



CHAPTER III EXPERIMENTAL

3.1 Materials

Bisphenol-A (BA, $C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde (CH_2O , analytical grade) was purchased from Merck, Germany. 1,6-Hexadiazine (hda, $C_6H_{16}N_2$) was purchased from Aldrich, Germany. 1,4-Dioxane ($C_4H_8O_2$, analytical grade) was purchased from Labscan, Ireland. All chemicals were used without further purification. Zeolite ammonium (ZSM-5) powder—Si/Al ratio is 24.3, the median particle size is 4.5μ , and surface area is $450 \text{ m}^2/\text{g}$ —was purchased from Zeolyst International, USA. In order to remove the adsorbed water vapour or other organic vapors, zeolite was dehydrated at 250°C for 7200 s (2 hours) under vacuum before use.

3.2 Equipment

1. Nicolet/Fourier Transform Infrared Spectrometer (FT-IR)
2. Nicolet/Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)
3. JNM-A500/Fourier Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR)
4. FE-SEM S4800/Scanning Electron Microscopy (SEM)
5. X-Ray Diffractometer (XRD)
6. Air-circulating Oven
7. Gas Permeability Apparatus Unit

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Membrane

3.3.1.1 *Synthesis of Polybenzoxazine Precursors*

The polybenzoxazine precursor was synthesized by using bisphenol-A (BA, $C_{15}H_{16}O_2$), formaldehyde (CH_2O) and 1,6-hexadiazine (hda,

$C_6H_{16}N_2$), with a molar ratio of 1:4:1, respectively. First, bisphenol-A (6.84 g) was dissolved in a 1,4-dioxane (15 ml) in 50 ml glass bottle and stirred until the clear solution was obtained. Formaldehyde solution (9.73 g) was then added into the bisphenol-A solution. The reaction was cooled with an ice bath. After that 1,6-hexadiazine (3.48 g) was added dropwise into the mixture and stirred continuously.

3.3.1.2 Preparation of Polybenzoxazine Membranes

The polybenzoxazine precursor obtained from the reactions was heated and stirred continuously until viscous liquid was obtained. Then the mixture was cast on the glass plate which is coated with foil at room temperature with a thickness of approximately 300 μm using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membrane was dried at room temperature in air for one day yielding the yellow transparent membrane. The membrane was then placed in the oven at 110 $^{\circ}$ C in an air-circulating oven for 24 hours. The thickness of the obtained membrane was around 150 $\mu\text{m} \pm 10 \mu\text{m}$.

The structural characteristics of polybenzoxazine membrane were measured using Fourier Transform Infrared Spectrometer (FT-IR) and Proton Nuclear Magnetic Resonance (^1H NMR). The morphology was observed by Scanning Electron Microscopy (SEM). Figure 3.1 depicts the chemical structure of polybenzoxazine.

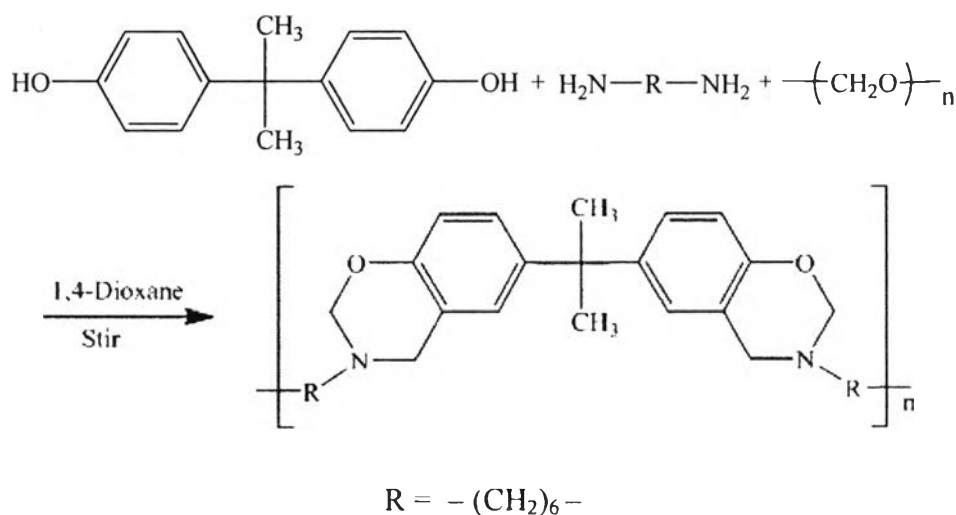


Figure 3.1 The structure of polybenzoxazine.

3.3.1.3 Polybenzoxazine Membrane Characterizations

3.3.1.3.1 Proton Nuclear Magnetic Resonance (^1H NMR)

^1H NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. To identify chemical composition in the range of 1–5 ppm. The prepared polybenzoxazine precursor was dissolved in deuterated chloroform (CDCl_3) for 24 hours prior to used.

3.3.1.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscope, FE–SEM S4800, was used to observe the surface morphology of polybenzoxazine membrane. The specimen was coated with platinum under vacuum before observation.

3.3.1.3.3 Fourier Transform Infrared Spectrometer (FT–IR)

Fourier Transform Infrared Spectra were obtained from a Thermo Nicolet with scans at a scanning resolution of 2 cm^{-1} .

3.3.2 Synthesis of Mixed Matrix Membranes (MMMs)

3.3.2.1 Varying concentration of ZSM–5

Various contents of ZSM–5 were dispersed in 1,4–Dioxane and stirred for 3 hours. After that, the zeolite mixed solution was sonicated for 10 minutes to improve the dispersion of zeolite particles in the solution. Zeolite particles were then “primed” by adding approximately 15 wt.% of total amount of polybenzoxazine, to increase the compatibility between zeolite and polymer, to minimize the aggregation of zeolite particles. The mixture was stirred using magnetic stirrer to enhance the homogeneity. After the remaining polybenzoxazine was added, the final mixture was further mixed for 2 hours to form mixed matrix membranes solution. The concentrations of zeolite in polybenzoxazine were varied at 1 wt.%, 5 wt.% and 10 wt.% on solvent–free basis (Singha–in, 2008).

3.3.2.2 Preparation of Mixed Matrix Membranes (MMMs)

Mixed matrix membranes solution obtained from the reactions were heated and stirred continuously until viscous liquid was obtained. Then the homogeneous solution were cast on the glass plate which is coated by foil at room temperature with thickness of approximately $300\ \mu\text{m}$ using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day yielding the yellow membranes. The

membranes were then further dried at 110°C in an air-circulating oven for 24 hours to obtain the polybenzoxazine/ZSM-5 membranes (MMM). The thickness of the obtained MMMs was around 150 $\mu\text{m} \pm 10 \mu\text{m}$.

3.3.2.3 *Mixed Matrix Membranes (MMMs) Characterizations*

3.3.2.3.1 *Scanning Electron Microscopy (SEM)*

The morphology of flat dense MMMs were investigated using SEM (FE-SEM S4800) to determine that the zeolite ZSM-5 particles were distributed homogenously in PBZ membrane matrix and whether voids existed between polymer and zeolite phases.

3.3.2.3.2 *X-Ray Diffractometer (XRD)*

XRD patterns of zeolite ZSM-5 before and after added into PBZ matrix were investigated to confirm the structure of zeolite ZSM-5 exists in the mixed matrix membrane.

3.3.2.3.3 *Fourier Transform Infrared Spectrometer (FT-IR)*

The IR spectra of MMM, PBZ and ZSM-5 were investigated to indicate the contact between the polymer and the ZSM-5 particle which might be due to the chemical interaction.

3.3.3 Gas Permeability Apparatus

In this study, CO₂ (Prax Air) and CH₄ (TIG) were used as testing gases for all membranes. All tested gases were of 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 experimental setup included gas sources, a membrane testing unit shown in Figure 3.3, and a bubble flow meter.

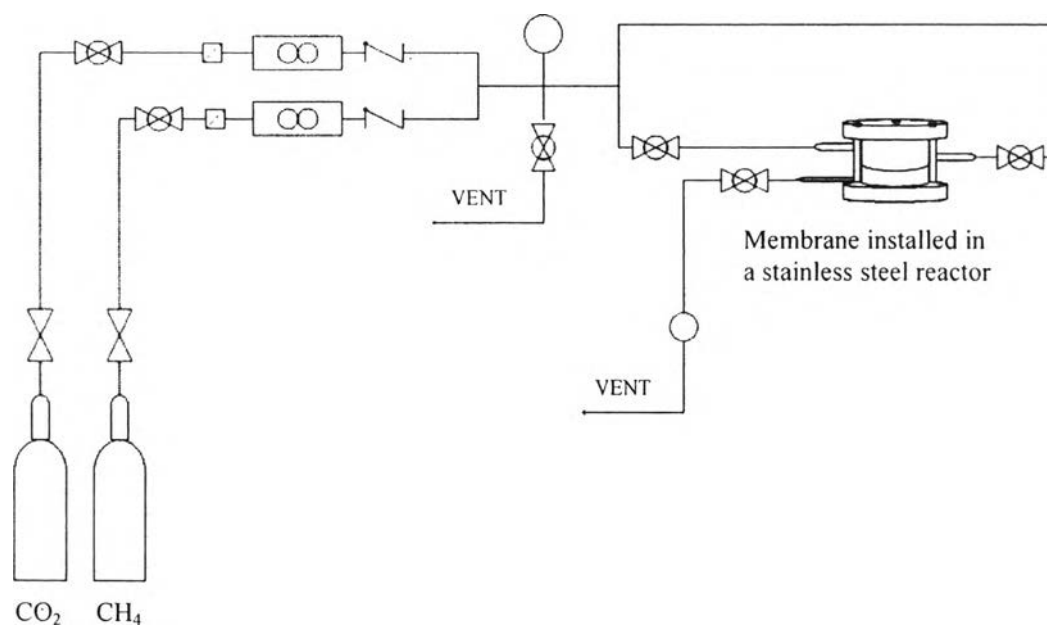


Figure 3.2 Experimental set up for the gas permeability apparatus.

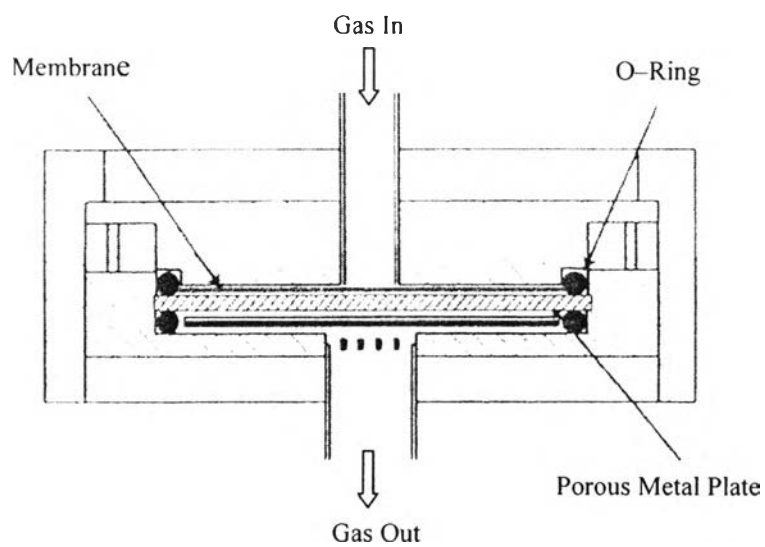


Figure 3.3 Schematic of the membrane testing unit (Singha-in, 2008).

3.3.4 Gas Permeation Measurements

3.3.4.1 Single-component gas permeation

The single-component gas permeation (CH₄ and CO₂) experiment through polybenzoxazine membrane and polybenzoxazine/ZSM-5 membranes (MMM) was carried out at 25° C in sequences by using a gas permeation testing unit in which the membrane was placed on a porous metal plate, then the two compartments were fixed together to prohibit the leakage. The area of the membrane in contact with the gas was 44.17 cm². The pressure difference across the membrane was maintained at 20 psi. Once reached the steady-state, individual gas flow rates were measured using a soap bubble flow meter. The attained data were used to calculate the gas permeance and selectivity. The permeability coefficient for the permeated gas can be obtained by equation 3.1:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \quad (3.1)$$

where $\left(\frac{P}{\delta}\right)_i$ = permeance of gas 'i' (GPU)
 P = permeability of gas 'i' (10⁻¹⁰ cm³ (STP) cm/cm² s cm Hg)
 (1 Barrer = 10⁻¹⁰ cm³ (STP) cm/cm² s cm Hg = 7.5 × 10⁻¹⁸ m² s⁻¹ Pa⁻¹)
 δ = thickness of membrane (μm)
 Q_i = volumetric flow rate of gas 'i' (cm³/sec)
 A = membrane area (cm²)
 ΔP = pressure difference between the feed side and the permeating side (psi)

3.3.4.2 Gas Selectivity

The ideal separation factor (Gas Selectivity, S_{A/B}) for component A and B is defined as the ratio of each component as shown in equation 3.2:

$$S_{A/B} = \frac{P_A}{P_B} \quad (3.2)$$

3.3.5 The interaction between penetrant gas and mixed matrix membrane

3.3.5.1 *Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)*

The IR spectra of MMM, MMM in CO₂ and CH₄ were investigated to indicate the effect of penetrant gas on membrane, a possible formation between MMM molecule and penetrant gas has been suggested.