



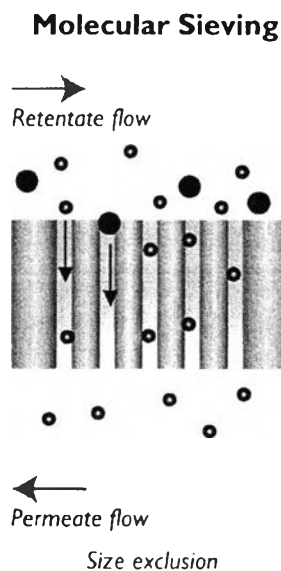
## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE SURVEY

#### 2.1 THEORETICAL BACKGROUND

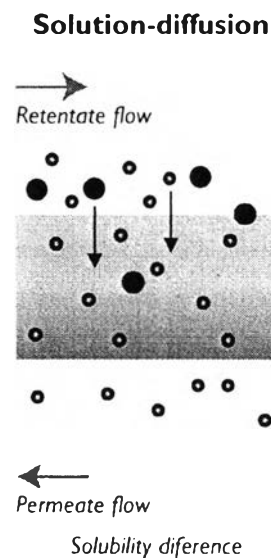
##### 2.1.1 Theory of Gas Transport in Membranes

Polymeric membrane is widely used due to its relatively easy to manufacture and is suitable for low temperature applications. There are three types of polymeric membrane based on mechanism of gas separation. First, porous membrane uses molecular sieve to one of molecule from other molecules by using diffusion mechanism. While passing through porous membrane with gases, the smaller molecule can diffuse into pores of membrane and pass through a permeate side. For bigger molecules, they cannot diffuse down into pores of membrane and cannot pass through permeate side, but they are rejected and stay at retentate side of the membrane. The molecular sieving mechanism is shown in Figure 2.1.



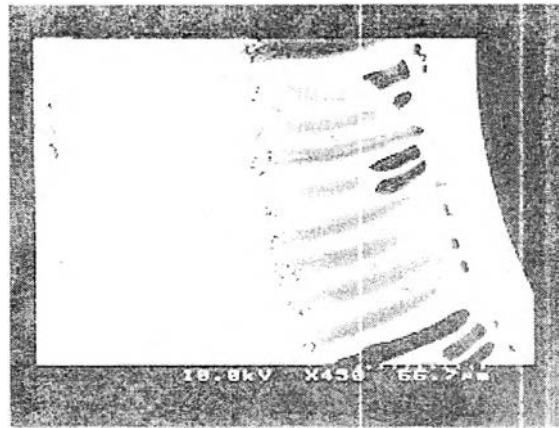
**Figure 2.1** The molecular sieving mechanism for porous membrane  
([www.co2crc.com.au/imagelibrary2/capture.html](http://www.co2crc.com.au/imagelibrary2/capture.html)).

The second type of membrane is nonporous membrane or dense membrane by using the difference in solution-diffusion of molecule. There three steps in solution-diffusion mechanism for dense membrane: (1) adsorption or absorption upon the upstream boundary. (2) diffusion through the polymeric membrane, (3) desorption or dissolution at the opposite interface of the membrane. This solution-diffusion mechanism is driven by a difference in thermodynamic activity between the interface of upstream and downstream. The solution-diffusion mechanism is shown in Figure 2.2.



**Figure 2.2** The solution-diffusion mechanism for dense membrane  
([www.co2crc.com.au/imagelibrary2/capture.html](http://www.co2crc.com.au/imagelibrary2/capture.html)).

The third type is called an asymmetric membrane. Asymmetric membrane denotes the structure consisting of a dense skin layer and a porous support layer, as shown in Figure 2.3. In the support layer, the polymer matrix and the pores are co-continuously connected across the layer. The three-dimensionally continuous polymer network exhibits the sufficient mechanical strength, and allows gases to pass through the three-dimensionally continuous pores without gas resistance.



**Figure 2.3** Structure of asymmetric membrane cross section ([www.eng.nus.edu.sg](http://www.eng.nus.edu.sg)).

Types of membranes most commonly used in membrane separation processes are polymeric and nonporous. The separation is based on a solution-diffusion mechanism, which involves molecular-scale interactions of the permeating molecule with the membrane polymer. The mechanism assumes that each molecule of gas is adsorbed by the membrane at one interface, transported by diffusion across the membrane through the voids between the polymeric chains (or called free volume), and desorbed at the other interface. According to the solution-diffusion model, the permeation of molecules through membrane is controlled by two major parameters: the thermodynamic factors, called the solubility coefficient ( $S$ ) and a kinetic parameter, called the diffusivity coefficient ( $D$ ). Diffusivity is a measure of the mobility of individual molecules passing through the void between polymeric chains in a membrane material. The solubility coefficient equals the ratio of sorption uptake normalized by some measure of uptake potential, such as partial pressure. Solubility coefficient ( $S$ ) reflects the number of molecules dissolved in membrane material. Flux or permeability ( $P$ ) defined in Eq. (2.1), represents the quantity of mass transport through the membrane.

$$P = D \times S \quad (2.1)$$

The ability of a membrane to separate two gas molecules called membrane selectivity,  $\alpha_{A/B}$  which is an ideal separation factor, can describe the ability of a membrane to separate gaseous mixture of A and B and can be written as a ratio of the permeability of component A and B.

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (2.2)$$

where  $P_A$  and  $P_B$  are the permeabilities of pure gas A and B that pass through the membrane, respectively.

Since permeability depended on both diffusion coefficient (D) which affected the mobility of each molecule in dense membrane, and solubility coefficient (S) which reflect the number of molecules dissolved in membrane material, so membrane selectivity ( $\alpha_{A/B}$ ) can be written as product of the diffusivity selectivity and solubility selectivity.

$$\alpha_{A/B} = \left( \frac{D_A}{D_B} \right) \left( \frac{S_A}{S_B} \right) \quad (2.3)$$

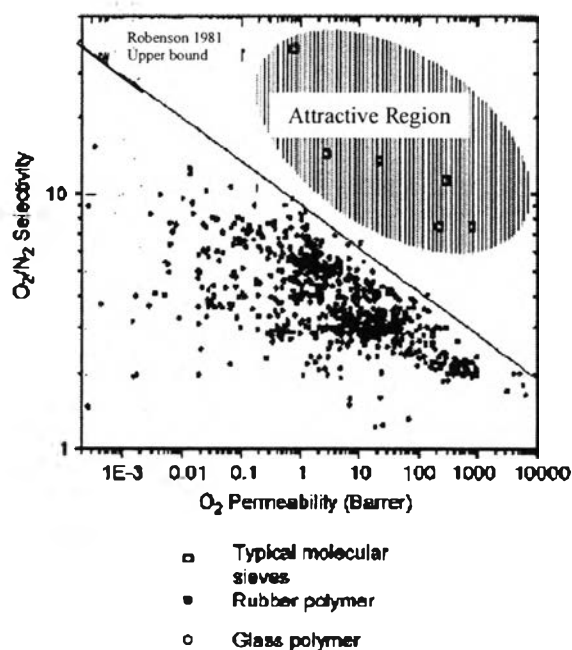
where  $D_A/D_B$  is the diffusivity selectivity and  $S_A/S_B$  is the solubility selectivity.

The diffusivity selectivity is based on the inherent ability of polymer matrix to function as size and shape selective media. This ability is determined by such factors 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 of which the membrane is composed.

## 2.2 LITERATURE REVIEW

### 2.2.1 Mixed Matrix Membranes (MMMs)

During the last two decades, the membrane gas separation process has become a predominant process for gas separation in the commercial scale. To increase the membrane performance or selectivity, either the diffusivity or the solubility needs to be enhanced. However, for a particular membrane polymer, these factors are fixed and difficult to alter without chemically modifying the molecular structure (Kulprathipanja et al, 1988). In addition, chemical modification and selectivity enhancement through gas diffusion mechanism are still difficult and have a limitation with gas separation. In early 1990s, Robeson asserted that the limitation of  $O_2/N_2$  separation for various types of membrane materials was predicted as shown in Figure 2.4.



**Figure 2.4** Relationship between the  $O_2/N_2$  selectivity and  $O_2$  permeability for polymeric membranes and inorganic membranes (Chung *et al.*, 2007).

For a polymeric materials, with an “upper-bound” in Figure 2.4, the limitation of selectivity and permeability based on the inherent structure property of material. To come across this limitation, the new type of membrane has been developed—mixed matrix membrane (MMM), which can enhance the membrane solubility and physical modification in the polymer membrane phase using molecular sieve particles as shown in attractive region in Figure 2.4.

Mixed matrix membranes (MMMs) consist of organic polymer and inorganic particle phases which help to improve the performance of membrane. There are two types of mixed matrix membranes base on the membrane materials that compose of. (Kulprathipanja et al, 1988). The first is an organic base membrane incorporate with adsorbent particle ( $MMM_{ADS}$ ). The adsorbent can be zeolites, such as NaX, AgX, NaA, NaY and silicalite, silica gel, alumina, activated carbon or any porous materials. The polymers can be cellulose acetate (CA), polyimide, silicone rubber, polyethersulfone or polysulfone. The second type of mixed matrix membrane is produced by casting polyethylene glycol (PEG) and silicone rubber on a porous polysulfone support ( $MMM_{PEG}$ ). Both types of mixed matrix membranes were evaluated for the separation of polar gas from non-polar gas, carbon dioxide from nitrogen and methane, and light paraffin from light olefin.

Kawakami *et al.* (1982) also reported cellulose nitrate/PEG blend membranes having up to 50 percent by weight of PEG. These membranes showed  $CO_2$  permselectivities of 29 to 38, with  $CO_2$  permeabilities of 1.4-8.2 Barrer. The permeability and  $CO_2$  permselectivity of cellulose nitrate/PEG blended membranes increase appreciably with increasing PEG fraction. The significant increase in  $CO_2$  permeability was attributed to the increments to both diffusivity and solubility of  $CO_2$ . It has been interpreted that an increase in diffusivity results from the spreading effect of the PEG plasticizer on the polymer chain.

Li *et al.* (1998) fabricated poly(ethylene glycol) (PEG)/cellulose acetate (CA) blended membranes for gas permeation studies. The apparent solubility coefficients of  $CO_2$  were reduced by blending PEG20000 (average molecular weight of 20,000). The blended membranes containing PEG exhibited

high apparent CO<sub>2</sub> diffusivity coefficients, resulting in high permeability coefficients for CO<sub>2</sub> compare to that of the CA membrane. They described that flexible main chain of PEG20000 in the amorphous domains in the blends permitted the large penetrants, CO<sub>2</sub>, and CH<sub>4</sub> to diffuse easily through the blended membranes, resulting in higher permeance of CO<sub>2</sub>, and CH<sub>4</sub> relative to that of N<sub>2</sub>. Hence, the CO<sub>2</sub>/ CH<sub>4</sub> permselectivities decreased by blending of PEG20000 with CA.

Suzuki *et al.* (1998) fabricated composite hollow fiber membranes composed of a thin and dense outer-layer of BPDA-PEO/ODA polyimide and a sponge-like layer of BPDA-ODA/DABA polyimide. The 1 mm thick outer layer was accountable for the gas separations. They had same results from mixed gas measurement, as well as from pure gas measurement. The CO<sub>2</sub> permeance and the CO<sub>2</sub>/N<sub>2</sub> permselectivity decreased in a month after the membrane preparation. The reduction of membrane performance was caused by densification of the inner layer at the interface to the outer layer, which might be caused by a plasticization effect of the PEO-containing polyimide. For this reason, the interface of the inner layer might become dense and act as an additional layer. Though, the membrane performance did not change a lot subsequent to the first month

### 2.2.2 Glassy polymer Mixed Matrix Membranes (Glassy MMMs)

Recently, many types of polymers (polyolefins, polyimides, polysulfones, cellulose, polycarbonates, etc.) have been explored for fabricating the practical gas separation membranes. In these polymeric membranes, polyimide membranes are the most promising due to their excellent properties of:

1. high selectivity and permeability
2. easy to prepare asymmetric structure
3. high thermal stability and high chemical stability
4. high mechanical strength
5. long durability

Membrane gas separation processes are widely used in many applications, especially in high valuable productivity such as olefin/paraffin separation. Srisilp (2004) studied the performance of Glassy MMMs which composed of

Silicalite-Polyimide (PI) polymer and with and without modification of zeolite surface. MMMs were fabricated and then tested the performance through the permeation rate of gases. It was found that introducing aminofunctional silane agent provided better adhesion between solid and polymer phases, but not improved selectivity of olefin/paraffin separation. Moreover, all type of zeolite studies were not suitable to develop MMMs with Ultem membrane as a consequence of remaining or decreasing of selectivity when compared to the pure Ultem membrane.

Furthermore, membrane gas separation process not only use for olefin/paraffin separation, but also use for valuable gases separation such as CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub>. Pechar *et al.* (2002) explored the effect of modified zeolites (ZSM-2) composed of a glassy polyimide in order to fabricate the defect-free Glassy MMMs. The ZSM-2 zeolites were functionalized with amine groups by reacting them with aminopropyltrimethoxysilane in toluene. Zeolites which interacted through the secondary forces with the carboxylic groups along the polymer backbone were observed in the FTIR spectra. This suggested that the zeolite and polymer had a good contact at the interface. Permeation data of He, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, were collected and analyzed. The permeabilities of He, CO<sub>2</sub>, and CH<sub>4</sub>, all decreased, while O<sub>2</sub>, and N<sub>2</sub>, increased.

In 2006, Pechar *et al.* (2006) developed Glassy MMMs composed of zeolite L dispersed in a 6FDA-6FpDA-DABA polyimide matrix. By changing type of zeolite, zeolite L was used to replace modified zeolites (ZSM-2), and amine-functionalized by reacting it with aminopropyl-triethoxysilane (APTES) in toluene. The non-defects interfacial contact of Glassy MMMs were fabricated and characterized. The results showed that the lack of an increase in permeability of He through the Glassy MMM as compared to the pure polyimide membrane indicated that there were no voids at the polymer-zeolite interface. O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> permeabilities increased, while those of He and CO<sub>2</sub> decreased. The permeabilities of CH<sub>4</sub> and CO<sub>2</sub> dropped with increasing pressure in both the mixed matrix and pure polymer systems.

Tin *et al.* (2005) investigated a carbon-zeolite Glassy MMMs in which zeolite was a dispersed phase in a carbon matrix. The investigation was performed to study the use of zeolite KY as the dispersed phase in the continuous matrix



phase of polyimide carbon membranes. A carbon-zeolite KY composite membrane was fabricated through the pyrolysis of a polymer-zeolite mixed matrix membrane. The results illustrated that the selectivity and permeability of the carbon-zeolite KY composite membrane increased to a great extent after carbonization. The carbon-zeolite KY composite membrane had higher separation performance in CO<sub>2</sub>/CH<sub>4</sub> than the carbon membrane derived from a pure Matrimid<sup>®</sup> dense film (CM-Matrimid<sup>®</sup>-800). The selectivity of CO<sub>2</sub>/CH<sub>4</sub> outstandingly enhanced from 61 to 124 for carbon-zeolite KY composite membrane, while the permeability decreased after carbonization, compared to CM-Matrimid<sup>®</sup>-800.

Husain and Koros (2007) fabricated mixed matrix asymmetric hollow fiber membranes by spinning via a dry jet-wet procedure using a surface modified small pore size zeolite, HSSZ-13, incorporated in an Ultem<sup>®</sup> 1000 polyetherimide matrix. Due to poor adhesion between the zeolite and the polymer phase, silane coupling agents were firstly chosen as a method to improve the zeolite-polymer compatibility and subsequent polymer “sizing” did not increase the selectivity of the Glassy MMMs. On the other hand, hollow fiber asymmetric membranes incorporating Grignard reagent-modified zeolite demonstrated a selectivity enhancement of 10%, 29%, and 17% for O<sub>2</sub>/N<sub>2</sub>, He/ N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub> pure gas pairs, respectively, and 25% for mixed gas CO<sub>2</sub>/CH<sub>4</sub>.

Vu *et al.* (2003) incorporated a carbon molecular sieve (CMS) as the disperse phase in Glassy MMM films using two different continuous polymer matrices (Matrimid<sup>®</sup> 5218 polyimide and Ultem<sup>®</sup> 1000 polyetherimide). The CMSs were prepared by the pyrolysis of a Matrimid<sup>®</sup> polyimide precursor to the final temperature of 800°C. Mixed matrix films containing a high loading of CMS particles (up to 35 wt. %) dispersed within the Matrimid<sup>®</sup> 5218 polyimide and the Ultem<sup>®</sup> 1000 polyetherimide polymer matrix were prepared by the flat-sheet solution casting method. The results showed that the Matrimid<sup>®</sup>-CMS and Ultem<sup>®</sup>-CMS mixed matrix membranes displayed significant enhancement in CO<sub>2</sub>/CH<sub>4</sub> selectivity, about 45 and 40% respectively compared to the pure polymer.

Anson *et al.* (2004) investigated the performance of various novel MMMs for CO<sub>2</sub>/CH<sub>4</sub> 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 CO<sub>2</sub>/CH<sub>4</sub> selectivities of ABS-AC mixed matrix composite membranes are simultaneously increased with increasing activated carbon loadings in the mixed matrix composite membrane, compared to that of the intrinsic ABS polymeric membranes.

Kim *et al.* (2007) fabricated and characterized novel nanocomposite membranes containing modified SWNTs inside a polysulfone matrix. To help the dispersion in the polysulfone, the carbon nanotubes were functionalized with long chain alkyl amines. Both permeabilities and diffusivities of the membranes increased with the weight fraction of carbon nanotubes at 4 atm.

### 2.2.3 Glassy MMMs with Plasticization Effect

In CO<sub>2</sub>/CH<sub>4</sub> membrane separation, plasticization phenomena occur when the CO<sub>2</sub> concentration in the polymer is high enough to increase free volume and segmental mobility. The polymer matrix swells upon sorption of CO<sub>2</sub>, accelerating the permeation of CH<sub>4</sub>. As a result, the polymer membrane lost its selectivity. For some polyimides with outstanding permeation performance a partial pressure of carbon dioxide of 8-10 bars is often sufficient to induce plasticization. To overcome this effect, plasticization should be minimized. Many attempts investigated several of methods to minimize the plasticization effect with polyimide-MMMs. Bos *et al.* (1998) studied the effect of thermal-treatment to the plasticization by heating polyimide (Matrimid® 5218) membrane at 350 °C for 15, 30, and 45 min. The result revealed that with heat-treated membrane, CO<sub>2</sub>-induced plasticization was successful suppressed but provided lower permeability.

Furthermore, the combing method between chemical cross-linking and heat treatments to minimize the plasticization effect was investigated. Shao *et al.* (2005) explored the chemical modification of polyimide. Ethylenediamine (EDA) was used to cross-link polyimides and the EDA modified polyimides

were further thermally treated at different conditions to enhance anti-plasticization characteristics. It was found that all EDA cross-linked samples have the higher  $H_2/N_2$ ,  $He/N_2$ ,  $O_2/N_2$  and  $CO_2/CH_4$  selectivity than those of the untreated one. Nevertheless, the plasticization resistance of polyimides can be practically achieved by EDA cross-linking followed by thermal treatment. The strong amide- $CO_2$  interactions and sorption advantages are reduced so that the  $CO_2/CH_4$  selectivity for mixed gas test increases.

In addition, the further study about Glassy MMMs for gas separation is introducing liquid additives into the polymer phase can alter the performance of membrane. For example, introducing butanediols such as polyethylene glycol (PEG) and some of diol isomers, into zeolite pores and then incorporated with silicon rubber MMMs (Vijitjunya, 2001). As an end result, the selectivity of olefin/paraffin separation was enhanced which refer to the group of butanediols play a significant role in the selectivity improvement.

Polyethylene glycol was introduced into pores of activated carbon and then admixed with silicon rubber in order to fabricate solid-liquid-MMMs Charoenphol (2002). The selectivity of  $CO_2/N_2$  was significantly improved as a result of increasing PEG concentration in the membrane.