

**CHAPTER IV**  
**SILVER-IMPREGNATED POLYBENZOXAZINE MEMBRANES**  
**FOR CO<sub>2</sub>/CH<sub>4</sub> GAS SEPARATION**

**4.1 Abstract**

Carbon dioxide and methane are the major components in flue gas which generally comes from industrial processes. Carbon dioxide is the main gas that causes global warming. This work investigated the effect of silver-impregnated polybenzoxazine membrane on CO<sub>2</sub>/CH<sub>4</sub> separation. Silver ions were impregnated into fully-cured polybenzoxazine to enhance the separation efficiency, since silver ions can react reversibly and selectively with CO<sub>2</sub> by  $\pi$ -complexation formation mechanism. DSC was used to observe the thermal behavior of polybenzoxazine. The silver-impregnated polybenzoxazine was characterized by FT-IR. The elemental composition on the surface was analyzed by energy dispersion of X-ray (EDX). The single gas experiments were conducted at room temperature under an absolute pressure of 24.59 psia, using the membranes with the thickness of 2 mm. The results showed that CO<sub>2</sub> permeability decreased when silver ions increased.

**Keywords:** Polybenzoxazine/ Gas separation membrane/ Silver

## 4.2 Introduction

Carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) are the important component in flue gas which is generally produced by the combustion of fossil fuels in the industrial processes. CO<sub>2</sub> emissions are concerned because it makes global climate change, commonly known as “greenhouse effect” (Xu X. *et al.*, 2005). Therefore, CO<sub>2</sub>/CH<sub>4</sub> separation is developed-

There are several post-combustion and capture technologies being investigated such as absorption, adsorption, cryogenic separation and membrane separation (Tirzha L.P. Dantas *et al.*, 2012). Traditional methods for CO<sub>2</sub> capture are based on reversible absorption such as amine scrubbing and cryogenic technologies, but these processes are costly and energy intensive. The membrane technology is attractive for CO<sub>2</sub> separation. The advantages of membrane gas separation over traditional techniques are low-energy consumption, ease of operation, and low environmental impact (Iarikov D. *et al.*, 2012).

Organic polymers are the most widely used as membranes for gas separation such as polyimide, cellulose acetate and polysulfone (Abetz V. *et al.*, 2006).. However, using polymer as membranes in CO<sub>2</sub>/CH<sub>4</sub> separations has been concerned since the membrane selectivity can be reduced because of CO<sub>2</sub>-induced plasticization (Bos A. *et al.*, 1998; Scholes C. A. *et al.*, 2010; Wessling M. *et al.*, 1991). But the effect of CO<sub>2</sub>-induced plasticization can be significantly improved by silver ionic modification approach. Moreover, the insertion of transition metal such as silver into the polymer membrane can be used to increase the selectivity (Li Y. and Chung T. S., 2010), since silver ions can react reversibly and selectively with CO<sub>2</sub> by  $\pi$ -complexation formation mechanism (Li, Y. *et al.*, 2007)

In this study, polybenzoxazine, which has many excellent properties such as high porosity, high heat resistance and excellent dimensional stability (Liu *et al.*, 2004) incorporated with silver ions and used as the membrane for CO<sub>2</sub>/CH<sub>4</sub> gas separation.

## 4.3 Experimental

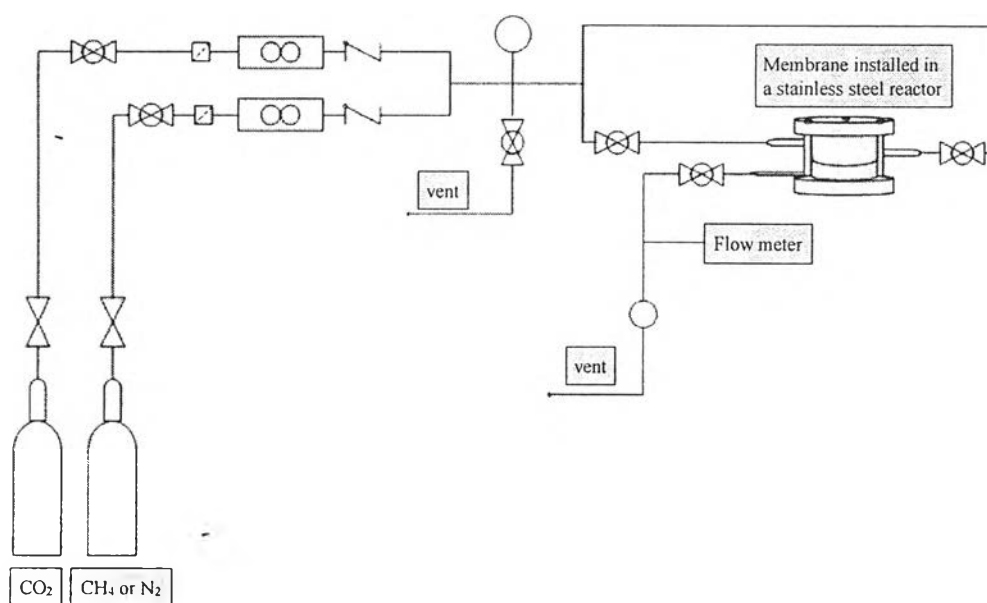
### 4.3.1 Materials

All chemicals were used without further purification. Bisphenol-A (100% purity) purchased from Sigma-Aldrich, formaldehyde (37 wt.% in water) purchased from Merck, tetraethylenepentamine (80% purity) purchased from Fluka were used as starting materials for polybenzoxazine synthesis. Silver nitrate purchased from Merck was used to impregnate into polybenzoxazine.

### 4.3.2 Measurements

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. 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. 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  $\text{cm}^{-1}$  with 64 scans at a resolution of 2  $\text{cm}^{-1}$ . KBr pellet technique was applied in the preparation of powder samples. 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. Elemental analysis of the silver-impregnated polybenzoxazine, particularly investigate by Axios WD XRAF, Panalytical.

In this study, CO<sub>2</sub> and CH<sub>4</sub> (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 Fig 4.1. 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 cm<sup>2</sup>. The testing gas was flowed for 1 hour in order to reach the equilibrium state.



**Figure 4.1** 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<sup>3</sup> (STP) cm/cm<sup>2</sup> s cm Hg)

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

$\delta$  = thickness of membrane ( $\mu$ m),

$Q_i$  = volumetric flow rate of gas 'i' (cm<sup>3</sup>/sec),

A = membrane area (cm<sup>2</sup>), and

$\Delta P$  = pressure difference between the feed side and the permeating side (psia).

### 4.3.3 Methodology

#### 4.3.3.1 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.

#### 4.3.3.2 Silver ions impregnation

Silver nitrate solution was prepared by dissolving silver nitrate in deionized water in 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 the reaction,

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 N<sub>2</sub> atmosphere overnight.

#### *4.3.3.3 Characterization of polybenzoxazine precursor and silver-impregnated polybenzoxazine*

The thermal behavior of benzoxazine precursor and fully-cured polybenzoxazine was analyzed by using DSC. TGA was used to characterize fully-cured polybenzoxazine and silver-impregnated polybenzoxazine. Chemical structure of polybenzoxazine was characterized by FT-IR. Microstructure and surface morphology of polybenzoxazine and silver-impregnated polybenzoxazine were observed by a field emission scanning electron microscope (FE-SEM)

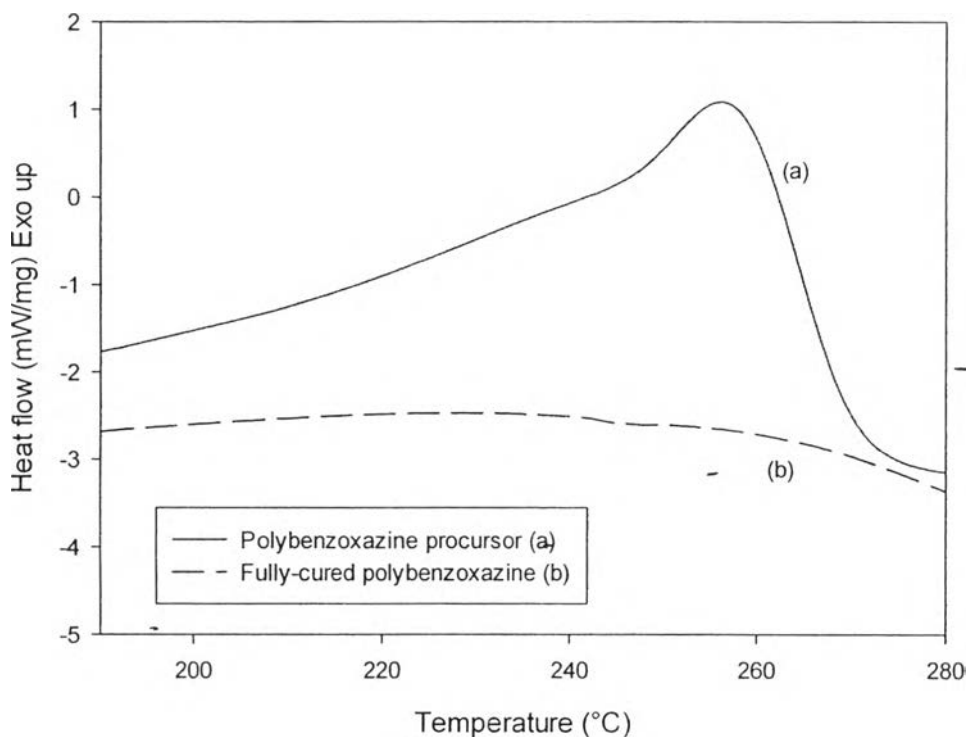
#### *4.3.3.4 Membranes preparation*

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

## **4.4 Results and discussion**

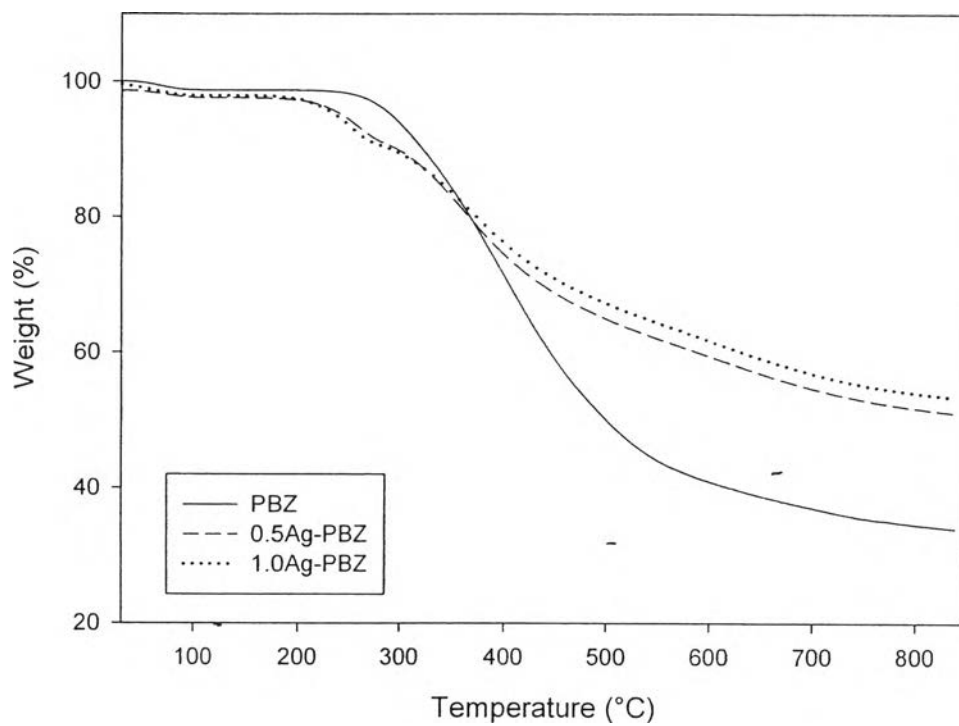
### 4.4.1 Thermal behavior of polybenzoxazine

The thermal behavior of benzoxazine precursor and polybenzoxazine was analyzed by using DSC technique as shown in Figure 4.2. Figure 4.2 (a) shows the exothermic peak of benzoxazine precursor which appears at 200-280 °C, representing the polymerization of benzoxazine precursor by ring-opening of oxazine. For the polybenzoxazine after heat treatment at 220 °C (b), no exothermic peak was found, confirming that the polybenzoxazine was completely polymerized. This result is similar to the work of Takeichi *et al.*

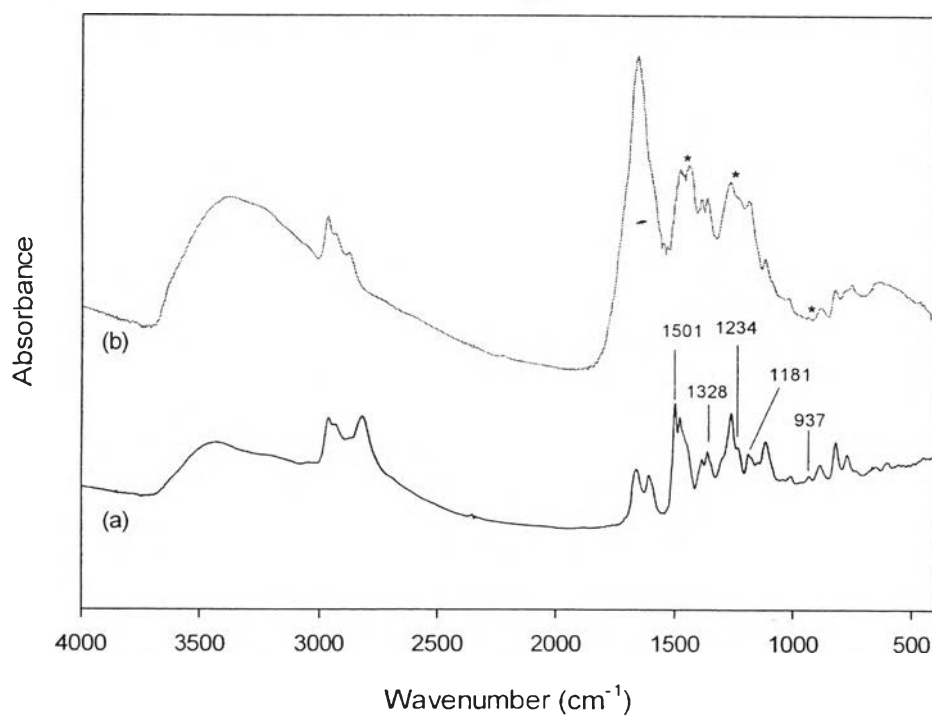


**Figure 4.2** DSC thermograms of (a) the benzoxazine precursor after drying at 80 °C (pre-cured) and (b) after heat treatment at 220 °C (fully-cured).

Figure 4.3 shows the TGA thermograms of polybenzoxazine and polybenzoxazine impregnated with silver nitrate. Polybenzoxazine decomposed at approximately 380 °C. For silver-impregnated polybenzoxazines, they decomposed at 280 °C which lower than pure polybenzoxazine. The possible explanation for this observation might be due to silver ions accepted electron from nitrogen of amine, leading to decrease bond strength of amine. Then, the degradation of the phenolic linkage occurred simultaneously with the degradation of the Mannich base which can be described by work of Low *et al.* (1999). Polybenzoxazine had char yield about 33 weight%. However, when 0.5M of  $\text{AgNO}_3$  was incorporated, the char yield of polybenzoxazine increases significantly (by about 20 weight%), meaning that silver enhances thermal stability of polybenzoxazine due to the complex formation between metal ions and polybenzoxazine, providing that char formation increased. This result is in agreement with the work of Low *et al.* (2006).



**Figure 4.3** TGA thermogram of PBZ (—), 0.5M Ag-PBZ (---), 1.0M AG-PBZ (.....).

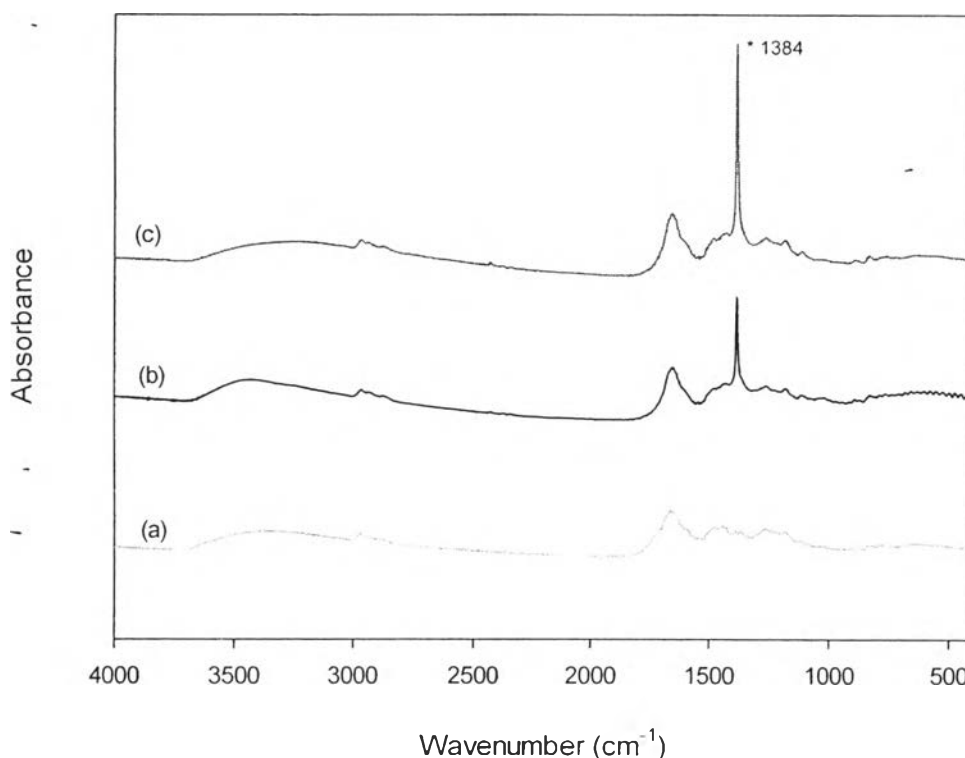


**Figure 4.4** FT-IR spectra of benzoxazine precursor (a) and fully-cured polybenzoxazine (b).



#### 4.4.2 Chemical structure of polybenzoxazine

The benzoxazine precursor was analyzed by FT-IR to confirm the chemical structure. IR spectra of benzoxazine precursor are shown in figure 4.4(a). The asymmetric stretching of C-O-C ( $1234\text{ cm}^{-1}$ ), the asymmetric stretching of C-N-C ( $1181\text{ cm}^{-1}$ ),  $\text{CH}_2$  wagging of oxazine ring ( $1328\text{ cm}^{-1}$ ) were observed. Additionally, the characteristic absorption bands at  $1501\text{ cm}^{-1}$  and  $937\text{ cm}^{-1}$  were assigned to trisubstituted benzene ring and out-of-plane bending vibrations of C-H of oxazine ring, respectively. This confirms that the benzoxazine precursor containing benzoxazine structure in the backbone. After polymerization at  $220\text{ }^\circ\text{C}$ , the intensity of those characteristic absorption bands decreased because of the completed ring-opening polymerization as shown in figure 4.4(b). This result is similar to Katanyoota *et al.* (2010) and Takeichi *et al.* (2005).



**Figure 4.5** FT-IR spectra of PBZ (a), 0.5M Ag-PBZ (b) and 1.0M Ag-PBZ (c).

FT-IR spectra of polybenzoxazine and silver-impregnated polybenzoxazine are compared in figure 4.5. The Schiff base and secondary amide are known to form complex with transition metals. Polybenzoxazines are nitrogen-containing phenolic resins. Significantly, the intensity of the absorption band at  $1384\text{ cm}^{-1}$  increases as increasing the  $\text{AgNO}_3$  concentration as shown in figure 4.5(b) and 4.5(c). This band is assigned to  $\text{CH}_2$  wagging vibration of amine and silver complex, meaning that there were Ag ions incorporated in the polybenzoxazine structure. These results agree with Takeichi *et al.* (2005).

#### 4.4.3 Silver-impregnated polybenzoxazine characterization

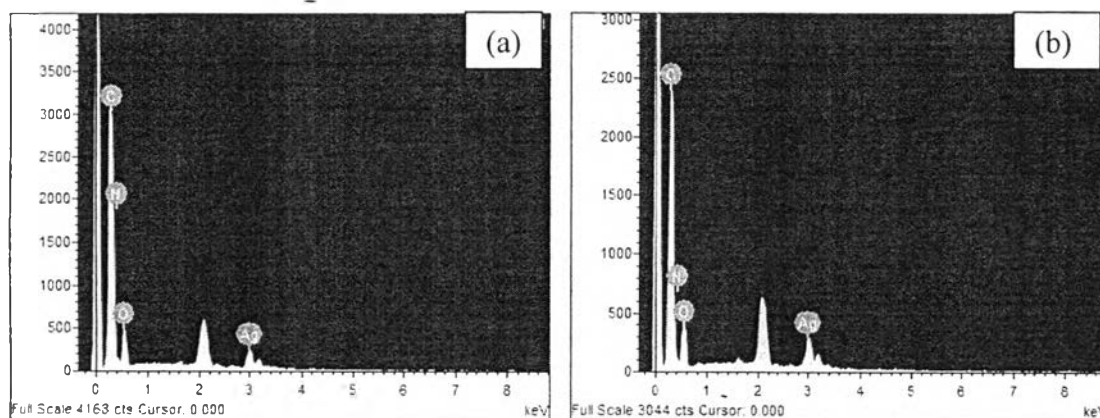
To determine the amount of silver ions impregnated in polybenzoxazine, the element composition was analyzed by SEM-EDX technique. The EDX spectrum shows that silver ions were impregnated in polybenzoxazine. The higher  $\text{AgNO}_3$  concentration, the higher Ag ions were impregnated on polybenzoxazine surface as shown in table 4.1. This results support the results of FT-IR that Ag ions incorporated in polybenzoxazine structure. The XRF principle enables the identification of the elements presenting in the sample and the determination of their mass or concentration. The XRF results indicated the amounts of silver concentration of 0.5M Ag-PBZ and 1.0M Ag-PBZ are approximately 0.061% and 0.095%, respectively.

**Table 4.1** Element composition of silver-impregnated polybenzoxazine

Elements	Weight %	
	0.5Ag-PBZ	1.0Ag-PBZ
C	50.95	49.54
N	18.72	17.72
O	22.72	22.08
Ag	7.61	10.66

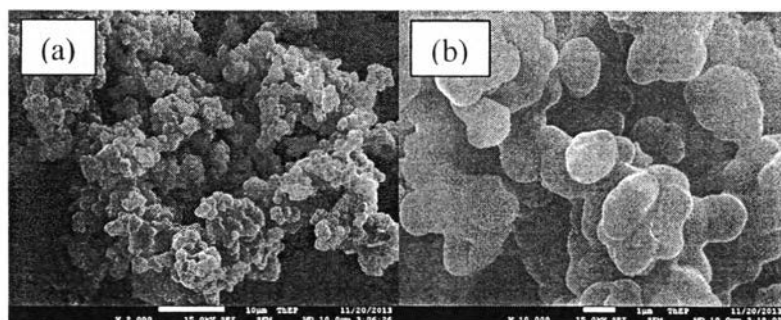
**Table 4.2** Amount of impregnated Ag ions on polybenzoxazine

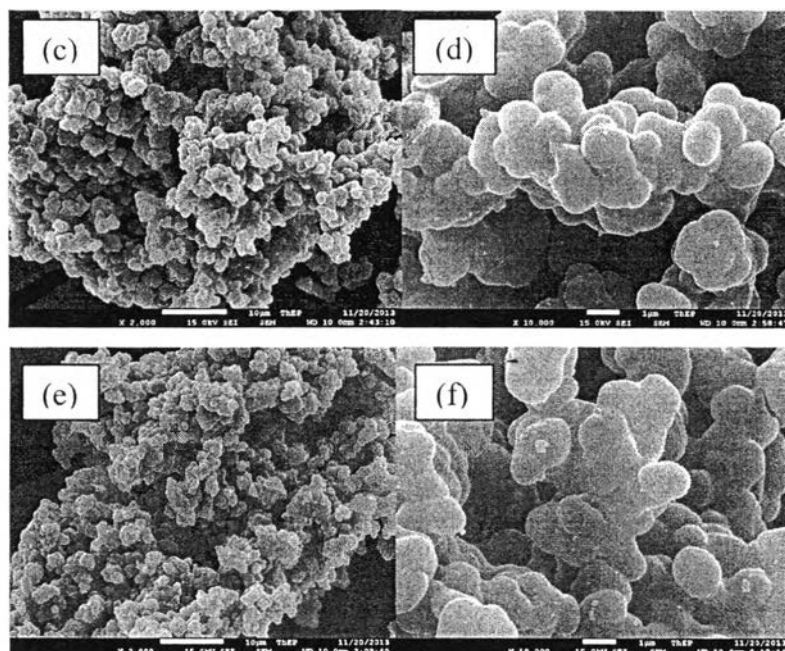
AgNO <sub>3</sub> concentration (Molar)	Ag ions concentration (Molar)
0.5	0.060
1.0	0.168

**Figure 4.6** EDX spectrum of 0.5M Ag-PBZ (a), 1.0M Ag-PBZ (b).

#### 4.4.4 Morphology of polybenzoxazine

The SEM micrographs of polybenzoxazine and Ag-impregnated polybenzoxazine are shown in figure 4.7. The porous structure of polybenzoxazine was obtained from the removal of solvent. In the structure of polybenzoxazine, the solid phase presents a smooth continuous polymer network incorporated with open macropores, similar to work of Thubsuang *et al.* (2012).



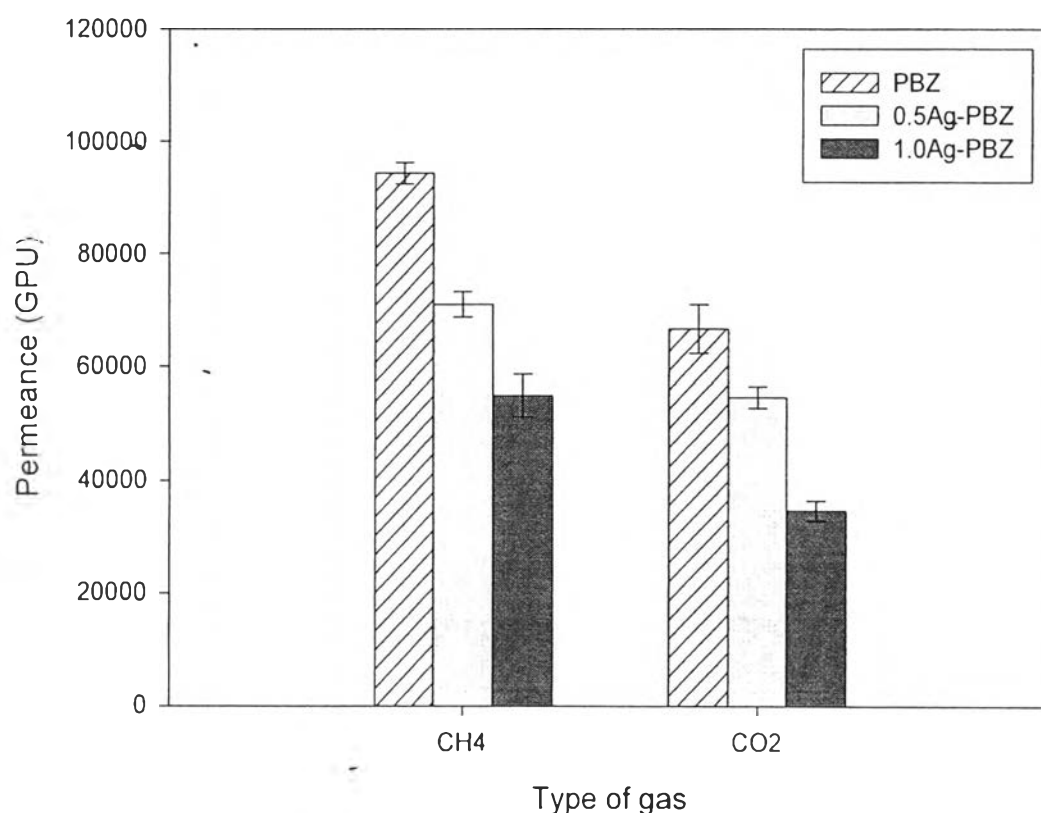


**Figure 4.7** SEM micrographs of PBZ with 2,000X (a) and 10,000X (b), 0.5M Ag-PBZ with 2,000X (c) and 10,000X (d), 1.0M Ag-PBZ with 2,000X (e) and 10,000X (f).

#### 4.4.5 Gas permeability

Neat polybenzoxazine membranes and silver-impregnated polybenzoxazine membranes were tested by single gas experiments at room temperature under trans-membrane pressure of 10 psi. Gas permeability was obtained in sequence of  $\text{CH}_4$  and  $\text{CO}_2$  as shown in figure 4.8. For neat polybenzoxazine membranes,  $\text{CH}_4$  show the highest permeability because  $\text{CH}_4$  is a non-polar gas which is no interaction with the membrane. But  $\text{CO}_2$  permeability is lower than  $\text{CH}_4$  permeability because amine groups in the polybenzoxazine structure can interact with  $\text{CO}_2$ , resulting lower permeability. For silver-impregnated polybenzoxazine membranes, the permeability of both gases decreases with an increase in silver nitrate concentration. This decreasing trend of gas permeability with silver nitrate concentration may be easily understandable because partial permeation pathway blockage of silver ions may lead to a decrease in the gas permeability. However,  $\text{CO}_2$  permeability is also lower than  $\text{CH}_4$  permeability because  $\text{CO}_2$  gas molecule can interact with silver ions. For 1.0M silver-impregnated polybenzoxazine membrane,

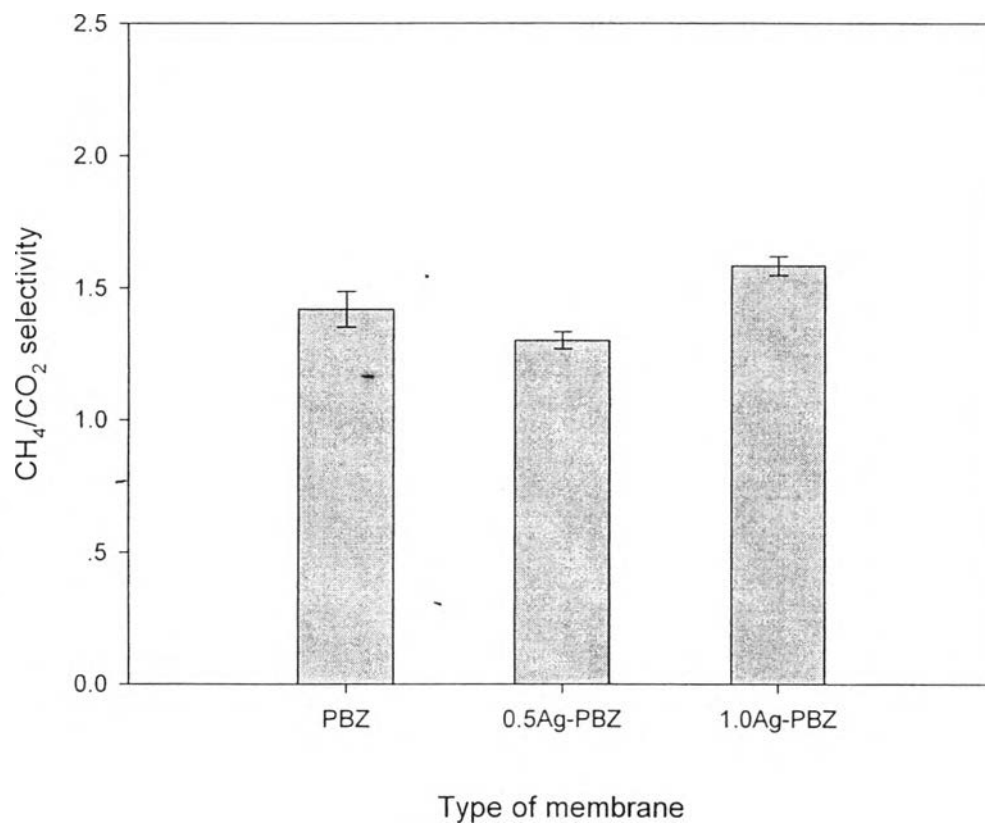
there were not only amine groups which could interact with  $\text{CO}_2$  but also double bond of  $\text{CO}_2$  molecules could react reversibly via  $\pi$ -complex bonding with silver ions, resulting that  $\text{CO}_2$  had the lowest permeability.



**Figure 4.8** Effect of silver nitrate concentrations on  $\text{CH}_4$  and  $\text{CO}_2$  on permeability.

#### 4.4.6 Gas selectivity

$\text{CH}_4/\text{CO}_2$  selectivity of neat polybenzoxazine and silver-impregnated polybenzoxazine are shown in figure 4.9. The results show that 1.0M silver-impregnated polybenzoxazine membranes showed the highest selectivity of  $\text{CH}_4/\text{CO}_2$ , meaning that these membranes allowed  $\text{CH}_4$  to permeate more than  $\text{CO}_2$ . However,  $\text{CH}_4/\text{CO}_2$  selectivity of 0.5M silver-impregnated polybenzoxazine membrane is lower than neat polybenzoxazine membrane because the amount of silver ions was not efficient to enhance selectivity.



**Figure 4.9** Effect of silver nitrate concentrations on CH<sub>4</sub> and CO<sub>2</sub> selectivity.

### Conclusion

Polybenzoxazine were successfully synthesized and impregnated with silver nitrate that used as membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. TGA thermogramme show that the char yield of silver-impregnated polybenzoxazine increase significantly with silver nitrate concentration. FT-IR spectra show the intensity of the absorption band at 1384 cm<sup>-1</sup> increase significantly with increasing the AgNO<sub>3</sub> concentration. For gas separation, 1.0M silver-impregnated polybenzoxazine membranes show the highest selectivity of CH<sub>4</sub>/CO<sub>2</sub> because of  $\pi$ -complex formation between silver ions and CO<sub>2</sub>.

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