



CHAPTER IV

HYBRID COMPOSITE MEMBRANE FOR CO₂/CH₄ SEPARATION

4.1 Abstract

A novel mixed matrix membrane (MMM), ZSM5-polybenzoxazine, has been successfully fabricated. MMM combines the advantages of both matrix and filler to improve the performance of gas separation. The SEM micrographs revealed good interfacial adhesion between the polybenzoxazine and ZSM-5 particles since no micron size void was observed. The XRD patterns showed no changes in the crystal structure of the ZSM-5 after mixing with the polymer matrix. CO₂ and CH₄ permeability were determined by using the single gas measurements. The CO₂ and CH₄ permeability of MMM was decreased with increasing zeolite content, while the CO₂/CH₄ selectivity was also increased with an increase in the zeolite loading.

Keywords: Mixed matrix membrane (MMM), Polybenzoxazine, Gas separation, ZSM-5, Hybrid composite membrane

4.2 Introduction

Normally, the types of gas presenting in the natural gas are H_2 , N_2 , O_2 , CH_4 and CO_2 , which are independent sources of the synthesis gas production. However, one problem commonly found in the natural gas processing is the pipeline corrosion, which is induced by the acidic gas such as acidic carbon dioxide gas, etc.

To reduce the pipeline corrosion and also to produce high-purity energy products, gas separation technique by membrane is the attractive approach to separate carbon dioxide gas (longer and slender molecule) from methane (more compact molecule with slightly longer cross-section) in the natural gas processing because it is low energy consumption, simple operation and low maintenance requirement [1].

One of the most important elements in gas separation technique is the membrane. In this study, polybenzoxazine, which is a high performance thermosetting resin, is selected as the membrane matrix. Polybenzoxazine exhibits excellent properties such as low shrinkage after curing, low water absorption, good thermal stability and high glass transition temperature [2]. However, in order to improve the selectivity of a dense membrane in the separation process, zeolite—which can act as a molecular sieve—is added to form a mixed matrix membrane (MMM) or composite membrane to enhance the separation performance, while still maintaining a low cost, simplicity of operation and great processing flexibility.

The purpose of this work is to develop a new MMM by using polybenzoxazine as the continuous phase mixed for gas separation and to study the ability of this MMM for the separation of carbon dioxide gas from methane.

4.3 Experimental

4.3.1 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.

4.3.2 Measurements

The structural characteristics of polybenzoxazine were measured using Fourier Transform Infrared Spectrometer (FT-IR) obtained from a Thermo Nicolet and Proton Nuclear Magnetic Resonance (^1H NMR) which were recorded on a Varian Mercury 300 (300 MHz) instrument. The prepared polybenzoxazine precursors were dissolved in deuterated chloroform ($CDCl_3$) for 24 hours prior to use. Attenuated Total Reflectance Infrared Spectrometer (ATR-IR) spectra of membranes were obtained from a Thermo Nicolet by using ZnSe 45° (flat plate) with a scanning resolution of 4 cm^{-1} to study the interaction between the gas molecule and the MMM. The membrane morphology was investigated by using Scanning Electron Microscopy (SEM) (FE-SEM S4800). X-Ray Diffractometer (XRD) was used to study the XRD patterns of zeolite ZSM-5 before and after added into PBZ matrix.

4.3.3 Methodology

4.3.3.1 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-hexadamine (3.48 g) was added dropwise into the mixture and stirred continuously.

Table 4.1 The chemical structure of reactants

Reactants	Chemical structures
Bisphenol A (BA)	
Formaldehyde	$\text{-(CH}_2\text{O)}_n\text{-}$
1,6-hexanediamine (hda)	

4.3.3.2 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^o C in an air-circulating oven for 24 hours. The thickness of the obtained membrane was around 150 $\mu\text{m} \pm 10 \mu\text{m}$. Figure 4.1 depicts the chemical structure of polybenzoxazine membranes.

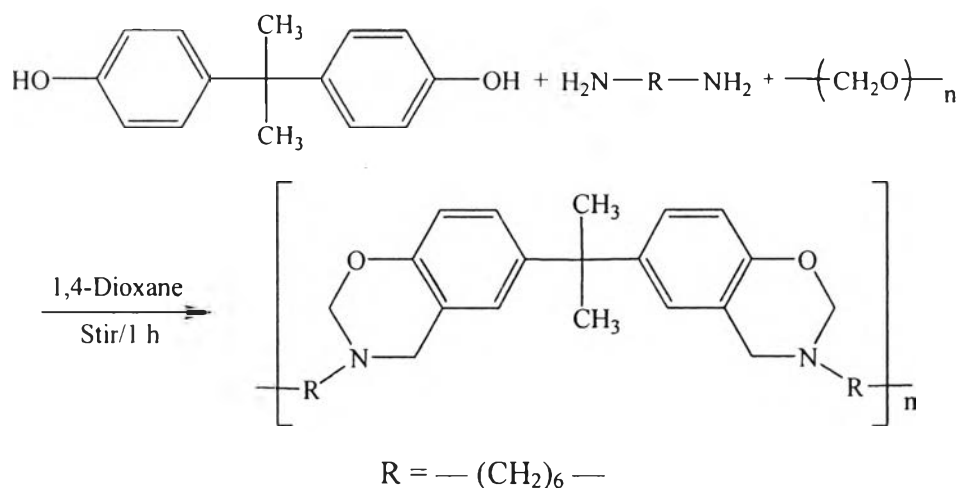


Figure 4.1 The chemical structure of polybenzoxazine membranes.

4.3.3.3 Preparation of Mixed Matrix Membranes

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 min 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 [3]. The mixed matrix membranes solution was heated until viscous liquid was obtained. The precursors obtained from the reactions were cast on the glass plate which is coated by foil at room temperature with thickness of approximately 300 μm using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day then further dried at 110°C in an air-circulating oven for 24 h.

4.3.3.4 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 4.2. The experimental setup included gas sources, a membrane testing unit shown in Figure 4.3, and a bubble flow meter.

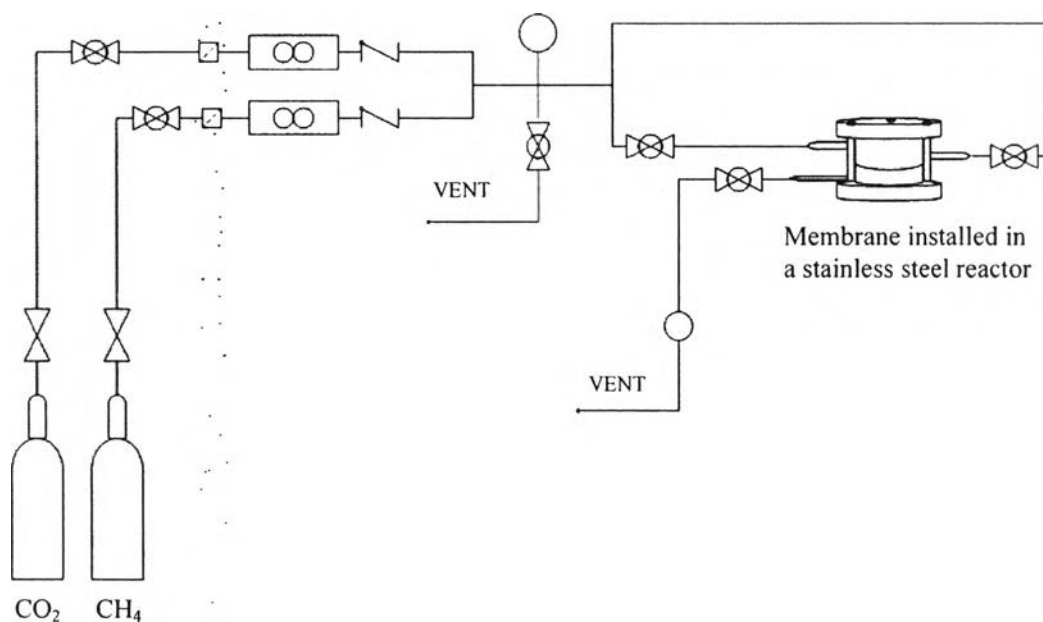


Figure 4.2 Experimental set up for the gas permeability apparatus.

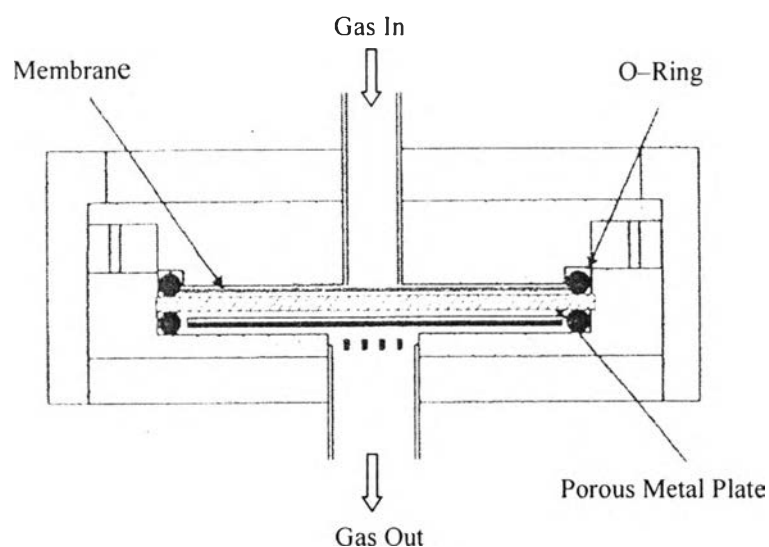


Figure 4.3 Schematic of the membrane testing unit [3].

4.3.3.5 Gas Permeation Measurements

4.3.3.5.1 *Single-component gas permeation*

The single-component gas permeation (CH_4 and CO_2) 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 cm^2 . 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 permeability and selectivity. The permeability coefficient for the permeated gas can be obtained by equation 4.1:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \quad (4.1)$$

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} 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)

4.3.3.5.2 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 4.2:

$$S_{A/B} = \frac{P_A}{P_B} \quad (4.2)$$

4.4 Results and Discussion

4.4.1 Polybenzoxazine Membrane Characterizations

Polybenzoxazine precursor, Poly(BA-hda) was derived from the reaction of bisphenol-A, formaldehyde and 1,6-hexadamine at a molar ratio of 1:4:1 via quasi-solventless method.

4.4.1.1 Proton Nuclear Magnetic Resonance (¹H NMR)

The results were in agreement with the work reported by Takeichi *et al.* (2005) [4] where the characteristic peaks assignable to methylene (O-CH₂-N) and methylene (Ar-CH₂-N) of oxazine ring in BA-hda were observed at 4.81 and 3.92 ppm, respectively. The peak of methyl protons of bisphenol-A and methylene protons of opened-ring polybenzoxazine were formed at 1.58 and 2.70 ppm, respectively.

The ¹H NMR measurement was conducted to confirm the synthesis process (Figure 4.4). The characteristic peaks of Poly(BA-hda) assigned to the methylene protons of O-CH₂-N (a) and Ar-CH₂-N (b) of oxazine ring were observed at around 4.80 and 3.90 ppm, respectively. The methyl protons of bisphenol-A (d) and methylene protons of opened-ring polybenzoxazine (c) were observed at 1.57 and 2.85 ppm, respectively.

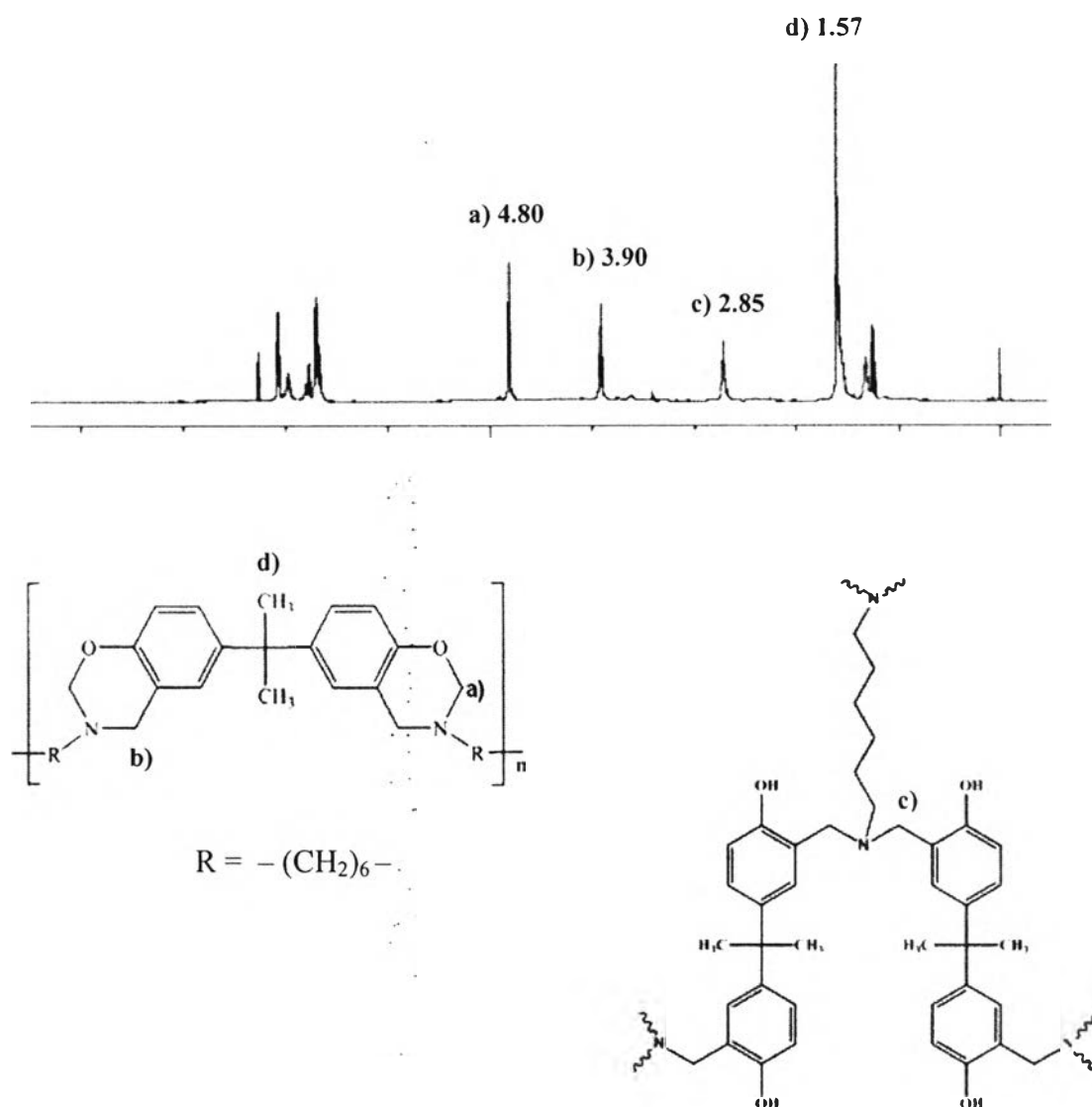


Figure 4.4 ^1H NMR spectra of polybenzoxazine precursors: Poly(BA-hda).

4.4.1.2 Preparation of Polybenzoxazine Membrane

The precursor was dissolved in 1,4-dioxane and cast on a glass plate which was coated with aluminum foil and then dried at 110°C for 24 hours yielding the membrane with the thickness around $150\ \mu\text{m} \pm 10\ \mu\text{m}$. The characteristic of polybenzoxazine membrane is shown in Figure 4.5.

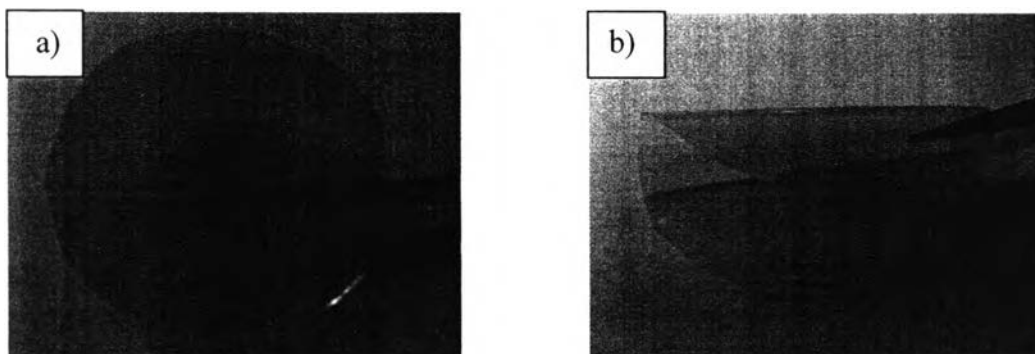


Figure 4.5 Appearance of polybenzoxazine membrane: Poly(BA-hda).

4.4.1.3 Scanning Electron Microscopy (SEM)

The polybenzoxazine membrane used in this study is a dense polymeric membrane, as can be seen from the SEM micrograph in Figure 4.6.



Figure 4.6 SEM micrograph of Poly(BA-hda).

4.4.1.4 Fourier Transform Infrared Spectrometer (FT-IR)

The chemical structure of prepared polybenzoxazine membrane was confirmed by using FT-IR (Figure 4.7).

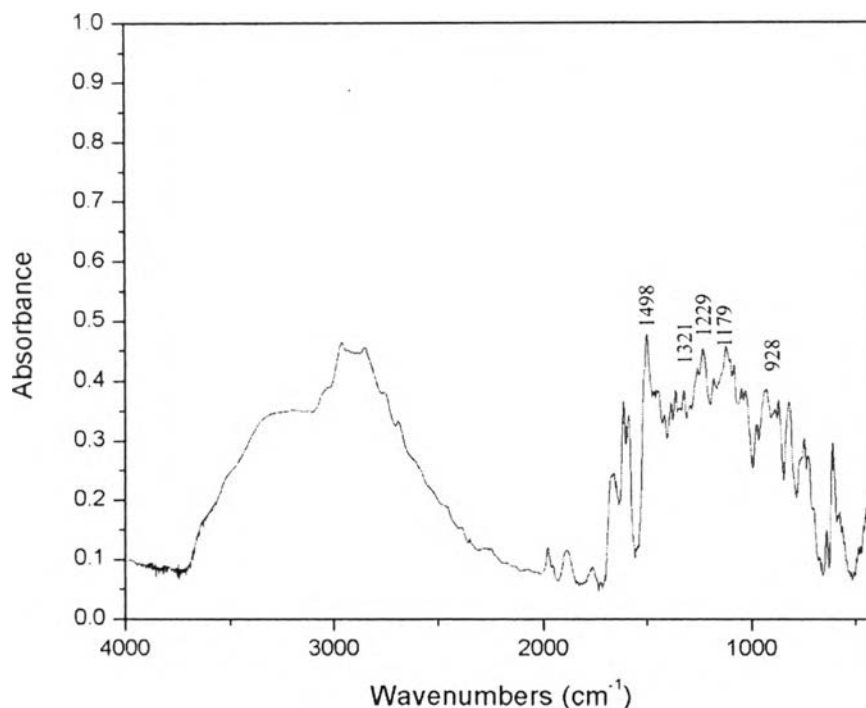


Figure 4.7 FT-IR spectra of polybenzoxazine membrane.

The structure of the precursor was examined by FT-IR. The asymmetric stretching of C–O–C (1234 cm^{-1}), the asymmetric stretching of C–N–C ($1180\text{--}1187\text{ cm}^{-1}$), and CH_2 wagging of oxazine ($1325\text{--}1328\text{ cm}^{-1}$) were observed. Additionally, the characteristic absorptions assigned to trisubstituted benzene ring at $1502\text{--}1511\text{ cm}^{-1}$ and the out-of-plane bending vibrations of C–H at $937\text{--}943\text{ cm}^{-1}$ were observed, indicating that precursors contained benzoxazine functionality [4].

4.4.2 Characterization of Mixed Matrix Membranes (MMMs)

4.4.2.1 Formation of Mixed Matrix Membranes

Various contents of ZSM-5 (1 wt.%, 5wt.% and 10 wt.%) were added into the polybenzoxazine solution and cast on a glass plate. The membranes were dried at 110°C for 24 hours yielding the mixed matrix membranes (MMMs) with the thickness around $150\text{ }\mu\text{m}\pm 10\text{ }\mu\text{m}$ and a testing diameter of 7.5 cm for the

permeability measurements. The characteristics of partially cured mixed matrix membranes are shown in Figure 4.8.

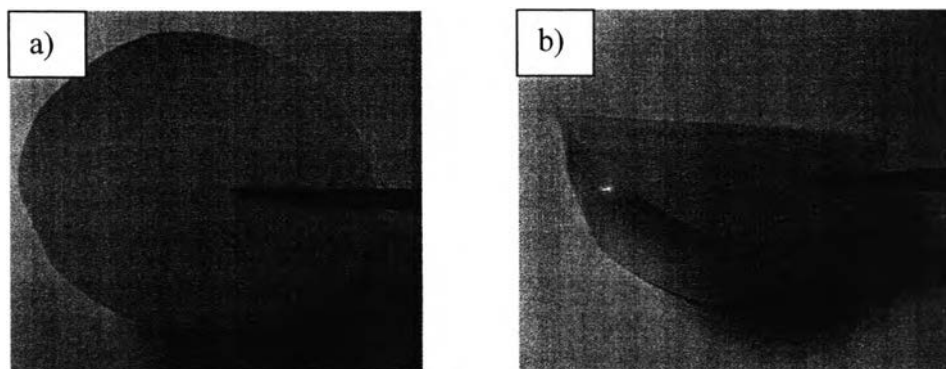


Figure 4.8 Appearance of mixed matrix membranes: Poly(BA-hda).

4.2.2.2 Scanning Electron Microscopy (SEM)

SEM micrographs of ZSM-5-polybenzoxazine mixed matrix membranes used in this study are shown in figure 4.9 and 4.10.

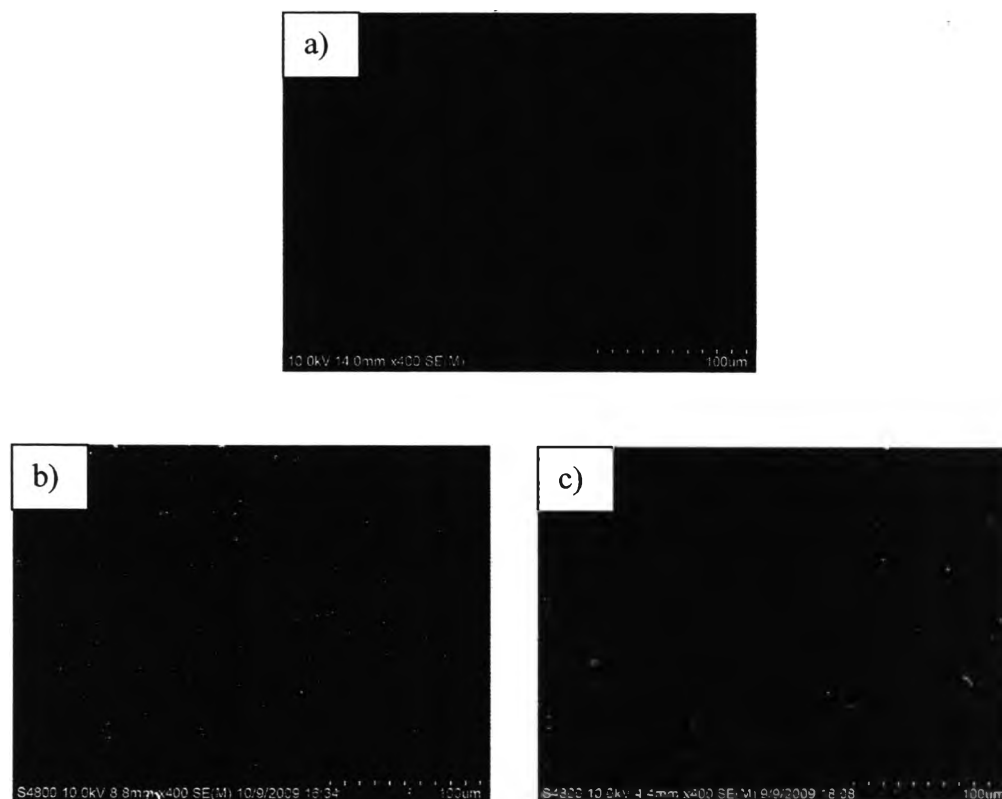


Figure 4.9 SEM surface image of PBZ-ZSM5 MMMs with (a) 1 wt. %, (b) 5 wt. % and (c) 10 wt. % of ZSM-5 loading.

The MMMs with different zeolite loadings were examined by SEM to determine that the zeolite ZSM-5 particles were homogeneously distributed in PBZ membrane matrix without forming any large agglomerate as shown (Figure 4.9).

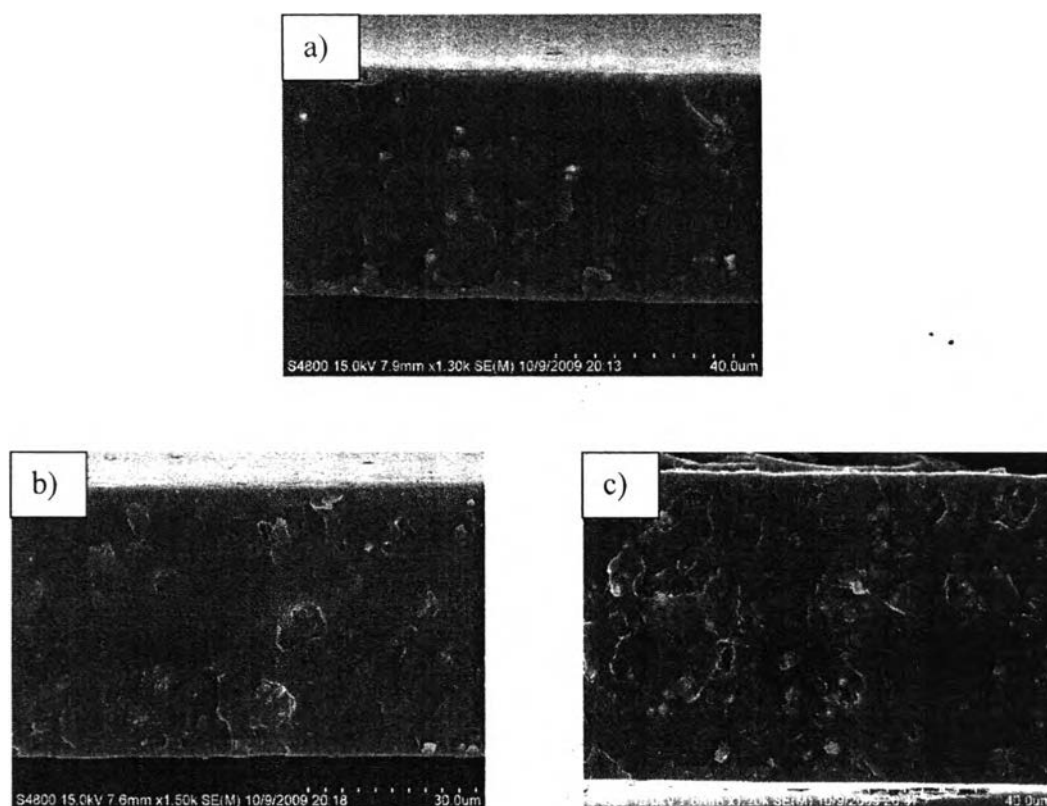


Figure 4.10 Cross-section SEM image of PBZ-ZSM5 MMMs with (a) 1 wt.%, (b) 5 wt.% and (c) 10 wt.% of ZSM-5 loading.

The SEM micrographs are shown in Fig 4.10 for the cross-section morphology of PBZ membrane filled with different zeolite loadings, where the cubic particles are zeolite ZSM-5 crystals, and the continuous phase is PBZ. At the interface between the polymer and ZSM-5 particles, there are no micron size void suggesting that the contact between the polymer and the ZSM-5 particles is good which might be due to the chemical interaction between the ZSM-5 particles and the PBZ. Further investigation will be carried out to confirm this hypothesis.

4.2.2.3 X-Ray Diffractometer (XRD)

The XRD patterns for the ZSM-5 and MMM are shown in Fig. 4.11. The XRD pattern of MMM shows the presence of all major peaks for ZSM-5 zeolite similar to that of the ZSM-5 reference pattern given by the JCPDS (Joint Committee on Powder Diffraction Standards) which suggests that the ZSM-5 zeolite structure was confirmed to exist in the MMMs.

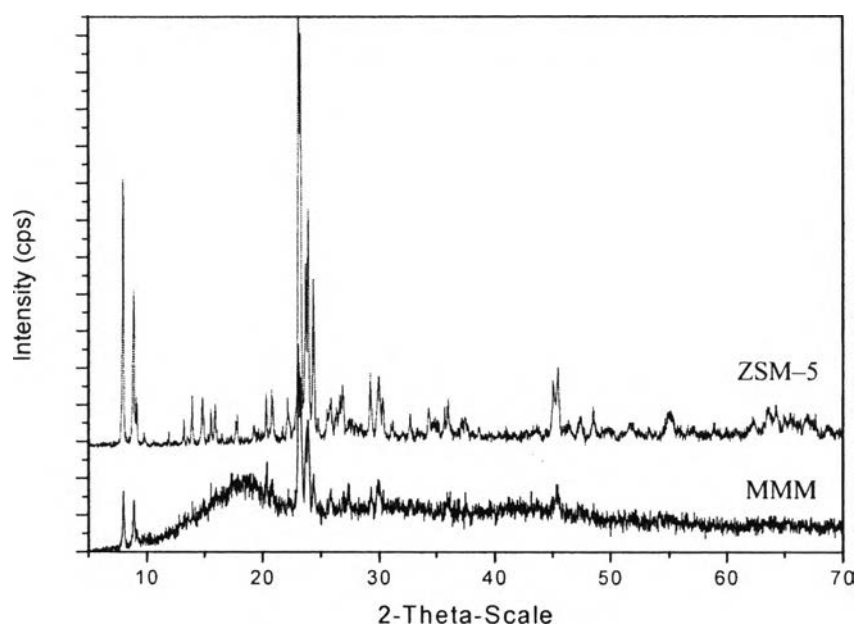


Figure 4.11 XRD patterns of ZSM-5 and MMM.

4.4.3 Interfacial interaction of ZSM-5 and polybenzoxazine (PBZ)

4.4.3.1 Fourier Transform Infrared Spectrometer (FT-IR)

The IR spectra of PBZ, MMM and ZSM-5 are shown in Fig. 4.12 to interfacial interaction between the polymer and the ZSM-5 particle.

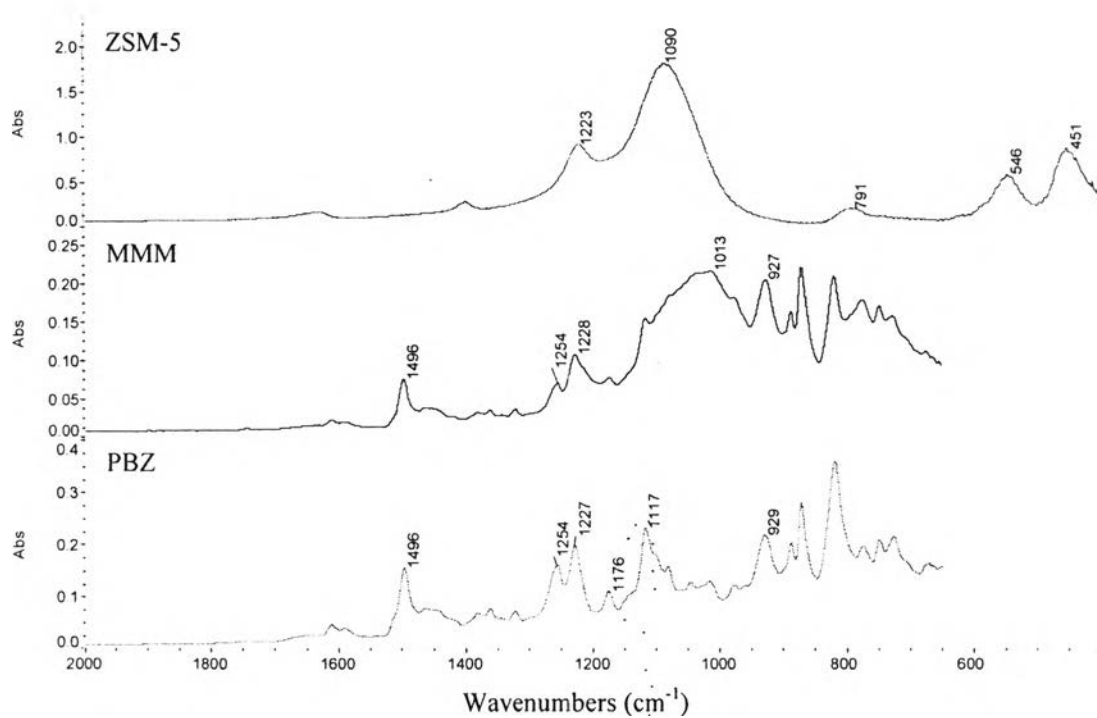
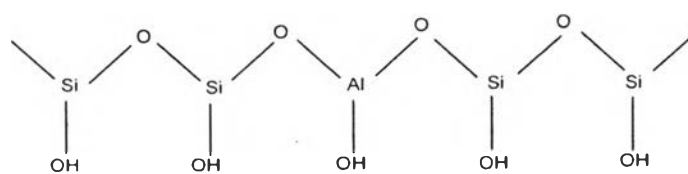
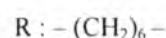
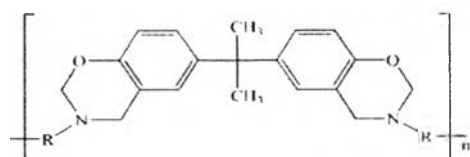


Figure 4.12 The IR spectra of polybenzoxazine membrane, MMM and ZSM-5.

For ZSM-5, Mohamed *et al.* (2005) [5] reported that the bands near 1219 and 542 cm^{-1} were the characteristics of double five membered ring, 1080 cm^{-1} represent the internal asymmetric stretching vibration of Si-O-T linkage (T represents Si or Al), while the peak at 790 cm^{-1} is attributed to the symmetric stretching of the external linkage. The peak at 450 cm^{-1} represents the T-O bending vibration of the SiO_4 and AlO_4 internal tetrahedral and the bands around 542 and 450 cm^{-1} are the characteristic peaks of the ZSM-5 crystalline structure (Fig. 4.12).



a) ZSM-5



b) PBZ

Figure 4.13 Chemical structure of (a) ZSM-5 and (b) PBZ.

As shown in Fig. 4.13, the chemical interaction between PBZ and zeolite ZSM-5 enables a good contact between the polymer and the ZSM-5 particles. The IR spectra of PBZ, MMM and ZSM-5 are given in Fig. 4.12.

Fig. 4.12, ZSM-5 shows the peak of internal asymmetric stretching vibration of Si-O-T linkage (1090 cm^{-1}) shifted to lower frequency (1013 cm^{-1}) in MMM which was suggested to Si-O-C and the peak was broadened with the overlapping peak of C-OH of PBZ (1117 cm^{-1}). The shifting and broadening of peaks distinctly reveal the chemical bonding between PBZ and zeolite ZSM-5 to form Si-O-C linkage resulting in no micron size voids suggesting that the contact between the polymer and the ZSM-5 particles is good.

4.4.4 Gas Permeability

Polybenzoxazine membrane and MMMs were tested in the single gas measurements. The permeability of these membranes was obtained in the sequence of CH_4 and CO_2 at room temperature and 20 psi. The permeability and selectivity of CO_2 and CH_4 in polybenzoxazine membranes and mixed matrix membrane are depicted in Figure 4.14–4.15.

4.4.4.1 The effect of zeolite loading on the CO₂ and CH₄ permeability

ZSM-5/PBZ composite membranes, MMMs, were successfully fabricated with different zeolite loadings. Their CO₂ and CH₄ permeability is shown in Figure 4.14.

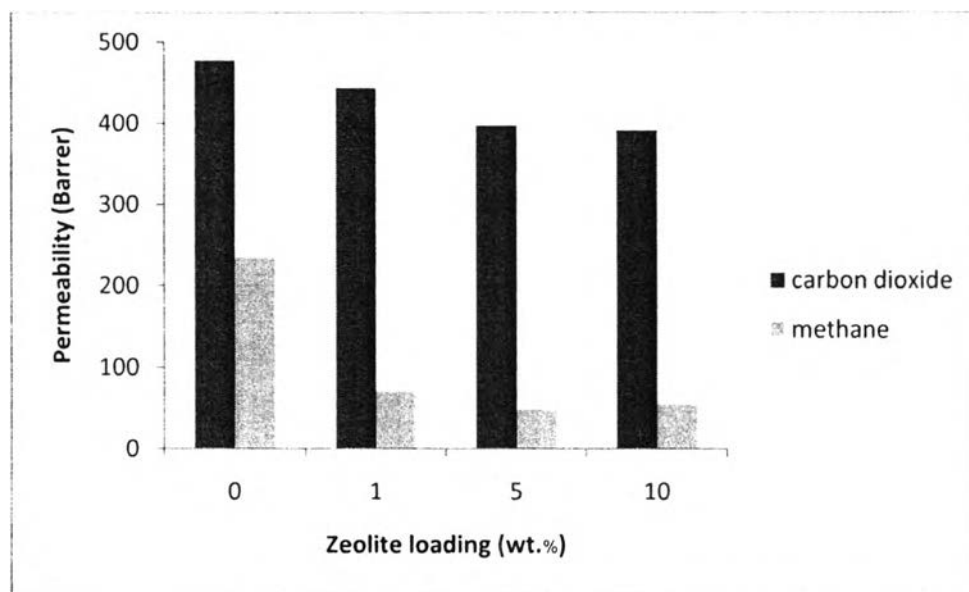


Figure 4.14 Effects of ZSM-5 loadings on CO₂ and CH₄ permeability.

Figure 4.14 shows that the CO₂ and CH₄ permeability of MMM were decreased with increasing zeolite contents. The combination of ZSM-5 into PBZ polymer matrix resulted in the drop-off CO₂ and CH₄ permeability as compare to the pure PBZ membrane. This is because zeolite particle disturbed the transient gap of polymer chains. This transient gap allowed penetrant molecules to pass through polymer matrix. The presence of zeolite obstructs the movement of the polymer chains and reduces polymer chain mobility [6]. Hence, CO₂ and CH₄ molecules are more difficult to penetrate through the membrane.

The gas permeability in polybenzoxazine decrease significantly as the penetrant size increases. In conventional glassy polymers, gas size has a much larger effect on diffusion than on solubility, which leads to a dramatic decrease in permeability as the size of the gas molecules increase [7]. The membranes are

selective for CO₂ because CO₂ preferentially adsorbs, and it also diffuses faster than CH₄ [8].

The molecular kinetic diameters of CO₂ and CH₄ are 3.3 Å and 3.8 Å, respectively. Due to the configurational diffusion, the small difference in molecular size between CO₂ and CH₄ results in a big difference in the rate of diffusion through the ZSM-5 zeolite channels; the diffusion of CO₂ is faster than that of CH₄ [8]. Therefore, CO₂ and CH₄ can be separated by a ZSM-5 zeolite mixed matrix membrane, which provides a new route for the separation of CO₂ and CH₄. However, as ZSM-5 loadings were increase, CO₂ and CH₄ permeability was not enhanced. This is because the pore opening of zeolite ZSM-5 (5 Å) is larger than kinetic diameters of both CO₂ (3.3 Å) and CH₄ (3.8 Å) molecules. Thus, allowing both gases to freely pass through them.

All these properties indicated that the gases mainly permeated through the channels of ZSM-5 zeolite and the gas permeation was controlled by the molecular kinetic diameter of penetrant gas and ZSM-5 zeolite and also the diffusion of gas through the membrane are the important role.

4.4.4.2 The effect of zeolite loading on the CO₂/CH₄ selectivity

The CO₂/CH₄ selectivity for ZSM-5 at different loadings are shown in Figure 4.15.

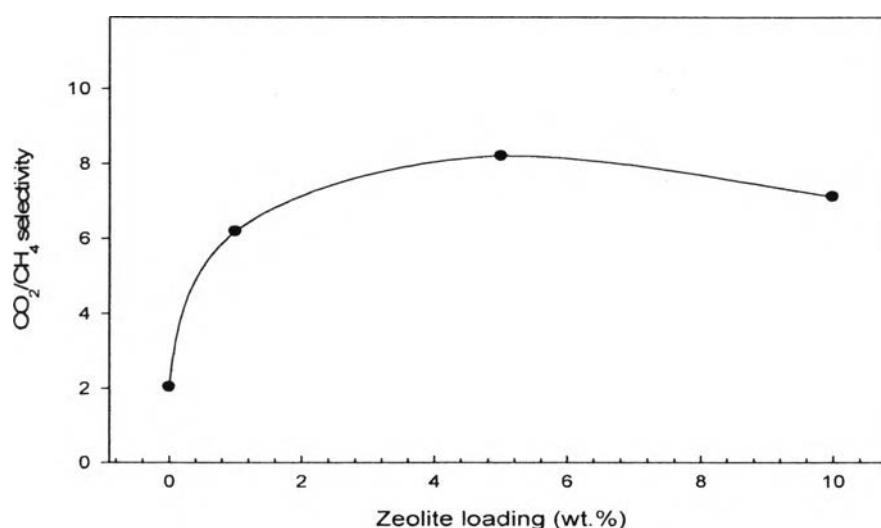


Figure 4.15 Effects of ZSM-5 loadings on CO₂/CH₄ selectivity.

Figure 4.15 shows the CO₂/CH₄ selectivity increased with an increase in the zeolite loadings. However, the increasing of ZSM-5 into the membrane did not enhance CO₂/CH₄ selectivity. This is due to its large pore opening compared to kinetic diameter of CO₂ and CH₄ molecules, or molecular sieving mechanism of ZSM-5 plays a minor role in CO₂/CH₄ separation [3].

Compared with the polybenzoxazine membrane, those MMMs showed better CO₂/CH₄ selectivity, the CO₂/CH₄ selectivity for 0 wt.%, 1 wt.%, 5 wt.% and 10 wt.% of zeolite loading were 2.04, 6.19, 8.21 and 7.12, respectively, suggesting that ZSM-5 zeolite improved the selectivity for CO₂ and CH₄ separation.

To make the gas separation process economically attractive, the 1 wt.% of zeolite loading showed the highest CO₂ and CH₄ permeability and great CO₂/CH₄ selectivity when compared with those with higher % of ZSM-5 loading content; thus, 1 wt.% of zeolite, it was chosen for further investigation.

Substitution of a silicon atom for an aluminium atom introduced a charge in the framework which must be balanced by a cation, hence, generating an acidic bridging hydroxyl group. These Bronsted hydroxyl groups are important for adsorption properties of zeolites [8]. Since the Si/Al ratio of zeolite ZSM-5 is 23, substitution of a silicon atom for an aluminium atom processes electric field gradients which can strongly interact with the permanent electric quadrupole moment of CO₂ molecules [3] and are able to selectively attract CO₂ molecules than CH₄ molecules resulting in obstructing other CO₂ molecules to pass freely through the MMMs. Thus, the CO₂/CH₄ separation performance is under estimated.

Since the pore size of ZSM-5 is around 5 Å which is larger than the kinetic diameters of both CO₂ (3.3 Å) and CH₄ (3.8 Å) molecules. The larger pore size exhibits higher gas penetration since gas can pass through MMMs. However, the interaction between the gas molecules and zeolite also has an influence on separation performance as previously discussed. Thus, the gas separation performance not only depend on the pore size but also the interaction between gas molecules and MMMs.

4.4.5 The interaction of penetrant gas on mixed matrix membrane

In general, CO₂ has higher permeation rate than CH₄. The presence of certain chemical groups in the polymer backbone may enhance or depress the permeation of

certain gas over another as a result of some interaction between the gas molecules and those chemical groups [9].

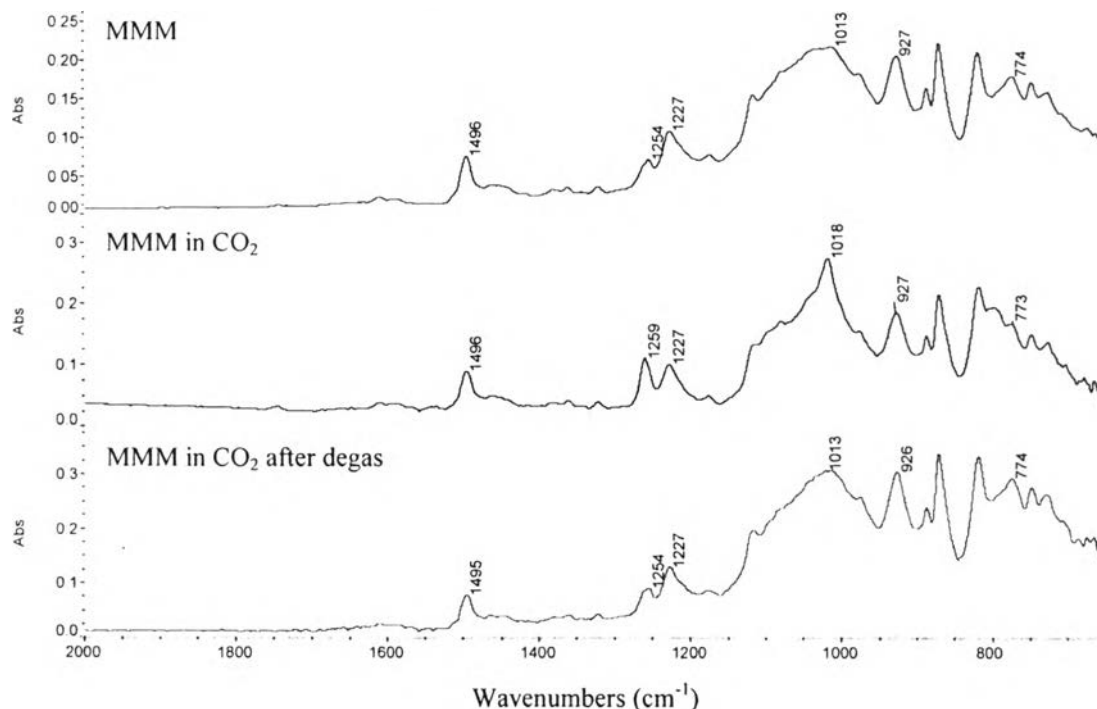


Figure 4.16 IR spectrum of MMM in CO₂ and after degas.

Fig. 4.16 compare the IR of MMM in CO₂ and after degas. The intensity of the C–O–C band at 1254 cm⁻¹ increased when CO₂ was purged into the system. The shape of the band 1013 cm⁻¹ (Si–O–T) changed and shifts to higher frequency (1018 cm⁻¹) and the peak at 774 cm⁻¹ disappeared. However, after degassing all bands returned to their original shape and intensity suggested that the MMM absence of CO₂. Thus the effect of CO₂ on the IR spectrum of MMM is reversible. This suggests that CO₂ molecule is interacting with the MMM and is forming an unstable complex.

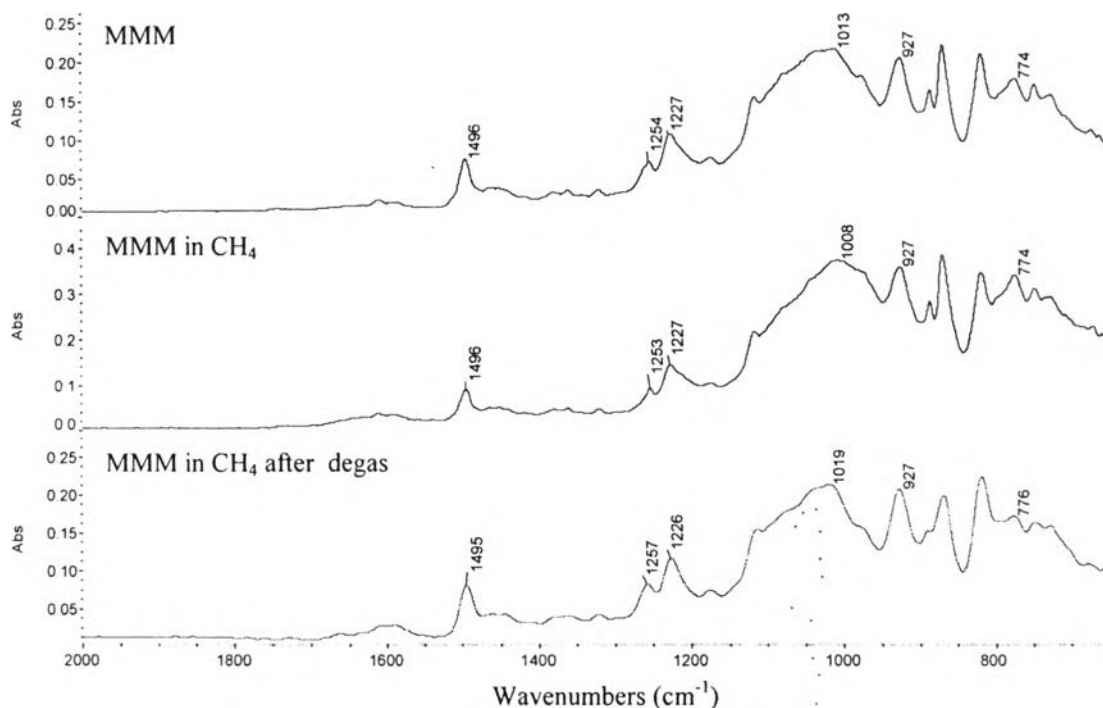


Figure 4.17 IR spectrum of MMM in CH₄ and after degas.

Fig. 4.17 compare the IR of MMM in CH₄ and after degas. The shape of the band 1013 cm⁻¹ (Si-O-T) changed and shifts to lower frequency (1008 cm⁻¹). However, after degassing they returned to their original shape and intensity suggested that the MMM absence of CH₄. Thus the effect of CH₄ on the IR spectrum of MMM is reversible. This suggests that CH₄ molecule is interacting with the MMM and is forming an unstable complex.

4.5 Conclusion

Mixed matrix membranes, ZSM5-polybenzoxazine, were successfully synthesized from bisphenol-A, formaldehyde and 1,6-hexadamine. The 1 wt.% of zeolite loading showed the highest CO₂ and CH₄ permeability and great CO₂/CH₄ selectivity when compared with those with higher % of ZSM-5 loading content. Increasing the zeolite loading did not significantly improve neither gas permeability nor CO₂/CH₄ selectivity since molecular sieving mechanism of ZSM-5 plays a minor role in CO₂/CH₄ separation.

4.6 Acknowledgements

I am grateful for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College, and by the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand.

4.7 References

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