CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Theory of Gas Transport in Membranes

The mechanism of gas separation by non-porous membranes is basically different from that of microporous membranes in which gasses are separated by differences in their molecular weights as they traverse pores by Knudsen diffusion. In non-porous membranes, the gas molecules actually dissolve and diffuse in the dense membrane matrix. Therefore, the mechanism of permeation is usually considered to consist 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. This solution-diffusion mechanism is driven by a difference in thermodynamic activity existing at the upstream and downstream faces of a membrane. The activity difference causes a concentration difference that leads to diffusion in the direction of decreasing activity (Kesting and Fritzsche, 1993).

Typical gradients for a binary mixture (A and B) are shown in Figure 2.1. Henry's law is assumed to apply for each gas, and equilibrium is assumed at the interface.
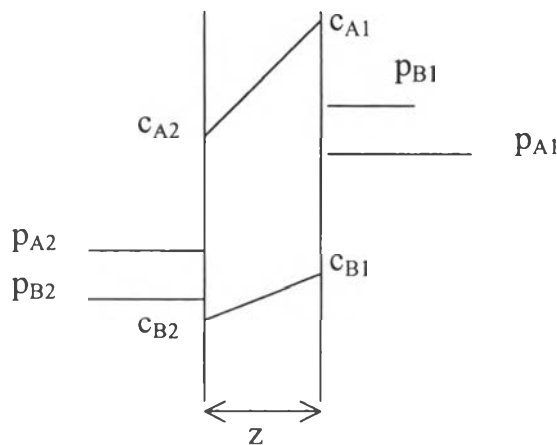

Figure 2.1 Gradients in a dense polymer membrane (McCabe *et al.*, 1993).

where

C_{A1}, C_{A2} = Concentration of A at upstream and downstream boundary, respectively

C_{B1}, C_{B2} = Concentration of B at upstream and downstream boundary, respectively

p_{A1}, p_{A2} = Partial pressure of A at upstream and downstream boundary, respectively

p_{B1}, p_{B2} = Partial pressure of B at upstream and downstream boundary, respectively

    Z = Membrane thickness

The gas-film resistances are neglected for this case, so the partial pressures at the gas-polymer interface are the same as those in the bulk. The flux for gas A, J_A, is

$$J_A = -D_A\left[\frac{dC_A}{dz}\right] = D_A\left[\frac{C_{A1} - C_{A2}}{z}\right] \tag{2.1}$$

where D_A =   Diffusion coefficient

The concentrations are related to the partial pressures by the solubility coefficient S, which has units such as mol/cm^3-atm (S is the reciprocal of the Henry's law coefficient).

$$C_A = p_A S_A \qquad\qquad C_B = p_B S_B \tag{2.2}$$

Using Eq.(2.2) to replace to the concentration gradient with a pressure gradient gives

$$J_A = \frac{D_A S_A (p_{A1} - p_{A2})}{z} \tag{2.3}$$

The product $D_A S_A$ is the flux per unit pressure gradient, which is called the permeability coefficient q_A and is often expressed in Barrers, where 1 Barrer = 10^{-10} cm^3(STP)-cm/cm^2-sec-cmHg

Since the actual membrane thickness is not always known or specified for commercial membranes, it is customary to use the flux per unit pressure difference, which is called the permeability, P_A : (McCabe *et al.*, 1993)

$$J_A = \frac{q_A (p_{A1} - p_{A2})}{z} = P_A (p_{A1} - p_{A2}) \tag{2.4}$$

P_A is a measure of the membrane's ability to permeate gas. The ability of a membrane to separate two gases, for example A and B, is the ratio of their permeabilities, α_{AB}, called the membrane selectivity.

$$\alpha_{AB} = \frac{P_A}{P_B} \qquad (2.5)$$

Since the permeability depends on both D_A reflecting the mobility of the individual molecules in the membrane material, and the other S_A reflecting the number of molecules dissolved in the membrane material. Thus Eq.(2.5) can also be rewritten as :

$$\alpha_{AB} = \frac{D_A}{D_B} \frac{S_A}{S_B} \qquad (2.6)$$

The ratio of D_A/D_B is the ratio of the diffusion coefficients of the two gases and can be viewed as the mobility selectivity, reflecting the different sizes of the two molecules. The ratio of S_A/S_B is the ratio of the Henry's law sorption coefficients of two gases and can be viewed as the sorption or solubility selectivity, reflecting the relative condensabilities of two gases. The balance between the sorption selectivity and the mobility selectivity determines whether a membrane material is selective for large or small molecules in a gas mixture. Membranes with both high permeability and selectivity are desirable. A higher permeability decreases the amount of membrane area required to treat a given amount of gas, thereby decreasing the capital cost of membrane units. The higher selectivity membrane gives, the higher purity product gas it produces (Orthmer, 1981).

2.2 Plasticization

In general permeability will not depend on different pressure. Because permeability is Flux divided by different pressure. It means that effect of pressure on permeability is eliminated. Therefore, the permeability will be constant at any pressure. However the permeability will increase with increasing pressure. Because penetrant acts as a plasticizer to decrease interaction between polymer chains. The

interaction between penetrant and membrane will change property of membrane. The net effect of decreased polymer-polymer interaction is introduction to increase free volume. On the macro level it means that increasing the softness and on the chain segmental level it means that increasing mobility. Therefore the permeability will increase due to plasticization. In mixture feed system if one component can plasticize in membrane it will increase the permeability of the other component. So membrane will loss selectivity.

2.3 Literature Review

2.3.1 Mixed Matrix Membranes

Over the past 30 years, relatively few attempts improved gas separation membrane performance with mixed matrix membranes. The permeability and selectivity values of membranes should be as high as possible for their efficient use in industrial gas separation applications. The attractive points of membrane are high energy efficiency and lower cost, so there are many separation processes that change from conventional processes such as distillation, absorption to membrane process. There are 2 types of mixed matrix membranes.

1) Dispersed Liquid-Polymer MMM

Kulprathipanja and Kulkrani (1986 and 1988) used membrane that was composed of polyethylene glycol (PEG) emulsified silicone rubber and porous polysulfone support. The results showed that the selectivities of silicone rubber/PEG on polysulfone were higher than the values obtained from the silicone rubber alone on polysulfone. The increase in selectivities was reached to higher permeation of polar gases through PEG that resulted from the solubility of polar gases in PEG. The efficiency of MMM depended on amount of PEG in silicone rubber phase.

Li et al. (1998) investigated about the effect of polyethylene glycol (PEG) on gas permeabilities and selectivities in a series of miscible cellulose acetate (CA) blend membranes. They used CO_2, H_2, N_2, CH_4, and O_2 as the sample gases. They found that 10 wt% PEG having molecular weight of 20000 exhibited higher permeability for CO_2 and higher permeability for CO_2 over N_2 and CH_4 than another membrane which contains 10wt%PEG of the molecular weight in the range 200-

6000. The CA blend membrane containing 60wt% PEG20000 showed that its permeability coefficients of CO_2 and ideal separation factors for CO_2 over N_2 reached above $2*10^{-8}$ cm^3(STP).cm/cm^2.s.cmHg and 22, respectively at 70°C and 20 cmHg. Solubility coefficients of all CA/PEG blend membranes for CO_2 were lower than those of the CA membrane. However, almost all the blend membranes containing PEG20000 showed higher diffusivity coefficients for CO_2, resulting in higher permeability coefficients of CO_2 with relation to those of the CA membrane.

Thanks to high performance of PEG, it can improve selectivity. However unstable PEG was, Vijitjunya (2001) used NaX zeolite to stabilize PEG by the adsorption of PEG into its pores. The objective of this work was to protect the PEG leakage from MMM. The propylene selectivity was enhanced and this was attributed to the presence of PEG in NaX pores.

2) Dispersed Solid-Polymer MMM

Silicalite had significant potential for increasing the permeabilities and selectivities of cellulose acetate for the separation of CO_2 from H_2(Kulprathipanja and Neuzil, 1992).

Furthermore, in 1993 Duval et al. investigated the effect of the introduction of specific adsorbents on the gas separation properties of polymeric membrane. Both carbon molecular sieves and zeolite were considered. The results showed that zeolites such as silicate-1, 13X and KY improved the separation properties of poorly selective rubbery polymer towards a mixture of carbon dioxide/methane. Some of the filled rubbery polymers achieved separation properties comparable to cellulose acetate, polysulfone or polyethersulfone. Using silicate-1 also resulted in an improvement of the oxygen/nitrogen separation properties. Carbon molecular sieves did not improve the separation performance or only to very small extent. This is caused by a mainly dead-end porous structure.

Suer, Bac and Yilmaz (1994) studied mixed matrix membrane which comprises of polyethersulfone (PES) and hydrophilic zeolites 13X and 4A. The permeation rates of N2, O2, Ar, CO2 and H2 were measured with a variety of membranes prepared at different zeolite loadings. They found that for both zeolitic additives, permeabilities and selectivities are enhanced at high zeolite loadings.

Additionally, the addition of zeolites silicalite-1, NaX and AgX to rubbery polymer (EPDM which is a copolymer of polyethylene and polypropylene) membranes was discussed by Boom, Bargeman and Strathmann in 1994. The membranes were used for pervaporation of methanol/toluene mixtures and for the separation of ethane and ethylene. Results showed that the addition of zeolites can lead to an increase in both permeability and selectivity of the membranes. The increase in selectivity results from a longer pathway for the slowest component around the zeolite particle, while the increase in permeability is explained by an increase in sorption experiments.

Singh and Koros (1996) compared diffusivity selectivity of O_2 over N_2 in the three different kinds of materials, namely, zeolite 4A, carbon molecular sieve (CMS), and upper bound polypyrrolone at $35^{o}C$. They found that D_{O2}/D_{N2} of 4A zeolite, CMS and upper bound polypyrrolone are 104, 25-45, and 5.1, respectively. Since diffusion was an activated process in both molecular sieving and polymeric media and limiting rotational degrees of freedom of nitrogen while allowing free rotation for the slightly smaller oxygen molecule.

Continuously, in 1997 Zimmerman et al. used Maxwell's equation and effective medium theory (EMT) to estimate mixed matrix composite (MMC) membrane performance by indicate that significant improvements should be achievable under optimum condition. It meant that good material selection and defect elimination. They found that CMS was attractive if a proper matrix polymer was selected to separate O_2 and N_2.

Birgul Tantekin-Ersolmaz et al. (2000) studied the effect of particle size on the performance of zeolite-polymer mixed matrix membrane as a function of the zeolite loading. Polydimethylsiloxane (PDMS, i.e. silicone rubber) was chosen as the polymer phase and silicalite was used as the zeolite filler. CO_2, N_2, and O_2 were the sample gases. They found that the permeabilities of the silicalite-PDMS MMM increase with increasing particle size. The variations occurring in the permeability values with changes made in the particle size were much more pronounced at the higher zeolite loading. The ideal selectivity values from MMM were less affected by the changes made in the particle size. The permeability of all

gases from MMM was higher than original polymer membrane only at higher zeolite loading and larger particle sizes.

Mahajan and Koros (2000) gave two key requirements for success to mach sieve and polymer transport properties: molecular adsorption of the polymer onto the sieve surface, and polymer flexibility during membrane formation. This work used poly(vinyl acetate)-zeolite 4A MMM to separate O_2 and N_2 by pure poly(vinyl acetate) gave $\alpha_{O2/N2}$ = 5.9 and 15 vol% zeolite 4A in poly(vinyl acetate) gave $\alpha_{O2/N2}$ = 7.3-7.6.

Birgul Tantekin-Ersolmaz et al. (2001) studied on the performances of various zeolite filled polymeric membranes in the separation of n-pentane from i-pentane as the function of zeolite loading and various experimental condition such as activation temperature and Si/Al ratio. They used polydimethylsiloxane (PDMS) as the polymer phase and HZSM-5, NaZSM-5, 4A and 5A as zeolite fillers. They found that none of the zeolite-PDMS mixed matrix membranes investigated in this study could provide n-pentane/i-pentane ideal selectivities higher than that of the unfilled polymeric membrane under the experimental conditions employed. But the binary permeation of these species may lead to a different result. n-Pentane showed lower permeability than for the pure polymer. On the other hand, i-pentane permeability was even increases with increased zeolite loading in case of 4A-PDMS. The relatively low n-pentane/i-pentane selectivities obtained in this study should not be generalized to all types of zeolite-polymer mixed matrix membranes, so the ability of the zeolite to separate between linear and branched paraffins in zeolite-polymer MMM should be continuous investigated.

Besides zeolite, carbon molecular sieves (CMSs) are interesting to use as a dispersed phase in mixed matrix membranes because of low price and high surface area.

In 2003 Vu, Koros and Miller used carbon molecular sieves that have been incorporated into two different polymer matrices to form mixed matrix membrane films for CO_2/CH_4 and O_2/N_2 separations. Mixed matrix films comprising high CMS particle loading (up to 35wt%) dispersed with in two polymer matrices (Matrimid[®]5218 and Ultem[®] 1000) were formed from flat-sheet solution casting. They found that for Ultem[®]-CMS mixed matrix membrane films, pure gas

permeability tests showed enhancements by as much as 40% in CO_2/CH_4 selectivity over pure Ultem[®] polymer matrix. For Matrimid[®]-CMS mixed matrix films, enhancements by as much as 45% in CO_2/CH_4 selectivity were observed. Like CO_2/CH_4 selectivity, O_2/N_2 selectivity showed as much as 8% for the Ultem[®]-CMS and 20% for Matrimid[®]-CMS mixed matrix films over pure polymer matrix. From this work MMM enhanced both selectivity and permeability.

2.3.2 Plasticization

Jordan and Koros (1990) investigated the effect of pressure on permeability of He, N_2, CH_4, CO_2, and C_2H_4 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 condensible penetrants (C_2H_4 and CO_2) while the reverse was true for the low sorbing N_2 and He.

Bos et al. (1999) investigated CO_2-induced plasticization phenomena in 11 different glassy polymers. They found that polar groups of the polymer increase the tendency of a polymer to be plasticized.

Wessling et al. (2001) used double layer composite membranes which consist of a silicone rubber support layer and a thin polyimide layer to determine the permeation properties of He, N_2, O_2 and CO_2. Helium permeation decreased with increasing feed pressure and no hysteresis behavior was found for successive increasing and decreasing feed pressure steps. For CO_2, its permeability increased with increasing feed pressure and showed a clear hysteresis effects. Another result was accelerated plasticization with decreasing film polyimide thickness.

Chan et al. (2002) investigated the transport of olefin and paraffin namely ethane, ethylene, propane and propylene in aromatic poly(1,5 - naphthalene 2,2' - bis(3,4 - phtalic)hexafluoropropane) diimide dense membranes. They found that plasticization effect was only found for propane and propylene.