

## Effect of CO<sub>2</sub> treated polycarbonate membranes on gas transport and sorption properties

Shih-Hsiung Chen<sup>a,\*</sup>, Shih-Liang Huang<sup>b</sup>, Kuang-Chang Yu<sup>a</sup>, Juin-Yih Lai<sup>c</sup>, Ming-Tsai Liang<sup>d</sup>

<sup>a</sup> Department of Environmental Engineering and Health, Chia-Nan College of Pharmacy and Science, Tainan 717, Taiwan

<sup>b</sup> Department of Chemical Engineering, National Chin-Yi Institute of Technology & Commerce, Taichung 41111, Taiwan

<sup>c</sup> Department of Chemical Engineering, Chung Yuan University, Chung Li 32023, Taiwan

<sup>d</sup> Department of Chemical Engineering, I-Shou University, Kaohsiung, county, Taiwan

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### Abstract

The effect of polycarbonate (PC) membranes treated with super critical carbon dioxide on gas sorption and transport properties was studied. It was found that the gas permeability of PC membranes hardly changed after the CO<sub>2</sub> treatment. However, the gas sorption and diffusion properties showed a significant change. The transport properties were determined by measuring the sorption and permeation properties. The oxygen and nitrogen sorption measurements were carried out at 35°C over the pressure range of 1–25 atm. It was found that exposed CO<sub>2</sub> treatment hardly changed the gas permeability but slightly increased the selectivity of oxygen to nitrogen. This study also showed that the increase in gas solubility was contributed by increasing Langmuir-type sorption of CO<sub>2</sub> treated membranes rather than Henry-type sorption. The change in polymer packing of membrane was evidenced by glass transition temperature measurements. This study showed that the free volume of membranes increased with the increase of exposed CO<sub>2</sub> density. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Super critical carbon dioxide; Polycarbonate; Membrane; Sorption; Diffusion

### 1. Introduction

There are numerous investigations regarding CO<sub>2</sub> conditioning of glassy polymers. CO<sub>2</sub> is highly sorbing and causes significant changes in the state and gas sorption behavior of the polymer. However, there are few studies of CO<sub>2</sub> conditioning on gas separation performance of CO<sub>2</sub> treated membrane [1–4]. Paul et al. [5] investigated glassy polycarbonate (PC) membranes exposed to a high pressure of CO<sub>2</sub> and found that plasticization effect existed at a high pressure of CO<sub>2</sub>. Their results showed that the CO<sub>2</sub> plasticizing

effect altered the sorption and permeation behavior of a polymer. N. Muruganan et al. [6] studied the effect of molecular structure manipulation of PC on sorption and transport of various gases. They found that exposing the polymer to CO<sub>2</sub> at pressure up to 20 atm did not increase the sorption level. However, it had a significant effect on permeation properties. B.J. Story et al. [7] investigated the sorption and permeation properties of CH<sub>4</sub> and CO<sub>2</sub> in polyphenylene oxide (PPO) and its derivatives and proposed that the PPO membrane had an upturn in CO<sub>2</sub> permeability at high pressure due to the plasticization effect. K. Toi [8] presented the pressure dependence of diffusion coefficients for CO<sub>2</sub> in glassy polymers. They indicated that the

\* Corresponding author. Fax: +886-6-266411.

permeation coefficient was constant, whereas the diffusion coefficient increased with pressure. Based on the solution–diffusion mechanism, the sorption properties of membranes should change at a high pressure of CO<sub>2</sub>.

In general, plasticization induces the dilation and the free volume expansion of a polymer membrane when the plasticization agent passes through membrane. But there are scarce studies of the effect of CO<sub>2</sub> treatment on gas transport properties of PC membranes. In order to understand the CO<sub>2</sub> plasticization effect on PC membrane, we exposed PC membranes to different CO<sub>2</sub> densities, and in some conditions, to densities even higher than the critical point of CO<sub>2</sub>. Gas permeability and solubility were measured independently. Glass transition temperature ( $T_g$ ) measurements and X-ray diffraction analyses were used to characterize the changes in treated membrane. The relationship between microstructural change in treated membranes and gas transport and sorption properties were discussed in this study.

## 2. Experimental

### 2.1. Materials

Polycarbonate (PC) (Uplion S-2000) with a molecular weight of 28 000 was supplied by Mitsubishi Gas Chemical. Chloroform (Merck) was used as solvent. All the chemicals are of reagent grade and were used without further purification.

### 2.2. Membrane preparation

Polycarbonate (PC) membrane was prepared from a solution of PC in chloroform. At room temperature, the solution (8 wt.%) was cast onto a glass plate to a predetermined thickness (35 μm) using a Gardner knife. The membrane was dried in vacuum at room temperature for 24 h before gas sorption and permeation measurements.

### 2.3. CO<sub>2</sub> treatment

Placing membranes in a stainless chamber, which was placed in a constant temperature tank, processed

the CO<sub>2</sub> treatment. CO<sub>2</sub> was pumped into a stainless chamber until the treated pressure and equilibrium were reached for at least 12 h. The CO<sub>2</sub> density was calculated by the Peng–Robinson equation [9]. The treated CO<sub>2</sub> was released from stainless chamber in at least 5 min. This exhaust rate was almost an order of magnitude more rapid than that practised by Paul and Wonders [5] and may be responsible for the somewhat different results observed here versus their work. The temperature loss was observed when the stainless chamber was depressurized to atmosphere. However, the temperature loss depended on the release rate of CO<sub>2</sub> and the temperature loss in this study was not recorded during the depressurization procedure.

### 2.4. Gas permeability measurements

The apparatus (Yanaco Gas Permeability Analyzer, model GTR-10) for measuring the gas permeability has been shown in our previous report [10]. The gas permeability was measured by the following equation:

$$P = \frac{l}{p_1 - p_2} \frac{q/t}{A}$$

where  $P$  is the gas permeability (cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cm Hg),  $q/t$  is the flow rate of gas permeate (cm<sup>3</sup>(STP)/s),  $l$  is the membrane thickness (cm), and  $p_1$ ,  $p_2$  are the pressures (cm Hg) on the high and the low pressure side of the membrane, respectively.  $A$  is the effective membrane area (cm<sup>2</sup>). The gas selectivity was calculated by the following expression using mixing gas permeability:

$$\text{Selectivity} = \frac{PO_2}{PN_2}$$

### 2.5. Gas sorption measurements

The experimental setup for gas sorption measurement has been shown in our previous report [11]. The amount of gas absorbed was measured by a microbalance. The microbalance (Cahn Model D-202 Electrobalance) was enclosed in a stainless chamber which was placed in a constant temperature box. The system was then vacuumed to about  $4 \times 10^{-3}$  Torr until constant weight before the gas sorption measurement. The gas sorption measurement was carried out under

measuring pressure until the constant weight to make sure that the sorption equilibrium was reached.

### 3. Results and discussions

#### 3.1. Effect of CO<sub>2</sub> plasticization on gas permeability and O<sub>2</sub>/N<sub>2</sub> selectivity

Polycarbonate (PC) membranes were exposed in the stainless tank to various CO<sub>2</sub> densities. Oxygen and nitrogen permeabilities were measured and O<sub>2</sub>/N<sub>2</sub> selectivity was calculated. As shown in Fig. 1, the oxygen permeability hardly changed with the increase in CO<sub>2</sub> density up to 720 kg/m<sup>3</sup>. After 720 kg/m<sup>3</sup>, there was a sharp increase in oxygen permeability. According to our microscopical observation, there were some defects on the membrane surface when the exposure CO<sub>2</sub> density was increased to 770 kg/m<sup>3</sup>. It was proposed that the defects were caused by rapid removal of sorbed CO<sub>2</sub> from the membrane matrix after CO<sub>2</sub> treatment. Those defects on the surface led to the increase in permeability and the decrease in selectivity ratio of oxygen to nitrogen. Normally, plasticization of a membrane would mobilize the polymer chains of a membrane by the plasticized agent, thereby enhancing gas sorption and permeation. For example, CO<sub>2</sub> in a super critical state is a good plasticizing agent for

a PC membrane. It was expected that an increase in gas permeability and a decrease in gas selectivity of PC membrane would be observed by CO<sub>2</sub> treatment. However, as shown in Fig. 1, an increase in the O<sub>2</sub>/N<sub>2</sub> selectivity of treated membrane was found with increasing CO<sub>2</sub> density up to 720 kg/m<sup>3</sup>. The increase in CO<sub>2</sub> density did not result in a decrease in the O<sub>2</sub>/N<sub>2</sub> selectivity, but the O<sub>2</sub>/N<sub>2</sub> selectivity increased. The CO<sub>2</sub> treated membrane showed no change in gas permeability with regard to CO<sub>2</sub> density. There are two possible explanations. One is attributed to the increased gas solubility and the decreased gas diffusivity on exposure and the other to the decreased gas solubility and the increased gas diffusivity of the treated PC membrane. In order to clarify gas solubility and diffusivity change, oxygen and nitrogen sorption measurements were carried out and those results are interpreted by the solution–diffusion mechanism and dual sorption model in the following sections.

#### 3.2. Effect of CO<sub>2</sub> plasticization on gas solubility and diffusivity

Gas solubility was calculated by the result of gas sorption measurements. Figs. 2 and 3 showed the pressure dependence of oxygen and nitrogen solubility. The gas diffusivity of the membrane was calculated by the relationship of  $P=DS$ , where  $P$  is the gas permeability,  $S$  the gas solubility coefficient and  $D$  the gas

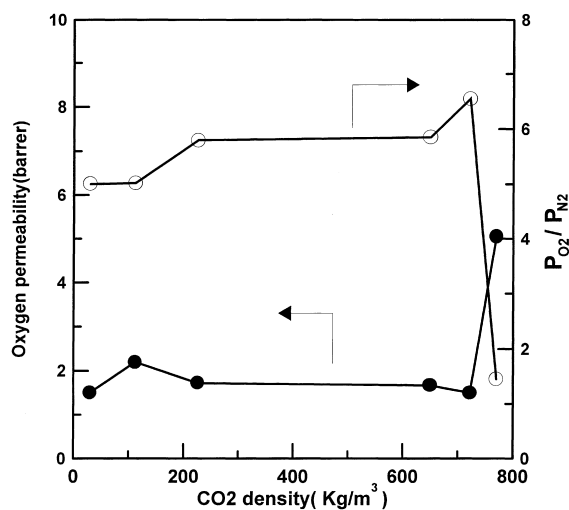


Fig. 1. Effect of CO<sub>2</sub> plasticization on gas permeability and O<sub>2</sub>/N<sub>2</sub> selectivity.

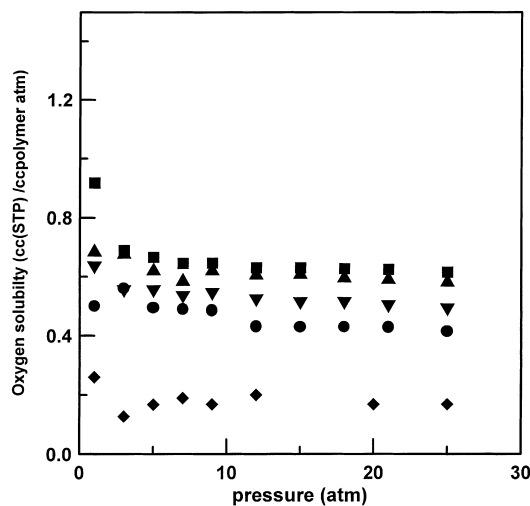


Fig. 2. Pressure dependence of oxygen solubility at 35°C.

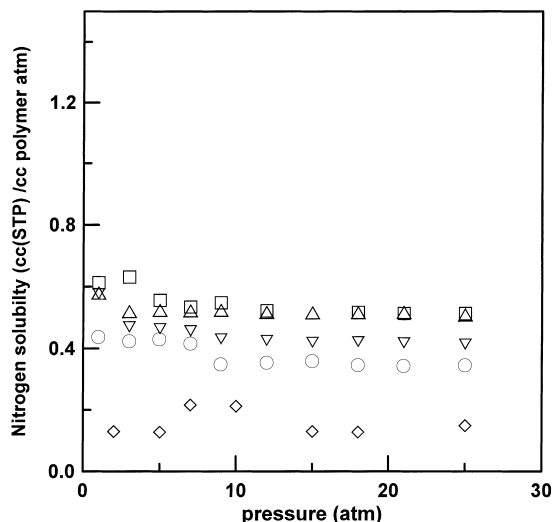


Fig. 3. Pressure dependence of nitrogen solubility at 35°C.

diffusion coefficient of the membrane. The effects of the various CO<sub>2</sub> density treatments on oxygen solubility and diffusivity are shown in Figs. 4 and 5. As can be seen in Fig. 4, the solubility and the solubility ratio of oxygen to nitrogen increased with increasing CO<sub>2</sub> density up to 720 kg/m<sup>3</sup>. On the other hand, the oxygen diffusivity decreased with increasing CO<sub>2</sub> density up to 720 kg/m<sup>3</sup>, as shown in Fig. 5. The nondependence of oxygen permeability on CO<sub>2</sub> density may be

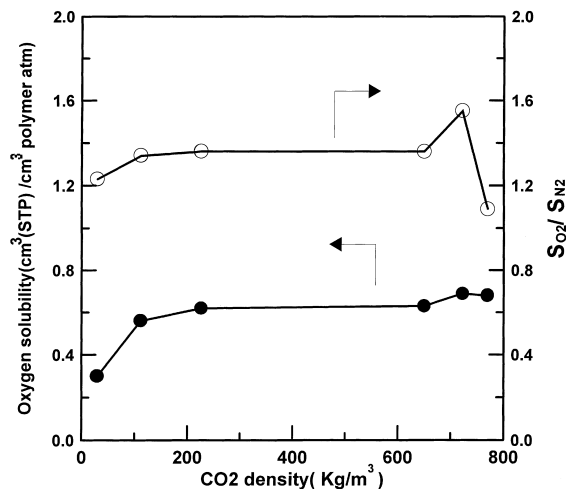


Fig. 4. Effect of CO<sub>2</sub> treatment on gas solubility and  $S_{O_2}/S_{N_2}$ .

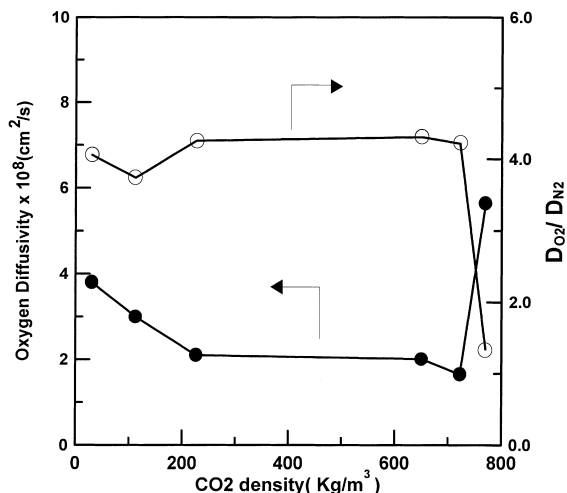


Fig. 5. Effect of CO<sub>2</sub> treatment on gas diffusivity and  $D_{O_2}/D_{N_2}$ .

due to an increase in gas solubility and a decrease in gas diffusivity after the CO<sub>2</sub> treatment.

If gas transport follows a solution–diffusion mechanism, the increase in gas selectivity is due to the increase in solubility ratio or the diffusivity ratio of oxygen to nitrogen. In order to clarify the matter, the solubility, and the diffusivity ratio of oxygen to nitrogen were measured. As shown in Figs. 4 and 5, the solubility selectivity of oxygen to nitrogen increased with CO<sub>2</sub> density. However, the effect of CO<sub>2</sub> treatment on the diffusivity ratio of a membrane was not identical. This result indicated that the increase in gas selectivity was contributed by an increase in the solubility ratio of treated membranes.

### 3.3. Effect of CO<sub>2</sub> treatment on free volume of a membrane

The gas diffusion rate of a membrane depends on the free volume of the membrane. Normally, it is proportional to the free volume of a membrane. An increase in the free volume leads to an increase in gas permeation of a polymer membrane. Glass transition temperature measurements and X-ray diffraction analysis were used to estimate the free volume of a membrane. Wide-angle X-ray diffraction measurements were used to determine the  $d$ -spacing of the treated membranes. It was expected that the increase in  $d$ -spacing proportional to the free volume of a membrane would be

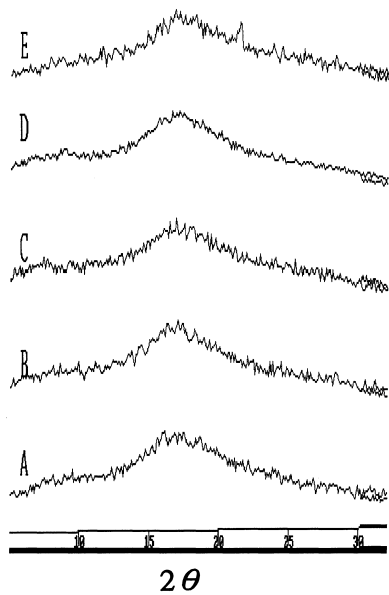


Fig. 6. X-ray diffraction patterns of CO<sub>2</sub> treated PC membrane: (A) CO<sub>2</sub> density: 30 kg/m<sup>3</sup>; (B) CO<sub>2</sub> density: 112 kg/m<sup>3</sup>; (C) CO<sub>2</sub> density: 226 kg/m<sup>3</sup>; (D) CO<sub>2</sub> density: 722 kg/m<sup>3</sup>; (E) CO<sub>2</sub> density: 770 kg/m<sup>3</sup>.

observed. As shown in Fig. 6, the broad peak center at 17.6° was attributed to the polymer interchain distance. The *d*-spacings can be calculated by applying the scattering angles ( $2\theta$ ) of the peak in Bragg's equation [12], namely  $n\lambda = 2d \sin\theta$ . It was found that the *d*-spacing hardly changed with exposure to different CO<sub>2</sub> densities. In order to show the change in free volume, another approach must be used.

As shown in Fig. 7, the glass transition temperature of the treated membrane decreased with increasing CO<sub>2</sub> density. This result indicates that the free volume of a CO<sub>2</sub> treated membrane increases with increasing CO<sub>2</sub> density. This result is different from the finding by Koros et al. [5]. They had showed that the free volume was not identical and the gas permeability was almost independent of CO<sub>2</sub> conditioning of membranes.

Generally, an increase in free volume of a membrane leads to an increase in gas permeability and a decrease in gas selectivity. However, as shown above, the increase in selectivity and the almost constant gas permeability were found for CO<sub>2</sub> treated membranes. It was assumed and proposed that uniform polymer

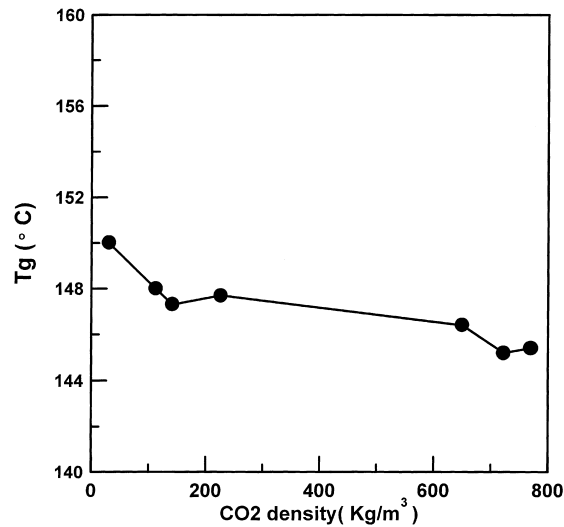


Fig. 7. Effect of CO<sub>2</sub> treatment on glassy transition temperature.

packing was formed after CO<sub>2</sub> treatment. The uniform polymer packing was expected to eliminate defects in the membrane and increase the Langmuir-type gas sorption area of treatment membranes. Therefore, oxygen and nitrogen sorption measurements were carried out and analyzed by dual sorption model to prove this.

### 3.4. Dual mode analysis

The solubility of a dual sorption model can be described by

$$S = S_H + S_L = K_D + \frac{C_H b}{1 + b p}$$

where  $S_H$  denotes Henry's mode solubility,  $S_L$  denotes the solubility caused by Langmuir sorption,  $K_D$  is the Henry's law dissolution constant, and  $C_H$  and  $b$  represent the maximum capacity and the affinity constant, respectively. The dual-model fitted parameters were obtained from nonlinear regression of the experimental sorption data to the above equation. The dual model parameters have a poor confidence and the relative error was about 30%. As can be seen in Table 1, the Langmuir-mode solubility increased with increasing CO<sub>2</sub> densities.

The effect of CO<sub>2</sub> exposure on oxygen and nitrogen solubility in the Langmuir mode is shown in Fig. 8. It was found that the Langmuir solubility of both oxygen

Table 1  
Dual sorption parameters of oxygen and nitrogen for different CO<sub>2</sub> density

| Oxygen                                       |   |   |                          | Nitrogen  |   |                          |
|--|---|---|--------------------------|---|---|--------------------------|
| CO <sub>2</sub> density (kg/m <sup>3</sup> ) | $K_D$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> atm) | $C_{H'}$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ) | $b$ (atm <sup>-1</sup> ) | $K_D$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> atm) | $C_{H'}$ (cm <sup>3</sup> (STP)/cm <sup>3</sup> ) | $b$ (atm <sup>-1</sup> ) |
| 30   | 0.18  | 0.2   | 0.08                     | 0.10  | 0.1   | 0.06                     |
| 112  | 0.18  | 7.2   | 0.08                     | 0.19  | 4.7   | 0.06                     |
| 226  | 0.18  | 8.8   | 0.08                     | 0.25  | 6.2   | 0.06                     |
| 722  | 0.18  | 11.0  | 0.08                     | 0.21  | 7.5   | 0.06                     |
| 770  | 0.18  | 12.4  | 0.08                     | 0.20  | 7.9   | 0.06                     |

and nitrogen increased with increasing CO<sub>2</sub> density. The increase in Langmuir solubility implied that the monolayer sorption area of a PC membrane increased after the CO<sub>2</sub> treatment. It was evident that the CO<sub>2</sub> treatment changed the polymer-packing density of a PC membrane and increased the Langmuir-type sorption site of treated membranes.

Generally, gas diffusion in Henry's law area is much higher than in Langmuir area. The same phenomena were observed in our previous report [13]. Gas diffusion in Henry's law area was greater than the diffusion in the Langmuir sorption area of PC/CoSalPr membranes. In order to explain the decrease in gas diffusivity of a PC membrane after CO<sub>2</sub> treatment, the sorption fraction of Henry's sorption at various CO<sub>2</sub> densities was examined by dual sorption model anal-

ysis. Fig. 9 shows the fraction of Henry's sorption at various CO<sub>2</sub> densities. It was found that the fraction of Henry's sorption decreased in the same way as gas diffusivity. This result indicated that the decrease in gas diffusivity was due to the decrease in Henry's sorption in a PC membrane. It also can be concluded that the increase in gas solubility was mostly contributed by the increase in Langmuir-type absorption of treated membranes.

### 3.5. Effect of free volume on gas transport properties

As shown in Fig. 1, the gas permeation test of treated PC membrane showed that the gas permeability was almost nondependent on the treated CO<sub>2</sub> den-

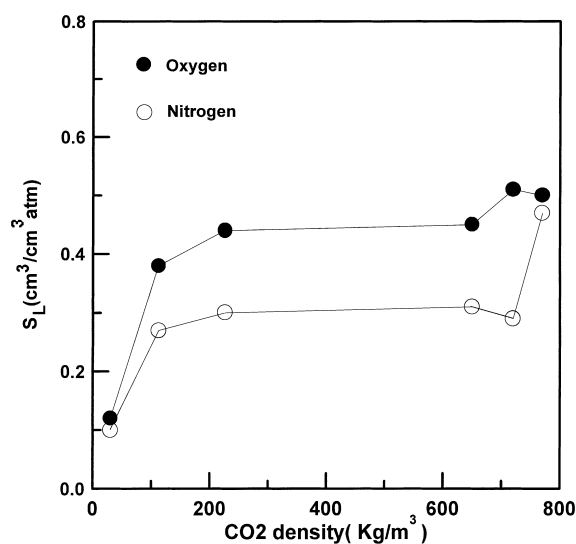


Fig. 8. Effect of CO<sub>2</sub> treatment on Langmuir-type gas solubility.

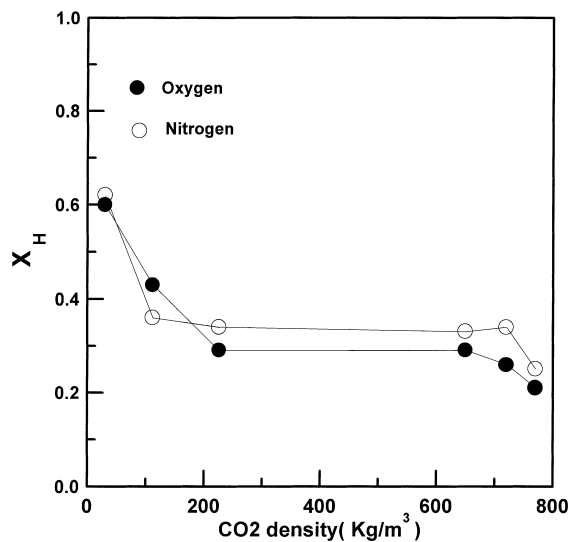


Fig. 9. Effect of CO<sub>2</sub> treatment on the fraction of Henry's solubility ( $X_H$ ).

sity. However, Fig. 9 showed an increase in Langmuir sorption and Fig. 5 showed a decrease in gas diffusion after CO<sub>2</sub> treatments. It was difficult to correlate the morphology change and gas transport properties of treated membranes. It was proposed that plasticized CO<sub>2</sub> absorbed into membranes and changed the membrane morphology. This morphology change led to an increase in excess free volume of treated membranes. If the excess free volume of membrane was contributed as microvoids of various sizes, the gas sorbed into microvoids would increase the excess free volume when the microvoids were smaller than the sorbed gas molecules. The gas sorbed into these microvoids would be in Langmuir form. A similar result was reported by Kamiya et al. [14] in poly(ethylene terephthalate) (PET) high pressure CO<sub>2</sub> treated membrane. The increases in Langmuir sorption implied that excess free volume of treated membranes would increase with increasing CO<sub>2</sub> density. As shown in Table 1, the gas solubility in Langmuir-type sorption increased with increasing CO<sub>2</sub> density. It was evidenced that CO<sub>2</sub> treatment increased the Langmuir sorption area in PC membrane. Generally, the gas diffusion through membrane was contributed by multilayer and monolayer diffusion in polymer matrix. The multilayer gas diffusion rate is usually much higher than the monolayer diffusion rate in the polymer. This phenomenon could also be found in our previous study [15]. If the multilayer diffusion area decreased significantly after CO<sub>2</sub> treatment, the gas diffusivity of CO<sub>2</sub> treated membrane should be decreased. It was proposed that the plasticization effect of PC membrane may have led to polymer chain redistribution and to a closer polymer packing. The decrease in gas diffusivity of plasticized membrane was contributed by polymer chain redistribution and this result was also reported by Sanders [16]. It was proposed that the decrease in gas diffusion rate may be due to the polymer chain redistribution, which reduced the multilayer diffusion rate after CO<sub>2</sub> treatment. The results of gas sorption and diffusion measurement implied that the monolayer diffusion rate increased and multilayer diffusion rate decreased after CO<sub>2</sub> treatment. It can be concluded that the decrease in gas diffusivity should be due to the decrease in multilayer diffusion rate of treated membranes. Therefore, membrane morphology change led to a decrease in gas diffusivity and an increase in gas solubility of treated membrane after

CO<sub>2</sub> treatment, but this morphology change did not significantly change the gas permeability.

#### 4. Conclusion

The effects of CO<sub>2</sub> treatment on gas transport and sorption properties of a membrane were assessed. When CO<sub>2</sub> density was increased, the effect of CO<sub>2</sub> treatment on gas permeability and diffusivity was not identical, but the effect of CO<sub>2</sub> treatment enhanced the selectivity of oxygen to nitrogen. The increase in gas selectivity was due to the improvement of the solubility ratio of oxygen to nitrogen. It was found that the increase in gas solubility was attributable to increasing Langmuir-type sorption of a treated membrane rather than to Henry-type sorption. The decrease in gas diffusivity was due to a decrease in the fraction of Henry's sorption in PC membrane after CO<sub>2</sub> treatment. It can be concluded that the increase in gas solubility was mostly contributed by the increase in Langmuir-type absorption. It was found that the free volume of a treated membrane increased after CO<sub>2</sub> conditioning, which was evident by glassy transition temperature measurements.

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