

# Gas Permeability and Permselectivity of Plasma-Treated Polypropylene Membranes

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**ABSTRACT:** The effects of NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment on rubbery polypropylene (PP) membrane upon permeation behavior for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> were investigated from their permeability measurements. The NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment on PP membranes could increase both the permeability coefficient for CO<sub>2</sub> and the ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub>. For O<sub>2</sub> transport, both the permeability coefficient for O<sub>2</sub> and the ideal separation factor for O<sub>2</sub> relative to N<sub>2</sub> also increased. NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment on PP membranes

possibly brings about an augmentation of permeability for CO<sub>2</sub> and permselectivity of CO<sub>2</sub> relative to N<sub>2</sub> simultaneously, but unfortunately the plasma-treated PP membrane does not reach the level of CO<sub>2</sub> separation membrane. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3236–3239, 2007

**Key words:** carbon dioxide; polypropylene membrane; plasma modification; permeability coefficient; ideal separation factor

## INTRODUCTION

Ever-increasing fossil fuel consumption has been causing atmospheric buildup of carbon dioxide (CO<sub>2</sub>). CO<sub>2</sub>, which is exhausted in massive amount, has been recognized as one of the most influential greenhouse gases. The fixation and removal of CO<sub>2</sub> from fossil fuel combustion facilities has been considered as a promising way to prevent CO<sub>2</sub> buildup in the atmospheric sphere. One possible process for this purpose is membrane-based separation. It was expected that the surface modification to the membrane by NH<sub>3</sub> plasma treatment, among others, would possibly induce an increase in the permeability to CO<sub>2</sub> through an interaction of dissolved CO<sub>2</sub> with the basic functional group (e.g., —NH<sub>2</sub>) by the treatment, whereas it would exert negligible influence on the permeability to N<sub>2</sub>. As a result, the plasma treatment would induce increases in both the permeability coefficient for CO<sub>2</sub> and the separation factor for CO<sub>2</sub> relative to N<sub>2</sub>.

In our preceding works,<sup>1–3</sup> the effects of NH<sub>3</sub>-plasma treatment on two kinds of glassy polymer membranes on the diffusion process for penetrant gases, CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> have been discussed; glassy poly(phenylene oxide) (PPO) membrane,<sup>1</sup> which has highly chemical and thermal stability and poly(methyl methacrylate) (PMMA) membrane<sup>2</sup> and poly

(ether sulfone) (PES) membrane,<sup>3</sup> both of which have been recognized to exhibit high permeability to CO<sub>2</sub>. The sorption equilibria and permeation behavior for O<sub>2</sub> and CO<sub>2</sub> in untreated PPO membranes were simulated well in terms of the dual-mode sorption and mobility model. For O<sub>2</sub> transport, the NH<sub>3</sub>-plasma treatment on PPO membrane had an influence on the diffusion process of Henry's law species, whereas for CO<sub>2</sub> transport, it promoted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant for CO<sub>2</sub>. The mean permeability coefficients for CO<sub>2</sub> in PMMA membrane decreased with increasing upstream pressure up to ~ 0.9 MPa, and the pressure dependency of mean permeability coefficient in this region could be interpreted by a dual-mode mobility model. Above 1.0 to 1.2 MPa of upstream pressure, the logarithmic permeability coefficients in treated as well as untreated membranes increased linearly with the upstream pressure, presumably due to the plasticization action of sorbed CO<sub>2</sub>. The mean permeability coefficients for O<sub>2</sub> and N<sub>2</sub> substantially remain constant irrespective of the upstream pressure. For O<sub>2</sub> transport, the permeability increases a little with increasing treatment power, and for N<sub>2</sub> transport, it was not affected by the treatment power. For CO<sub>2</sub> transport, NH<sub>3</sub>-plasma treatment promoted the transport of Langmuir mode, presumably through an increased Langmuir capacity constant for CO<sub>2</sub>, whereas it had only an influence on the mobility of Henry's law species. The permeation behavior for O<sub>2</sub> and CO<sub>2</sub> in untreated and NH<sub>3</sub>-plasma-treated PES membranes was also simulated well in terms of the dual-mode mobility model. For O<sub>2</sub> transport, NH<sub>3</sub>-

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plasma treatment on PES membrane had a little influence on the diffusion process of Langmuir species, and very little influence on the diffusion process of Henry's law species. For CO<sub>2</sub> transport, it promoted the transport of Henry's law mode, but had very little influence on the transport process of Langmuir species. Both the mean permeability coefficient to CO<sub>2</sub> and the ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub> took maximum values at a treatment power of 40 W.

The NH<sub>3</sub>-plasma treatment to PPO, PMMA, and PES membranes resulted in an increase in the ideal separation factor of CO<sub>2</sub> relative to N<sub>2</sub> as well as the permeability to CO<sub>2</sub>. It is desirable that this speculation for CO<sub>2</sub> transport through NH<sub>3</sub>-plasma-treated glassy polymer membrane is confirmed also for rubbery polymer membranes as well as the other glassy polymer ones.

In the other preceding work,<sup>4</sup> NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment was applied on a typical rubbery polymer membrane, polyethylene (PE) membrane under plasma discharge powers up to 100 W and a plasma exposure time of 1 min. The degrees of improvement of both permeability for CO<sub>2</sub> and permselectivity for CO<sub>2</sub> relative to N<sub>2</sub> induced by NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment were investigated from measurements of permeability coefficients to CO<sub>2</sub> and N<sub>2</sub>. As a result, NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment on PE membranes could increase both the permeation coefficient for CO<sub>2</sub> and the ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub>. NH<sub>3</sub> and N<sub>2</sub> plasma treatment on rubbery polymer membranes also possibly brings about an augmentation of CO<sub>2</sub> permeability and separation factor for CO<sub>2</sub> relative to N<sub>2</sub> simultaneously.

In the present work, thus, a similar surface modification by plasma treatment was executed on the other typical rubbery polymer membrane, polypropylene (PP) membrane. The degrees of improvement of both permeability for CO<sub>2</sub> and permselectivity for CO<sub>2</sub> relative to N<sub>2</sub> induced by NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment were investigated from measurements of permeability coefficients to CO<sub>2</sub> and N<sub>2</sub>.

## EXPERIMENTAL

Homogeneous dense polypropylene (PP) membrane used was supplied from Tosero Co., Japan. The glass-transition temperature was reported to be -35°C by the manufacturer.

The plasma treatment was performed in a flow-type cylindrical plasma reactor with an external electrode (Yamato, PR-510A), employed in our preceding works.<sup>1-3</sup> The internal diameter and length of the reactor are 21.5 and 27.5 cm, respectively. N<sub>2</sub> as well as NH<sub>3</sub> balanced with N<sub>2</sub> at 2010 ppm was used as the treatment gas, and the flow rate was maintained at

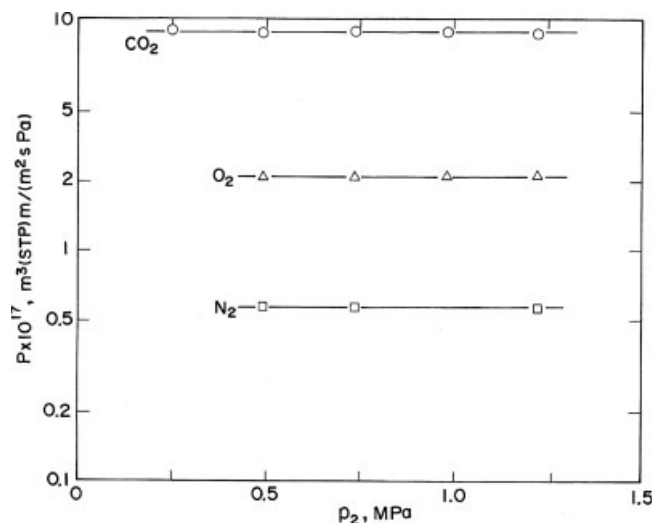
10 cm<sup>3</sup> (STP)/min. The glow discharge was generated under a pressure of 0.5 mm Hg at a fixed frequency of 13.56 Hz. The electric power of discharge was varied up to 100 W. The duration of plasma discharge was fixed at 1 min and 5 min. Argon (Ar) was used as a cleansing gas for the plasma reactor.

The steady-state permeation rates for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> through PP membranes with and without treated NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma were measured at a constant temperature of 30°C by a variable-volume method employed by Stern et al.<sup>5</sup> The gas to be permeated was fed into the upstream side, whereas the downstream side was filled with the same gas at an atmospheric pressure. The volumetric flow rate through the membrane to the downstream side was measured by observing the displacement of a small amount of 1-propanol in a capillary tube connected to the downstream pressure side. The permeability coefficient was calculated from this steady-state permeation rate. The permeation area of the cell was 19.6 cm<sup>2</sup>.

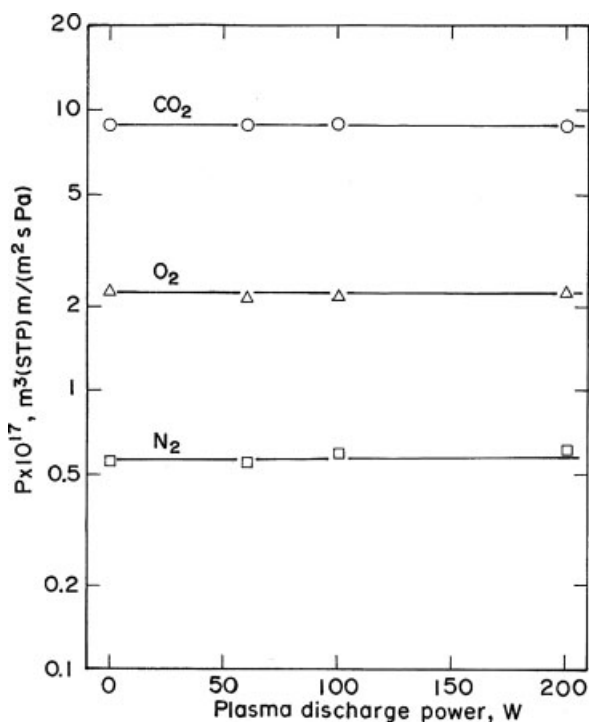
## RESULTS AND DISCUSSION

The experimental results on permeability coefficients for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in the untreated PP membrane at 30°C were plotted against the upstream pressure in Figure 1. It is apparent that the permeability coefficients for these gases are almost independent of the upstream pressure, characteristic of typical rubbery polymer membranes. In both NH<sub>3</sub>-plasma-treated and N<sub>2</sub>-plasma-treated PP membranes, the permeability coefficients for these three gases were also almost independent of the upstream pressure up to 1.2 MPa.

Figure 2 shows the relationship between the permeability coefficients for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in NH<sub>3</sub>-plasma-treated PP membrane and the plasma dis-

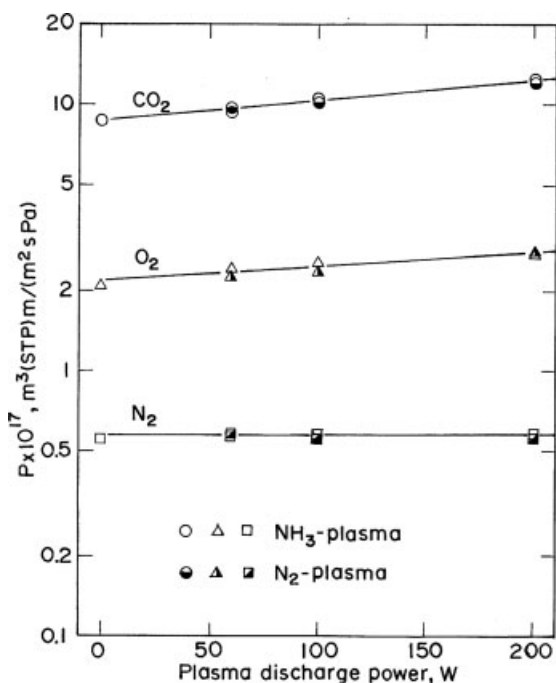


**Figure 1** Pressure dependencies of permeability coefficients for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in untreated PP membrane at 30°C.



**Figure 2** Relationship between gas permeability coefficient and plasma discharge power at a NH<sub>3</sub>-plasma discharge duration of 1 min.

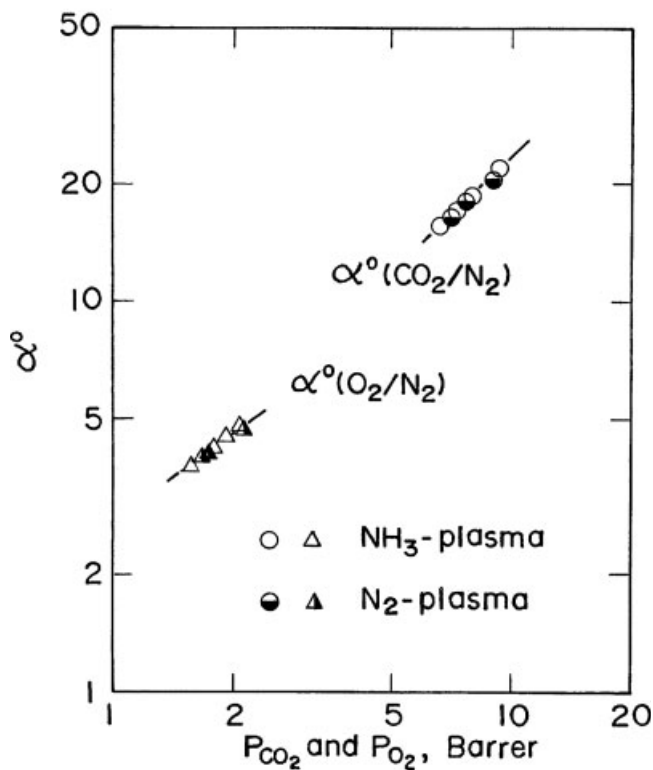
charge power up to 200 W at a plasma exposure time of 1 min. The effect of NH<sub>3</sub>-plasma treatment on the gas permeability coefficients is shown to be negligibly small.



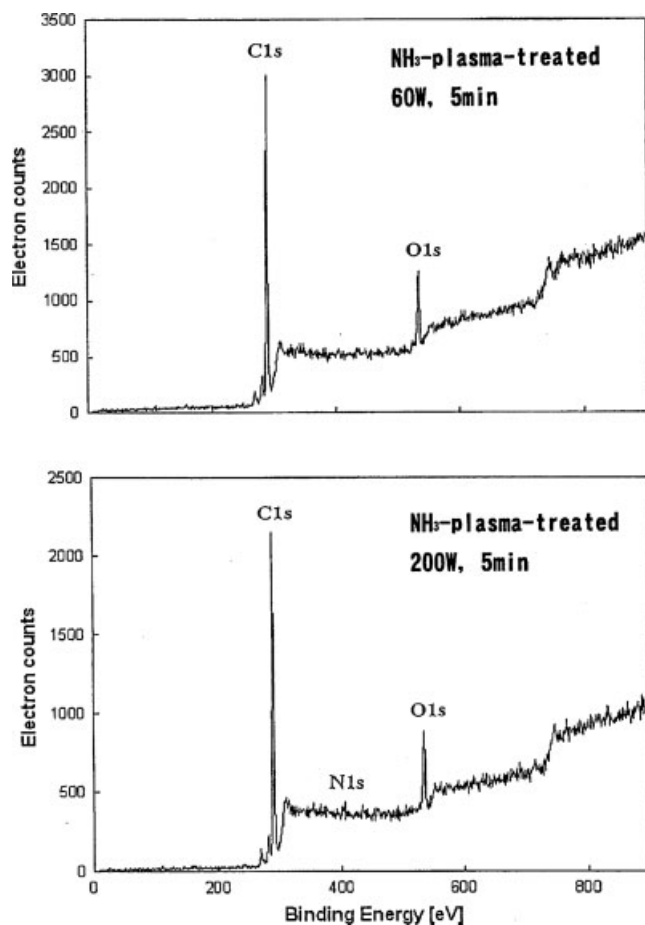
**Figure 3** Relationship between gas permeability coefficient and plasma discharge power at NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma discharge duration of 1 min.

Figure 3 indicates the relations of permeability coefficients for CO<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> in both NH<sub>3</sub>-plasma-treated and N<sub>2</sub>-plasma-treated PP membranes to the plasma discharge power up to 200 W at a plasma exposure time of 5 min. The effect of NH<sub>3</sub>-plasma treatment is found to be very similar to that of N<sub>2</sub>-plasma on the gas permeability coefficients. It should be emphasized here that the permeability to N<sub>2</sub> is not affected by the plasma treatment, whereas with increasing plasma discharge power at a plasma exposure time of 5 min, those to CO<sub>2</sub> and O<sub>2</sub> increase.

Next, the ideal separation factors for CO<sub>2</sub> relative to N<sub>2</sub>,  $\alpha^{\circ}(\text{CO}_2/\text{N}_2)$ , and for O<sub>2</sub> relative to N<sub>2</sub>,  $\alpha^{\circ}(\text{O}_2/\text{N}_2)$ , which are defined by permeability ratio,  $P_{\text{CO}_2}/P_{\text{N}_2}$  and  $P_{\text{O}_2}/P_{\text{N}_2}$ , respectively, were plotted against the permeability coefficients  $P_{\text{CO}_2}$  and  $P_{\text{O}_2}$  in Figure 4. This figure clearly reveals that with increasing permeability coefficient, the ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub> is somewhat improved when compared with that for O<sub>2</sub> relative to N<sub>2</sub>. The NH<sub>3</sub>-plasma treatment on the PP membrane tends to induce considerable increase in both the permeability for CO<sub>2</sub> and the permselectivity of CO<sub>2</sub> relative to N<sub>2</sub>, simultaneously. The N<sub>2</sub>-plasma treatment also induces the similar promotion effect.



**Figure 4** Relations of ideal separation factors for CO<sub>2</sub> relative to N<sub>2</sub> and for O<sub>2</sub> relative to N<sub>2</sub> to permeability coefficients for CO<sub>2</sub> and O<sub>2</sub>, respectively, in NH<sub>3</sub>-plasma-treated and N<sub>2</sub>-plasma-treated PP membranes at an exposure time of 5 min at 30°C.



**Figure 5** ESCA spectra of NH<sub>3</sub>-plasma-treated PP membranes.

The direction of research and development (R and D) for CO<sub>2</sub> separation membranes is a simultaneous increase in both increases in CO<sub>2</sub> permeability and ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub>. Actually, the NH<sub>3</sub>- and N<sub>2</sub>-plasma treatment on the PP membrane brings about both increases in CO<sub>2</sub> permeability and separation factor for CO<sub>2</sub> relative to N<sub>2</sub> simultaneously. Such a trend coincides with the direction of R and D. But unfortunately, NH<sub>3</sub>- and N<sub>2</sub>-plasma-treated PP membranes do not reach the level of the CO<sub>2</sub> separation membrane.

Figure 5 reveals the ESCA spectra of PP membranes with treated NH<sub>3</sub>-plasma, where the plasma treatment was executed at powers of 60 and 200 W for 5 min. With the PP membrane treated at a power of 200 W, a slight but definite peak of N1s appears at a binding energy of 400–405 eV, presumably based on the NH<sub>2</sub> group, whereas the membrane treated at 60 W has no N1s peak there. The solubility of CO<sub>2</sub> in the NH<sub>3</sub>-plasma-treated PP membrane can be augmented through an interaction with the basic functional group, NH<sub>2</sub>. In case of CO<sub>2</sub> transport in NH<sub>3</sub>-plasma treated PPO membranes,<sup>1</sup> such an

increase was observed and interpreted qualitatively by the interaction of sorbed CO<sub>2</sub> with basic groups generated by NH<sub>3</sub>-plasma treatment as follows:

Sorbed CO<sub>2</sub> (A) is assumed to react reversibly with the basic groups (B) (A + B = AB), so that at an equilibrium

$$K = \frac{[AB]_e}{([A]_e[B]_e)} = \frac{([B]_0 - [B]_e)}{([A]_e[B]_e)} \quad (1)$$

where  $K$  refers to the equilibrium constant, subscript  $e$  to the concentration at an equilibrium and subscript 0 to the initial value. The total concentration of sorbed CO<sub>2</sub> at the equilibrium,  $[A]_{\text{tot}}$  can be given as

$$[A]_{\text{tot}} = [A]_e + [AB]_e = [A]_e + K[B]_0[A]_e / (1 + K[A]_e) \quad (2)$$

The above equation implies that the solubility coefficient for CO<sub>2</sub> in PP membrane is augmented by NH<sub>3</sub>-plasma treatment. Thus, the permeability coefficient to CO<sub>2</sub> can be increased, while that to N<sub>2</sub> remains unchanged. The permeability coefficient to O<sub>2</sub> can also be increased as shown in Figure 3, although the interaction of sorbed O<sub>2</sub> with the NH<sub>2</sub> group has not been understood yet.

## CONCLUSIONS

NH<sub>3</sub>-plasma and N<sub>2</sub>-plasma treatment on PP membranes with a plasma exposure time of 5 min can increase both the permeation coefficient for CO<sub>2</sub> and the ideal separation factor for CO<sub>2</sub> relative to N<sub>2</sub>. Such a favorable trend coincides with the direction of R and D for CO<sub>2</sub> separation membranes. NH<sub>3</sub> and N<sub>2</sub> plasma treatment on polymer membranes possibly brings about an augmentation of permeability and permselectivity simultaneously.

## NOMENCLATURE

$P$	Permeability coefficient [m <sup>3</sup> (STP) m / (m <sup>2</sup> s Pa)] or (Barrer), [1 Barrer = 1.33 × 10 <sup>-17</sup> m <sup>3</sup> (STP) m / (m <sup>2</sup> s Pa)]
$p$	Pressure of penetrant gas, (Pa) or (MPa)
$\alpha^o$	Ideal separation factor defined by permeability coefficient ratio

## Subscript

2	upstream side of membrane
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