# CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE SURVEY

2.1 Theoretical Background

2.1.1 Theory of Gas Transport in Membranes

Polymeric membrane based separation is widely used at moderate temperature and pressure. There are three types of polymeric membranes based on the mechanism of gas separation. First, a porous membrane uses molecular sieve to separate one type of molecule from another type in that the smaller molecule can diffuse through the pore of the membrane and pass through the permeate side. On the other hand, the bigger molecules which are bigger than the pore of the membrane cannot pass through the permeate side but is rejected and stays at the retentate side of the membrane. Second, a nonporous membrane or dense membrane uses the difference in solution-diffusion of a molecule (Figure 2.1). The mechanism occurs in three successive steps: (1) sorption of penetrant in the polymer film; (2) diffusion of the penetrant through the polymer film; (3) desorption at the opposite interface. This solution-diffusion model is widely used in gas separation applications to control the permeation of different species. The chemical potential gradient across the membrane is expressed as a concentration gradient but not a pressure gradient. A third type is called asymmetric membrane (Figure 2.2) which consists of two layers: a very thin active dense layer on the top surface, and a thick porous layer on the other side. The latter is effective for both high permeation rate (not for selectivity) and mechanical support of the thin dense layer. The thin active dense membrane is essential in the separation of small molecules by the membrane system. Therefore, in order to fully understand the asymmetric membrane's transport properties, studied on sorption, diffusion, and permeation of small molecules through the dense membrane must first be established.
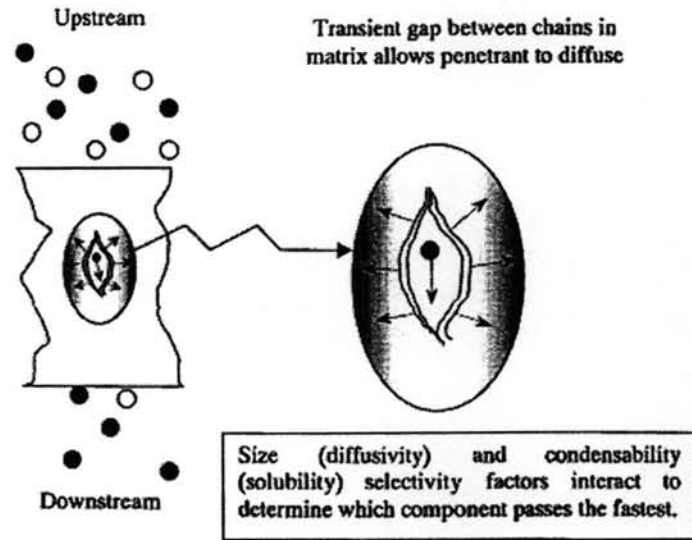
Figure2.1 Solution-diffusion mechanism. (Ismail and Lorna, 2002)
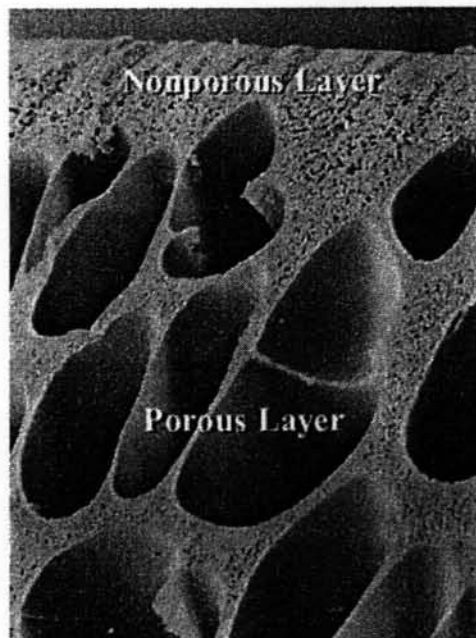
Figure 2.2 Asymmetric membrane. (Dortmundt and Doshi, 1999)

A quantitative measure of mass transported through the polymeric membrane is characterized by the permeability. According to the solution-diffusion model, the permeability P_A is a product of a thermodynamic factor, called the solubility coefficient S_A, and a kinetic parameter, called the diffusion coefficient D_A.

$$P_A = D_A * S_A \qquad (2.1)$$

Therefore, gas permeability is not a fundamental property of these materials. It is the product of a mobility (kinetic)-related term and a solubility (thermodynamic)-related term. The diffusion coefficient is a measure of the amount of energy necessary for the penetrant to execute a diffusive jump through the polymer matrix and the intrinsic degree of segmental packing in the matrix. It is determined by the packing and motion of the polymer segments and by the size and shape of penetrating molecules. On the other hand, the solubility coefficient depends on the condensability of the penetrant, the extent of the polymer-penetrant interaction, and the amount of excess volume existing in the polymer.

The ability of a membrane to separate a gaseous mixture of A and B in a single-stage membrane process may be characterized by the ideal separation factor or permselectivity, $\alpha_{A/B}$, which is defined by

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

where P_A and P_B are the permeabilities of pure gases A and B, respectively.

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

$$\alpha_{A/B} = \frac{D_A * S_A}{D_B * S_B} \qquad (2.3)$$

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 the polymer matrix to function as a size- and shape-selective media. This ability is primarily 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 condensibities of the two penetrants as well as the physical interaction of the penetrants with the particular polymer that the membrane is composed of.

2.1.2 Influence of Carbon Dioxide on Polymer Plasticization

2.1.2.1 Gas-polymer interactions

Nowadays, it would be of great interest to study the interaction between gases and polymers as a result of the rapid progress in the advanced technology of membrane separations. Since then, the sorption and transport behavior

of CO_2 in glassy polymers has been extensively studied because of its potential applications in several areas. However, it is recognized that CO_2 acts as a plasticizer at a sufficiently high level of concentration. CO_2 at elevated pressure resembles common organic solvents in its ability to swell and plasticize polymers. Gases like CO_2, with higher critical temperature, are considerably more soluble, particularly in glassy polymers. Furthermore, high gas solubilities can contribute to plasticization due to the fact that strong interactions between polymer and penetrant can lead to low gas diffusivities. In other words, every sorbed CO_2 molecule contributes instantaneously in the dilation of the polymer. Thus, it was thought that CO_2-induced plasticization might significantly alter the membrane performance in high-pressure CO_2/CH_4 separations.

It was thought that in polymethyl-methacrylate (PMMA), polyethyl-methacrylate (PEMA) and cellulose acetate (CA) polar and flexible pendent groups, such as $-OCOCH_3$ or $COOCH_3$, contribute to the plasticization behavior of CO_2. CA also contains polar hydroxyl groups, but it is speculated that the ester unit is more important in the plasticization process since both CA and the polyacrylates have this functional group in common. The polar groups of the polymer could have dipolar interactions with the polarizable carbon dioxide molecules. The solubility selectivity increases with increasing concentration of the polar groups.

The interactions of CO_2 with polar groups in the polymer chain are stronger than the interactions between chain segments. Thus, CO_2 breaks these interactions, which provides additional diffusion pathways for the CO_2 molecules. It is also clear why it is suggested that the pendant group should be flexible in addition to being polarity. As the interaction between the pendant groups is broken, the polymer segments become highly mobile; this provides more opportunities for penetrant molecules to execute diffusive jumps.

To get more insight into the effect of the concentration of sorbed CO_2 on plasticization, the plasticization pressure should be correlated with the concentration of CO_2 sorbed by the polymer at the plasticization pressure. It is hypothesized that each polymer needs the same CO_2 concentration to induce

plasticization, but that each polymer requires a different pressure (the plasticization pressure) to reach this concentration.

2.1.2.2 CO_2-permeation behavior

Typically, three types of pressure dependencies of the CO_2 permeability in polymeric membranes can be distinguished, as shown in Figure 2.3:
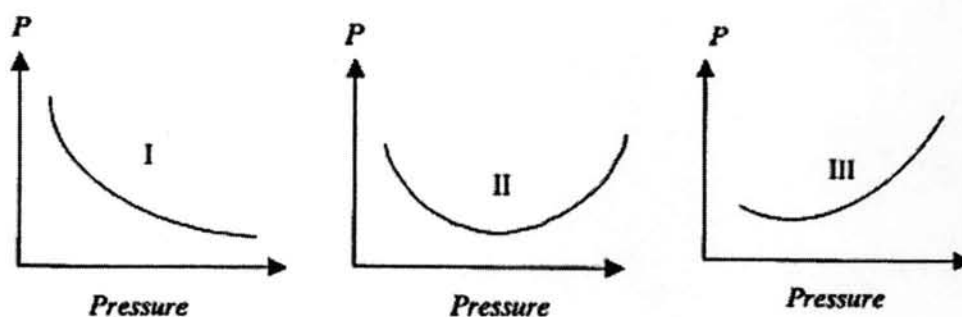
Figure 2.3 Representation of the possible shapes of the permeability (P) of several glassy polymers to CO_2. (Ismail, 2002)

Type I The gas permeability of the polymer decreases with increasing pressure; for polymers without large substituents on the backbone, such as polysulfone and polycarbonate for pressures up to 30 bar.

Type II shows that the permeability initially decreases at low feed pressure. As the pressure is increased to a critical pressure, the permeability of gas begins to increase with increasing pressure, e.g. various polyimides.

Type III has been found for polyarylate, such as polymethylmethacrylate (PMMA) and polyethylmethacrylate (PEMA) and cellulose acetate (CA). Although these polymers are in the glassy state, they show a similar permeation behavior as found for rubbers as they have permeability to CO_2 that progressively increases as a function of pressure.

Considering the solution-diffusion model, the increase in permeability is attributed to the concentration dependence of the diffusion coefficient. The pressure dependence of solubility coefficient is comparable for different polymers. Hence, differences in permeability are determined mainly by the diffusivity. Furthermore, the diffusivity generally increases with increasing pressure,

whereas the solubility decreases. An increase in permeability is therefore possible because the diffusion coefficient increases with concentration much more rapidly than the solubility coefficient decreases with pressure. However, this does not imply that the solubility of a penetrant is unimportant. On the contrary, solubility indirectly contributes to the increase in diffusivity. Ultimately, the diffusion coefficient can only increase because the CO_2 concentration in the polymer increases.

2.2 Literature Review

2.2.1 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 membranes composed of a variety of materials. Both types are made from many polymers. During the period of 1980-1985, the installation of membrane plants using carbon dioxide selective cellulose acetate membrane began. This membrane has a CO_2/CH_4 selectivity of about 12-15. Cellulose acetate is only now being slowly replaced by polyimide and polyaramide membranes with a selectivity of 20-25. Though the advantages are a simple flow configuration and low-maintenance operation, membrane systems cannot compete with the current amine systems for most CO_2 removal applications. The problem is low selectivity and flux.

To separate 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, this shows the ideal propylene/propane selectivity of 9.1 at 323 K with permeability of 2.3 barrer (Ilinich and Zamaraev, 1993). 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)

The effect of polymer structure on permeation characteristics was investigated by Stern et al. (1989). The investigation included the development of nine types of polyimide membranes. Permeability results showed improved selectivity for polyimide versus conventional glassy polymers, which include cellulose acetate, polysulfone, and polycarbonate. This behavior is attributed to chain stiffness and packing density. It can be concluded that calibration of the packing density as a function of the properties of penetrant molecules is necessary to achieve the required permeation rates. In addition, Ettouney and Majeed (1997) developed permeability functions for pure gases and mixtures of N_2, CH_4, CO_2 and O_2 as a function of driving pressure for polysulfone and silicone rubber membranes. For polysulfone membranes, the presence of the faster permeating species enhanced the permeation rates of slower species. This behavior was found for N_2 in air and in the CO_2 mixture, where the permeability of N_2 in both mixtures was higher than the permeability for pure N_2. Similarly, the O_2 permeability measured in the CO_2 mixture is higher than the pure gas permeability. In addition, reduction in the faster species permeability was caused by the presence of the slower permeation species. However, the permeation behavior of various gases in silicone rubber was distinguished from that in polysulfone. In this regard, small variations were found in the measured permeability for various gases in the mixture and pure states.

The use of a combined polymeric membrane (hydrophilic-hydrophobic, SLM type), which has been proposed as an effective support for CO_2 absorbent solutions, was studied by Freni et al. (2004). They use different liquid absorbents (2-ethanolamine, K_2CO_3, H_2O) as a carrier. The experimental results pointed out that the performances, in terms 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 a type of adsorbent with greater affinity toward CO_2. Furthermore, Yi et al. (2006) facilitated the transport of CO_2 through polyvinylamine/polyethylene glycol (PEG)

blend membranes. The blend membrane with 10 wt% PEG had the highest pure CO_2 permeation rate and the highest selectivity. The effects of cross-linking and the coupling effects between CO_2 and CH_4 were also investigated. The selectivity increases remarkably when the membrane is cross-linked. For mixed gas of constant CH_4 partial pressure and changing CO_2 partial pressure, the CH_4 permeation rate increases with an increase of CO_2 partial pressure due to the coupling effects.

To improve the separation effectiveness of the hollow-fiber membranes from Matrimid® 5218 and flat-sheet membranes from polyvinyltrimethylsilane (PVTMS), Syrtsova et al. (2004) studied the effect of gas phase fluorination on the membranes. It was found that this modification significantly increases selectivity of separation of CO_2/CH_4, He/CH_4 and He/N_2 at a negligible decrease of permeability for He and CO_2

2.2.2 Plasticization

In CO_2/CH_4 membrane separation it is well known that CO_2 acts as a plasticizer. Plasticization occurs when the CO_2 concentration in the polymer is high enough to increase the free volume and segmental mobility. Due to the swelling of the polymer matrix, the permeation of CH_4 is accelerated and as a consequence of polymer loses its selectivity. Bos et al. (1999) investigated a CO_2-induced plasticization phenomenon in eleven different glassy polymers. They tried to search for relationships between the plasticization pressure and the chemical structure or 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. However, no dependence of the plasticization pressure on the carbonyl or sulfone density of the polymers considered was observed. Instead, it was proposed that all polymers need a similar CO_2 concentration to be plasticized, but required different pressures to achieve it.

Since plasticization generally leads to a loss in the selectivity of a membrane, plasticization should be minimized. Plasticization effects can be suppressed by various means. A method is defined as successful if the permeability

as a function of pressure does not increase anymore. There are several methods used to suppress the plasticization:

2.2.2.1 Chemical cross-linking treatment

Staudt-Bickel and Koros (1999) studied the uncross-linked and cross-linked polyimide with copolyimide in order to increase selectivity without the plasticization phenomenon. They found that chemical cross-linking of the free carboxylic acid group of 6FDA-mPD/DABA 9:1 with ethylene glycol can reduce the swelling effects by CO_2 at least up to a pure CO_2 feed pressure of 35 atm. Furthermore, copolyimides containing a carboxylic acid group in every tenth polymer unit can strongly reduce permeability. They also found that 6FDA/mPD (uncross-linked) showed a plasticization pressure at 4 atm but 6FDA-mPD/DABA copolyimide shifted the plasticization pressure up to 14 atm due to the hydrogen bonding between the carboxylic acid groups. However, 6FDA-mPD/DABA 9:1 and 6FDA/DABA cross-linked did not show any signs of plasticization. Because of the high degree of cross-linking, a very rigid polyimide structure was obtained.

Hibshman *et al.* (2004) determined the degree of CO_2 plasticization by studying the permeability coefficients of methane and carbon dioxide as a function of feed pressure for two polyimides, 6FDA-6FpDA and 6FDA-6FpDA-DABA, and two polyimide-organosilicate hybrid membranes. For methane, the permeability coefficient decreased with increasing pressure. For carbon dioxide, plasticization dominated the permeation mechanisms above 17 atm. The degree of plasticization was dependent upon the degree of cross-linking, being the lowest in a highly cross-linked hybrid membrane. In addition, separate analysis of the diffusion and sorption behavior of CO_2 and CH_4 suggested that the plasticization results more from changes in local chain dynamics rather than from increases in free volume due to swelling.

2.2.2.2 Chemical cross-linking and heat treatment

Bos *et al.* (1998) studied the effect of thermal treatment on the plasticization by heating a polyimide (Matrimid® 5218) membrane to 350°C for 15, 30, and 45 min. They found that the treated membrane reached a steady-state value

of permeance. It can be concluded that the cross-linking method is effective in suppressing the CO_2-induced plasticization. Also, the CO_2/CH_4 selectivity of a treated film is higher than the untreated one due to the permeability of CH_4 decreasing more than the permeability of CO_2. In 2001, they studied the effect of blending Polyimide (Matrimid® 5218) with copolyimide, P84 (60/40) on the plasticization phenomenon. They found that the blend polymer can shift the plasticization pressure to higher feed pressure due to the densification of the polymer matrix, and hence there is reduction of free volume. Also, a blending of polymers not only suppresses plasticization but also increases selectivity. They concluded that the blending of a polymer that is highly susceptible to plasticization with a polymer that hardly ever plasticization presents a simple method to suppress plasticization.

Krol *et al.* (2001) studied the plasticization phenomenon in polyimide hollow fiber gas separation membranes of propane/propylene and ways to suppress it (i.e. heat treatment). They found that propylene can plasticize a membrane like CO_2 and it was clear that heat treatment reduces the permeance (the more intense the treatment, the larger the decrease in permeance). The results showed that mild heat treatment is not sufficient to suppress plasticization completely at high feed pressure, but if using a temperature more than 200°C (still below the glass transition temperature, T_g), it can completely suppress plasticization due to the thermal curing. Therefore, it is not always necessary to have cross linking to suppress plasticization. Thermal curing can already be sufficient.

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 CO_2 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 in suppressing CO_2 plasticization on an asymmetric polysulfone membrane. Experimental results showed that the membranes were stabilized against CO_2 plasticization after the heat treatment process. However, permeation rates were reduced with the intensity of heat treatment.

Wind *et al.* (2004) developed polyimide membranes cross-linked with 1,4-butylene glycol and 1,4-cyclohexanedimethanol to separate CO_2/CH_4 mixtures and multicomponent synthetic natural gas mixtures. It was successful in reducing CO_2 plasticization effects by thermal annealing and cross-linking. Furthermore, CO_2 permeabilities also increased without a loss in selectivity.

Shao *et al.* (2006) investigated 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. They 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 unmodified one. Furthermore, the plasticization resistance of polyimides can be practically achieved by EDA cross-linking followed by thermal treatment. After thermal annealing to high enough temperatures, the amide groups decrease and imide groups increase. The strong amide-CO_2 interactions and sorption advantages are reduced so that the CO_2/CH_4 selectivity for mixed-gas test increases.

2.2.3 Mixed Matrix Membranes

During the 1980s, membrane gas separation emerged as a commercial process on a grand scale. This led to intensified academic interest, with the result that published research in this field increased substantially. The mixed matrix membranes have been developed by modifying the 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 selectivity significantly higher than polymeric membranes. Two types of mixed matrix membranes (Kulprathipanja *et al.*, 1986 and 1988), solid-polymer and liquid-polymer, have been developed. The first is a membrane with a solid adsorbent embedded in the polymer phase (MMM_{ADS}). The adsorbent can be zeolites, such as NaX, AgX, NaA and silicalite, silica gel, alumina, or activated carbon. The polymers can be cellulose acetate (CA), polyimide, silicone rubber, polyethersulfone or polysulfone. The second type of mixed matrix membrane is a membrane with a liquid adsorbent (polyethylene glycol: PEG) and silicone

rubber cast on a porous polymer support (MMM$_{PEG}$) such as polysulfone. 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 paraffins from light olefins (Kulprathipanja *et al.*, 1986 and 1988).

2.2.3.1 Introducing zeolite as an adsorbent into the polymer phase

Interfacial void-free Matrimid polyimide (PI) membranes filled with zeolite were prepared by introducing 2,4,6-triaminopyrimidine (TAP) by Yong *et al.* (2001). They found that TAP enhanced the contact of zeolite particles with polyimide chains presumably forming hydrogen bonding among them. The void-free PI/13X zeolite/TAP showed higher gas permeability for He, N_2, O_2, CO_2 and CH_4 with a small expense of selectivity compared with the PI/TAP membrane, while PI/4A zeolite/TAP membrane showed the lower permeability but higher selectivity.

Tantekin-Ersolmaz *et al.* (2000) investigated the effect of particle size on the performance of zeolite-polymer mixed matrix membranes as a function of the zeolite loading. Polydimethylsiloxane (PDMS, i.e. silicone rubber) was chosen as the polymer phase and silicalite was used as a zeolite filler. The separation properties of the mixed matrix membranes prepared were characterized by permeability measurements for O_2, N_2 and CO_2 gases. The permeability of the silicalite-PDMS mixed matrix membranes increase with increasing particle size of the silicalite crystallites. The permeability values corresponding to the mixed matrix membranes exceed those pertaining to the original polymer membrane only at relatively higher zeolite loadings and/or for relatively larger particle sizes.

Srisilp (2004) studied the effect of two types of zeolites, silicalite and NaX, on the performance of Ultem mixed matrix membranes. She concluded that the both types of zeolite studies were not suitable to develop MMMs with Ultem membrane. The molecular sieve effect of zeolite and the interactions between molecules of gas and zeolite might give the explanation for increasing in the permeability in this study. Appropriate selection of the specific dispersed material and polymer membrane are important consideration.

Li *et al.* (2005) demonstrated that the factors resulting from the interaction between polymer and zeolite phases may remarkably influence the gas separation performance (H_2/N_2 and O_2/N_2 separation) of mixed matrix membranes, such as the partial pore blockage of zeolites by the polymer chains. Zeolite-3A, 4A and 5A were used as the dispersed phase. Polyethersulfone (PES) was chosen as the continuous polymer matrix. They concluded that the permeability of all gases for PES-zeolite-3A, PES-zeolite-4A and PES-zeolite-5A membranes generally increase with an increase in zeolite pore size. This phenomenon only confirmed that the partial pore blockage of zeolites by the polymer chains may significantly affect the gas separation performance of mixed matrix membranes.

Pechar *et al.* (2006) found that the separation performance of mixed matrix membranes can be improved with the incorporation of a larger pore size zeolite. Mixed matrix membranes composed of zeolite-L dispersed in a 6FDA-6FpDA-DABA polyimide matrix were fabricated and characterized for gas separation performance. At 4 atm, oxygen, nitrogen and methane permeabilities through the MMM increased in accordance with the observed higher gas solubilities in the zeolite-L, while those of He and CO_2 decreased. The permeabilities of CH_4 and CO_2 dropped with increasing pressure in both the mixed matrix and pure polymer systems, suggesting that the gases were not accessing the zeolite pores.

Hu *et al.* (2006) investigated the pure gas permeation and sorption of surface modification zeolite-filled polymethyl methacrylate (PMMA) membranes. Interfacial void-free PMMA membranes filled with zeolite-4A were prepared by introducing 3-(trimethoxysilyl propylmethacrylate (TMOPMA) as a way to improve the gas separation properties of the polymeric membranes by making the zeolite more compatible with the polymer phase. The zeolite used in this work exhibited relatively high gas solubility compared to the pure PMMA membrane. The oxygen permeability of zeolite-filled PMMA membranes decreased with increasing zeolite-4A loading. At the same zeolite composition, zeolite surface modification with TMOPMA significantly improved the solubility and diffusivity coefficients of the zeolite-filled PMMA membranes, while the PMMA/zeolite-4A showed lower permeability but higher selectivity.

2.2.3.2 Introducing other types of adsorbents into the polymer phase

Vu *et al.* (2003) examined the use of a carbon molecular sieve (CMS) as the disperse phase in mixed matrix membrane films using two different continuous polymer matrices (Matrimid® 5218 polyimide and Ultem® 1000 polyetherimide). The results showed that Matrimid and Ultem mixed matrix membranes displayed significant enhancements in CO_2/CH_4 selectivity which increased 52% for the Matrimid and 38% for the Ultem, over the pure polymers. Similar enhancements were observed for O_2/N_2 selectivity for both mixed matrix films. Effective permeabilities of the penetrants (CO_2 and O_2) through the mixed matrix membranes are also significantly enhanced over the intrinsic permabilities of the Matrimid and Ultem polymer matrices.

Anson *et al.* (2004) investigated the performance of various novel mixed matrix membranes for the separation of CO_2 from CH_4 as a function of carbon loading. Acrylonitrile-butadiene-styrene (ABS) copolymer was used as the polymer matrix and two micro- and mesoporous activated carbons (AC) were chosen as inorganic fillers. The results showed that the pure gas permeabilities and CO_2/CH_4 selectivities of ABS-AC membranes are substantially increased over the intrinsic ABS permselectivities by increasing activated carbon loadings in the mixed matrix composite membrane.

Sridhar *et al.* (2006) developed the modified poly(phenylene oxide) (PPO) membranes to enhance the gas permeability characteristics of high-performance PPO membranes for the separation of CO_2/CH_4 gaseous mixtures. PPO was successfully modified physically by the incorporation of a heteropolyacid (HPA) filler and chemically by sulfonation. Incorporation of an inorganic filler into the PPO matrix, as well as modification by sulfonation rendered the polymer amorphous. Modified PPO membranes have shown good potential for separating the CO_2/CH_4 gaseous mixtures by increasing the CO_2 selectivity over the pristine PPO membranes.