

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Theory of Gas Transportation in Membranes

Membrane separation has gained attractive in chemical technology and is being used increasingly in a broad range of applications. There are two types of polymeric membranes based 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 molecules 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 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.

A quantitative measure of the amount of mass transported through the polymeric membrane is characterized by the permeability. The gas permeability of polymeric membrane is measure by a mean permeability coefficient ( $P$ ), which is defined by the isothermal relation and usually expressed in Barrers, in which 1 Barrer is equivalent to  $10^{-10} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$

$$P = \frac{Q \cdot l}{P_o - P_1} \quad (2.1)$$

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.

However, the effective thickness of membrane is much smaller than its actual thickness and may not be known. So, the gas permeability of membrane is often characterized by its permeance.

The permeability coefficient,  $P_A$  of penetrant A is the product of a kinetic parameter,  $D_A$ , the average diffusion coefficient, and thermodynamic parameter,  $S_A$ , the solubility coefficient

$$P_A = D_A * S_A \quad (2.2)$$

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 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

$$\alpha_{A/B} = P_A/P_B \quad (2.3)$$

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.

$$\alpha_{A/B} = \frac{D_A * S_A}{D_B * S_B} \quad (2.4)$$

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.

## 2.2 Plasticization

Gas separation process based on glassy solution-diffusion membranes frequently suffer from plasticization of the stiff polymer matrix by the sorbed penetrant molecule. It seems like hardly to identify the fundamental description or definition of plasticization. Moreover, we have been no method until now which can be used to predict precisely whether a material will be plasticized by a penetrant.

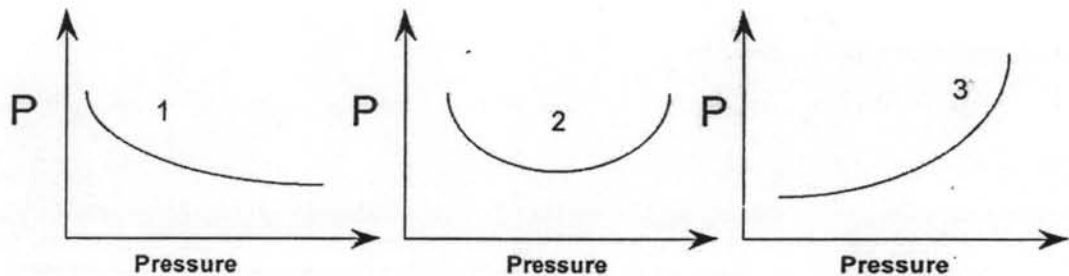
Generally, the permeability will be constant at any pressure. However, the permeability will increase with increasing pressure. Because penetrant acts as a plasticizer to decrease interaction between penetrant and membrane will change property of membranes. As a consequence, the polymer chains are separated by penetrant molecules, which lead to the loosening of matrix plus the increasing of the free volume and segmental mobility of the polymer matrix. Due to the swelling of the polymer matrix, the polymer losses its separation ability and unable to discriminate anymore on a basis of size and shape. In other words, the film has lost its molecular sieving and therefore causing the reduction in selectivity.

In the area of  $\text{CO}_2/\text{CH}_4$  separation with membranes, the removal of  $\text{CO}_2$  in natural gas, landfill gas, and  $\text{CO}_2$  removal from fractured well as well as the removal of  $\text{CO}_2$  in enhanced oil recovery application (EOR) are of interest. In some of these separation applications, the membranes are exposed to high  $\text{CO}_2$  concentration in the feed stream. The resulting strong interaction between the  $\text{CO}_2$  and the polymer material often affects flux and permselectivity properties.

Typically, three types of pressure-dependencies of the  $\text{CO}_2$ -permeability in polymeric membranes can be distinguished:

- 1) a decreasing permeability ( $P$ ) as a function of pressure over the pressure range considered,
- 2) a minimum in the permeability as a function of pressure, and
- 3) a progressive increase in permeability with increasing feed pressure.

The three types of permeation behavior are schematically given in Figure 2.1.



**Figure 2.1** Schematic representation of the possible shapes of the permeability ( $P$ ) versus pressure curves. (Ismail, A.I., and Lorna, W. 2002)

The three trends are found among polymers that differ over an order of magnitude in permeability. Polysulfone (PSF) and polycarbonate (PC), for example, show type 1 permeation behavior for pressure up to 30 bar. Polyimide (PI) shows a permeation curve represented by type 2. A relatively low partial  $\text{CO}_2$  pressure is necessary to induce plasticization. In this case, plasticization is defined as the increase in permeability with increasing feed pressure above a certain threshold pressure value. Type 3 has been found for polyarylate, such as polymethyl-

methacrylate (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.

Considering the solution-diffusion model, an 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. The 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<sub>2</sub> concentration in the polymer increases.

#### *Polarity of the polymer chain*

It was thought that in PMMA, PEMA and CA polar and flexible pendent groups, such as  $-\text{OCOCH}_3$  or  $\text{COOCH}_3$ , attribute to the plasticization behavior of CO<sub>2</sub>. 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 polyarylates 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 increased with increasing concentration of the polar groups.

The interactions of CO<sub>2</sub> with polar groups in the polymer chain are stronger than the interactions between chain segments. Thus, CO<sub>2</sub> breaks these interactions, which provides additional diffusion pathways for the CO<sub>2</sub> molecules. It is also clear why it is suggested that the pendant group should be flexible in addition to being polar. As the interaction between the pendant groups is broken, the polymer segments become highly mobile, which provides more opportunities for penetrant molecules to execute diffusive jumps.

To get more insight in the effect of the concentration of sorbed CO<sub>2</sub> on plasticization, the plasticization pressure should be correlated with the concentration

of CO<sub>2</sub> sorbed by the polymer at the plasticization pressure. It is hypothesized that each polymer needs the same concentration CO<sub>2</sub> to induce plasticization, but that each polymer requires a different pressure (the plasticization pressure) to reach this concentration.

## 2.3 Literature Review

### 2.3.1 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 membrane composed of a variety of materials. Both types are made from many polymers. In natural gas separation, almost natural gas requires some treatment to meet its specifications before delivered to the pipeline. About 17% of all domestic natural gas must be treated to remove CO<sub>2</sub>. The technology most widely used is amine absorption, but amine plants suffer from a number of problems such as high capital cost, labor-intensive, full-time supervision and complex operation. During period 1980-1985, installation of membrane plants using carbon dioxide selective cellulose acetate membrane began. It has a CO<sub>2</sub>/CH<sub>4</sub> selectivity of about 12-15. Cellulose acetate is only now being slowly replaced by polyimide and polyaramide membranes with selectivities of 20-25. Though the advantages of a simple flow configuration and low-maintenance operation, membrane systems cannot compete with current amine systems for most CO<sub>2</sub> removal applications. The problem is low selectivity and flux. 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 *et al.*, 2002).

Several investigators analyzed the conditioning effects of CO<sub>2</sub> on glassy polymers. Chiou and Paul (1987) studied the effect of CO<sub>2</sub> conditioning in polycarbonate and poly (methyl methacrylate). The results show different performances for the two membranes as a function of CO<sub>2</sub> conditioning and driving

pressure. For the polycarbonate membranes, permeability for pure CO<sub>2</sub> and CH<sub>4</sub> are reduced upon conditioning with CO<sub>2</sub> and increase of the driving pressure. On the other hand, the permeability for two gases in the acrylic membranes is attributed to high levels of CO<sub>2</sub> plasticization and subsequently increased rates of segmental motion of polymer chains. This behavior is the opposite of that found in the polycarbonate membranes. In this regard, it is assumed that exposure of the polycarbonate membranes to carbon dioxide alters the segmental organization, which does not recover to its original state upon removal of CO<sub>2</sub>.

Effect of polymer structure on permeation characteristics is investigated by Stern *et al.* (1989). The investigation included development of nine types of polyimide membranes. Permeability results show 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 properties of penetrant molecules is necessary to achieve the required permeation rates.

Pfromm *et al.* (1993) studied effects of preparation methods for polysulfone, polycarbonate and poly (ester carbonate). The measurements focused comparison of separation characteristics for dense and asymmetric membranes. Higher selectivity is reported for asymmetric films. This behavior is attributed to free volume distribution in the skin layer of asymmetric membranes.

Species permeability in commercial type membranes, which includes silicone rubber and cellulose acetate, were measured for pure and mixture gases. Ettouney *et al.* (1994) considered separation properties of mixtures of CO<sub>2</sub>/N<sub>2</sub> in silicone rubber and cellulose acetate membranes. The results show that the pure gas permeability is independent of the system pressure. This behavior is also observed for mixtures with lean or rich gas compositions, i.e., 90% CO<sub>2</sub> in N<sub>2</sub>. Permeability dependence on the system pressure is found in feed mixtures with compositions of 50% CO<sub>2</sub> in N<sub>2</sub>. Comparison of separation factors for silicone rubber and cellulose acetate is found to be similar for the mixture gases. This is irrespective of the fact that separation factors for the pure gas in cellulose acetate are 5-7 times higher. In addition, Hughes *et al.* (1995) examined possibilities of separation of nitrous oxide

from mixtures with  $O_2$  and  $CO_2$  by using cellulose acetate or silicone rubber membranes. Results show  $N_2O/CO_2$  membrane selectivity close unity in cellulose acetate and around 1.3 for silicone rubber. System operation at various temperatures or feed pressures did not improve the separation characteristics for either membrane.

Pellegrino and Kang (1995) measured  $CO_2$  and  $CH_4$  gas permeation through polyfluorosulfonate ionomer (PSFI) that was solvated with water, methanol, ethanol, and 1-propanol. The increased permeabilities of  $CO_2$  when the membrane was swelled by the solvent in the sequence of ethanol>methanol>water implied the effect of polar solvents. The higher permeability of  $CH_4$  compared to value measured from the dry PSFI film was observed. They suggested that the solvents penetrated into polymer phase and increased the permeability, which was resulted from the increase in diffusivity.

Barbari and Datwani (1995) modified polysulfone membranes by using bromine to form charge transfer complexes with unpaired electrons along a polymer backbone. The bromine molecules would alter the free volume distribution in such a way as to hinder the transport of large gas molecules without a significant reduction in the flux of the more permeable gas. After bromine treatment, the selectivity of a polysulfone membrane for  $CO_2$  over  $CH_4$  was increased over 100% at 10 atm upstream pressure with only a 36% reduction in  $CO_2$  permeability.

Hughes and Jiang (1995) measured the permeability of  $N_2O$ ,  $CO_2$ , and  $O_2$  through silicone rubber and cellulose acetate membranes using a flat sheet permeator. Measurements have also been made of individual gas permeabilities from a mixed feed stream.  $N_2O$  has the highest permeability when using the silicone rubber membrane, followed by  $CO_2$ , with  $O_2$  an order of magnitude less. All three gas permeability coefficients were independent of feed pressure, but both  $N_2O$  and  $CO_2$  permeability coefficients were temperature independent. For the cellulose acetate membrane,  $N_2O$  and permeabilities varied with feed pressure and all three gases gave positive temperature coefficients. No separation of  $CO_2$  from  $N_2O$  could be achieved under any conditions with the cellulose acetate membrane.

Yamasaki *et al.* (1997) prepared asymmetric membranes by the phase inversion technique under different gelation conditions from polysulfone/*N,N*-dimethylacetamide(DMAc) solutions. The dual bath method was employed to



control the skin layer properties. A thin layer of silicone rubber was laminated on the surface of each asymmetric polysulfone membrane to eliminate the effect of defects in the skin layer. The oxygen permeance was inversely proportional to the square root of immersion time in the first (2-propanol) bath. The skin layer thickness increased with an increase in the immersion time. Also, the oxygen permeance decreased with an increase in the polymer concentration in the casting solution. Selectivity of oxygen over nitrogen also depends both on the polymer concentration and the immersion time.

Ettouney and Majeed (1997) developed permeabilities functions for pure gases and mixture 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, presence of faster permeating species enhanced 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 presence of the slower permeation species. However, permeation behavior of various gases in silicone rubber was distinguished from that in polysulfone. In this regard, small variations are found in the measured permeability for various gases in the mixture and pure state.

The use of combined polymeric membrane (hydrophilic-hydrophobic, SLM type) has been proposed as effective support for  $CO_2$  absorbent solutions. They use different liquid absorbents (2-ethanolamine,  $K_2CO_3$ ,  $H_2O$ ) as carrier. The experimental results pointed out that the performances in term 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 the type of adsorbent with the greater affinity toward  $CO_2$  (Freni *et al.*, 2004).

### 2.3.2 Mixed Matrix Membranes

The mixed matrix membranes had been developed in the late 1980's. The desirable characteristics of mixed matrix membrane that must be possessed by

the membranes include a high selectivity of one or more gases from other gases as well as relatively high flux (Kulprathipanja *et al.*, 1988).

The first type of mixed matrix membrane was silicone rubber with polyethylene glycol (PEG) emulsified silicone rubber casting on a polysulfone support. It was found that the glycol plasticizer (PEG) was a good solvent for the polar gases, but it was not a good solvent for the non polar gases, the former will pass through the membrane at a much more rapid rate due to the solubility of gases in the glycol (PEG). Therefore, the selectivities of PEG /SR/PS were higher than a SR/PS. Additionally, the efficiency of MMM depended on amount of PEG in silicone rubber phase (Kulprathipanja and Kulkarni, 1986). The permeation rates of SO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were evaluated through a dense silicone rubber membrane and silicone rubber-PEG mixed matrix membrane. The results showed that the gas permeance was a function of critical temperature while the gas selectivities were observed to be similar for each of the dense silicone rubber membranes. For the mixed matrix membrane, the gas permeance slightly decreased while the selectivities of polar/non-polar gas were significantly improved due to the enhancement in solubility of polar gas in PEG. PEG not only had the capacity of altering the permeability of silicone rubber but also acted on the polymeric support material by softening it and causing its pores to shrink (Serivalsatit, 1999).

The other type of mixed matrix membrane was silicalite/cellulose acetate. It was developed to separate CO<sub>2</sub> from H<sub>2</sub>. It had been known that a plain cellulose acetate membrane had a greater permeability for H<sub>2</sub> whereas a silicalite had a greater adsorption affinity for CO<sub>2</sub>. The mixed matrix membrane comprising cellulose acetate having silicalite as the solid participate adsorbent showed a reverse selectivity for CO<sub>2</sub> over H<sub>2</sub> when compared to a pure cellulose acetate membrane (Kulprathipanja *et al.*, 1992).

Li *et al.* (1998) studied the effect of polyethylene glycol (PEG) on gas permeabilities and selectivities in a 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. 10 wt% PEG 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 blended 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  $2 \times 10^{-8}$  cm<sup>3</sup>(STP).cm/cm<sup>2</sup>.s.cmHg and 22, respectively at 70°C and 20 cmHg. Solubility coefficients of all CA/PEG membranes for CO<sub>2</sub> were lower than those of the CA membrane. However, almost all the blended 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.

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. The results showed that none of the zeolite-PDMS mixed matrix membranes could provide n-pentane/i-pentane ideal selectivities higher than that of the unfilled polymeric membrane under the experimental conditions employed. For permeability study, n-pentane showed lower permeability than for the pure polymer whereas i-pentane permeability was even increases with increased zeolite loading in case of 4A-PDMS.

Vu *et al.* (2003) determined the permeation properties of a mixed matrix membranes with 10%CO<sub>2</sub>/90%CH<sub>4</sub> gas feeds containing a vapor impurity of toluene (70ppm). The mixed matrix membrane was comprised of fine particles of high-selective carbon molecular sieves (CMS) dispersed within a glassy polyimide matrix (Matrimide5218). As the results, the CMS-polyimide membranes have significantly enhanced effective permselectivities over the intrinsic properties of the neat polymer matrix phase alone. Both Matrimide mixed matrix membrane and the pure Matrimide film exhibited fairly stable properties in the presence of the low-concentration toluene impurity. It was hypothesized that larger-sized impurities, such as toluene, may only be successful in blocking or occupying the larger, non-selective pores of the CMS particles and may not access the smaller, selective pores that are accessible to CO<sub>2</sub>.

Kalapanulak (2003) prepared mixed matrix membranes by solution-casting method and tested the permeabilities and selectivities of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/H<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> at room temperature and single gas measurement. For the selectivities of

all membranes, activated carbon in activated carbon/silicone rubber/polsulfone MMM had a strong effect on  $\text{CO}_2/\text{N}_2$  selectivity and did not significantly change  $\text{CO}_2/\text{H}_2$  and  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$  selectivities. PEG can show the effect to enhance selectivity when PEG suspended in polymer phase of mixed matrix membranes. For plasticization phenomenon, plasticization effect of  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$  and  $\text{CO}_2$  decreased with increasing amount of PEG.

Anson *et al.* (2004) investigated the performance of various mixed matrix membranes for separation of  $\text{CO}_2$  from  $\text{CH}_4$  as a function of carbon loading. Acrylonitrile-butadiene-styrene (ABS) copolymer was used as the polymer matrix and two micro-mesoporous activated carbons (AC) were chosen as inorganic fillers. The results showed the pure gas permeabilities and  $\text{CO}_2/\text{CH}_4$  selectivities were substantially enhanced with the increasing activated carbons loadings in the matrix ABS polymer.

### 2.3.3 Plasticization

In  $\text{CO}_2/\text{CH}_4$  membrane separation it is well known that  $\text{CO}_2$  acts as plasticizer. Plasticization occurs when the  $\text{CO}_2$  concentration in the polymer is high enough to increase free volume and segmental mobility. Due to the swelling of the polymer matrix, the permeation of  $\text{CH}_4$  is accelerated and as a consequence of polymer loses its selectivity.

Sanders (1988) studied the  $\text{CO}_2$ -induced changes in polyethersulfone(PES). The results showed that the glass transition temperature ( $T_g$ ) decreased by  $76^\circ\text{C}$  after equilibration with  $\text{CO}_2$  at 7.8 atm and  $100^\circ\text{C}$  as the pressure was increased to 35 atm. From these results it was concluded that PES was highly plasticized by  $\text{CO}_2$ .

Jordan and Koros (1990) investigated the effect of pressure on permeability of He,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$  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 condensable penetrants ( $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ ) while the reverse was found for the low sorbing  $\text{N}_2$  and He.

Bos *et al.* (1999) investigated a CO<sub>2</sub>-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<sub>2</sub> concentration to be plasticized, but required different pressures to achieve it.

Wessling *et al.* (2001) used double layer composite membranes consisted of a silicone rubber support layer and a thin polyimide layer to determine the permeation properties of He, N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>. Helium permeation decreased with increasing feed pressure and no hysteresis behavior was found for successive increasing and decreasing feed pressure steps. For CO<sub>2</sub>, its permeability increased with increasing feed pressure and showed a clear hysteresis effects. Another result was accelerated plasticization with decreasing film polyimide thickness.

Since the plasticization generally leads to a loss in 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 two major methods used to suppress the plasticization, which are:

#### 2.3.3.1 Heat treatment

Bos *et al.* (1998) studied effects of thermal-treatment on the plasticization by heating polyimide (Matrimid 5218) membrane at 350°C for 15, 30, and 45 minutes. They found that the treated membrane reached a steady-state value of permeance. It can be concluded that the heat-treatment method was effective in suppressing the CO<sub>2</sub>-induced plasticization. Also, the CO<sub>2</sub>/CH<sub>4</sub> selectivity of treated film was higher than the untreated one due to the permeability of CH<sub>4</sub> decreased more than the permeability of CO<sub>2</sub>. In addition, they stated that the longer treated time, the lower permeance but not significant difference.

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 membrane like CO<sub>2</sub> and it was clear that a heat-treatment reduced the permeance (the more intense the treatment, the larger the decrease in permeance). The results showed that mild heat treatment was not sufficient to suppress plasticization completely at high feed pressure but if using 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 was not always necessary to have cross linking to suppress plasticization. Thermal curing can already be sufficient.

Ismail and Lorna. (2003) studied the effect of heat treatment on PSF membranes. They used different heating temperature (100,120,140,160,180 °C) and different treatment time (10, 30, 60,300 Minutes) to investigate the suppression of CO<sub>2</sub> plasticization. They stated that the mild temperature (100 °C,120°C) were not sufficient to suppress plasticization but can shifted the plasticization pressure to higher value. Also, at too high temperature (180°C) the temperature had a particular tremendous effect on the gas transport. At this temperature membranes exhibited serious collapse of the porous structure. Therefore, the best temperature to completely suppress the plasticization was at 140 °C. The results showed that the heat treatment may induce reorientation of polymer chains, and as a result the treated membranes had a better or more perfect chain -packing in polymer. For treatment time, the differences due to the different curing time were not large enough to be pronounced.

Chung *et al.* (2003) developed hollow fiber membrane (Polyimide) with high permeance and high selectivity for separation of CO<sub>2</sub>/CH<sub>4</sub> and found possible ways to suppress the plasticization phenomenon. They found that the CO<sub>2</sub>-induced plasticization can be gradually suppressed when treatment temperature arised from room temperature to 320 °C. If temperature was greater than 250 °C, the CO<sub>2</sub>-induced plasticization can be removed completely. When we increased the heating temperature, the selectivity slightly increased due to combined effects of heat treatment on the dense selective layer and on the permeation of gas molecules. They

conclude that this membrane showed the optimal heat treatment temperature at about 250 °C.

#### 2.3.3.2 Chemical cross-linked treatment

Staudt-Bickel and Koros (1999) studied the uncross-linked and cross-linked polyimide with copolyimide in order to increase selectivity without plasticization phenomenon. They found that chemical cross linking of the free carboxylic acid group of 6FDA-mPD/DABA 9:1 with ethylene glycol can reduced the swelling effects by CO<sub>2</sub> at least up to pure CO<sub>2</sub> feed pressure of 35 atm. Moreover, copolyimides containing a carboxylic acid group in every tenth polymer unit can strongly reduced 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 sign of plasticization because of high degree of cross linking a very rigid polyimide structure was obtained.

Bos *et al.* (2001) studied the effect of blending Polyimide (matrimid) with copolyimide, P84 (60/40) to plasticization phenomenon. They found that the blend polymer can shifted the plasticization pressure to higher feed pressure due to the densification of polymer matrix, and hence a reduction of free volume. Also, Blending polymer not only suppress plasticization phenomenon but also increase selectivity. They concluded that blending of a polymer that is highly susceptible to plasticization with a polymer that hardly plasticizes presents a simple method to suppress plasticization.

Tin *et al.* (2003) studied the effect of chemical cross linking modification on the permeability and selectivity. The cross-linked membrane was performed by immersing the membrane film at room temperature into the cross linking reagent (10% p-xylenediamine in methanol) for a period of time. The results showed that after completely cross-linked, the imides group peak will fully disappear and substituted by the amide group. Increasing degree of cross linking resulted in the reduction of free volume, chain mobility and the interstitial space among chains attribute to the decrease of permeability with immersion time. For plasticization, the untreated membrane shows the plasticization pressure at 15 atm whereas 7-day cross-

linked membrane can improve the plasticization effect by shifting the plasticization pressure to higher value. In addition, 32-day cross-linked membrane can completely suppress the plasticization.

Chun *et al.* (2003) studied the effect of chemical cross linking of 6FDA,2,6-DAT by immersing them into a p-xylenediamine or m-xylenediamine in methanol solution at room temperature. They proposed the mechanism of cross linking process: the amino groups of p-xylenediamine or m-xylenediamine break the C-N bonds of the imide group of 6FDA,2,6-DAT polyimide. Therefore, some of the imide groups are converted to amide groups. The cross linking polymer can effectively enhance nodule integrity and suppress the CO<sub>2</sub>-induced plasticization. In comparison, m-xylenediamine gave less permeance and higher selectivity than p-xylenediamine did due to the closer of N-N distance of m-xylenediamine.