CHAPTER III
METHODOLOGY

3.1 Materials and Instruments

3.1.1 Materials

Polysulfone (PSF; Aldrich) was fabricated as polymer based membranes. Concentrated sulfuric acid (98% H_2SO_4; Univar, Ar grade) was used as a sulfonating agent to introduce sulfonic groups onto the polymer backbones by the sulfonation process. Dichloromethane (DCM; RCI Labscan, Ar grade), and dimethylacetamide (DMAc; RCI Labscan, Ar grade) were used as solvents. Methanol (Univar, Ar grade) was used in the methanol permeation study. Zeolite Y (Si/Al ratio = 5.1; Zeolyte International) and graphene oxide (Top New Energy Co., Ltd.) were used as fillers in S-PSF membrane.

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 (S-PSF). The structure of S-PSF was determined by a ^{1}H-NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer). 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 polymer membranes. Gas chromatography (GC; Agilent, 7820A) 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. X-ray photoelectron spectroscopy (XPS; Thermo VG scientific, hemisphere analyzer) was used for determination the surface composition of the GO and S-GO. Scanning electron microscopy (SEM; Hitachi, Model S4800) was used for investigation the surface morphology of the GO and S-GO.

3.2 Experimental

3.2.1 Sulfonated Polysulfone and Sulfonated Graphene Oxide

3.2.1.1 Preparation of Sulfonated Polysulfone (S-PSF)

The polymer solution was prepared by dissolving PSF (2 g) in a 10 mL of DCM. The concentrated H_2SO_4 was added into the polymer solution at the acid per polymer mole ratio of 80 at room temperatures. The sulfonated solution was continuously stirred for 4 h, and then the solution was precipitated by methanol in an ice bath. The precipitate was washed with deionized water until the pH of precipitate reached 7. The S-PSF was dried at 100 °C for 24 h (Macksasitorn et al., 2012).

3.2.1.2 Preparation of Sulfonated Graphene Oxide (S-GO)

50 mg of graphene oxide was added to 8 mL of 0.06 M sulfanilic acid solution at 70 °C. Under continuous stirring, 2 ml of 0.006 M sodium nitrite solution was added dropwise and held at 70 °C for 12 h. After reaction, the mixture was collected by filtration and washed with deionized water several times until the pH reached 7. The S-GO was then dried at 70 °C for 24 h (Chien et al., 2013).

3.2.2 Composite Membrane Preparation

3.2.2.1 S-PSF/Zeolite Y Composite Membrane

1 g of S-PSF was dissolved in a 12 mL of DMAc to prepare a polymer solution. The polymer solution was continuously stirred until homogenous. Zeolite Y was added into the polymer solution (5, 10, 15, and 20 % v/v) and stirred continuously for 24 h. The film was formed by a casting method and heated at 70 °C for 24 h under a vacuum.

3.2.2.2 S-PSF/S-GO Composite Membrane

1 g of S-PSF was dissolved in a 10 mL of DMAc to prepare a polymer solution. The polymer solution was continuously stirred until homogenous.

S-GO was added into the polymer solution (1, 2, 3, 5, and 7 % v/v) and stirred continuously for 24 h. The film was formed by a casting method and heated at 70 °C for 24 h under a vacuum.

3.3 Characterizations

3.3.1 Characterizations of S-PSF

3.3.1.1 Chemical Structure by FT-IR

The PSF and S-PSF functional groups were determined using the FT-IR spectrometer (Nicolet, Nexus 670). The PSF and S-PSF were determined in a powder form using potassium bromide (KBr; dried at 100 °C for 24 h) as a background. The samples were measured in the wave number range of 400-1600 cm^{-1} with 64 scans. The sample was prepared by compressing into pellets and inserted in a sample holder (Macksasitorn et al., 2012).

3.3.1.2 Chemical Structure by Nuclear Magnetic Resonance (NMR)

The structure of S-PSF was determined by the ^{1}H-NMR spectrometer (Bruker Biospin Avance 500 MHz NMR spectrometer) using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent at room temperature.

3.3.2 Characterizations of S-GO

3.3.2.1 Chemical Structure of S-GO by FT-IR

The GO and S-GO functional groups were determined using the FT-IR spectrometer (Nicolet, Nexus 670). The GO and S-GO were collected after 64 scans in the 4000 - 500 cm^{-1} region in the ATR mode at a resolution of 4 cm^{-1} (Heo et al., 2012).

3.3.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS used for determination the surface composition of the GO and S-GO. The XPS spectra were obtained by using an incident achromatic MgKa X-ray source (1253.6 eV) operated at 14.8 kV and 20 mA for excitation and a

hemisphere analyzer (Thermo VG scientific). The high-resolution XPS spectra were composite averages of 10 scans with a passing energy of 50 eV. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The binding energy was adjusted to the C1s peak at 285.1 eV. Data analysis and curve de-convolution were accomplished by using the Thermo Advantage Spectra Data Processor software.

3.3.2.3 Scanning Electron Microscopy (SEM)

The surface morphology of GO and S-GO was investigated using a scanning electron microscope (Hitachi, Model S4800) operated at 5kV and 15 mA.

3.3.3 Characterizations of Composite Membrane

3.3.3.1 Thermal Stability of Composite Membrane

The thermal property of composite membrane was conducted using a Thermo-Gravimetric/Differential Thermal Analyzer (TG/DTA; Perkin Elmer, Pyris Diamond). 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 from 50 to 700 °C at a heating rate of 10 °C min^{-1} (Zhang et al., 2011).

3.3.3.2 Mechanical Properties of Composite Membrane

The mechanical properties: tensile strength, yield strain, and Young's modulus, were measured and recorded using a universal testing machine (Lloyd, model SMT2-500N) at room temperature with a gauge length 30 mm and 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.

3.3.3.3 Water Uptake

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 and weighed again (noted as W_d). The percentage of water uptake was then calculated as in the following Eq. (3.3):

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

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

3.3.3.4 Proton Conductivity (σ)

Proton conductivity of membrane was measured by an impedance phase analyzer (HP, 4194) at various frequencies from 20 Hz to 2 MHz at room temperature. The membranes were cut into a form 5×5 cm^2 specimen for the measurement. Proton conductivity was calculated as in the following Eq. (3.4)

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

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 (Ahmad *et al.*, 2006).

3.3.3.5 Methanol Permeability (P)

The methanol permeability refers the amount of methanol that permeates through the membrane and was measured by using two compartment diffusion cell techniques. The permeation cell for methanol permeability measurement consisted of chamber A and chamber B separated by a polymer membrane. Chamber A was filled with 250 ml of methanol solution (2.5 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)

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

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 (Zhai *et al.*, 2007).