CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Gas Separation Membrane

The separation of CO_2 from CH_4 is one of the important process in many industrial areas including flue gas treatment, natural gas processing, biogas purification and enhanced oil recovery. (Chun *et al.*, 2003) CO_2 in flue gas should be removed because it causes global warming. There are several techniques for gas separation such as membrane, absorption, adsorption and cryogenic process.

Presently, membrane gas separation is considered to be a proven technology, and widely used in a broad range of applications since it has many advantages such as low capital investment, simplicity and ease of installation and operation, low maintenance requirements, low weight and space requirements, and high process flexibility.

For CO_2 gas separation, membrane materials should have the following characteristics: (1) inherently high permselectivity for CO_2 and CH_4 gas pair and (2) immunity to plasticization induced by CO_2. The CO_2-induced plasticization usually results in a severe deterioration of membrane separation performance (Hui *et al.*, 2007). Moreover, Petropoulos (Petropoulos *et al.* 1992) recognized that CO_2 acted as a plasticizer with high level of CO_2 concentration.

Due to most of the membrane materials swell upon sorption of CO_2 and accelerating the permeation of CH_4. Thus, it needs to develop a membrane for CO_2/CH_4 gas separation.(Ismail *et al.*, 2002)

Comparing of CO_2 and CH_4 molecule, CO_2 is a longer and slender molecule than CH_4 which is a more compact molecule with a slightly larger cross-section. The differences in the molecular dimensions of the two molecules can be exploited by allowing them to adsorb, and subsequently diffuse, across zeolite membranes. From a practical point of view it is advantageous to use a membrane separation process in which CH_4 is retained on the high pressure side and CO_2 permeates selectively across to the membrane (Balamurali *et al.*, 2007).

Developing new membrane morphologies and blending with low molecular-weight additives may be promising alternatives to increase the polymeric membrane performances. Mixed matrix membranes are expected to combine the separation properties of polymers with those of fillers to obtain membranes with better separation performances than pure polymeric membranes. With some reports of improvements in separation performance associated with adding zeolites to rubber polymers (Duval *et al.*, 1993), focusing on mixing zeolites with glassy polymers. Due to the weak contact between rubbery polymers and zeolites at their interfaces resulted in the presence of voids between the polymer and zeolite. This reduced the separation performance of the composite membrane relative to the pure polymer. Efforts to eliminate these voids usually focused on using a coupling agent to improve interactions between the polymer and zeolite (Yong *et al.*, 2001), adding a plasticizer to increase the flexibility of the polymer matrix or by chemically linking the two components together.

Süer (Murat *et al.*, 1994) studied the permeation rates of N_2, O_2, Ar, CO_2 and H_2 of polyethersulfone (PES) membranes filled with zeolites 13X and 4A. They concluded that both permeabilities and selectivities were increased at high zeolite loading (42–50 wt.%). Permeability were decreased first and then increased with increasing zeolite loading

To improve separation performance and to solve plasticization problem, carbon membrane prepared by sol-gel method, which can control pore size to separate CO_2 and CH_4 without plasticization. The carbon molecular sieve membranes (CMSMs) was prepared by pyrolysis of P84 polyimide precursor. CMSMs were carbonized at three different pyrolysis (Tin *et al.*, 2004) temperatures of 550, 650 and 800°C. From the results showed high pyrolysis temperature give more selective but less permeable CMSMs. The carbon membrane pyrolyze at 800°C had excellent ideal permeation properties.

For the mix gas system, permeability of CH_4 for mixed gas system decreased when compared with pure gas system. Moreover, the pure gas measurement underestimated the separation efficiency of carbon membranes. This was owing to the restriction of CH_4 penetration by the presence of absorbed CO_2 molecules in carbon membrane's micropores.

2.2 Benzoxazine

Polybenzoxazines are a newly developed type of addition cured phenolic system, which have attracted the interest of many researchers during the last decade because the attractive properties of polybenzoxazines such as near-zero volumetric change upon curing, low water absorption, and for some polybenzoxazines, T_g much higher than curing temperature, high char yield, no strong acid catalysts required for curing, and release of no toxic by-product during curing. The molecular structure of polybenzoxazines offers great design flexibility, which allows tailoring the properties of the cured materials for a wide range of applications. (Ghosh et al., 2007) These benzoxazines were first synthesized by Holly and Cope (Holly et al., 1994). No further details about structure and properties were included. A benzoxazine precursor based on bisphenol A, formaldehyde, and aniline, was synthesized following the general method outlined in figure 2.1 (Ishida et al., 1995)
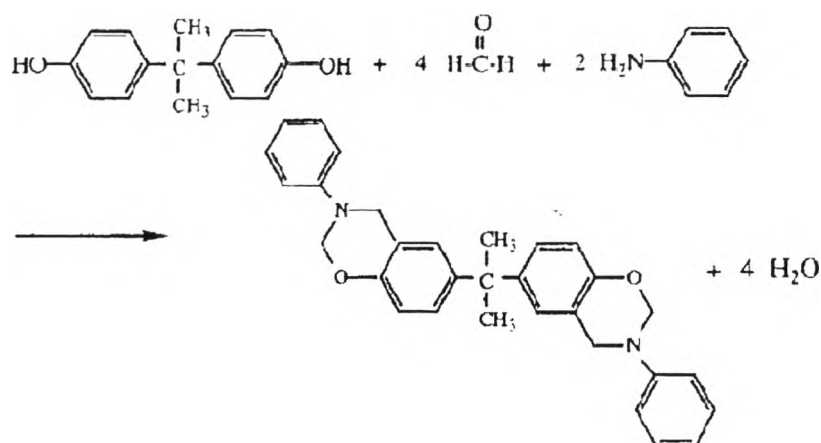

Figure 2.1 Schematic drawing of first synthesize of benzoxazine

Then, polybenzoxazines are formed by the ring-opening of the cyclic monomers only by heat treatment without any catalyst and without generating any by-product (figure 2.2) (Burke et al., 1950)
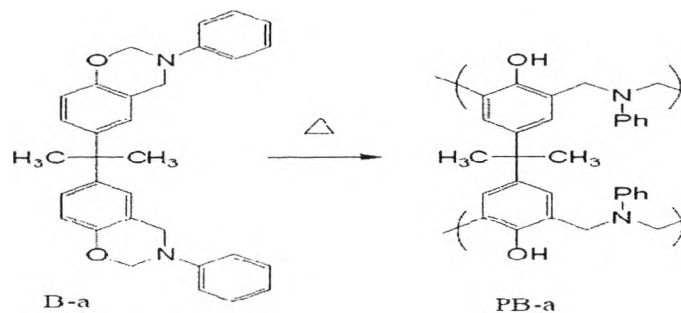
Figure 2.2 Schematic drawing of ring-opening of cyclic monomers

2.2.1 Chemical Methodologies for Synthesis of Benzoxazine Precursor

Generally, benzoxazine monomer are synthesized from mono/diphenols , aliphatic/aromatic mono/diamines and formaldehyde. Holly and Cope discovered the chemistry for the aromatic oxazines in 1944 using phenols, formaldehyde and amines via Mannich reaction Later (Holly *et al.,* 1994), *Burke et al.,* (1950, 1952) found the benzoxazine ring usually reacted with the free ortho positions of a phenolic compound and form Mannich-bridge with phenolic. After that, they systhesized Mannich condensation via a solvent proceed by firstly amine was added to formaldehyde at low temperature to form an N,N-dihydroxymethylamine derivative product which then reacted with the active hydrogen of the hydroxyl group and ortho position of the phenol at a higher temperature to form the oxazine ring as shown in figure 2.3
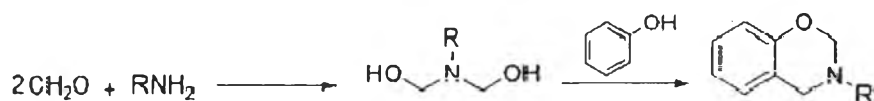

$$2CH_2O + RNH_2 \longrightarrow$$

Figure 2.3 Schematic drawing of oxazine ring formation

This synthesis required large amount of solvent and the poor solubility of the precursors was the disadvantage when using solvent synthesis technique. The use of an organic solvent also increased the cost of the products and caused environmental problems. Additionally, the solvent residue in the precursors also caused

problems during processing of the benzoxazine resins. To prevent these shortcomings, Ishida (Ishida *et al.,* 1996) developed a solventless synthesis.

Since the low molecular weight benzoxazines was obtained after formation of only oligomeric structure from mono amine and phenol, high molecular weight polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde in figure 2.4(Takeichi *et al.,* 2005).
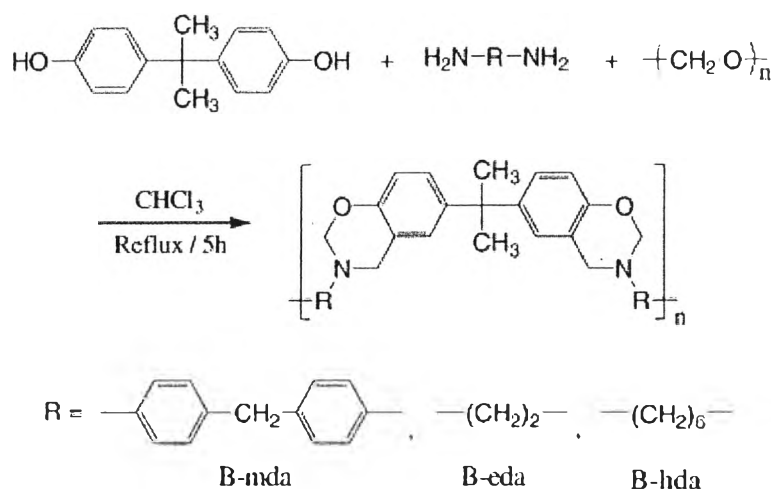

Figure 2.4 Schematic drawing of high molecular weight benzoxazine

The toughness of the crosslinked polybenzoxazine films from the high molecular weight precursors was highly enhanced compared with the cured film from the typical low molecular weight monomer , exhibited the highest strength and modulus and higher elongation at break. Additionally, these polybenzoxazine thermosets showed excellent thermal stability. (Takeichi *et al.,* 2005), Sorina et *al.,*(2007) synthesized difunctional benzoxazine monomer ;bis(4-benzyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane from a bisphenol (bisphenolA or bisphenol F), an amine (benzylamine or cyclohexylamine), and formaldehyde as shown in figure 2.5
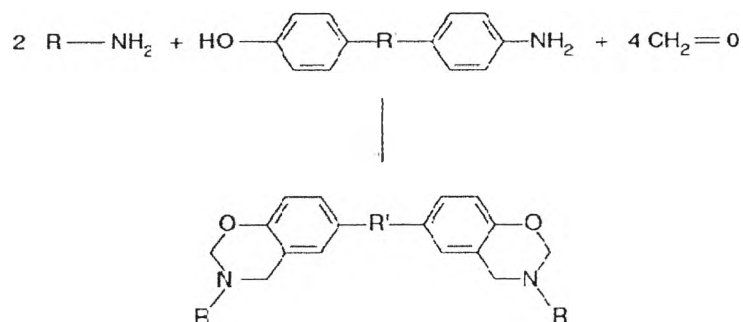
$$2\ R\text{—}NH_2\ +\ HO\text{—}\langle\text{benzene}\rangle\text{—}R\text{—}\langle\text{benzene}\rangle\text{—}NH_2\ +\ 4\,CH_2{=}O$$

$$\downarrow$$

(difunctional benzoxazine monomer structure: O—⟨benzene⟩—R'—⟨benzene⟩—O with N–R groups)

Figure 2.5 Schematic drawing of difunctional benzoxazine monomer.

2.3 Improvement Properties of Polybenzoxazine

There are still some shortcomings of polybenzoxazine; the cured materials are brittle. Moreover, their brittleness caused polybenzoxazine derived from monomers cannot be easily processed into thin films (Kayanomori *et al.*, 2009). To improve mechanical properties and reducing polymerization temperature , many methods have been investigated. Agag *et al.*, (2000) showed that the onset of the temperature of the ring opening of B-a in the presence of OMMT to form polybenzoxazine–OMMT Nano composites occurred at relatively low temperatures in comparison with neat B-a polybenzoxazine due to the catalytic effect of the OMMT surface on the ring-opening polymerization.

Another way to improve mechanical and thermal properties are was to prepare polybenzoxazine composites. such as, blending of epoxy resins with polybenzoxazine to the hydroxyl groups on the polybenzoxazine reacted with epoxy resins providing additional crosslinking points in the resulting network structure.(Agag *et al.*, 2002) Moreover , the incorporation of epoxy in the polybenzoxazine matrix resulted in an increase in T_g of the materials over that of pure polybenzoxazine. It was also reported that T_g was reduced with increasing molecular weight of epoxy. The crosslinking density ofthe network played an important role in determining the thermal properties of the material (Rao *et al.*, 2005). L. Jin *et al* (2010) improved thermal stability and processibility of polybenzoxazine by introducing maleimide group in to benzoxazine, namely poly bis(benzoxazine-maleimide), resulted in an

increased char yield and glass-transition temperature without increasing the viscosity of the monomer significantly.

2.4 Carbon xerogel

Carbon xerogels are porous materials that highly sensitive to the conditions in which they are synthesized. They are very easy to tailor in terms of shape, porous texture and surface chemistry (Kang *et al.*, 2008).These features, along with their very low inorganic matter content, make them more suitable for use in super capacitors than traditional activated carbons. Moreover, they have a low mass density and a high electrical conductivity which also make them ideally appropriate for use in super capacitors (Kang *et al.*, 2008).

Carbon xerogels can be obtained by different procedures *(*Zubizarreta *et al.*, 2008), but the preparation basically consists of three steps: (i) gel synthesis involving the formation of a three-dimensional polymer in a solvent followed by a gelling process, (ii) gel drying, in which the solvent is removed to obtain an organic gel, and finally (iii) pyrolysis under an inert atmosphere to form the porous carbon material, i.e. the so-called carbon xerogel.

The meso- or macro porosity formed using the synthesis is barely altered during thermal stabilization (i.e. the pyrolysis step). The micro porosity created during the pyrolysis can be increased through an activation process. These carbon materials are constituted of interconnected sphere-like nodules, whose size can be controlled by the synthesis conditions. Hence, the size of the voids between the nodules can be tailored (Zubizarreta, 2008; Conceicao, 2009).

2.5 Gas Separation System

A schematic diagram of the system used to carry out the gas separation experiments is shown in Fig 2.6. The membrane is supported on a O-ring which separated the cell into two compartments. The feed was maintained pressure at 2 bar 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 measure by universal gas flow meter (Agilent Technologies ADM1000)
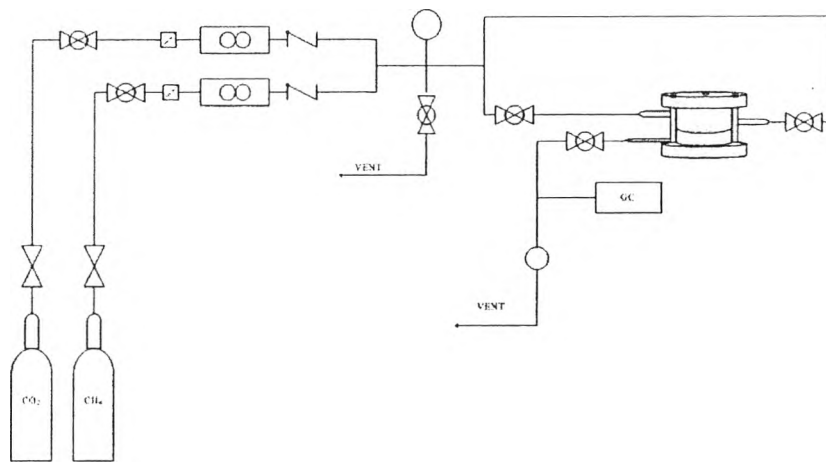

Figure 2.6 Experimental set up for the gas separation apparatus.

2.6 Gas Permeation Measurements

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 1:

$$S_{A/B} = \frac{P_A}{P_B} \tag{1}$$

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

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

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

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

(1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm Hg = 7.5×10^{-18} m^2 s^{-1} 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 (psi)