

# Polymeric Membranes Used in Natural Gas Processing to Separate Carbon Dioxide: the Facing Problems and Solutions

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**Abstract:** For the last two decades polymeric membranes have been used in several gas separation processes. For the high selectivity and permeability various types of membranes have been developed. Thin layers to high dense and hollow fiber to asymmetric wounded materials to determine the effective separation of CO<sub>2</sub> from CH<sub>4</sub> were used. Ideal membrane materials must have provisions of durability, chemical and thermal resistance, effective separation and economical production and operation. In this review it is observed that most of the polymeric materials face plasticization problem in the separation of CO<sub>2</sub> from CH<sub>4</sub>. This is due to the condensable nature of carbon dioxide that causes swelling in most of the polymeric membranes due to which the efficiency of selectivity and permeability is affected. Most extensive works have been carried out in developing the chemical structure and compositions of polymeric materials to improve the separation properties. Cross-linking and blending of molecular sieving called “mixed-matrix” are the most useful approaches applied in this regard, but no where it is found to be fully effective and ideal polymeric membranes commercially fit to replace the existing systems of CO<sub>2</sub> separation from the natural gas. Still area is open to work on to produce more worth full materials and switch towards liquid membranes and hybrid systems.

**Key words:** Carbon dioxide, gas separation, natural gas, polymer membranes.

## 1. Introduction

Recently the G8 summit held in Japan ended to conclude the joint declaration on to slow, stop and reverse global growth of emissions and move towards a low-carbon society. The all member countries committed to share with all Parties in the United Nations Framework Convention on Climate Change (UNFCCC) process by 2009 to develop the vision of, and together with them to consider and adopt in the UNFCCC, the goal of achieving at least 50% reduction of global emissions by 2050. Developed or under

developed countries around the world are facing the problem of CO<sub>2</sub> production by all human activities. Fossil fuel reservoirs and the combustion processes of the fossil fuels are the major sources of CO<sub>2</sub> production. In addition to this the biogas generation as renewable energy source is also rich in the amount of CO<sub>2</sub> along with the methane gas. To protect the echo system and provide the green future to next generations the scientist around the globe are in combat to develop various methods to separate the CO<sub>2</sub> from fuel, fuel gases and flue gases. Mostly the amine solutions, alkaline sorbents and scrubbing solution are used to separate the carbon dioxide. Cryogenic system is also common for the similar purpose [1]. All the existing systems are old fashioned and cost ineffective. Since last two decade polymer membranes has been

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experimented for the gas separation processes because of their efficiency and selectivity to permeate. Membrane separation processes are energy efficient and versatile in application due to the no power consumption and water requirement. But it is still so far to transfer the overall separation processes of CO<sub>2</sub> from CH<sub>4</sub> because of the various complexes and difficulties faced by the researchers in their work [2, 3].

Ultra thin layer polymer membranes of > 1 μm to 50 μm densities and the wound hollow fiber cylinders of simple and layered, plain and cross linked chains of functional groups are considered by the various researchers to assess the improved effectiveness of CO<sub>2</sub> separation from the natural gas. Polymer membrane selectivity, crystallinity, diffusivity, plasticity and permeability were the foremost factors to be observed in the majority of works [4].

Since now more than 2000 documents are prepared for the patent in two decades, but the number of research publications of membrane technology is three times higher than that. It is indicating that the researchers are more interested in the scientific benefit instead of the commercial interests. The two types of polymers glossy and rubbery are the dominating in the selective layer membrane system. Therefore it is important to consider the physico-chemical regularities of hydrocarbon mass transfer through the polymer membranes [5-7].

In this review research papers on polyamide, polyimide and polysulfone materials, and membranes used to separate the carbon dioxide from natural gas, published in rated journals are considered. The permeability, plasticization, and selectivity of these polymeric membranes are considered to study and the critical review is presented to understand the issues and problems to develop more strong research in the future in this area.

## 2. Permeability

### 2.1 Permeability Measuring Methods

In very old methods Henis and Tripodi's model [8] is used to analyze permeability. This model is based on resistance of membrane thickness (m) to the gas transport rate (mol·s<sup>-1</sup>).

$$R = l/PA = \Delta p/Q \quad (1)$$

Where  $R$  is membrane resistance (Pa·s·mol<sup>-1</sup>),  $l$  is membrane thickness (m),  $A$  is membrane area (m<sup>2</sup>),  $\Delta p$  is pressure difference (Pa) and  $Q$  is permeation rate (mol·s<sup>-1</sup>). Due to the more assumptions in over all calculation to analyze the separation process it is not commonly applied.

The constant volume and variable pressure is most common to determine the gas permeabilities. It is determined from the rate of downstream pressure rise taken place when the steady state condition of permeation is reached [9].

$$P = 273 \times 10^{10} / 760 \times VL/AT(p_2 \times 76/14.7) (dp/dt) \quad (2)$$

Where  $P$  is the permeability of a membrane to a gas, it is denoted with the unit Barrer. 1 Barrer = 1 × 10<sup>-10</sup> cm<sup>3</sup> (STP) cm/cm<sup>2</sup> s cmHg),  $V$  is the volume of downstream chamber (cm<sup>3</sup>),  $L$  is the film thickness (cm),  $A$  is the area of the membrane (cm<sup>2</sup>),  $T$  is the temperature (K), and  $p$  is the pressure of feed gas in the upstream (psia).

Above these equations are mostly used for the thin layers and film polymeric membranes of different densities and thicknesses, where as permeance of the hollow fiber is calculated by pressure normalized flux [10] which is presented as

$$P/l = N/\Delta p \quad (3)$$

Where  $P$  is the permeance,  $l$  is the length of fiber,  $N$  is the number of fibers and  $\Delta p$  is the pressure difference. The unit of permeance is denoted with GPU and this is represented as

$$1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ s cmHg} \quad (4)$$

CO<sub>2</sub>' permeability of polymeric membranes.

#### 2.2.1 Polyacryl Acetate

In 1991, Meyert et al. used commercial scale single stage wound asymmetric cellulose acetate membrane to separate carbon dioxide to up grade the low quality natural gas produced from a well in East Texas. First

time for the 20 months of long period data from the field was recorded and the concentration of CO<sub>2</sub> as per pipeline specifications was maintained. Spiral wound membrane designed to treat 500 MSCF/Day used on well containing 6 mole % CO<sub>2</sub> at 750 psig of feed gas pressure. In the 573 days of operating period the 95000MSCF of natural gas was processed and the CO<sub>2</sub> concentration in the product remained below the 2 mole %, which is the pipe line specification, all the time [11]. In this work the loss of methane is reported with increasing the membrane area. In permeate stream loss of methane indicates the defect of membrane which is commonly observed by most of the researchers in the glossy polymeric membranes. Hirayama et al. (0000) studied the permeation properties polymeric membrane containing cross linked polymer films for CO<sub>2</sub> and N<sub>2</sub>. They achieved 510 Barrer permeability ratios for the CO<sub>2</sub> over N<sub>2</sub> [12]. Where as economical feasibility of membrane is counted when it is exceeding the 100 Barrer [13]. They prepared membranes of monomethacrylate and dimethacrylate of long chains of 9-23 and 9-69 molecules and observed that much longer blocks of polyethylene oxide were partially crystallized at low temperature and also loss of permeability, diffusivity and solubility coefficient faced. They did not apply it to experiment these polymeric membranes on CO<sub>2</sub> and CH<sub>4</sub> group gases. It is possible that same can be having good results for the CO<sub>2</sub> separation from CH<sub>4</sub> because of the high tendency to tolerate the pressure and good permeability coefficient for CO<sub>2</sub>.

Polymer containing polar moieties like ether group due to the dipole-quadrupole interactions increases the CO<sub>2</sub> attachment capability and with this membranes can be developed which may have more permeability to CO<sub>2</sub> and can be used for selective separation of gases.

### 2.2.2 Poly Ethylene Oxide

Pure PEO has high crystallinity and low transport property values for the acid gas selective separation. Solution cast PEO films used to test the physical

characterization and gas transport properties with effect of pressure on gas permeability, diffusivity and solubility of non polar gases and a series of olefinic and aliphatic hydrocarbons.

PEO permeability Barrer for CO<sub>2</sub> at 14.6 atm pressure and 45°C temperature is recorded 52, which is high enough but that temperature is melting point of the PEO and it can not be longer continued, therefore for the higher temperatures this membrane will not suit and decreasing the temperature its permeability for CO<sub>2</sub> also decreases.

Pure gas selectivity of CO<sub>2</sub> in semi-crystalline PEO at 14.6 atm and 45°C temperature decreases to 7.7 Barrer and it is recorded 12 at 25°C, which is higher, but the selectivity of CO<sub>2</sub> in the CO<sub>2</sub>/CH<sub>4</sub> group is not reported, where as some where else in Koros work it is reported that increasing the mass density of polar carbonyl or sulfone groups in the polymer system the solubility selectivity of CO<sub>2</sub>/CH<sub>4</sub> system increases [14].

In poly ether block amide (PEBA) membrane at 25 °C the permeance (GPU) of CO<sub>2</sub> increases as the number of layers of each 0.3µm thick is increased. For five layers at 345 KPa feed pressure and 25 °C is measured to permeate 70.9 GPU of CO<sub>2</sub> where as the selectivity of CO<sub>2</sub>/N<sub>2</sub> observed 32.7.

It is reported that the poly sulfone-supported multilayer PEBA membranes have a carbon dioxide permeation of 20-70GPU at temperature 25°C and feed pressure of 345 kPa, where as with carbon dioxide/nitrogen group gases selectivity is 34-44. In Liu et al. work on PEBA it is estimated that when a single layer of the thin PEBA membrane used, the permeance would be 3-5 times greater with the selectivity remaining same. although membranes as thin as 0.3 mm had been prepared, the supported membrane laminates with 3-5 layers of PEBA membrane but it could not tolerate the transmembrane pressure used in the experiment, mainly due to the relatively large pore size and rough surface of the polysulfone substrates. Substrate with finer pores and

smoother surfaces would be needed to prevent the burst of the ultra thin membrane under pressure [15]. The hardness of PEBA is low because of the polyamide content due to which when higher pressure may applied the membrane compaction will take place and permeability will decrease.

### 2.2.3 Polphosphazene

Improving the chemical structure of polymeric membrane is the common task to the membrane technologist. Most of the researchers are engaged in developing more and more effective membranes. Due to unique structure polyphosphazene are ideal for membrane studies. Containing the nitrogen and phosphorus atoms on the back bone makes it highly resistant to heat and degradation agents like acids and solvent. Orme et al. were attracted on this quality of polyphosphazene and worked on synthesizing material of block and cross linked chain polymers.

Synthesizing of homopolymers is simpler and the crystalline behavior by using one pendent group lowers the gas permeability. Semi-crystalline and hydrophobic in nature, Poly[bis-(phenoxy)phosphazene] (PPOP) polymer, is excellent in film forming characteristics. Efficient chain of homogeneous structure of mers develops the crystallinity of PPOP. 80-150 mm PPOP membrane supported with 0.2 mm pore size ceramic membrane 25 mm thickness was fed with 206 kPa gas. Permselectivities of carbon dioxide/ methane is 4 at 30 °C, which is very low as compared to the other works. Solubility characteristic of CO<sub>2</sub> and phosphazene polymers is more complicated due to the high condensability of these gases.

As over all the selectivity and permeance of PPOP for CO<sub>2</sub> from natural gas is not favorable. PPOP density was measured 1.3318 g/ml and the degree of crystallinity measured from this value approximated 45%. Results reported for the permeability of CO<sub>2</sub> are very small. At 50% crystallinity the permeability of CO<sub>2</sub> was 4.73 Barrer and 9.26 Barrer at 20% crystallinity. The crystalline and amorphous phase showed small difference of transport behavior and the

permeability is very low as compared to the other works. Permeability is more complicated in the CO<sub>2</sub>/CH<sub>4</sub> gas pair due to the high condensability and it is observed that CO<sub>2</sub> separation factor is very low in PPOP.

In the last it is concluded after comparing this membrane to the poly[bis-(3,5-di-tert-butylphenoxy)1.2 (chloro)0.8 phosphazene] that the attachment of alkyl substituents to the aromatic portions of the polymer increases the permeability and ideal separation factors with respect to PPOP [16].

### 2.2.4 Polimide-amide

To increase the intra-and inter-chain hydrogen bonding polyimide-amide polymer, Trorlon is used to suppress the plasticization effect. It was expected by Madhava and William that such hydrogen bonds may prevent the CO<sub>2</sub>-induced segmental mobility to suppress the plasticity.

Mixed gas of CO<sub>2</sub> and CH<sub>4</sub> (90 mol% CO<sub>2</sub> and 10 mol% CH<sub>4</sub>) was tested at 1220 psi total pressure at 35 °C, at this point 1100 psi is the partial pressure of CO<sub>2</sub> which is above the critical pressure level. The permeance of CO<sub>2</sub> observed constant up to 1220 psi without swelling. This shows the high efficiency of membrane to un-plasticize at high pressure as compared to the other polyimide membranes. Swelling effect of membrane on the separation efficiency is studied by mixed gas selectivity performance during the pressurization and depressurization cycle and plotted without and with fugacity corrections (Figs. 1-2, [10]).

Without fugacity taking into account the selectivity decreased about 60%, from 46.3 to 19.5. This decrease is caused due to the non- ideality of gas phase. Taking fugacity into consideration the non-ideality is corrected and the selectivity decreases about 20% from 50.4 to 39.6, which is comparatively moderate. The work done by Madhava and William comparing the pure gas CO<sub>2</sub> permeability and selectivity to other Permeate at the supercritical pressure membrane swelled due to the

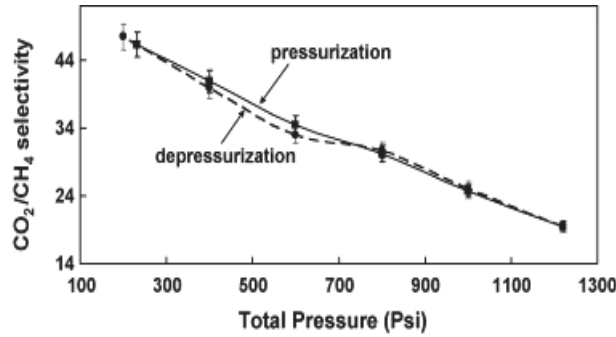


Fig. 1 Mixed gas selectivities of  $\text{CO}_2/\text{CH}_4$  (without fugacity corrections) during the pressurization and depressurization cycle. The experiment is performed with 90 mol%  $\text{CO}_2$  and 10 mol%  $\text{CH}_4$  gas mixture. Solid line corresponds to pressurization step and dashed line corresponds to depressurization step.

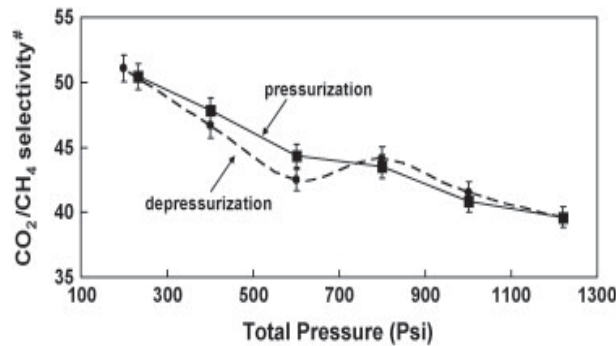


Fig. 2 Mixed gas selectivities of  $\text{CO}_2/\text{CH}_4$  (with fugacity corrections) during the pressurization and depressurization cycle. The superscript # indicates fugacity corrected selectivities. The experiment is performed with 90 mol%  $\text{CO}_2$  and 10 mol%  $\text{CH}_4$  gas mixture. Solid line corresponds to pressurization step and dashed line corresponds to depressurization step.

high sorption of  $\text{CO}_2$  and while depressurization as the  $\text{CO}_2$  desorbs the extra free volume is produced as the equilibrium state is not attained immediately. This free volume results to increase the permeance due to which the selectivity decreases. Torlon is proved to control the plasticization but on the contrary it is not totally supported to be good enough by all means. It is identical (Table 1, [10]) that Torlon has lower separation performance compared to the other polyimide membranes.

As compared to the polycarbonate, polysulfone and other polymeric materials considered for gas separation, polyimides are found to have high gas permeability and high intrinsic perm selectivity [20, 21]. By synthesizes

of polyimide with dianhydride or diamines for cross linking modifications the gas transport performance and anti-plasticity character can be improved [22-25]. L. Shao et al. [9] worked to study the transport properties of polyimide membranes with cross linking of diaminobutane (DAB) dendrimers. The study was conducted to examine if Cross Linking agents for polyimide membranes of DAB dendrimers can be employed and also the gas transport properties effectiveness on chemical modifications effect of various generation DAB dendrimers was analyzed. Gel content, FTIR, and X-ray photoelectron spectroscopy (XPS) was used for characterization of DAB dendrimers cross-linked membranes. For gas transport properties constant volume and variable pressure method used to determine the pure gas permeability. The generation 1 (G1) polypropylenimine tetra amine dendrimers (trade name: DAB-AM-4) was modified to examine the gas pair of  $\text{CO}_2$  and  $\text{CH}_4$ . The permeability for  $\text{CO}_2$  and  $\text{CH}_4$  were obtained at  $35^\circ\text{C}$  and upstream pressure  $1.01325 \times 10^6$  Pa (10 atm). The behavior of permeability ratio versus cross-linking time plotted for various gases is presented (Fig. 3 [9]).

Fig. 3 depicts the trends of permeability ratio versus cross-linking time for various gases before and after G1 cross-linking. The common feature is that the decreases with cross-linking time after 5 min of cross-linking.

After 5 min of cross-linking the permeability starts decreasing. The permeability of  $\text{CH}_4$  after 60 min cross-linking is observed 45.1 Barrer, which is the lowest one. And for  $\text{CO}_2$  it is 612 Barrer. The significant decrease of  $\text{CO}_2$  and  $\text{CH}_4$  diffusion coefficient-

**Table 1** Pure gas  $\text{CO}_2$  permeabilities and  $\text{CO}_2/\text{CH}_4$  selectivities of different polyimides: Matrimid® [17], Ultem® [18], 6FDA-DAM:DABA 2:1 [19], and Torlon®

| Polymer           | $\text{CO}_2$ permeability (Barrer) | $\alpha_{\text{CO}_2/\text{CH}_4}$ |
|-------------------|-------------------------------------|------------------------------------|
| Matrimid®         | 12.5                                | 57                                 |
| Ultem®            | 1.3                                 | 37                                 |
| 6FDA-DAM:DABA 2:1 | 133                                 | 29                                 |
| Torlon®           | 0.47                                | 52                                 |

All the values are obtained at pressures less than 10 atm.

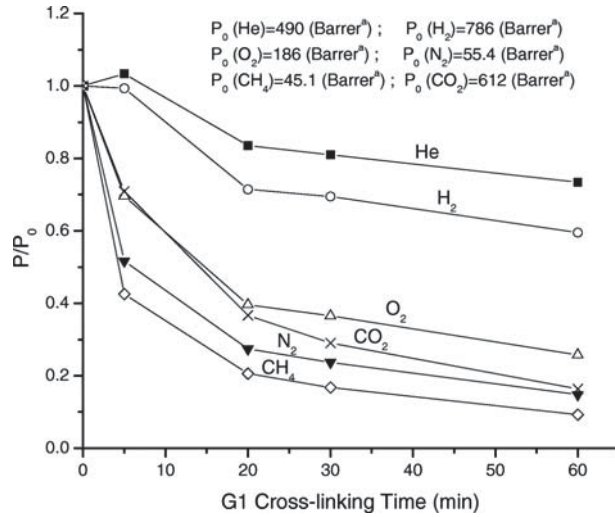


**Fig. 3** The effect of cross-linking time on the relative permeability.

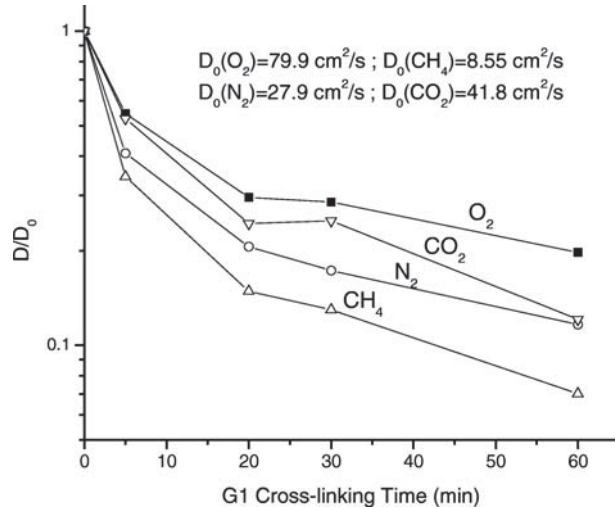


**Fig. 4** The effect of G1 cross-linking time on relative diffusion coefficients.

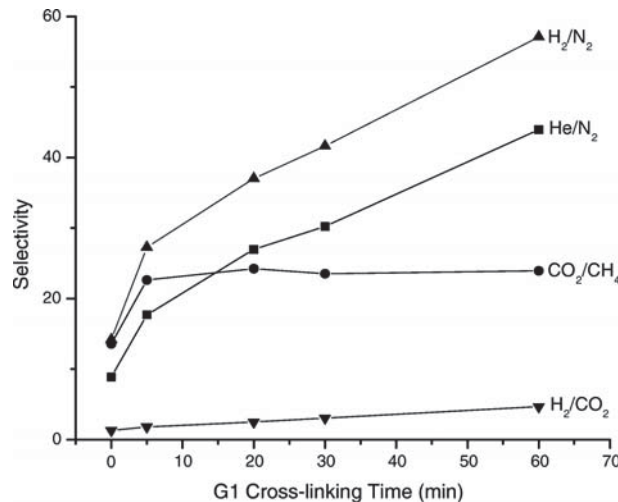


**Fig. 5** The effect of G1 cross-linking on selectivity.

ent  $41.8 \text{ cm}^2/\text{s}$  and  $8.55 \text{ cm}^2/\text{s}$  respectively is evident (Fig. 4 [9]).

Sudden drop in permeability of  $\text{CO}_2$  and  $\text{CH}_4$  is resulted after five minutes it may be due to an isometric molecules effect during the diffusion and the highly condensable nature [26]. It indicates that it is not good enough for the  $\text{CO}_2/\text{CH}_4$  gas pair separation process. For the  $\text{CO}_2/\text{CH}_4$  gas pair selectivity the maximum increment is about 74% after 20 min of cross-linking and after this it becomes constant up to 60 min (Fig 5 [9]). Due to the faster decrease of diffusion coefficient of  $\text{CH}_4$  with cross-linking time than that of  $\text{CO}_2$  the selectivity increases for the  $\text{CO}_2/\text{CH}_4$  gas pair.

A. T. Mohammadi et al. (1995) worked on silicon coated dry asymmetric polyamide membrane. Along with other gases the  $\text{CO}_2/\text{CH}_4$  gas pair was also analyzed. Separation factor of carbon dioxide from methane is recorded 64-166 at an operating pressure 700 kPa, which is higher than the ideal separation factor it indicates that there may be some error in the calculation done on the basis of detectable limit of permeability for methane [1].

### 3. Issues and Solutions of Polymer Membranes

Polymeric membranes swell at high pressure of  $\text{CO}_2$  feed, due to this segmental mobility of the polymeric chain increases. This undesired phenomenon is known as plasticization, which causes to decrease the membrane selectivity for the  $\text{CO}_2/\text{CH}_4$  system. This plasticization effect is caused due to the solubility or interaction of carbon dioxide with polymeric chain. Because of the swelling permeability increases while the selectivity is effected to decrease. Due to the plasticization, aging phenomena, low process ability and high cost only eight to nine types of polymers are used in 90% of commercial applications.

In literature it is found that many researchers are working on polymers to reduce the extent of plasticization effect. Mostly flat sheet membranes were tested to apply the annealing, thermally induced

cross-linking, chemical cross linking, interpenetrating networks and polymer blending. In most of the CO<sub>2</sub> plasticization suppression caused gas permeability reduction [27].

Increasing the gas pressure the gas uptake in the membrane increases, this increase is less than proportional because of the Langmuir sorption, where the active sorption sites are gradually saturated, after that the gas permeability and solubility of membrane reduces. There after the passing gas tends to plasticize or swell the polymer membranes.

Glassy polymer membranes are good to separate non condensable gases like O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO etc, but their separation properties are deteriorated in the presence of condensable gases and organic vapors. Commercial polyimide Matrimid 5218 has high selectivity coefficient at low feed pressure of CO<sub>2</sub>, while increasing the partial pressure of CO<sub>2</sub> selectivity reduces. A. Bos et al. (1998) reported the cross-linking and heat treatment of polyimide Matrimid 5218 for plasticization resistance effect of CO<sub>2</sub> and CO<sub>4</sub> separation. The heat-treated membrane of 15 and 30 min compared with untreated one showed the increase up to 11 to 30 % in all values at elevated pressure in mixed gas permeation experiments of CO<sub>2</sub>/ CH<sub>4</sub>. The permeation isotherms comparison of treated and untreated (Fig. 6 [28]) film shows that treated one at elevated pressure suppresses the plasticization and does not increase permeability [28].

Barsema et al. reported that ultra thin dense or asymmetric hollow fiber membranes exhibit difference in physicochemical properties, like aging phenomena and plasticization behaviour when compared to the thicker membranes prepared from the same polymeric materials [29].

A high penetrant concentration of CO<sub>2</sub> causes plasticize the polymer matrix. PEO was plasticized by CO<sub>2</sub> at 10cm<sup>3</sup>(STP)/(cm<sup>3</sup> amorphous polymer) and the solubility of condensable components typically increases by pressure rise and because of this permeability coefficient factor also increase [14].

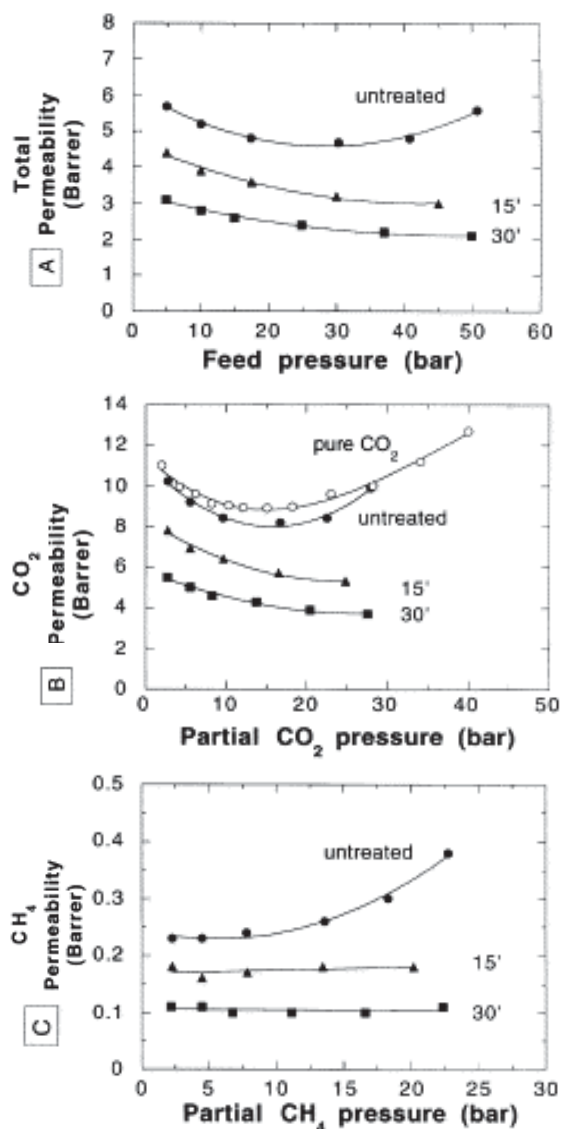


Fig. 6 Permeability–pressure curves obtained with a 55/45 mol% CO<sub>2</sub>/CH<sub>4</sub> mixture at 35°C for an untreated and two heat-treated Matrimid films.

It is observed by L. Liu et al. (2004) that the solubility of carbon dioxide in PEBA is 14-29 times higher than the nitrogen and oxygen, therefore carbon dioxide will plasticize and swell the membrane. If the plasticization effect is higher the increasing gas pressure will tend to increase the membrane permeability [15].

To increase the intra-and inter-chain hydrogen bonding polyimide-amide polymer, Trorlon is used to suppress the plasticization effect. In the work of Madhava and William [10], it is presented that such

hydrogen bonds may prevent the CO<sub>2</sub>-induced segmental mobility to suppress the plasticity [30].

#### 4. Conclusion and Suggestions

It is concluded that most of the polymeric membrane are non ideal due to the plasticization effect and may not be as much suitable for commercial applications of CO<sub>2</sub> separation from natural gas. The research work considered in this study has developed the view that elevated pressure in CO<sub>2</sub>/CH<sub>4</sub> pair of gas separation may not prevent the membrane from swelling. It is observed that polyimide membranes are more preferable than other polymers due to their permselectivity and performance for CO<sub>2</sub>/CH<sub>4</sub>. The majority of work is produced to only identify the permeability and selectivity of CO<sub>2</sub> and CH<sub>4</sub> not much concern is given to the effects of plasticization. From over all view it is evident that cross linking of polymeric membrane is the more suitable area to develop further investigations. But it is also identical that polymeric membranes are mainly composed of hydrocarbon derived materials therefore they will always be providing such difficulties in this group of gas separation. Instead of polymer membranes the gas liquid contact membranes and liquid emulsion membranes may be more suitable as compared to this.

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