

CHAPTER III EXPERIMENTAL

3.1 Materials

Chemicals

- Bisphenol-A (Sigma-Aldrich), (100% purity)
- Formaldehyde (Merck), (37 wt.% in water)
- Tetraethylenepentamine (TEPA) (Fluka), (80% purity)
- Silver nitrate (Merck)

Solvents

- *N,N* Dimethylformamide (DMF) (Lab-Scan)
- Acetone
- Deionized water

3.2 Measurements

3.2.1 Differential Scanning Calorimetry (DSC)

The curing behavior of the polybenzoxazine precursor and fully-cured polybenzoxazine were investigated by using a PerkinElmer Differential Scanning Calorimeter, DSC 7. Approximately 5–10 mg samples were sealed in aluminum pans. The sample was heated from 30 °C to 300°C at a heating rate of 10 °C/min under nitrogen flow rate of 10 ml/min.

3.2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was analyzed by using Perkin Elmer Thermogravimetric/Differential Thermal Analyzer (TG-DTA). The sample was heated from 30 °C to 800 °C at a heating rate of 20 °C/min under nitrogen flow rate of 50 ml/min.

3.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups related to structure of materials were investigated by using FT-IR technique. The FT-IR spectra of fully-cured polybenzoxazine and silver-impregnated polybenzoxazine were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm^{-1} with 64 scans at a resolution of 2 cm^{-1} . KBr pellet technique was applied in the preparation of powder samples.

3.2.4 Scanning Electron Microscope (SEM)

Microstructure and surface morphology of polybenzoxazine and silver-impregnated polybenzoxazine were observed by a field emission scanning electron microscope (FE-SEM; JSM-7001F) at voltage of 15 kV. The samples were coated with platinum under vacuum before observation. Furthermore, the amount of Ag ions on the surface can be determined by Energy Dispersive X-Ray Spectrometer (EDX) mode.

3.2.5 X-ray Fluorescence (XRF)

Elemental analysis of the silver-impregnated polybenzoxazine was investigated by Axios WD XRAF, Panalytical.

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine

Bisphenol-A and formaldehyde were dissolved in dimethylformamide and stirred continuously. After that tetraethylenepentamine (TEPA) was added dropwise into the mixture and stirred continuously for approximately 20 minutes while the reaction was cooled with the ice bath until transparent yellow viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde: tetraethylenepentamine was 1:4:1. The pre-polymer was then put in a closed system and left for 1 day, followed by heating at 80 °C for 2 days in an oil bath to let the gel set. Benzoxazine gel was immersed in acetone for 3 days before solvent removal by ambient pressure drying. The resulting organogel was then cured at 160 °C, 180 °C and 200 °C for 3 hours at each temperature and 220 °C for 30 minutes to obtain the fully-cured polybenzoxazine. The synthetic reaction is shown in Figure 3.1.

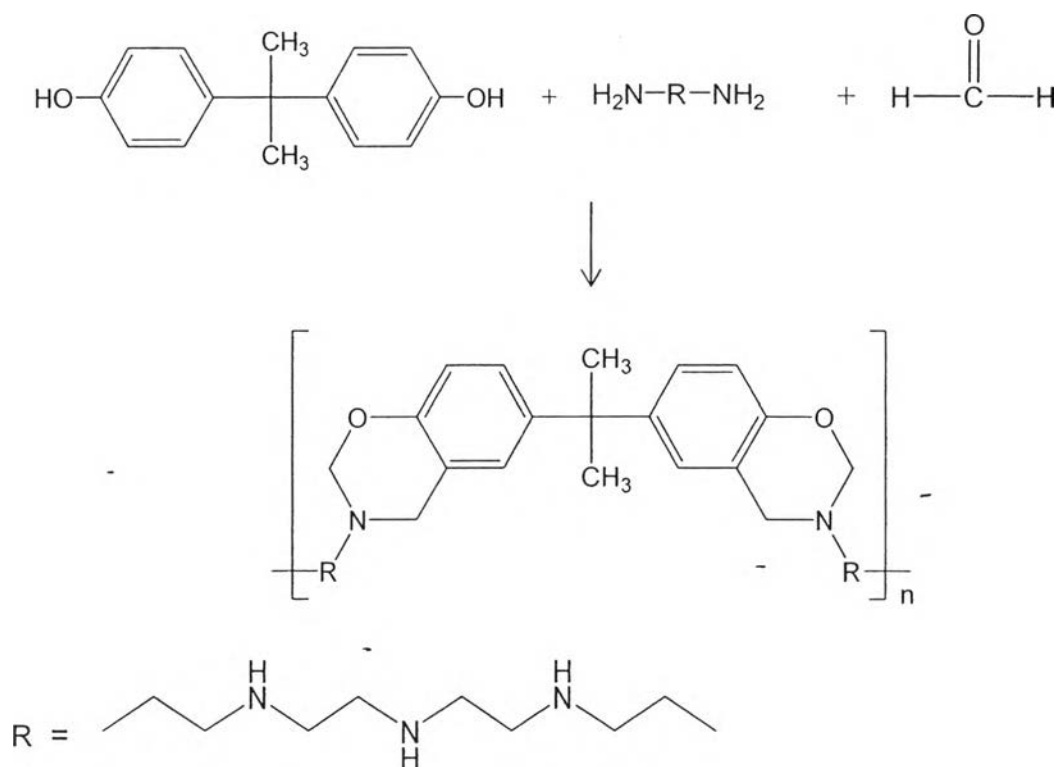


Figure 3.1 Preparation of polybenzoxazine precursor.

3.3.2 Silver Ions Impregnation

Silver nitrate solution was prepared by dissolving silver nitrate in deionized water in a glass bottle and stirred until the clear solution was obtained. The concentration of silver nitrate solutions were 0.5M and 1.0M. Polybenzoxazine was grinded into powder and then soaked into silver nitrate solution and stirred for 1 day at 60 °C in a temperature-controlled water bath. After that, polybenzoxazine with silver ion was filtered and washed with 500 mL of deionized water to remove unreacted ions. Then, it was dried at 100 °C in N₂ atmosphere overnight.

3.3.3 Membranes Preparation

Polybenzoxazine powder and silver-impregnated polybenzoxazine powder were compressed at 4 MPa for 30 seconds to obtain the membranes with thickness of 2 mm.

3.4 Gas Permeability Experiment

In this study, CO₂, N₂ (Prax Air) and CH₄ (TIG) were used as testing gases for all membranes. All tested gases were a high purity (HP) grade and used as received. A schematic diagram of the system used to carry out the gas permeability experiments is shown in Figure 3.2. The experiments were conducted at room temperature under an absolute pressure of 24.59 psia. (Absolute pressure = gauge pressure 10 psig + local atmospheric pressure 14.59 psi) The area of the membrane in contact with the gas was 0.50 cm². The testing gas was flowed for 1 hour in order to reach the equilibrium state.

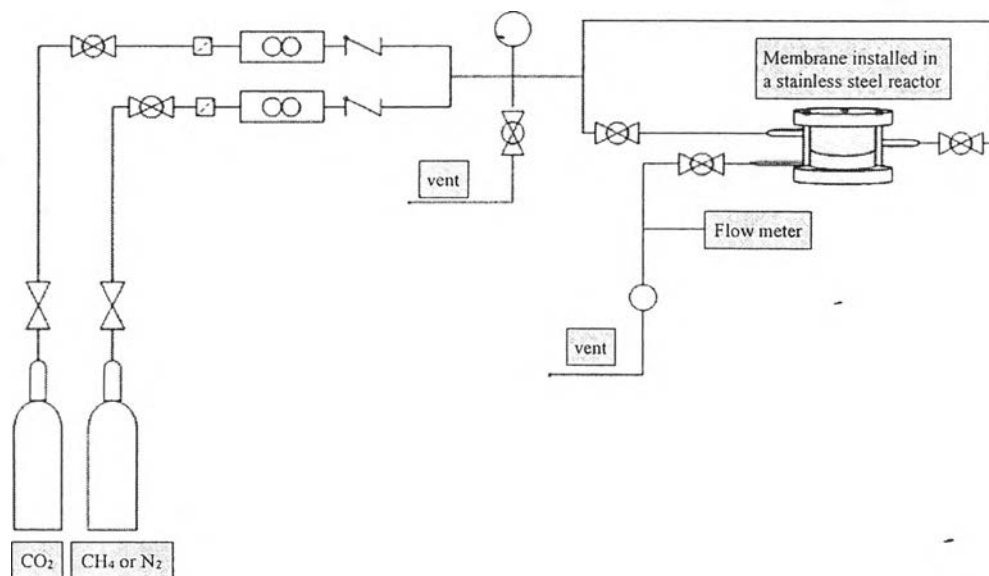


Figure 3.2 Schematic diagram of gas permeability experiments.

The equilibrium state was obtained by measuring the constant permeate rate. Once reached the steady-state, individual gas flow rate was measured using an ADM1000 universal gas flow meter (Agilent technology). The results of each sample were determined from an average of at least 3 tests. The attained data were used to calculate the gas permeability and selectivity. The ideal separation factor (Gas Selectivity, $S_{A/B}$) for component A and B is defined as the ratio of permeance of each component as shown in equation 1:

$$S_{A/B} = \frac{P_A}{P_B} \quad (1)$$

The permeance for the permeated gas can be obtained by equation 2:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \quad (2)$$

Where; $\left(\frac{P}{\delta}\right)_i$ = permeance of gas 'i' (GPU),

P = permeability of gas 'i' (10^{-10} cm^3 (STP) $\text{cm}/\text{cm}^2 \text{ s cm Hg}$)

(1 Barrer = 10^{-10} cm^3 (STP) $\text{cm}/\text{cm}^2 \text{ s cm Hg} = 7.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$),

δ = thickness of membrane (μm),

Q_i = volumetric flow rate of gas 'i' (cm^3/sec),

A = membrane area (cm^2), and

ΔP = pressure difference between the feed side and the permeating side (psia).