



CHAPTER II

LITERATURE REVIEW

The separation of carbon dioxide from methane in the process of natural gas and landfill gas treatment is essential to reduce pipeline corrossions induced by acid CO₂ gas as well as to produce high-purity energy products. To meet pipeline requirements, CO₂ must comply with such a concentration specification (< 2%). Available techniques for natural gas separation include membrane, absorption, adsorption, and cryogenic distillation. Membrane processes have been proven to be technically and economically superior to other competing technologies in many industrial applications. This superiority is explained by many advantages of membrane separation technology, which include low capital investment, simplicity and ease of installation and operation, low maintenance requirements, low weight and space requirements, and high process flexibility.

The membrane material for natural gas separation should possess the following characteristics: (1) inherently high permselectivity for CO₂ and CH₄ gas pair and (2) immunity to plasticization induced by CO₂. The CO₂-induced plasticization usually results in a severe deterioration of membrane separation performance (Li *et al.*, 2007).

2.1 Gas Transport in Membranes

Membrane morphology may determine the transport mechanism and therefore affects the separation performance strongly. The membranes usually have three types of morphologies: dense, asymmetric and composite. Dense membranes are homogenous films of a single polymer layer, whereas the asymmetric membranes consist of a dense top layer supported by a porous sublayer. In composite membranes, both layers may originate from different materials (Şen *et al.*, 2007).

2.1.1 Solution-Diffusion Model

Mass transport behaviour through a dense, selective polymeric membrane has been thoroughly investigated experimentally and theoretically in the last 40 years. It is well known that the penetrant transports through a glassy polymer

membrane is understood to proceed by a solution–diffusion mechanism, which takes place in three successive steps (Wijmans *et al.*, 1995): (1) the sorption of the penetrant in the polymer film; (2) the diffusion of the penetrant through the polymer film; and (3) the desorption at the opposite interface.

This solution–diffusion model is widely used in the gas separation applications to control the permeation of different species. The chemical potential gradient across the membrane is expressed as a concentration gradient but not a pressure gradient. A quantitative measurement of the amount of mass transported through the polymeric membrane is characterized by the permeability. According to the solution–diffusion model, the permeability is a product of a thermodynamic factor, called the solubility coefficient S_i , and a kinetic parameter, called the diffusion coefficient D_i .

$$P_i = [D_i][S_i]. \quad (2.1)$$

The ability of a membrane to separate a gaseous mixtures of i and j in a single–stage membrane process may be characterized by the ideal permselectivity, α , which is defined by:

$$\alpha_{ij} = [P_i]/[P_j], \quad (2.2)$$

where P_i and P_j are the permeabilities of pure gases i and j , respectively (Ismail *et al.*, 2002). The natural gas stream is available at high pressures of a few megapascals, and can be considered to be primarily methane (CH₄). CO₂ is a longer, slender molecule; CH₄ is a more compact molecule with a slightly larger cross–section. The subtle differences in the molecular dimensions of the two molecules can be exploited by allowing them to adsorb, and subsequently diffuse across zeolite–filled polymeric membranes. From a practical point of view, it is advantageous to use a membrane separation process in which CH₄ is retained on the high pressure side and CO₂ permeates selectively across the membrane (Krishna *et al.*, 2007).

2.2 Membrane Materials

2.2.1 Polymeric Membranes

Kim *et al.* (2001) prepared pore-filled membranes by using porous polyacrylonitrile membrane as a support and methoxy poly(ethylene glycol) acrylate (MePEGA) as a filler by UV-irradiated photografting. They achieved high CO₂/N₂ permselectivity (32.5) with very low CO₂ permselectivity (5.65×10^{-4} Barrer) from this pore-filled membrane at a temperature of 30 °C.

Li *et al.* (1998) fabricated poly(ethylene glycol) (PEG)/cellulose acetate (CA) blended membranes for gas permeation studies. The apparent solubility coefficients of CO₂ were reduced by blending PEG20000 (average molecular weight of 20,000). The blended membranes containing PEG exhibited high apparent CO₂ diffusivity coefficients, resulting in high permeability coefficients for CO₂ when compare with that of the pristine CA membrane. They claimed that the flexible main chain of PEG20000 in the amorphous domains in the blends permitted the large penetrants, CO₂, and CH₄ to diffuse easily through the blended membranes, leading to higher permeance of CO₂, and CH₄ relative to that of N₂. Hence, the CO₂/CH₄ selectivity decreased by blending of PEG20000 with CA.

2.2.2 Mixed Matrix Membranes (MMMs)

Mixed matrix membranes (MMMs) have recently emerged as a promising material for gas separation. They are obtained by embedding a filler material such as carbon or zeolites acting as molecular sieves into a polymer matrix. MMMs are expected to combine the separation properties of polymers with those of fillers to obtain membranes with better separation performances than pure polymeric membranes. A significant effort has been devoted to prepare membranes using zeolites as the filler, due to their size and shape selective properties, and glassy polymers as the polymer matrix, due to their rigidities and higher intrinsic selectivities (Şen *et al.*, 2007).

2.2.2.1 *Introducing Zeolite as an Adsorbent into Polymer Matrix*

To extend the industrial applications of membrane separation technology, it is essential to synthesize and develop high-performance membrane materials. Progress has been made in the polymer-zeolite MMMs for natural gas

separation, which showed a significant increase in CO₂/CH₄ selectivity of roughly 44% at 50 wt % zeolite loading compared with that of neat polymer dense film (Li *et al.*, 2006).

In another work done by Li *et al.* (2007) both CO₂ and CH₄ gases possessed little or no affinity for the polymer matrix and zeolite 4A; therefore, it was the precise tailoring of pore size [3.8×10^{-10} m (3.8 Å)] of zeolite 4A that resulted in a significant increment in CO₂/CH₄ selectivity of MMMs. However, to achieve even higher separation performance, it is necessary to go beyond the tailoring of pore sizes.

The incorporation of zeolites into rubbery polymers has been shown experimentally to enhance both the permeability and selectivity in pervaporative separation of organic compounds out of water. Since then, there is a great interest in zeolite-filled polymeric membranes for gas separation. Zeolite-filled rubbery polymer membranes were first investigated by Jia *et al.* (1991) They studied the permeation properties of various gases through polydimethylsiloxane (PDMS) membranes filled with silicalite-1, from which the permeability of He, H₂, O₂ and CO₂ was observed to increase, while that of N₂, CH₄ and C₄H₁₀ was observed to decrease. They concluded from their results that silicalite played the role of a molecular sieve, although its pore size was larger than the kinetic diameters of gases. It meant that the shape-selective effect was not only inherent in the equilibrium adsorption of gas molecules into zeolites but also in the kinetic adsorption and diffusion.

Duval *et al.* (1993) studied the effect of zeolites incorporation into PDMS, ethylene-propylene rubber (EPDM), polychloroprene (PCP) and nitrile butadiene rubber (NBR). The results showed that silicalite-1, zeolites 13X and KY improved the gas separation properties of membranes, which was attributed to both CO₂ sorption enhancement and molecular sieving effects embodied by zeolites. However, zeolites 3A, 4A and 5A were totally ineffective in improving the permselectivity of the rubbery polymers. This behavior was attributed to the slow diffusion of the sorbed molecules from zeolite to polymer phase.

Süer *et al.* (1994) studied the permeation rates of N₂, O₂, Ar, CO₂ and H₂ 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.%). The permeabilities were decreased at first and then increased with increasing zeolite loading.

The intent of the MMMs is to take the advantage of the low cost and good processability of polymers with the excellent separation performance of zeolites. Early attempts at designing MMMs were focused on using rubbery polymers to serve as the polymer matrices (Hennepe *et al.*, 1987).

With some reports of improvements in separation performance associated with adding zeolites to rubber polymers (Duval *et al.*, 1993), the focus began to shift to mixing zeolites with glassy polymers. Unlike the good contact between rubbery polymers and zeolites at their interfaces, the initial attempts at fabricating MMM using glassy polymers and zeolites resulted in the presence of voids between the polymer and zeolite which reduced the separation performance of the composite membrane relative to the pure polymer (Zimerman *et al.*, 1997).

Efforts to eliminate these unselective gaps often focused on the use of a coupling agent to introduce favorable interactions between the polymer and zeolite (Yong *et al.*, 2001) by adding a plasticizer to increase the flexibility of the polymer matrix or by chemically linking the two components together (Koros *et al.*, 2002). While some efforts appeared to eliminate the presence of voids between the polymer and zeolite, the resulting permeability of the MMM was often sacrificed in the process (Pechar *et al.*, 2006).

2.2.2.2 *Introducing Other Materials as an Adsorbent into Polymer Matrix*

Vu *et al.* (2003) incorporated a carbon molecular sieve (CMS) as the disperse phase in mixed matrix membranes using two different continuous polymer matrices (Matrimid[®] 5218 polyimide and Ultem[®] 1000 polyetherimide). The CMSs were prepared by the pyrolysis of a Matrimid[®] polyimide precursor to the final temperature of 800° C. Mixed matrix membranes containing a high loading of CMS particles (up to 35 wt. %) dispersed within the Matrimid[®] 5218 polyimide and Ultem[®] 1000 polyetherimide polymer matrix prepared by the flat-sheet solution casting method. The results showed that the Matrimid[®]-CMS and Ultem[®]-CMS

mixed matrix membranes displayed significant enhancement in CO₂/CH₄ selectivity, about 45 and 40% respectively compared to the pure polymer.

Anson *et al.* (2004) investigated the performance of various novel mixed matrix membranes for CO₂/CH₄ separation as a function of carbon loading. Acrylonitrile–butadiene–styrene (ABS) copolymers were used as the polymer matrix and two micro–mesoporous activated carbons (AC) were chosen as inorganic fillers. The results showed that the pure gas permeabilities and CO₂/CH₄ selectivities of ABS–AC mixed matrix membranes were simultaneously increased with increasing activated carbon loadings in the mixed matrix membrane, compared to that of the intrinsic ABS polymeric membranes.

2.3 Polybenzoxazine

Polybenzoxazines are a relatively new class of versatile materials that can be used in many fields, such as electronics and aerospace industries, because they have a good combination of attractive properties which include nearly zero shrinkage upon curing, high thermal stability, and good chemical resistance. Polybenzoxazines can be prepared by thermally activated ring–opening polymerization of the corresponding benzoxazines without any catalyst and without generating any by–products (Figure 2.1) (Kiskan *et al.*, 2008).

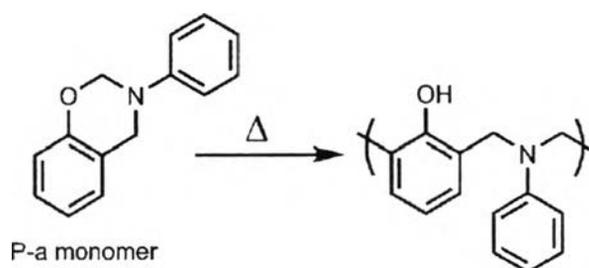


Figure 2.1 Ring–opening polymerization of polybenzoxazine.

The development of the benzoxazine-based family of phenolic resins has attracted significant attention. Particular attention was devoted to the synthesis of polybenzoxazines, one of a series of phenolic-type polymers with good thermal and mechanical properties. In fact, these new materials combine the thermal properties and flame retardance of phenolics and the mechanical performance and molecular design flexibility of advanced composites. For this reason, the new polybenzoxazines showed physical and mechanical properties comparable with those of conventional phenolic and epoxy resins. Benzoxazines are bicyclic heterocycles (Figure 2.2) generated by the Mannich-like condensation of a phenol, formaldehyde and an amine. Moreover, polybenzoxazines, one of a series of phenolic-type polymers, which are generated upon thermal polymerization from various types of substituted 3,4-dihydro-2H-1,3-benzoxazines, offer excellent mechanical, physical and thermal properties due to the phenolic groups, Mannich base linkages and the existence of extensive inter- and intramolecular hydrogen bonds. A great deal of effort was expanded towards the understanding of the curing chemistry of these resins (Calò *et al.*, 2007).

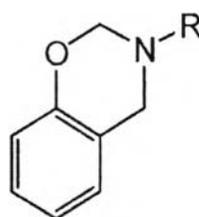


Figure 2.2 Structure of a 3,4-dihydro-2H-1,3-benzoxazine.

2.3.1 Synthesis of Benzoxazine Monomer

Benzoxazine monomers can be prepared simply from inexpensive and commercially available phenols, primary amines, and formaldehyde. Additionally, the chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility; by using appropriate starting materials, the polybenzoxazine properties can be tailored (Kiskan *et al.*, 2008). In 1944., Holly and Cope discovered the synthesis of aromatic oxazines using phenol, formaldehyde, and amines through the

Mannich reaction. Ishida and coworkers subsequently reported the synthesis of bisphenol A–based polybenzoxazines (Figure 2.3). Kimura et al. (1999) prepared the terpenediphenol–based benzoxazine and modified with epoxy resin or bisoxazoline. Agag et al. (2000) prepared bisphenol A–based polybenzoxazine/inorganic hybrid nanocomposites. Liu et al. (2004) developed bisphenol A–based polybenzoxazines containing maleimide and furan groups (Men *et al.*, 2007).

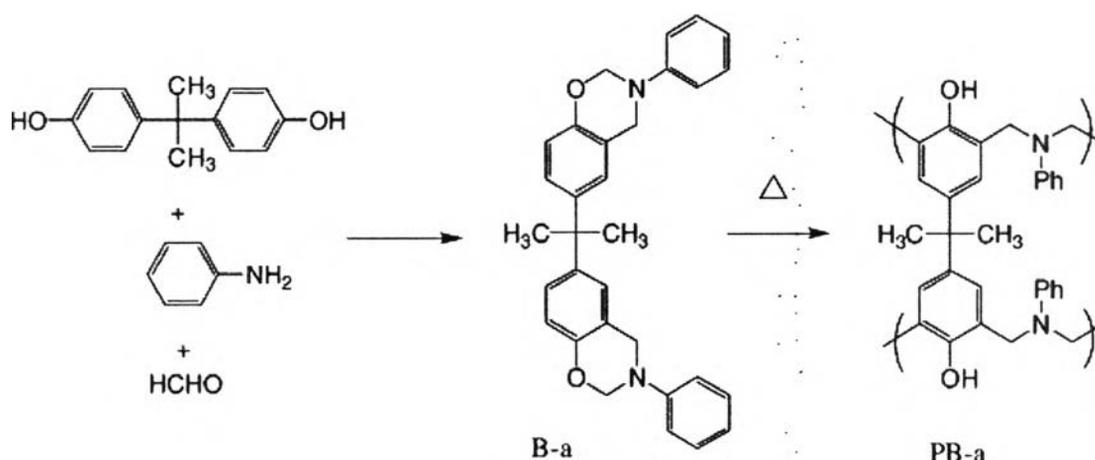


Figure 2.3 Synthetic route to bisphenol A–based polybenzoxazines.

Benzoxazine rings can also be opened at room temperature by cationic initiators resulting in the polymers consist of phenoxy–type repeating units. Recently, polybenzoxazines obtained via photopolymerization has also been reported. The structures of the polymers prepared by photoinitiated cationic polymerization were complex and related to the ring–opening process of the protonated monomer either at the oxygen or nitrogen atoms (Kiskan *et al.*, 2005).

2.3.2 Preparation of High Molecular Weight Benzoxazine Precursors

Takeichi *et al.* (2005) prepared high molecular weight polybenzoxazine precursors from aromatic or aliphatic diamine and bisphenol–A with paraformaldehyde in Figure 2.4. The precursors were obtained as soluble white powder. The structure of the precursors was confirmed by IR, ^1H NMR and elemental analysis, indicating the presence of cyclic benzoxazine structure. The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were thermally cured up to 240°C to give brown transparent

polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films revealed that polybenzoxazine from aromatic diamine exhibited the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The viscoelastic analyses showed that the glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238–260 ° C. Additionally, these novel polybenzoxazine thermosets showed excellent thermal stability

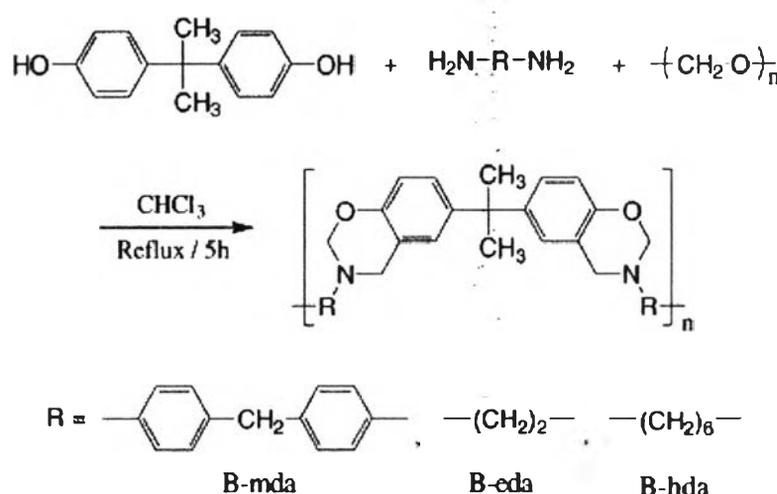


Figure 2.4 Synthesis of polybenzoxazine precursors.

Agag *et al.* (2006) synthesized polybenzoxazine matrix through high molecular weight polybenzoxazine precursors. They have used AB-type aminophenols instead of amines and phenols separately. The self-standing thin films were obtained from the precursors before curing by casting the precursor solutions onto glass plates. After the thermal treatment of the AB polybenzoxazine precursor films up to 250 ° C, reddish-brown, transparent polybenzoxazines were attained. Both viscoelastic analyses and TGA indicated that the thermosets derived from these novel AB precursors have excellent thermomechanical properties as well as high thermal stability. This enhancement in the thermal properties can be attributed to the

increase in the crosslinking density and hence suggesting that the use of AB precursors is an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties.

2.3.3 Properties Improvement of Polybenzoxazine

Aiming for performance enhancement and lowering the polymerization temperature, various approaches have been examined. One approach is the modification of monomer. Introduction of another crosslinkable functional units is very effective to enhance the thermal properties. Moreover, polymer alloys of polybenzoxazine with high performance polymers or with elastomers resulted in high performance and tough films. The third approach involving hybridization with inorganic materials such as layered clay and metal oxide nanoparticles was also successful in obtaining polybenzoxazine with improved properties (Takeichi *et al.*, 2005).

By taking the advantage of the molecular design flexibility of benzoxazine chemistry, thermal and thermo-oxidative stabilities of polybenzoxazine have been improved by altering the functional group on the amine and/or phenol. Low and Ishida (1998) had studied the thermal and thermo-oxidative degradation of polybenzoxazines and concluded that the thermal degradation of bisphenol-based polybenzoxazines involved three stages. Evaporation of amine moiety first occurred below 300° C followed by degradation of the schiff base between 300° C and 400° C. Finally, above 400° C, the evaporation of phenolic moiety took place. This observation gave rise to the postulation that, if amine evaporation was reduced, the char yield could be greatly increased. Kim *et al.* (1999) synthesized acetylene-functionalized benzoxazines, in which acetylene-functionalized side chain could further crosslink upon thermal activation. Recently, Ishida and Ohba (2005) synthesized monofunctional benzoxazine with maleimide and aniline to develop low-viscosity benzoxazine monomers with a glass-transition temperature above 200° C. Incorporation of the maleimide functionality into the monofunctional benzoxazine resulted in an increased char yield and glass-transition temperature without significantly increasing the viscosity of the monomer (Chaisuwan *et al.*, 2006).

2.4 Zeolite

Zeolites, which are microporous crystalline materials, can act as molecular sieves because of their particular structure—a three-dimensional pore structure consisting of a network of interconnected tunnels and cages—and nearly uniform pore and channel sizes. Therefore, zeolites possess the ability to separate and remove one gas from a similarly sized gas mixture based on their size- and shape-selective nature (Li *et al.*, 2007). Zeolite membranes with well-defined crystalline structures and good characteristics such as higher mechanical strength, chemical and thermal stability compared with other inorganic and polymeric membrane materials can be used in broad applications including gas separation, pervaporation, membrane reactors chemical sensors, and components in the microelectronic devices. Different types of zeolite membranes, including LTA, MFI (ZSM-5, silicalite-1), FAU, X, Y, MCM-22, MOR, FAU, FER, SAPO and AlPO_4 have been successfully prepared in recent years (Cheng *et al.*, 2006).

Zeolites are of prime importance as catalysts for many industrial processes, mainly due to their shape-selectivity and Bronsted acidity (Limtrakul, 1995). Substitution of a silicon atom for an aluminium atom introduces a charge in the framework which must be balanced by a cation or a proton, hence, generating an acidic bridging hydroxyl group. These Bronsted hydroxyl groups are acknowledged to be prime importance for the adsorption properties led to numerous industrially important applications (Lomratsiri *et al.*, 2006).

2.4.1 ZSM-5*

ZSM-5 (structure type MFI) is an aluminosilicate zeolite mineral belonging to the pentasil family of zeolites. Its chemical formula is $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$ ($0 < n < 27$). Patented by Mobil Oil Company in 1975, it is widely used in the petroleum industry as a heterogeneous catalyst for hydrocarbon isomerization reactions.

ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings. In these rings, the vertices are Al or Si and an O is assumed to be bonded between the vertices.

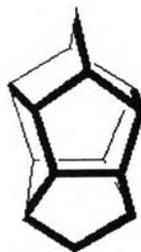


Figure 2.5 Pentasil unit.