

Effect of High Pressure Carbon Dioxide Exposure on the Permeation Properties of Asymmetric Polysulfone Membranes for Gas Separation

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ABSTRACT

In this study, the dependence of permeability on the feed pressure for glassy asymmetric polysulfone membranes has been investigated. Pure CO₂ and CH₄ were used as test gases. In pure gas experiments with CO₂, the untreated membrane showed that the carbon dioxide permeation rate increased with increasing feed pressure from one bar onwards. This is because carbon dioxide behaves as a plasticizing agent by expanding the polymer lattice and increased the frequency of molecular motions of the polymer. Moreover, high carbon dioxide concentration in the polymer film disrupts the chain packing, thereby leading to a larger free volume and enhanced rates of segmental motions. Due to swelling of the polymer matrix, the structure of the polymer matrix is loosened and consequently polymer chains become more flexible. For the treated membrane, the permeability of carbon dioxide does not increase with feed pressure but gives a steady state value over the feed pressure ranges investigated. This was in agreement with scanning electron microscopy studies, which revealed that heat treatment densified the membrane skin layer. Thus, a subsequent heat treatment to the membrane is necessary in suppressing the plasticization effect.

Keywords: Carbon dioxide, plasticization, gas separation

1.0 INTRODUCTION

Gas separation using integrally skinned asymmetric membranes made from glassy polymers is a proven technology that has found a wide range of industrial applications [1]. These membranes as illustrated in Figure 1 consist of an extremely thin and dense surface layer (0.1 μm to 1 μm) and a much thicker porous sub-layer (100 μm to 200 μm) of the same material, on which the dense layer is supported. The skin layer performs the separation with a high flux because of its high density and thinness. The porous sublayer provides the mechanical strength while the gases may permeate

through it with little resistance [2]. However, problems arise due to plasticization of glassy polymer [3]. This phenomenon is related to the dilation in the polymeric matrix induced by the

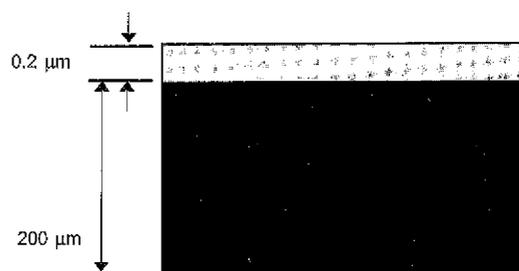


Figure 1 A schematic illustration of the structure of integrally-skinned asymmetric membranes

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highly sorbed penetrant molecules. This becomes larger as the penetrant concentration increases, which further allows greater mobility of the chain segments and higher diffusion rates [4]. Consequently, membrane plasticization flexibilizes the discriminating matrix with a reduction in the permselectivity of the membrane at sufficiently high driving pressure. In other words, plasticization may be interpreted as a weakening effect on the polymer, which eventually results in the swollen materials unsuitable for gas separation applications. Therefore, understanding of plasticization phenomenon is essential especially at high pressure condition in order to develop high performance glassy polymer membrane [5, 6].

Efforts have therefore been made to improve the separation performance of asymmetric membranes through either phase inversion process optimization and/or post treatment methods [6].

In this paper the effect of exposure of asymmetric polysulfone membranes to high pressure CO_2 on their gas permeation properties is thoroughly studied since through the best of our knowledge only few studies have been made for this particular case. Another novel aspect of this study is the study of the effect of the heat-treatment polysulfone membranes on their stability in gas separation performance.

2.0 EXPERIMENTAL

2.1 Membrane Preparation

Polysulfone (PSF) manufactured by Amoco Chemical (Europe) S.A. under the trade name "Udel polysulfone P-1700" was selected as the polymer for this study primarily because of its low cost and widespread use as a commercial membrane material for gas separation. Although the polysulfone have a reasonably high T_g , the polymers are significantly plasticized by highly sorbing penetrants at high pressure [7].

Asymmetric flat sheet membranes were prepared by the dry/wet phase inversion process from casting solutions composed of polysulfone, N,N' -dimethylacetamide (less volatile solvent), tetrahydrofuran (more volatile solvent) and ethanol

(nonsolvent). The polymer solution was cast on a clean glass plate using a pneumatically controlled flat sheet membrane casting system constructed in our laboratory. Forced convective evaporation was induced on the cast polymer solution film before it was immersed in a water bath overnight at room temperature. The membrane was further transferred to a methanol bath where the membrane was kept for two hour for solvent exchange and then air-dried at least for one day at room temperature. Some membranes were further heat-treated by placing them in a forced hot air oven at a predetermined temperature.

Before testing, the membrane was coated with a highly permeable elastomeric silicone polymer (polydimethylsiloxane) (Slygard 184, Dow Corning). The top skin side of the membrane was kept in contact with a 3% w/w silicone solution in n-hexane for 3 minutes. Then, the membrane was placed in an oven at 60°C for 2hrs to allow curing of the silicone layer. The coating is a standard method, which can repair any imperfections in the active layer, and will not alter the permeation characteristics of the asymmetric membrane material (Figure 2). Thus, coating allows the membrane to exhibit permeation properties close to the inherent characteristics of the membrane polymer itself [8, 9].

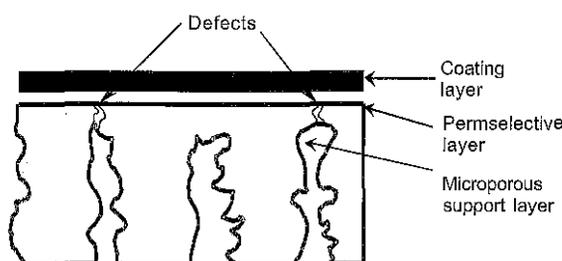


Figure 2 Schematic of coated gas-separation membranes

2.2 Gas Permeation Experiments

The high pressure permeation setup is a constant pressure system as illustrated schematically in Figure 3. The gas permeation tests were performed using a permeation cell. The permeation cell was constructed using stainless steel 316, allowed the

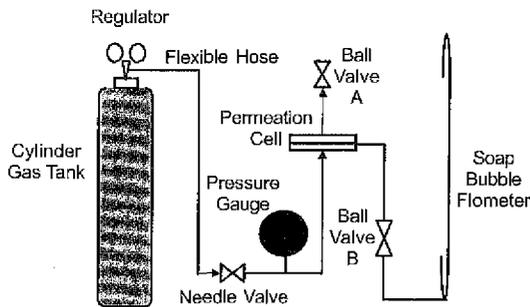


Figure 3 Pre gas permeation testing system

permeation tests at elevated pressures (up to 13 bars). In the permeation cell, the membrane samples were placed on a Bekipor ST-CL3 filter medium that is durable and pleated 316L stainless steel medium sintered into a graded pore structure. The volumetric gas flow rates were determined using a soap bubble flow meter reading to 0.05 cm^3 , attached to the permeation cell with a thick-walled rubber hose or tubing. The effective membrane area was 13.5 cm^2 . All permeation experiments were single gas experiments performed at $25 \pm 2^\circ\text{C}$.

The permeance, P/l , and was calculated by

$$\left(\frac{P}{l}\right)_i = \frac{Q_{i0} \cdot 10^6}{(\Delta p)(A)} \quad (1)$$

where Q_i is the volumetric flow rate of gas 'i' at standard temperature and pressure (cm^3/s), Δp is the transmembrane pressure difference (cmHg), and A is the effective area of the membrane (cm^2). Permeances are expressed in gas permeation units, GPU, where

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

2.3 Differential Scanning Calorimetry

A membrane sample was loaded into a sample pan for thermal analysis with a differential scanning calorimeter (Perkin-Elmer DSC-7) equipped with a Thermal Analysis Data Station (TADS). The glass transition temperatures obtained from two samples were averaged and reported.

2.4 Scanning Electron Microscopy

Membrane morphology was studied by scanning electron microscopy (SEM) technique. The membrane samples were prepared by cryogenic breaking of the membranes, followed by coating with a thin layer of gold.

3.0 RESULTS AND DISCUSSION

Figure 4 shows CH_4 and CO_2 permeance versus feed gas pressure. As stated earlier, the data were obtained from pure gas permeation experiments. From Figure 4, CH_4 permeance is almost independent from the feed gas pressure, as documented and adequately explained by the dual-mode model. According to Sanders [10], decrease in permeability stems from a stronger decreasing tendency of solubility than increasing tendency of diffusivity. Sanders also mentioned that a 'microvoid-situation' would appear at low levels of penetrant in the polymer, while at higher penetrant concentrations, such microvoids would become saturated, causing the decrease in gas permeability.

From Figure 4, CO_2 permeance exhibited an increasing tendency with an increase in the feed pressure. This is very typical for CO_2 Permeance through membranes made of glassy-polymers. According to Bos *et al.* [11], the increase in permeability due to is possible because of an

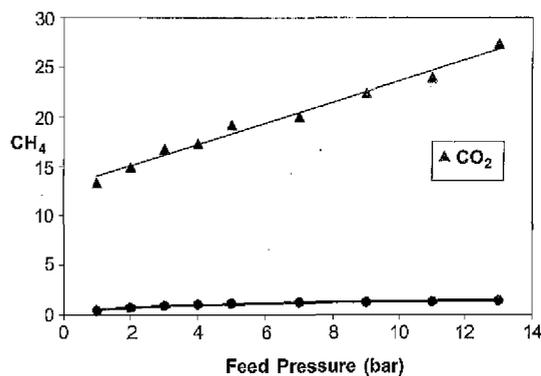


Figure 4 CO_2 and CH_4 permeability of the asymmetric polysulfone as a function of the feed pressures

increase in chain mobility. A large amount of penetrant in a polymeric membrane disrupts chain packing, leading to increased segmental motions. This phenomenon is well known as plasticization effect.

Another explanation is that the diffusion coefficient increases with the pressure much more rapidly than the decrease in solubility [10]. Moreover, some researchers [12–14] have found the CO₂ sorption results in dilation of polymers, which allows easy passage of the carbon dioxide molecules and influence the mass transport. In other words, the activation energy for diffusion decreases with increasing of penetrant concentration because of the presence of CO₂ may loosen the polymer matrix by separation of chain segments for a diffusional jump.

White *et al.* [14], on the other hand, proposed that the asymmetric membranes prepared by precipitation process possess morphology where small nodules of polymer are tied together with regions of lower density polymer chains. The exposure to highly soluble plasticizer such as CO₂ results in the loosely packed chains which are more susceptible to movement and structural change.

Figure 5 shows CO₂ permeance versus feed pressure for both heat-treated and untreated membranes. Regarding the data for the untreated membrane, the data in Figure 6 is slightly different from the ones in Figure 5 since different membrane

samples were used in permeation experiments. Hence, there is slight difference in the permeance data. Plasticization effect is clearly observed for the untreated membrane. For the heat-treated membrane, the permeance was nearly equal to that of the untreated membrane at 1 bar. The decreased with an increase in pressure but the change was significantly less than untreated membrane, indicating improvement of performance stability. This is due to better packing of polymer chains and decrease in free volume in the heat-treated membrane. This is also probably due in part to the lower segmental (rotational) mobility, i.e., greater chain stiffness, of the polysulfone. This phenomenon is in agreement with that reported by Paul and Yampol [16].

Increase in the packing density of the polymer is further supported by the SEM pictures (Figure 6). The figure shows that the size of the pores underneath the thin skin layer decreased by the heat-treatment. This seems consistent with denser polymer packing and lower free volume in the thin skin layer of the heat-treated membrane. Similar observations have been reported by Bos *et al.* [3] and Krol [17]. Thermal treatment induces rearrangements of polymer chains towards a new configurationally state. It was observed that restriction of the polymer chain mobility after heat-treatment could impede gas transport [18]. Thus,

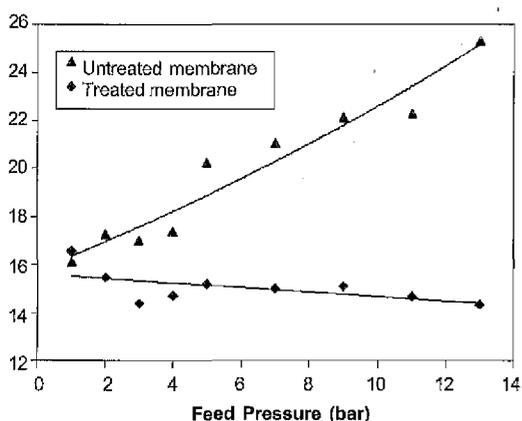


Figure 5 Carbon dioxide permeability of the asymmetric polysulfone as a function of the feed pressures

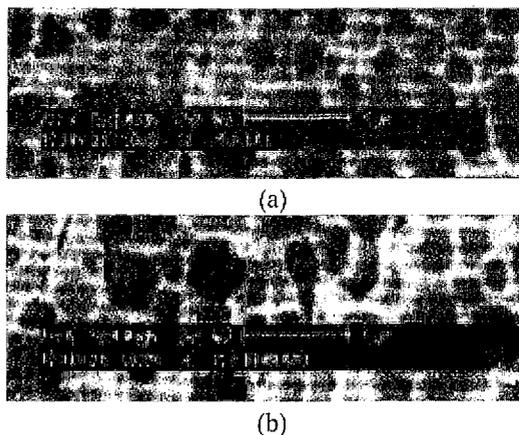


Figure 6 SEM pictures of (a) before heat treatment and (b) after heat treatment at 140°C for polysulfone flat sheet membranes

heat-treatment method is effective to stabilize the performance of asymmetric membranes.

4.0 CONCLUSION

The following conclusions can be drawn from the experimental work in this study.

- (1) The CH₄ permeance of the asymmetric polysulfone membrane fabricated by the phase inversion technique followed by silicone rubber coating decreases as the feed CH₄ pressure increases in accordance with the dual-sorption behavior of membranes made of glassy polymers.
- (2) The CO₂ permeance, on the other hand, increases with an increase in the feed CO₂ pressure. This is due to much reported plasticization effect.
- (3) Heat-treatment of the asymmetric polysulfone membrane suppresses the plasticization effect significantly.
- (4) The stabilization by heat-treatment is due to the denser packing of macromolecules and free volume reduction. This is evidenced, at least indirectly, by SEM observation which revealed shrinkage of the pores immediately underneath the dense skin layer.

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