

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Theory of Gas Transport in Membranes

The polymeric membrane materials are typically used in processes in which a feed gas mixture contacts the upstream or feed side of the membrane, resulting in a permeate mixture on the downstream or permeate side with a greater concentration of one of the components of the original feed gas mixture. A pressure differential is maintained between the upstream and downstream side, providing the driving force for permeation. 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 molecule that bigger than pore of membrane can not pass through permeate side but it is rejected and stays at retentate side of membrane. Second, nonporous membrane or dense membrane, which is currently used in most commercial application 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 membrane performance is characterized by the flux of gas component across the membrane. This flux can be expressed as a quantity called the permeability (P) which is generally defined as a pressure- and thickness-normalized flux of a given component and usually expressed in Barrers, in which 1 Barrers is equivalent of  $10^{-10} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$

$$P = \frac{Q \cdot l}{p_0 - p_1} \quad (1)$$

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 pressures of the component, respectively.

The separation of gas mixture is achieved because of differences in the relative transport rates of the feed component.

In these materials, permeation is the solution-diffusion process so the permeability can be expressed as a product of a diffusion coefficient ( $D$ ) and a solubility coefficient ( $S$ )

$$P = D \cdot S \quad (2)$$

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

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

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (3)$$

Since the permeability depends on both  $D_A$  which reflects the mobility of the individual molecules in the membrane material, and  $S_A$  which reflects the number of molecules dissolved in the membrane material, thus Eq.(3) can also be rewritten as

:

$$\alpha_{A/B} = \frac{D_A S_A}{D_B S_B} \quad (4)$$

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.

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, the higher purity product gas (Benny, 1998).

## 2.2 Literature Review

### 2.2.1 Polymeric Membrane

To separation of olefin/paraffin mixtures through various polymeric membranes without carriers has been studied recently. Rubbery polymers show poor separation performance for olefin and paraffin mixtures. For example, Ito and Hwang (1989) found that ideal propylene/propane selectivity of 1 for silicone rubber and 3.8 for cellulose acetate at 313 K. For PDMS and for 1,2-polybutadiene, ideal propylene/propane selectivity of 1.1 and 1.7 at 323 K, respectively (Tanaka *et al.*, 1996). More suitable as membrane material for the olefin/paraffin separation seems to be PPO, which shows the ideal propylene/propane selectivity of 9.1 at 323 K with permeability of 2.3 barrer. (Ilinich and Zamaraev, 1993). For polyethylene as membrane material also, a rather low ideal selectivity of 1.6 was found (Shimazu *et al.*, 1998). Currently, the most interesting membrane materials for the separation olefin/paraffin mixtures seem to be polyimide, glassy polymer, especially 6FDA-based ones.

Polyimides based on 4,4-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) membrane were tested concerning the permeation and sorption properties of pure ethane, ethylene, propane and propylene and for determining separation factor for 50:50 olefin/paraffin feed mixtures. The ideal selectivity of

ethylene to ethane was between 3.3 and 4.4 and propylene to propane was between 10 and 16. In the mixed gas permeation experiments, up to 20% lower selectivity was found for ethylene/ethane separation and up to 50% lower selectivity was found for propylene/propane separation compared to the ideal selectivity (Staudt and Koros, 2000).

Chan *et al.* (2002) explored the possibility of using 6FDA-1,5-NDA membranes to separate unsaturated hydrocarbon especially C<sub>2</sub> and C<sub>3</sub> systems. The result showed that the ideal selectivity of 5.8 for the separation of ethylene/ethane, 10 for propylene/propane. The plasticization effect was also found for propylene and propane at the pressure above 5 atm in 6FDA-1,5-NDA membrane, while ethylene and ethane was not observed at pressure up to 16 atm.

Asymmetric hollow fiber membranes of 6FDA/BPDA-DDBT copolyimide displayed better performance for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>/C<sub>4</sub>H<sub>10</sub> : for example, permeances of C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>/C<sub>4</sub>H<sub>10</sub> of 3.6 and 7.4 GPU, respectively, and separation factor of 15 and 69 for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>6</sub>/C<sub>4</sub>H<sub>10</sub> (50/50 mol% in feed) at 373 K and 1 atm (Yoshino *et al.*, 2002).

### 2.2.2 Mixed Matrix Membranes

Over the past 30 years, relatively few attempts improved gas separation membrane performance with mixed matrix membrane. 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 process such as distillation, absorption to membrane process.

#### 2.2.2.1 *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<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and O<sub>2</sub> as the sample gases. They found that 10 wt% PEG that molecular weight is 20000 exhibited higher permeability for CO<sub>2</sub> and higher permeability for CO<sub>2</sub> over N<sub>2</sub> and CH<sub>4</sub> 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<sub>2</sub> and ideal separation factors for CO<sub>2</sub> over N<sub>2</sub> reached above  $2 \times 10^{-8} \text{ cm}^3(\text{STP}).\text{cm}/\text{cm}^2.\text{s}.\text{cmHg}$  and 22, respectively at 70°C and 20 cmHg. Solubility coefficients of all CA/PEG blend membranes for CO<sub>2</sub> were lower than those of the CA membrane. However, almost all the blend membranes containing PEG20000 showed higher diffusivity coefficients for CO<sub>2</sub>, resulting in higher permeability coefficients of CO<sub>2</sub> with relation to those of the CA membrane. Vijitjunya *et al.* (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.

#### 2.2.2.2 Dispersed Solid-Polymer MMM

Silicalite had significant potential for increasing the permeabilities and selectivities of cellulose acetate for the separation of CO<sub>2</sub> from H<sub>2</sub>(Kulprathipanja and Neuzil, 1992).

Singh and Koros (1996) compared diffusivity selectivity of O<sub>2</sub> over N<sub>2</sub> in the three different classes of material, namely, zeolite 4A, carbon molecular sieve (CMS), and upper bound polypyrrolone at 35°C. They found that  $D_{\text{O}_2}/D_{\text{N}_2}$  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<sub>2</sub> and N<sub>2</sub>.

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<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> 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<sub>2</sub> and N<sub>2</sub> by pure poly(vinyl acetate) gave  $\alpha_{O_2/N_2} = 5.9$  and 15 vol% zeolite 4A in poly(vinyl acetate) gave  $\alpha_{O_2/N_2} = 7.3-7.6$ .

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.

### 2.2.3 Modification of Zeolite Surface

Previous researchers noted difficulties in achieving good adhesion between molecular sieve material and polymer chain which ultimately results in gas bypassing around the sieve, thus higher permeability with no selectivity increase. These voids are probably caused by polymer chain delaminating from the sieve because of the rigid nature of the polymer. One way to solve this problem is to modify the surface properties of the molecular sieve materials to make them more compatible with the polymer matrix by means of the silane coupling agents in which this compound becomes bonded to the surface of the molecular sieve. This step is often called “Silanation” of the sieve. The silanation step for treating the molecular sieve involves a chemical reaction to condense the monofunctional organosilicon compound onto the molecular sieve. The monofunctional organosilicon compound acts as “linking groups” which have affinity for or which chemically react with the polymeric continuous phase. Hence, attraction between treated molecular sieve and the polymer phase is enhanced. This reduces the formation of voids at the molecular sieve-polymer interface.

Duval *et al.* (1994) studied the modification of silicalite surface by grafting with aminopropyltriethoxy silane incorporated into polyetherimide polymer. The improvement of the external surface as seen from the decreasing in the permeability compared to the membrane prepared with unmodified silicalite because less voids can be observed. However the selectivity remained the same and lower than that of the pure polymer.

Pechar *et al.* (2002) investigated MMMs that were fabricated from 6FDA-6FpDA-DABA polyimide incorporated with modified ZSM-2 zeolite with aminopropyltriethoxy silane. The morphology of the MMM was documented by

SEM and TEM studies and verified the absence of voids around the zeolite. The results suggested that zeolite and polymer had good contact at the interface.

Modified 3A zeolite-polysulfone aldehyde was developed by Guiver *et al.* (2002) for H<sub>2</sub>/CO<sub>2</sub> separation. Aminopropyltrimethoxy silane was employed to modified 3A zeolite surface. As a result, significant enhancement was observed in both permeability and selectivity compared to pure polysulfone and unmodified 3A-polysulfone aldehyde MMM.

Interfacial void-free Matrimide polyimide (PI) membranes filled with zeolite were prepared by introducing 2,4,6-triaminopyrimidine (TAP) by Yong *et al.* (2000). They found that TAP enhanced the contact of zeolite particles with polyimide chains presumably forming hydrogen bonding between them. The void-free PI/13X zeolite /TAP could show the higher gas permeability for He, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> with a little expense of selectivity compared with the PI/TAP membrane, while the PI/4A zeolite/TAP membrane showed the lower permeability but higher selectivity.