

CHAPTER II

LITERATURE SURVEY

2.1 Theory of Gas Transportation in Membranes

Polymeric membrane based separation is widely used at moderate temperature and pressure. There are two types of polymeric membrane base on mechanism of gas separation. First, porous membrane uses molecular sieve to separate one type of molecule from another type by smaller molecule can diffuse in pore of membrane and pass through permeate side. On the other hand, the bigger molecules that bigger than pore of membrane cannot pass through permeate side but it is rejected and stays at retentive side of membrane. Second, nonporous membrane or dense membrane uses difference in solution-diffusion of molecule. The mechanism of permeation consists of three steps: (1) absorption or adsorption upon the upstream boundary, (2) activated diffusion through the membrane, and (3) dissolution or evaporation from the downstream boundary. The driving forces of solution-diffusion mechanism depend on a difference in thermodynamic and kinetic activity between upstream and downstream faces of a membrane.

The gas permeability of polymer membrane is measured by a mean permeability coefficient (P), which is defined by the isothermal relation and usually expressed in Barrers, in which 1 Barrers is equivalent to $10^{-10} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$

$$P = \frac{Q \cdot l}{p_0 - p_1} \quad (2.1)$$

where Q is the steady state rate of gas permeation through unit area of a membrane (Flux);
l is the effective thickness;
 p_0 and p_1 are the upstream and downstream partial pressure of the component, respectively.

However, the effective thickness of membrane is much smaller than its actual thickness and may not be known. So, the gas permeability of membrane is often characterized by its permeance.

The permeability coefficient, P_A of penetrant A is the product of a kinetic parameter, D_A , the average diffusion coefficient, and thermodynamic parameter, S_A , the solubility coefficient

$$P_A = D_A * S_A \quad (2.2)$$

The ideal separation factor or permselectivity, $\varphi_{A/B}$, describes the ideal ability of a membrane to separate gases A and B and may be written as the ratio of permeabilities of components A and B.

$$\varphi_{A/B} = P_A/P_B \quad (2.3)$$

$\varphi_{A/B}$ can be written as the product of the diffusivity selectivity and solubility selectivity of the gas pair, viz.

$$(2.4) \quad \varphi_{A/B} = \frac{D_A * S_A}{D_B * S_B}$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity. The diffusivity selectivity is based on the inherent ability of polymer matrix to function as size and shape selective media. This ability is primarily determined by such factor as polymer segmental mobility and intersegmental packing. The solubility selectivity, on the other hand, is determined by the difference of the condensibilities of the two penetrants as well as physical interaction of the penetrants with the particular polymer that the membrane is composed of.

2.2 Plasticization

An understanding of plasticization phenomenon is essential to develop and achieve a highly performance polymeric membrane. It seems like hardly to identify the fundamental description or definition of plasticization. Moreover, we have been no methods until now which can be used to predict precisely whether a material will be plasticized by a penetrant. A typical effect of plasticization on polymers is the reduction of the interaction between adjacent segments of neighboring polymer chains. The phenomenon on the macro scale shows the increasing of softness, and ductility, while on the chain segmental scale reflects enhancement of mobility and permeability but reduction of selectivity. In other words, plasticization may be interpreted as a weakening effect on the polymer and finally resulting the swollen polymer losses its selective properties. In addition, this plasticization effect usually can be observed as an anomalous sorption and permeation during measurements at elevated pressures.

It is well known that the gas streams often contain high levels of plasticizing or condensable agent. Plasticization problem is the major problem faced by CO₂-selective polymeric membrane. CO₂ permeability is pressure dependence. In general, it can be classified to three categories, which are in the following:

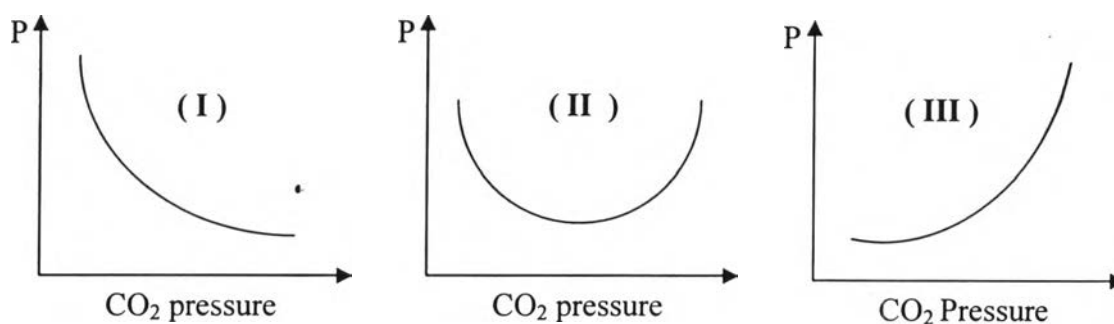


Figure 2.1 Representation graph of CO₂ permeabilities (P) for several polymers.

1. For polymers without large substituents on the backbone, such as PSF and PC are two examples of type (I). The gas permeability of the polymer decreases with the increasing of pressure. It stated that a microvoid-situation appears at low

concentration of the penetrant that allows the gas molecules pass through easily. However, such microvoid becomes saturated at higher of penetrant and resulting the decreasing of gas permeability.

2. Type (II) shows that the permeability initially decreases at low feed pressure. As the pressure is increased up to a critical pressure, the permeability of gas begins to increase with the increasing pressure, e.g. various of polyimides. The decrease in permeability at low pressures is dominated by a decrease in solubility with increasing pressure. On the other hand, for polymers in which the permeability increases with pressure, the diffusion coefficient increases with concentration much more rapidly than the solubility coefficient.

3. Polyacrylates, such as PEMA, CA, PMMA and polystyrene (PSt) which containing large side groups on the main chain show type (III) trend can be regarded as atypical. These polymers exhibit similar permeation behavior as found for rubbers as they have permeability to CO₂ that progressively increases as a function of pressure. The higher the acetyl contents of the CA, the greater the conditioning effect by CO₂.

2.3 Literature Review

The mixed matrix membranes have been developed by modifying morphology of polymeric membrane to enhance the permeability of gases and selectivity for gas separation. There are several kinds of adsorbents which are used in mixed matrix membranes. Some of them offer very attractive performance and selectivities significantly higher than polymeric membranes.

2.3.1 Polymeric Membranes

In the early 1960s, the Loeb-Sourirajan process was developed making defect-free, high flux, ultrathin skinned reverse osmosis membranes by cellulose acetate. It was continually developed for gas separation. It is divided into 2 types, which are asymmetric membranes composed of one material and composite membrane composed of a variety of materials. Both types are made from many polymers. In natural gas separation, almost natural gas requires some treatment to

meet its specifications before delivered to the pipeline. About 17% of all domestic natural gas must be treated to remove CO₂. The technology most widely used is amine absorption, but amine plants suffer from a number of problems such as high capital cost, labor-intensive, full-time supervision and complex operation. During period 1980-1985, installation of membrane plants using carbon dioxide selective cellulose acetate membrane began. It has a CO₂/CH₄ selectivity of about 12-15. Cellulose acetate is only now being slowly replaced by polyimide and polyamide membranes with selectivities of 20-25. Though the advantages of a simple flow configuration and low-maintenance operation, membrane systems cannot compete with current amine systems for most CO₂ removal applications. The problem is low selectivity and flux. Permeability and selectivity are only two of the criteria that must be met to produce a useful membrane; others include the ability to form stable, thin, low-cost membranes that can be packaged into high-surface-area modules. (Baker, 2002).

Pellegrino and Kang (1995) measured CO₂ and CH₄ gas permeation through polyfluorosulfonate ionomer (PSFI) that was solvated with water, methanol, ethanol, and 1-propanol. The increased permeabilities of CO₂ when the membrane was swelled by the solvent in the sequence of ethanol>methanol>water implied the effect of polar solvents. The higher permeability of CH₄ compared to value measured from the dry PSFI film was observed. They suggested that the solvents penetrated into polymer phase and increased the permeability, which was resulted from the increase in solubility.

Barbari and Datwani (1995) modified polysulfone membranes by using bromine to form charge transfer complexes with unpaired electrons along a polymer backbone. The bromine molecules would alter the free volume distribution in such a way as to hinder the transport of large gas molecules without a significant reduction in the flux of the more permeable gas. After bromine treatment, the selectivity of a polysulfone membrane for CO₂ over CH₄ was increased over 100% at 10 atm upstream pressure with only a 36% reduction in CO₂ permeability.

Hughes and Jiang (1995) measured the permeability of N₂O, CO₂, and O₂ through silicone rubber and cellulose acetate membranes using a flat sheet permeator. Measurements have also been made of individual gas permeabilities

from a mixed feed stream. N_2O has the highest permeability when using the silicone rubber membrane, followed by CO_2 , with O_2 an order of magnitude less. All three gas permeability coefficients were independent of feed pressure, but both N_2O and CO_2 permeability coefficients were temperature independent. For the cellulose acetate membranes, N_2O and CO_2 permeabilities varied with feed pressure and all three gases gave positive temperature coefficients. No separation of CO_2 from N_2O could be achieved under any conditions with the cellulose acetate membrane.

The use of combined polymeric membrane (hydrophilic-hydrophobic, SLM type) has been proposed as effective support for CO_2 absorbent solutions. They use different liquid absorbents (2-ethanolamine, K_2CO_3 , H_2O) as carrier. The experimental results pointed out that the performances in term of permeability of the coupled membranes are higher than that of the polymeric hydrophilic and hydrophobic membranes prepared by polyethylene fluoride (PTFE) deposition. 2-ethanolamine is the type of adsorbent with the greater affinity toward CO_2 (Freni *et al.*, 2004).

2.3.2 Mixed Matrix Membranes

The mixed matrix membranes had been developed in the late 1980's at UOP. The desirable characteristics of mixed matrix membrane that must be possessed by the membranes include a high selectivity of one or more gases from other gases as well as relatively high flux (Kulprathipanja *et al.*, 1988).

The first type of mixed matrix membrane was silicone rubber with polyethylene glycol (PEG) emulsified silicone rubber casting on a polysulfone support. The results showed that the selectivities of PEG /SR/PS were higher than a SR/PS. The increase in selectivities was reached to higher permeation from the solubility of polar gases in PEG. The efficiency of MMM depended on amount of PEG in silicone rubber phase (Kulprathipanja and Kulkarni, 1986).

The other type of mixed matrix membrane was silicalite/cellulose acetate. It was developed to separate CO_2 from H_2 . It had been known that a plain cellulose acetate membrane had a greater permeability for H_2 whereas a silicalite had a greater adsorption affinity for CO_2 . The mixed matrix membrane comprising cellulose acetate having silicalite as the solid participate adsorbent showed a reverse

selectivity for CO₂ over H₂ when compared to a pure cellulose acetate membrane (Kulprathipanja *et al.*, 1992).

Li *et al.* (1998) studied the effect of polyethylene glycol (PEG) on gas permeabilities and selectivities in a miscible cellulose acetate (CA) blend membranes. They used CO₂, H₂, N₂, CH₄, and O₂ as the sample gases. 10 wt% PEG 20000 exhibited higher permeability for CO₂ over N₂ and CH₄ than another membrane which contains 10wt%PEG of the molecular weight in the range 200-6000. The CA blended membrane containing 60wt% PEG20000 showed that its permeability coefficients of CO₂ and ideal separation factors for CO₂ over N₂ reached above $2 \cdot 10^{-8} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ and 22, respectively at 70°C and 20 cmHg. Solubility coefficients of all CA/PEG membranes for CO₂ were lower than those of the CA membrane. However, almost all the blended membranes containing PEG20000 showed higher diffusivity coefficients for CO₂, resulting in higher permeability coefficients of CO₂ with relation to those of the CA membrane.

The permeation rates of SO₂, H₂S, NH₃, CO₂, H₂, N₂ and C₂H₆ were evaluated through a dense silicone rubber membrane and silicone rubber-PEG mixed matrix membrane. The results showed that the gas permeance was a function of critical temperature while the gas selectivities were observed to be similar for each of the dense silicone rubber membranes. For the mixed matrix membrane, the gas permeance slightly decreased while the selectivities of polar/non-polar gas were significantly improved due to the enhancement in solubility of polar gas in PEG. PEG not only had the capacity of altering the permeability of silicone rubber but also acted on the polymeric support material by softening it and causing its pores to shrink (Serivalsatit, 1999).

Reid *et al.* (2001) explored the first use of the siliceous MCM-41 molecular sieve as an additive to enhance the gas permeability characteristics of a high-performance polysulfone. For all gases tested (N₂, O₂, CO₂, CH₄), the permeability increased in proportion to the weight percent of MCM-41 present in the film. Calculated ideal selectivities were remained almost constant irrespective of MCM-41 loading. It supposed that the hydroxyl groups, which decorate the internal surface of MCM-41, provide the necessary functionality for hydrogen bonding, while the 40°A pore size is large enough to readily enable penetration of the polymer.

Using a mesoporous molecular sieve as the adsorbent additive enhances contact and penetration of polymer is a alternative technology to increase in permeability, without a loss in selectivity, which is not observed with dense silica or zeolites.

Vu *et al.* (2003) determined the permeation properties of a mixed matrix membranes with 10%CO₂/90%CH₄ gas feeds containing a vapor impurity of toluene (70ppm). The mixed matrix membrane was comprised of fine particles of high-selective carbon molecular sieves (CMS) dispersed within a glassy polyimide matrix (Matrimide5218). As the results, the CMS-polyimide membranes have significantly enhanced effective permselectivities over the intrinsic properties of the neat polymer matrix phase alone. Both Matrimide mixed matrix membrane and the pure Matrimide film exhibited fairly stable properties in the presence of the low-concentration toluene impurity. It was hypothesized that larger-sized impurities, such as toluene, may only be successful in blocking or occupying the larger, non-selective pores of the CMS particles and may not access the smaller, selective pores that are accessible to CO₂.

2.3.3 Facilitated Transport Membranes

Nonporous and glassy polymeric membranes possess rather low CO₂/CH₄ selectivity around 15-35. The problem becomes particularly acute at lower CO₂ feed partial pressures thus the CO₂ flux becomes quite low. Facilitated transport membranes (FTMs) have been investigated wherein reactive carriers increase the CO₂ permeability. FTMs are often in the form of an appropriately immobilized thin liquid layer containing carrier species which react reversibly with CO₂ in the pores of a porous polymer. The FTM investigated employ generally an aqueous solution containing a carrier species e.g., K₂CO₃, diethanolamine (DEA), ethylenediamine (EDA). The CO₂ permeability drastically increased even in (Kovvali *et al.*, 2000).

Saha and Chakma (1994) studied selective CO₂ separation from CO₂/C₂H₆ mixtures using immobilized diethanolamine/PEG membranes. The better separation was achieved with a counter-current flow pattern. The reactive membranes with DEA showed higher permeation rates for CO₂ compared to the non-reactive PEG membranes. The CO₂ permeability increased with increasing concentration of alkanolamine although the change was not proportional. Higher

selectivities were obtained at lower CO₂ partial pressure differential conditions. An increasing CO₂ partial pressure differential across the membrane resulted in the saturation of DEA carrier and decreasing of rate of flux variation with the driving force.

Quinn *et al.* (1995) developed new facilitated transport membranes for the separation of carbon dioxide from hydrogen and methane by using melts of the salt hydrates tetramethylammonium fluoride tetrahydrate, [(CH₃)₄N]F·4H₂O, or tetraethylammonium acetate tetrahydrate, [(C₂H₅)₄N]CH₃CO₂·4H₂O, immobilized in micro porous supports (PTMSP). Both membranes exhibited CO₂ permeability which increased with decreasing feed partial pressure of CO₂. Selectivity of CO₂/H₂ and CO₂/CH₄ increased with decreasing feed pressure since H₂ and CH₄ permeances were independent of feed pressure. Modeling of membrane properties was consistent with permeation of CO₂ by a carrier-mediated pathway and resulted in reasonable values for the diffusivities of HCO₃⁻, the chemically bound form of CO₂.

Park *et al.* (2000) focused on the characteristics of facilitated transport of CO₂ through hydrophilic polymeric membranes with an immobilized aqueous potassium carbonate (K₂CO₃) solution. The rate of permeation for CO₂ increased with increasing K₂CO₃ concentration, decreasing membrane thickness, and decreasing CO₂ partial pressure. The permeation rate for CO₂ was predicted by a theoretical model based on mass transfer accompanied by a reversible chemical reaction, such as hydration rate of CO₂, reaction of CO₂ with OH⁻, or dissociation of HCO₃⁻. The permeation rate of CO₂ was increased by adding K₂SO₄, PEG, or DBC into the aqueous K₂CO₃ solution. By assuming that these additives enhanced the hydration reaction of CO₂, these forward-reaction rate constants were higher than those without additives about 15-36 times.

Chen *et al.* (2000) developed immobilized glycerol-based liquid membranes in hollow fibers for selective separation of CO₂ from a mixed gas (CO₂ and N₂) feed having low concentration of CO₂. The immobilized liquid membranes (ILMs) investigated consisted of sodium carbonate (Na₂CO₃)-glycerol solution. The hollow fiber-based ILMs were studied at selected CO₂ partial pressure differences, relative humidity (RH), as well as carrier concentration. The sweep gas was always dry helium and flowed on the shell side. Generally, lower permeance but greater

CO₂/N₂ selectivity values were observed at lower feed stream RH and also lower CO₂ partial pressure differential.

Chen *et al.* (2001) continued to develop glycerol-based ILMs for selective separation of CO₂ from a mixed gas (CO₂, N₂) feed. The items of specific interest are replacement of the carrier sodium carbonate (Na₂CO₃) by glycine-Na in glycerol, ILM thickness reduction performance of environmentally benign carriers, e.g., glycine-Na vis-a-vis toxic and volatile carriers, e.g., ethylenediamine. As the glycine-Na concentration was increased, N₂ permeability decreased while CO₂ permeability increased drastically at lower glycinate concentrations and level off at higher glycinate concentrations. The effect of feed relative humidity, lower feed stream RH yielded lower species permeances but greater CO₂/N₂ selectivities.

The effect of convective flow of a carrier solution through a facilitated transport membrane on the CO₂ permeation was investigated using diethanolamine (DEA) as a carrier of CO₂. The mixture of CO₂ and CH₄ was supplied to the feed side and the liquid transfer to the sweep side was recycled to the feed side. The CO₂ permeance was enhanced remarkably by the circulation of the carrier solution between the feed and the sweep side, and very high CO₂ permeance was observed at high circulation rate. (Teramoto *et al.*, 2001)

2.3.4 CO₂ – Induced Plasticization

Jordan and Koros (1990) investigated the effect of pressure on permeability of He, N₂, CH₄, CO₂, and C₂H₄ to consider plasticization and hydrostatic compression effects in the range of pressure up to 60 atm. They found that plasticization effects tended to dominate hydrostatic compression effect for the more condensable penetrants (C₂H₄ and CO₂) while the reverse was found for the low sorbing N₂ and He.

Bos *et al.* (1998) investigated CO₂-induced plasticization phenomena in eleven different glassy polymers. They tried to search for relationships between the plasticization pressure and the chemical structure or the physical properties but no relationship were found with respect to the glass transition temperature or fractional free volume. Furthermore, it was thought that polar groups of the polymer,

which have dipolar interactions with carbon dioxide molecules, increase the tendency of a polymer to be plasticized.

Wessling *et al.* (2001) used double layer composite membranes consisted of a silicone rubber support layer and a thin polyimide layer to determine the permeation properties of He, N₂, O₂ and CO₂. He permeation decreased with increasing feed pressure and no hysteresis behavior was found for successive increasing and decreasing feed pressure steps. For CO₂, its permeability increased with increasing feed pressure and showed a clear hysteresis effects. Another result was accelerated plasticization with decreasing film polyimide thickness.

Ismail and Lorna (2002 and 2003) concluded that the plasticization of the polymer matrix by penetrant gases can be attributed to the swelling stresses on the polymer network. Sorption of CO₂ in glassy polymers can facilitate the local segmental organization with a reduction of selectivity and substantially affect membrane morphological performance. One year later, the heat treatment method was successful to suppress CO₂ plasticization on asymmetric polysulfone membrane. Experimental results showed that the membranes were stabilized against CO₂ plasticization after heat treatment process. However, permeation rates were reduced with the intensity of heat treatment.

Wind *et al.*, (2004) developed polyimide membranes crosslinked with 1,4-butylene glycol and 1,4-cyclohexanedimethanol to separate CO₂/CH₄ mixtures and multicomponent synthetic natural gas mixtures. It was successful to reduce CO₂ plasticization effects by thermal annealing and crosslinking. Moreover, CO₂ permeabilities also increased without a loss in selectivity.