CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Theory

Polymeric membranes have become widely used for the separation of gases at moderate temperature and pressure. The mechanism of gas separation by porous membranes is basically different from that of nonporous membrane, in which gases are separated by differences in their molecular weights as they transverse pores by Knudsen diffusion. In nonporous membrane, the gas molecules actually dissolve and diffuse in the dense 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. The 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. (Koros *et al.*, 1987)

The gas permeability of polymer membrane is characterized by a mean permeability coefficient P, which is defined by the isothermal relation (Yamamoto *et al.*, 1990, Kamaruddin and Koros, 1997) and usually expressed in Barrers, which 1 Barrers is $10^{-10}cm^3(STP)/(cm^2\text{-sec-cmHg})$

$$P = \frac{j_s * \delta}{p_h - p_l} \qquad (2.1)$$

Where J_S is the steady-state rate of gas permeation through unit area of a membrane.

δ is the effective thickness.

p_h and p_l are the upstream and downstream partial pressure of the component, respectively.

The effective thickness of asymmetric or composite membrane is much smaller than their actual thickness (Koros *et al.*, 1996, Seader and Henley, 1998) and may not be known. Therefore, the gas permeability of such membrane is often characterized by their "permeance", P/δ.

When the downstream pressure is much less than the upstream pressure and Fick's law describes penetrant flux, permeability is written as (Yamamoto *et al.*, 1990, Kesting and Fritzsche, 1993):

$$P = S \times D \qquad (2.2)$$

Where S, the apparent solubility coefficient, is the ratio of the dissolve penetrant concentration in the upstream face of the polymer to the upstream pressure in the contiguous gas or vapor phase, and is D the concentration averaged penetrant diffusion coefficient.

The ideal separation factor $\alpha_{a/b}$ is determined by dividing by the individual permeability of single gases, expressed as (Kim *et al.*, 1998):

$$\alpha_{a/b} = P_a / P_b \qquad (2.3)$$

Factoring permeability into diffusivity and solubility terms, the selectivity may be expressed for gas/polymer separations as (Singh *et al.*, 1998):

$$\alpha_{a/b} = \frac{D_a S_a}{D_b S_b} \qquad (2.4)$$

Where D_a/D_b is called 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 condensibities of the two penetrants as well as physical interaction of the penetrants with the particular polymer that the membrane is composed of.

2.2 Literature Review

2.2.1 The Gas Transport

Understanding the nature of transport phenomena involved during gas permeation through membrane is fundamental and practical interest. The solution-diffusion model: a review was studied by Wijmans and Baker (1995). In this review, the appropriate transport equations for dialysis, reverse osmosis, gas separation and pervaporation membrane were derived using the solution-diffusion model. The fundamental equations describing transport in these processes can be derived from simple, basic principle without resource to process-specific factor. These equations provided an accurate description of the behavior of these membranes and the dependence of membrane transport on pressure, concentration and so on.

Dhingra and Marand (1998) studied mixed gas transport study through polymeric membranes. The use of single gas permeation data to estimate the separation properties of such a membrane can lead to erroneous results, particularly in the case of condensable components or when there is a specific interaction of one component with the polymer matrix. The design and

development of an experimental setup for observing mixed gas permeation through non-porous membrane has been focused. It was concluded that the transport parameters of individual gases involved in a mixed gas permeation can be estimated. Eventhough, the individual gas permeation under mixed gas permeation can not be valid for the full range of operations.

Gas permeation through plasma polymer membrane was studied by Oh and Zurawsky (1996) by using composite membrane consisting poly (dimethylsiloxane) (PDMS) substrates coated with fluorine. The results showed the permeabilities of the composites depend linearly on the thickness of the plasma polymer coating and the properties of the composite were described by a modified resistance in series model.

Polotsky and Polotskaya (1998) focused on study on top layer of composite membranes. Poly(phenylene oxide) (PPO) of different molecular weights and sulfonated PPO were used as top layer polymers. This work showed that the top layer of composite membranes were inhomogeneous through their thickness. Moreover, the degree of inhomogeneous increases with the molecular weight of the polymer. This fact must be taken into account in developing composite membranes because the use of polymers with high molecular weight can lead to considerable losses in permeability without any gain in selectivity.

Morisato et al. (1995) studied gas separation of aromatic polyamides containing hexafluoroisopropylidene groups. The synthesis and gas transport of aromatic polyisophthalamides (PIPAs), based on isophthaloyl chloride derivative bearing pendent groups and hexafluoroisopropylidene (6F) linkage in the main chain, were investigated and compared with properties of a similar series of PIPAs containing sulfonyl (SO_2) rather than 6F in the main chain. It was found that the polymer containing 6F groups were markedly more permeable and less selective than sulfonyl analog. This resulted from the

markedly higher fractional free volume values in the 6F-containing polymer. Polymer containing a t-butyl pendent group at the 5 position of the isophthaloyl linkage was much more permeable than those bearing only a hydrogen atom at this position, although a strong decrease in permselectivity accompanied the large increase in permeability. The t-butyl substituted polymer had a significant higher glass transition temperature than the unsubstituted analog. This observation exhibited substantial local scale rotational motion, which is relatively non-selective for the penetrants.

Chatterjee *et al.* (1997) prepared a rubbery polymer with high H_2S/CH_4 selectivity for possible use as membrane material for the separation of H_2S from low-quality natural gas in order to meet US pipeline specification. The poly(ether urethane) PU1 and PU3 and the poly(ether urethane ureas) PU2 and PU4 were synthesized and cast in the form of dense homogeneous membranes. Polyurethane exhibits high H_2S/CH_4 solubility selectivity, and hence high H_2S/CH_4 overall selectivity, due to interaction between H_2S molecule and the polymer chain. It was believed that the polar H_2S molecule interacted strongly with the carbonyl groups in polyurethane. Moreover, the amine groups can enhance this interaction, and increase the solubility of the H_2S relative to CH_4.

2.2.2 Asymmetric Membrane

Membrane technology requires skill in chemical synthesis, analytical chemistry, and the chemical engineering. Method of membrane preparation also affects the characteristics of membrane separation. Surface treatment (Kulprathipanja, 1986) is used to alter separation properties of the membrane. Study of this technique focused on comparison of separation properties for treated porous support membrane with a polyhydric alcohol versus untreated

porous support membrane. The results showed that the treated porous support membrane exhibited a much greater selectivity than the treated porous support membrane because polyhydric alcohol altered the micropores of the porous support.

Ongoing research strives to improve process by enhancing the selectivity and flux rates. Henis and Tripodi (1980) explained the membranes prepared by the Leob method were composed of two distinct regions made of the same cellulose acetate material, a thin dense semi-permeable skin and a less dense, void containing, non-selective support region. The Loeb-type membranes have been shown to have superior permeate flux when compared to the older style compact membrane. The improvement in the permeation rate has been attributed to the decrease in the thickness of the dense selective region. The less dense region in such a membrane provides sufficient structural support to prevent rupture of the membrane under operating pressure.

Further developments for providing advantageous separation membranes have led to composite membranes consisting a porous support being sufficient strong to withstand operating conditions and thin selective layer. Cabasso and Lundy (1986) invented a method for making a composite membrane for the oxygen enrichment of air by passing the air mixture through the composite membrane, consisting essentially of coating an amino organofunctional polysiloxane on a highly porous substrate. The characteristics of this membrane were good permselectivity for oxygen, reasonable high flux, and adapted to hollow fiber technology.

Williams, *et al.* (1989) reported improved permselectivities for the separation of air by using composite permeable membranes prepared by applying a thin coating of a permeable membrane material to a porous base material. An ethyl cellulose was well known as a membrane material being selectively permeable with respect to oxygen rather than nitrogen.

Nevertheless, dense film of ethyl cellulose had not been suitable for economical air separation because of the low oxygen rates. Because of good selectivity characteristics of this membrane material, an ethyl cellulose/polysulfone composite membrane was preferably prepared by applying a coating of ethyl cellulose to a hollow fiber polysulfone substrate.

In order to achieve commercial membrane separation, the multicomponent membranes formed through the combination of a porous support and a coating, which combines different material having their own excellent properties have been proposed. Riley and Grabowsky (1981) used the multicomponent membrane utilizing dimethy silicone as the semi-permeable forming prepolymer with trifluorotrichloroethane, which was composited on a finely porous membrane such as cellulose nitrate-cellulose acetate. This multicomponent membrane was possible to affect selective separations for specific mixture of gases. The results showed that when utilizing dimethyl-silicone as the prepolymer, which forms the thin film, it is possible to obtain a relatively high transport of oxygen whereas by utilizing nylon-6 of teflon as the polymer a relatively low oxygen occurred.

Kulprathipanja and Kulkarni (1986) studied the separation of polar gases from non-polar gases by using multicomponent membrane consisting of a mixture of a glycol plasticizer and an organic polymer composited on highly porous support. It was found that a multicomponent membrane composed of polyethylene glycol incorporated with silicone rubber as the first polymer and porous polysulfone membrane support as the second polymer had significant utility. The effect of polyethylene glycol and its amount introduced into a multicomponent membrane were considered. The results showed that the silicone rubber and polyethylene glycol combination on polysulfone yielded a higher selectivity than the silicone rubber on polysulfone alone. The increasing in selectivity resulted from the fact that the different component, that is, the

polar and non-polar gases passed through a membrane at different rates due to different diffusivity and solubility characteristics.

In another attempt to improve membrane performances by making mixed matrix composite membrane, incorporating molecular sieving materials within polymeric substrates, has been reported. Zimmerman *et al.* (1997) investigated the separation of O_2/N_2 by mixed matrix composite membrane of zeolite 4A and carbon molecular sieves in Utem® and Udel® and found that improved selectivity resulted from the successful discrimination between the similar size of O_2 and N_2 molecules by the molecular sieving phase.

The introduction of zeolite on the gas separation membrane was also studied by Suer *et al.* (1994). It was found that the type of membrane preparation procedure and the type of zeolite strongly affect the transport properties of membrane. Significant changes in the membrane morphologies of PES-13X and PES-4A matrices were observed. SEM studies showed that the addition of zeolite particles induced a microporous cavity and channeling system. For both zeolite 13X and 4A, the permeabilities and ideal separation factors were enhanced at high zeolite loading for certain commercially important gas pairs due to faster permeation of H_2 and CO_2 through the membrane matrix. It was concluded that the increasing selectivities with increasing filler content could not be solely due to a molecular sieving mechanism. Shape selective properties of zeolites, the polarities of gases, and the microstructures of membranes might play rules in increasing permselectivities.

Kulprathipanja and Neuzil (1988) studied the separation of fluids by mean of mixed matrix membrane, which consist of an organic polymer having a solid particulate adsorbent. It was found that a mixed matrix membrane having silicalite incorporated with cellulose acetate had significant utility,

especially in separation carbon dioxide from hydrogen. It can be seen that the selectivities of CO_2/H_2 were significantly improved. This is probably due to a greater adsorbtive affinity for carbon dioxide of silicalite.