



CHAPTER IV

NANOPOROUS CARBON MEMBRANE FOR CO₂ SEPARATION

4.1 Abstract

Polybenzoxazine xerogel membrane for gas separation was prepared via sol-gel synthesis and cost-effective ambient drying. After pyrolysis at 800 °C under nitrogen atmosphere, carbon xerogel was obtained. The Brunauer, Emmett, Teller (BET) surface area of the carbon xerogel film was approximately 360 m²/g. Activation of the carbon xerogels under CO₂ atmosphere and thermal treatment at 900 °C was also investigated in order to compare gas separation performance. The BET surface area of the CO₂ activated carbon xerogels increased approximately 2 times in comparison to the unactivated porous carbon membrane. On the other hand, the BET surface area of the heat treated carbon xerogel film decreased to 110 m²/g due to the re-alignment of the pore structure of carbon. The gas separation measurement showed that polybenzoxazine-derived carbon xerogel exhibited good gas separation performance. It was also found that the gas separation selectivity could be modified by varying the surface treatment of the resulting porous carbon.

Keywords: Polybenzoxazine, Gas separation membrane, Xerogel

4.2 Introduction

The separation of CO₂ from CH₄ is important in natural gas processing because CO₂ reduces energy content of natural gas. In addition, CO₂ is acidic and corrosive in the presence of water which can cause problems when used in the transportation or storage system. Possible processes for CO₂ separation include physical and chemical absorption, membrane separation, gas-solid absorption and cryogenic separation [1]. The use of carbon membranes for gas separation process is very attractive because it consumes lower energy and there is no problem regarding membrane swelling unlike polymeric membrane for gas separation. Moreover it provides better selectivity, thermal stability and chemical stability [2] than those gas separation techniques already exist, such as polymeric membrane and distillation. Polybenzoxazine is one of the candidate materials that used to make carbon membrane due to wide varieties of available phenol and amine derivatives which offer great opportunities in molecular design [3] to tailor effective pore structures for carbon membranes used for separation. It also provides many advantages properties, such as high heat resistance and good flame retardance, excellent dimensional stability, low water absorption and good dielectric properties[4,5]

In this study, polybenzoxazines based carbon membrane for CO₂/CH₄ separation has been prepared by using aniline, bisphenol A and para-formaldehyde as starting materials, following Lorjai et al's work [6] since the resulting porous carbon contained mostly micropores which was suitable for this application. The effects of carbon microstructure, thermal treatment, and acid treatment surface on gas separation efficiency have been investigated.

4.3 Experimental

4.3.1 Materials

All chemicals were used without further purification. Bisphenol-A was purchased from Aldrich, Germany. Aniline was purchased from Sigma. Formaldehyde solution (37% by weight) was purchased from Merck, Germany. *N,N*-Dimethylformamide (DMF) was purchased from Labscan Asia Co., Ltd., Thailand.

4.3.2 Measurements

The FT-IR spectrum of benzoxazine precursor was obtained using a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. DSC analyses were carried out using a Perkin-Elmer DSC instrument. The samples were heated from 30 ° to 300 °C at a heating rate of 10 °C/min under a N₂ atmosphere with a flow rate of 10 ml/min. TG-DTA curve was collected on a Perkin-Elmer Pyris Diamond TG/TGA instrument. The sample was loaded on the platinum pan and heated from 30° to 900 °C at a heating rate of 20 °C/min under N₂ flow of 50 mL/min. HITACHI S-4800 scanning electron microscope was used to observe the surface morphology of polybenzoxazine-based xerogel and carbon xerogel. N₂ adsorption-desorption isotherms were obtained at -196 °C on a Quantachrome Autosorb-1 MP. Samples were degassed at 300 °C for 15 hrs in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The mesopore volume and mesopore surface area were constructed based on Barrett, Joyner and Halenda (BJH) method, using the adsorption branch of the nitrogen isotherm. X-Ray Diffractometer (XRD) was used to study the XRD patterns of carbon membrane. The gas flow pass the membrane will be measured by universal gas flow meter (Agilent Technologies ADM1000).

4.3.3 Methodology

4.3.3.1 *Preparation of Benzoxazine Monomer*

The benzoxazine monomer was synthesized via solventless method proposed by Ishida [7]. Bisphenol-A, aniline and para-formaldehyde were mixed together at a 1:2:4 molar ratio and heated 110 °C for 60 min until the mixture

appeared a transparent pale yellow color. The synthesis reaction of benzoxazine monomer is shown in Figure 4.1

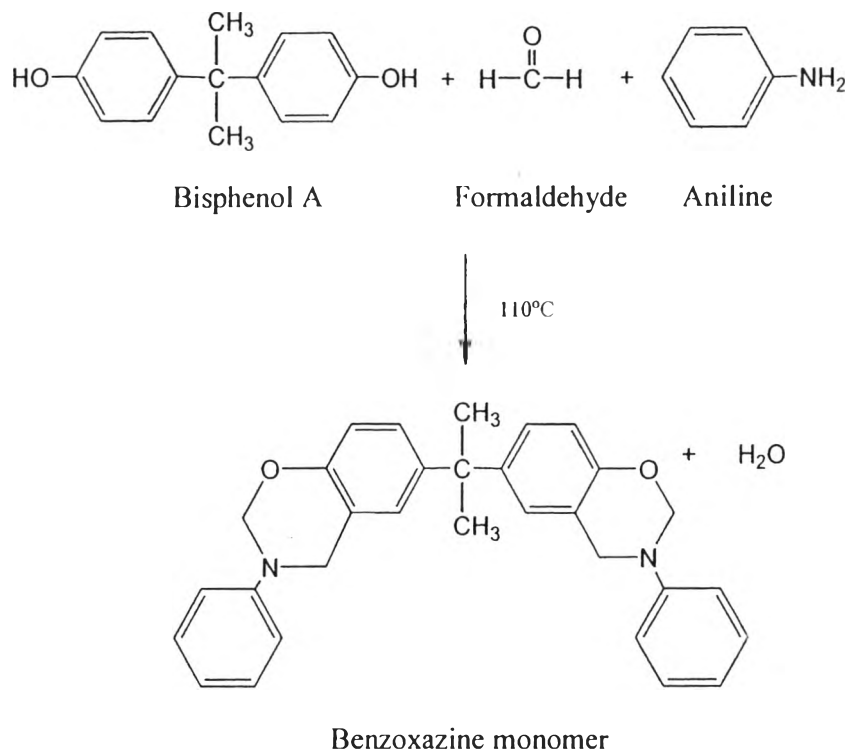


Figure 4.1 Synthesis of benzoxazine monomer

4.3.3.2 Preparation of Polybenzoxazine Xerogel Membrane

Benzoxazine solution was prepared from the benzoxazine monomer using xylene as a solvent at a concentration of 40 wt%. After that, the mixture was transferred into a vial and sealed at room temperature then the temperature was slowly raised with the heating rate of 0.02°C/min to 130 °C for 96 hours in an oven. The attained products which was partially cured benzoxazine xerogel was then cut into disk-shape with a thickness of approximately 2 mm. by diamond saw before drying at ambient temperature and pressure for 2 days to remove xylene from the matrix. Finally the xerogel was fully cured in an oven at 160 and 180 °C for an hour, and 200 °C for 2 hours

4.3.3.3 Preparation of Polybenzoxazine Xerogel-based Carbon Membrane at 800 °C

Polybenzoxazine membranes were pyrolyzed into carbon xerogel membrane under a nitrogen flow rate of 550cm³/min. using the following

ramp cycle: 30-250 °C in 1 hour, 250-600 °C in 5 hours, 600-800 °C in 1 hour, and holding at 800°C for 1 hour.

4.3.3.4 Preparation of Polybenzoxazine Xerogel-based Carbon Membrane at 900 °C

Polybenzoxazine membranes were pyrolyzed into carbon xerogel membrane under a nitrogen flow rate of 550cm³/min. using the following ramp cycle from Lorjai and coworker [6]: 30-250 °C in 1 hour, 250-600 °C in 5 hours, 600-900 °C in 1.5 hour, and holding at 900°C for 1 hour. Here, the carbon xerogel was denoted as CX-xxx where the xxx denotes the pyrolysis temperature.

4.3.3.5 Preparation of Polybenzoxazine Xerogel-based Activated Carbon Membrane

Activated carbon membrane (CX-A) was obtained by pyrolysis of carbon xerogel from 4.3.3.3 in a quartz reactor using the following ramp cycle: 900 °C for 180 min. The system was carried out in CO₂ flow at 550 cm³/min in order to have more surface area.

4.3.3.6 Characteristics of Polybenzoxazine and Carbon Xerogel Derived From Polybenzoxazine

The chemical structure of benzoxazine precursor was characterized by Fourier transform infrared (FT-IR) spectroscopy, which recorded on a Nicolet Nexus 670 FT-IR spectrometer by using KBr pellet technique. The surface area of carbon xerogel and activated carbon xerogels was calculated from nitrogen adsorption isotherms at 77 K, based on the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated with the adsorption data based on the Barret-Joyner-Halenda method (BJH). The surface morphology was characterized using the field emission scanning electron microscope (FE-SEM); the samples were coated with platinum under vacuum prior to investigation.

4.3.3.7 Gas permeability and Selectivity Measurements of their Carbon Xerogel Membrane for Gas Separation.

The membrane is supported on a O-ring which separated the cell into two compartments. The feed was maintained pressure at 20 psi in the cell. The carbon dioxide and methane gas were used as the feed respectively. A Teflon gasket was applied on the membrane. After the membrane was placed in the

chamber, then the two compartments were fixed together to prohibit the leakage. The area of the membrane in contact with the gas is 1.13 cm^2 . Then the gas flow pass the membrane will be measured by universal gas flow meter. Figure 4.2 shows the scheme of the gas separation measurement.

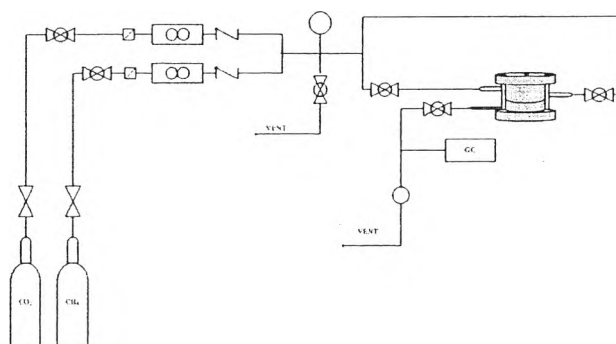


Figure 4.2 The scheme of the gas separation measurement.

4.4 Results and Discussion

4.4.1 Characterization of Polybenzoxazine-based Carbon Xerogel

The chemical structure of benzoxazine precursor was examined by FTIR spectra as shown in Figure 4.3. The asymmetric stretching of C–O–C (1224 cm^{-1}) and C–N–C (1176 cm^{-1}) and the CH_2 wagging of oxazine (1317 cm^{-1}) were observed. Additionally, the characteristic adsorptions assigned to trisubstituted benzene ring at 1480 cm^{-1} , C=C unsaturated aromatic at 1653 cm^{-1} and out of plane bending vibrations of C–H at 938 cm^{-1} were also observed, indicating that the precursor containing benzoxazine structure was obtained. On the other hand, the intensity of adsorption band at 1480 cm^{-1} was decreased while the band at 1653 cm^{-1} were increased confirming the polymerization of benzoxazine precursor. These results also correspond to the result reported by Takachi and coworkers [5] who suggested the completion of ring-opening polymerization of polybenzoxazine was attained when these adsorption peaks were observed.

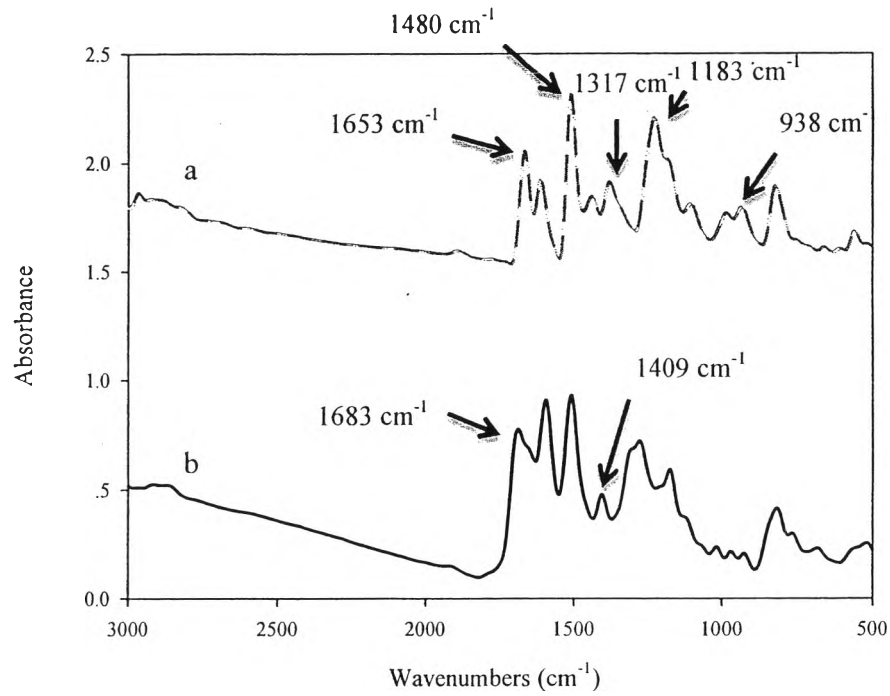


Figure 4.3 FT-IR spectrum of (a) benzoxazine monomer and (b) polybenzoxazine.

DSC was used to investigate the curing behavior of the benzoxazine monomer. The measurement was conducted with a heating rate 10 °C/min.

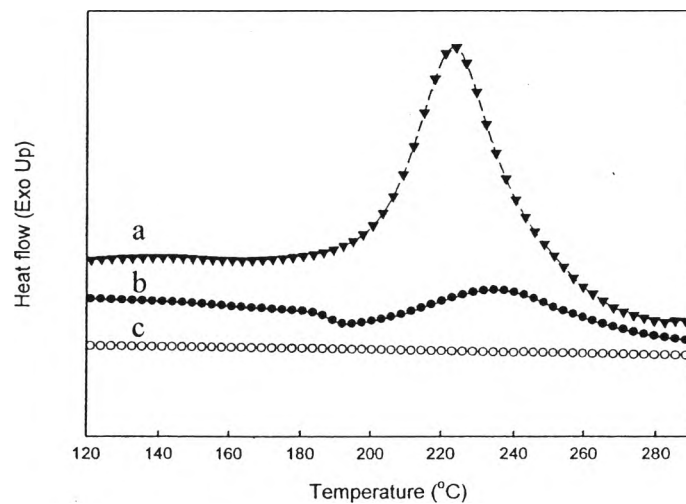


Figure 4.4 DSC thermograms of (a) benzoxazine monomer, (b) polybenzoxazine xerogel before and (c) after step cured.

From the DSC thermograms, the heat of reaction determined from the area under the exothermic peak was 292.75 J/g for the benzoxazine monomer. After heated at 130 °C for 96 hours, the area was reduced to 62.98 J/g indicating that the curing conversion was 78.5% and the exothermic peak of the xerogel after step curing was disappeared implying that the curing reaction of the polybenzoxazine xerogel was completed [6]. Furthermore, as clearly seen in this figure, the exothermic peaks at around 180–300 °C of the xerogels which were step cured disappeared. This evidence could imply that the curing reaction of polybenzoxazine xerogels became practically complete.

TGA was used to investigate the thermal properties of Ba-a polybenzoxazine xerogel

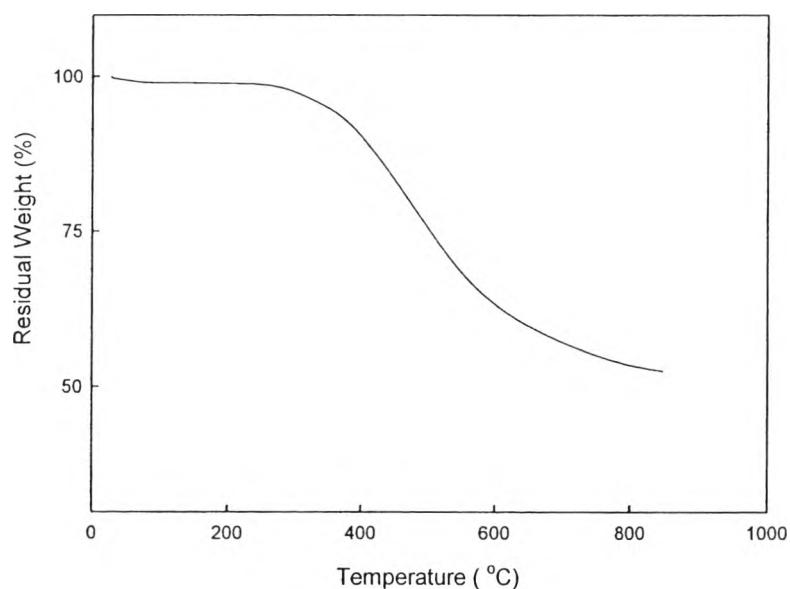


Figure 4.5 TGA thermogram of polybenzoxazine xerogel under nitrogen atmosphere

The TGA thermogram of the polybenzoxazine is shown in Figure 4.5. It began to lose weight at 250 °C, and the maximum weight loss rate was observed in the temperature range of 250 to 600 °C, which was caused by the production of a large amount of volatile materials. The rate of weight loss became slower after 600 °C and an obvious weight loss could not be observed beyond 800 °C.

Moreover, from the thermo-gram, it can be seen that the degradation temperature at 5% weight loss and the char yield at 800 °C of the synthesized polybenzoxazine was 310 °C and 55 wt%, respectively when compare with BA-teta, BA-tepa and BA-hda as shown in table 6.1, BA-a show higher char yield due to the presence of aromatic groups. According to this result, it can be inferred that the polybenzoxazine derived from aniline is a one candidate material to produce a carbon membrane.

Table 4.1 Thermal stability of the polybenzoxazine membranes.

Type of benzoxazines	% Char yield	Reference
Poly(BA-hda)	23	[8]
Poly(BA-teta)	21	[8]
Poly(BA-tepa)	20	[8]
Poly(BA-a)	55	This study

SEM micrographs of polybenzoxazine xerogel and polybenzoxazine derived carbon xerogel are shown in Figure 4.6(a)-(d).The structure of the organic xerogel and CX-800 at °C exhibits the network of 3D-interconnected particles with continuous opened-macropore as shown in Figure 3(a) and (b), respectively. In case of the heat-treated carbon xerogel at 900 °C (figure3c) the surface area decrease drastically due to the agglomerated of 3D-interconnected particle and structure realignment as confirmed later by the XRD technique

In case of the activated of carbon xerogels prepared by heat treated carbon aerogel with CO₂ at 900 °C, the denser mesoporous structure was obtained as shown in figure 3(d). The micrograph also shows similar morphology compared with the unactivated one.. However, the micropores are generated cause higher surface area and slightly lower average pore size[9]We will discuss this rearrangement in the next section.

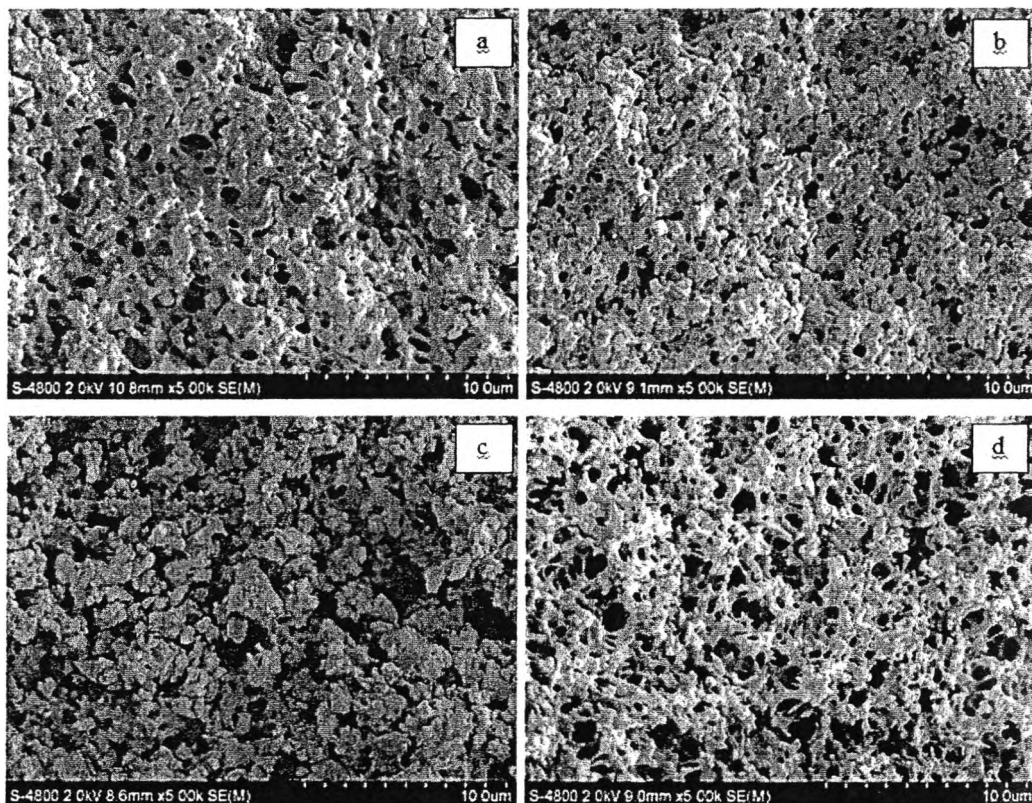


Figure 4.6 SEM micrographs of (a) Polybenzoxazine (b) carbon xerogel 800°C (c) carbon xerogel 900°C (d) activated carbon xerogel

Figure 4.7(a),(b) shows the X-ray diffraction (XRD) pattern of polybenzoxazine-based carbon xerogel 800 °C and 900 °C. The intensity of the peak at $2\theta=23^\circ$ and 43° increase when the pyrolysis temperature increase. The diffraction patterns of the samples show the existence of the peaks at 23° and 43° corresponding to (d002) and (Lc002) which confirm the graphite with rhombohedral cubic structure[10], suggesting that at 900 °C can be induced polybenzoxazine-base carbon xerogel to have more graphite structure.

The structure of material is the one that has an effect on the surface area, pore size directly. The table 4.2 shows the physical characteristics of polybenzoxazine base carbon xerogel. The surface area of carbon xerogel 800 °C is $335 \text{ m}^2/\text{g}$ with average pore size 2.3 nm, the surface area of carbon xerogel 900 °C is $110 \text{ m}^2/\text{g}$ with average pore size 5.08 nm. Moreover, pore volume reduce from 0.19

to 0.14. We found that when the pyrolysis temperature was increased, the BET surface area and average pore size of the derived carbon xerogel decreased and increased respectively. It might be from the rearrangement of unstructured to graphite structure combine with shrinkage of the structure. However, the surface area of AC carbon xerogel(CX-A) increased up to 2 times from carbon xerogel 800 °C and the pore volume increased up to 2 times from 0.19 to 0.41., depending on the exposure temperature [11].

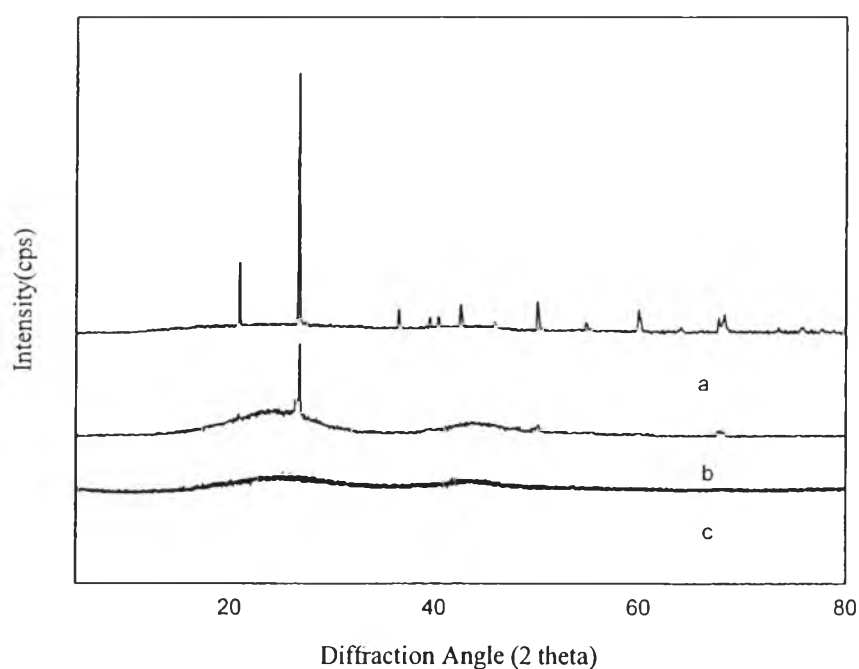


Figure 4.7 X-ray diffraction (XRD) pattern of polybenzoxazine-base carbon xerogel (a) 900 °C (b) 800 °C and (c) activated carbon xerogel

Table 4.2 The physical characteristics of polybenzoxazine base carbon xerogel

Material	Surface area (m ² /g)	Average pore size (nm)	Micro Pore volume (cc/g)	Meso pore volume (cc/g)	Micro porosity(%)	O ₂ wt.%
CX 800	335	2.30	0.17	0.015	72.5	0
CX 900	110	5.08	0.06	0.018	42.8	0
CX-A	729	2.24	0.36	0.03	90.7	16.3

4.4.2 Gas Permeation

All of carbon xerogel membranes were tested in the single gas measurements. The permeability of these membranes was obtained in the sequence of CH₄ and CO₂ after in steady state by let gas pass for 1 hour at 25 °C temperature and 20 psi. The permeability and selectivity of CO₂ and CH₄ of their carbon xerogel are shown in Figure 4.8 and Table 4.3.

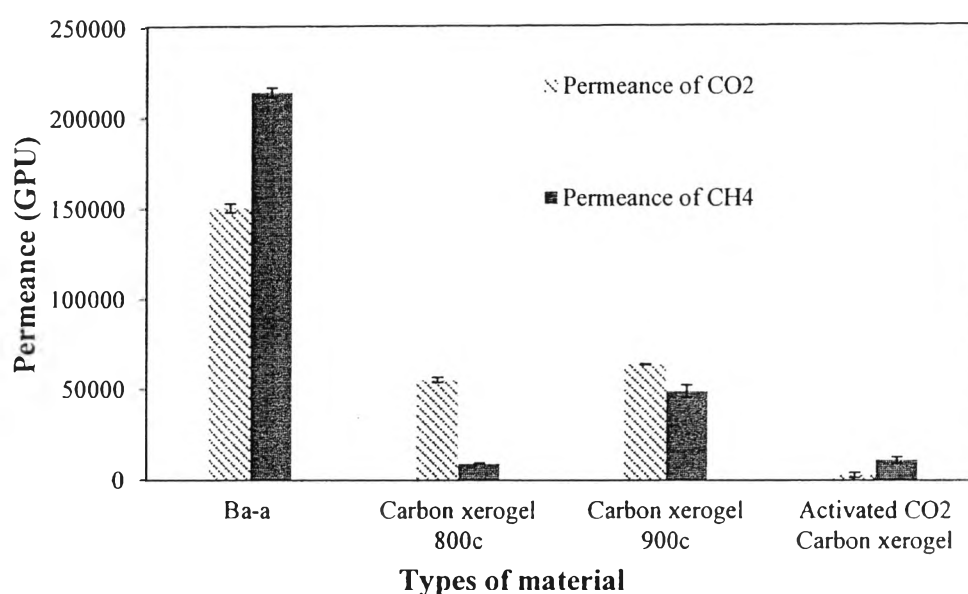


Figure 4.8 CO₂ and CH₄ permeability of materials.

4.4.2.1 The Effect of Pyrolysis Temperature on The CO₂ and CH₄ Permeability and Selectivity.

The CO₂ and CH₄ permeance and selectivity of carbon xerogel at different pyrolysis temperature are shown in Figure 4 and table 2. For CX-800, the CO₂/CH₄ selectivity is 5.94. The permeance of CO₂ was higher than that of CH₄ due to its larger amounts of micropore, that allowed gas molecules to pass through with different rates depended on the kinetic diameter of gas molecules. This carbon was selective for CO₂ because of CO₂ preferentially adsorbed, and also diffused faster than CH₄ molecules[12,13]. For CX-900 when compare with CX-800, the selectivity dropped from 5.94 to 1.30 while the permeance of both gas increased. This result might be from the rearrangement of amorphous structure to graphite structure and the

agglomeration of 3D-interconnected particles. This result also correspond to the results from SAA and XRD.

Table 4.3 Permeability and selectivity values for carbon membranes using a driving pressure of 20 psi.

Materials	Permeability (Barrel)		Selectivity	
	CO ₂	CH ₄	S _{CO₂/CH₄}	S _{CH₄/CO₂}
Ba-a polybenzoxazine	1.505	2.142	-	1.42
Carbon xerogel 800 °C	0.552	0.093	5.94	-
Carbon xerogel 900 °C	0.640	0.491	1.30	-
Activated carbon xerogel	0.029	0.112	-	3.79

4.4.2.2 The Effect of CO₂ Treated on the CO₂ and CH₄ Permeability and Selectivity.

Generally gas separation membrane usually allows the smaller molecule gases to pass through while the bigger molecule are obstructed by molecular sieves or surface diffusion/selective adsorption. In this part we tried to fabricate membrane that capture small molecules while the larger molecule can pass through. For BA-a derived xerogel, the permeance of CH₄ is higher than permeance of CO₂ because polybenzoxazine tends to form physical interaction (dipole-dipole) between O atom in the main chains and CO₂ gas molecule. This interaction resulting in obstructed other CO₂ molecules to pass freely though polybenzoxazine membrane. The CH₄/CO₂ selectivity of BA-a derived xerogel was 1.42. In the case of CX-A, the oxygen-containing functional groups was generated[11] in addition to the micropores structure. This combination resulted in increase of CH₄/CO₂ selectivity from 1.42 to 3.79 when compared with BA-a derived xerogel membrane

Table 4.4 Performance of the polymer membranes in CO₂/CH₄ separation

Membrane	Conditions studies			CO ₂ Permeability (Barrer)	CH ₄ Permeability (Barrer)	CO ₂ /CH ₄ Selectivity	Reference
	Temperature (°C)	Pressure Δ P (psia)	Thickness of membrane (μ m)				
PDMS	20	low pressure vacuum	85-102	25.7	7.40	3.5	[14]
Poly(St-co-MAH- graft-DMS)	20	low pressure vacuum	85-102	29.8	7.52	4.0	[14]
41 wt% PDMS– 6FDA–6FpDA–20 wt% Zeolite L	35	58.78	152.4 \pm 12.7	199.41	41.61	4.79	[15]
Polybenzoxazine based carbon polybenzoxazine base carbon xerogel membrane 800 °C	25	20	1000	0.55	0.09	5.94	this work

4.4.2.3 Comparison of Gas Separation Performance

The CO₂/CH₄ selectivity of carbon xerogel 800 °C was compared with previous works as shown in Table 2. The performance of our membranes shows good results with pretty good selectivity. Previous work presented rather low selectivity but high permeability [14,15].

4.5 Conclusions

Carbon xerogel membranes were successfully synthesized from bisphenol-A, formaldehyde and aniline. CX-800 showed the highest CO₂/CH₄ selectivity when compared with CX-900 since the rearrangement of structure and the agglomeration of 3-D network particles causing lower surface area and larger average pore size CX-A, obtained from the carbonization of carbon xerogel under carbon dioxide atmosphere at 900 °C for 3 hours, showed the highest CH₄/CO₂ selectivity when compared with polybenzoxazine xerogel due to the oxygen-containing functional groups on the carbon surface.

4.6 Acknowledgements

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4.7 References

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