heating rate of 10°C/min under nitrogen flow was used to study thermal property of the polymers. Gas chromatography (GC; Pr2100) was used to measure methanol concentration through the membranes. An impedance phase analyzer (HP, model 4194) was used to determine the proton conductivity of membrane.

3.2 Experimental Methods

3.2.1 Sulfonated polysulfone and sulfonated polyvinylidene fluoride

3.2.1.1 *Preparation of sulfonated polysulfone (S-PSF)*

The polymer solution was prepared by dissolved PSF (2 g) in a 10 ml of DCM. The concentrated H_2SO_4 was added into the polymer solution at

various acids per polymer ratios solution and at various reaction temperatures between 25 and 50 °C. The sulfonated solution was continuously stirred for 4 h, then the solution was precipitated by methanol in ice bath. The precipitate was washed using DI water until pH of precipitate reached to neutral. The S-PSF as a sulfonated polymer was dried at 100 °C for 24h (Macksasitorn *et al.*, 2012).

3.2.1.2 Preparation of sulfonated poly(vinylidene fluoride) (S-PVDF)

The polymer solution was prepared by dissolved PVDF (1.2g) in NMP (60 ml). The concentrated H₂SO₄ was added in the polymer solution at various acid per polymer ratios and at various reaction temperatures between 25 and 50 °C. The sulfonated solution was continuously stirred for 4 h, then the solution was precipitated by methanol in ice bath. The precipitate was washed using DI water until pH of precipitate reached neutral. The S-PVDF as a sulfonated polymer was dried at 100 °C for 24h (Saxena *et al.*, 2009).

3.2.2 Membrane Preparations

Either S-PSF or S-PVDF was put in a round bottom flask and dissolved in a DMAc solvent to form a polymer solution. The polymer solution was continuously stirred until homogenous. The film was formed by a casting method and heated at 80 °C for 24 h.

3.3 Characterizations and Testing

3.3.1 Characterizations

The polymers and sulfonated polymers functional groups were determined using the FT-IR spectrometer (Nicolet, Nexus 670). The polymer and sulfonated polymer were determined in powder sample. The samples were measured directly in the wave number range of 400-1600 cm⁻¹ and 64 scans, after they were grinded with potassium bromide (dried at 100 °C for 24 h) as background. The composite was compressed into pellets and inserted in the sample holder (Macksasitorn *et al.*, 2012).

The thermal property of sulfonated membrane was conducted using a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA; Perkin Elmer,

PyrisDiamond). The samples were weighed in the range of 4-10 mg and inserted into an alumina pan. The measurements were carried out under nitrogen flow, and the samples were conditioned at 25 °C to 700 °C at a heating rate of 10 °C. min⁻¹ (Zhang *et al.*, 2011).

The mechanical properties: tensile strength, yield strain, and Young's modulus, were recorded using a universal testing machine (Lloyd, model SMT2-500N) at room temperature with a 25 mm.min⁻¹ speed. The membranes with 200 µm thick were cut to 1 cm × 5 cm. The measurements were taken at least 5 times from 5 fresh samples.

3.3.2 Degree of Sulfonation (DS)

The degree of sulfonation was determined using a titration method. The polymer membranes were acidified by 0.1 M of hydrochloric solution at room temperature for 24 h. Then the membranes were washed with deionization water and dried at 80 °C for 24 h. After that the membranes were placed in a sodium chloride solution for 24 h. The degree of sulfonation of polymer solution was determined by the titration with 0.01 M of sodium hydroxide using phenolphthalein as an indicator. The degree of sulfonation was calculated as in the following Eq. (3.1):

$$DS(\%) = \frac{(V_{NaOH} \times C_{NaOH}) / 1000}{\text{Mole of polymer membrane}} \times 100\% \quad (3.1)$$

where V_{NaOH} refers to the volume of sodium hydroxide solution, C_{NaOH} refers to the concentration of sodium hydroxide solution.

3.3.3 Ion Exchange Capacity (IEC) (Macksasitorn *et al.*, 2012)

Ion exchange capacity of membrane was determined by a titration method. Ion exchange capacity is a method to determine the number of milliequivalent of ions in 1 g of dry polymer (meq./g). The membranes were soaked in 0.1 M NaCl solution for 24 h to exchange H⁺ with Na⁺. H⁺ were titrated with 0.01 M NaOH solution with using phenolphthalein as an indicator. Ion exchange capacity of membrane was calculated using following Eq. (3.2):

$$IEC (\text{mmol } g^{-1}) = \frac{\text{Consumed ml}(\text{NaOH}) \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (3.2)$$

where consumed ml (NaOH) is the consumed volume of NaOH solution. Molarity NaOH is molar of NaOH solution. Weight dried membrane is the weight of membrane in a dry state.

3.3.4 Water Uptake

In the Water uptake measurement, the membranes were immersed into DI water for 24 h at room temperature. Excess water was removed from the membrane surface with a wipe paper and the membranes were weighed (noted as W_s). The membranes were dried at 100 °C for 24 h in a vacuum oven and weighed (noted as W_d). The percentage of water uptake was then calculated as in the following Eq. (3.3):

$$\text{Water uptake} = \frac{(W_s - W_d) \times 100}{W_d} \quad (3.3)$$

where W_d refers to the weight of dried polymer, and W_s is weight of swelled polymer

3.3.5 Proton conductivity

Proton conductivity of membrane was measured by an impedance phase analyzer HP 4194 at various frequencies from 100 Hz to 2 MHz and at room temperature (known as dry state). The membranes were cut into a form $5 \times 5 \text{ cm}^2$ specimen for the measurement. Proton conductivity was calculated as in the following Eq. (3.4)

$$\sigma(S/cm) = \frac{d}{R \times A} \quad (3.4)$$

where σ is the proton conductivity(S/cm), d is the thickness of the membrane (cm), A is the area of the interface of membrane in contact with the electrodes (cm^2), and R refers to the measured resistance of the membrane derived from the high frequency semi-circle on the complex impedance plane with the Z axis (ohm).

3.3.6 Methanol Permeability

The methanol permeability refers the amount of methanol that permeates through the membrane. The permeation cell for methanol permeability measurement consisted of chamber A and chamber B as separated by the sulfonated polymer membrane. Chamber A was filled with 250 ml of methanol solution (2.0 M). Chamber B was filled with 250 ml of DI water. The membrane was placed

between chamber A and chamber B. The methanol permeability was calculated as in the following Eq. (3.5)

$$P \text{ (cm}^2\text{/s)} = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \quad (3.5)$$

where P is the methanol permeability, C_A and C_B are the methanol concentrations in the compartments A and B respectively, A and L are the area and the thickness of a membrane respectively, V_B is the volume of the solution in the compartment B, k_B is the slope of the methanol concentration profile in the compartment B. The methanol concentrations were measured with a thermal conductivity detector (TCD) in gas chromatography; ethanol was used as the internal standard.