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Effect of top layer swelling on the oxygen/nitrogen separation by surface modified polyurethane membranes

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Abstract

Cobalt(II) was chelated on the surface of a hydroxyl terminated polybutadiene (HTPB) based polyurethane (PU) membrane. The surface of a HTPB based PU membrane was first modified by ethylenediamine (EA) plasma. The cobalt chelated membrane was prepared by immersing the plasma treated membrane into a cobalt(II)/formamide solution for various length of time. For a fair comparison, the untreated and plasma treated membranes were also immersed in formamide solution. The gas transport properties of all three membranes were compared. Without solvent immersion, the O_2/N_2 selectivity increased from 2.6 to 3.1 after EA plasma treatment. But the permeability decreased from 0.88 GPU to 0.35 GPU. The selectivity was further improved to 4.4 by immersing the plasma treated membrane in a solution of $CoCl_2{\cdot}6H_2O$/formamide for 1 h, but the permeability decreased to 0.23 GPU. The solvent immersion had little effect on the transport properties of the untreated membrane. But the transport properties of the plasma treated and cobalt chelated membranes were greatly affected by the formamide immersion. The oxygen and nitrogen permeabilities of the modified top layers could be calculated from a series model for composite membranes. It was found that both the permeability and selectivity of the top layer of the plasma treated membrane increased with the solvent immersing time. For the top layer of the cobalt chelated membrane, the gas permeability first decreased after 1 h immersion and then increased after further immersion in $CoCl_2{\cdot}6H_2O$/formamide solution. The selectivity of cobalt chelated membrane increased as the gas permeability decreased and vice versa. These results implied that the EA grafting enhanced the O_2/N_2 selectivity by increasing its oxygen affinity but the cobalt chelating increased the O_2/N_2 selectivity by enhancing the size sieving effect. © 1998 Elsevier Science B.V.

Keywords: Polyurethane membrane; Ethylenediamine; Plasma treatment; Cobalt chelating; Gas separations

1. Introduction

Polyurethane was a promising material for gas separation because of its low temperature flexibility and good mechanical strength. A lot of efforts were put for the improvement of the gas separation performance of polyurethane (PU) membranes by adjusting the hard segment content or by going through various chemical modifications[1]. Hseih [2] has reported that the gas permeability depended on the types of soft and hard segment in PU membranes. Huang [3] reported that the polymerization methods, one-step or two-step polymerization, also affected the gas permeability of PU membranes. In most cases, the

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increase of gas permeability lead to a decrease in gas selectivity.

In recent years, selectivity improvement by metal chelated membranes for oxygen enrichment has attracted many attentions [4]. Bick [5] and Park [6] significantly improved the O_2/N_2 selectivity by cobalt(II) chelated membranes. The selectivity of those complexed membranes usually increased as the content of chelated metal increased. However, the disadvantage of those membranes were the relative low gas permeability. A lot of efforts [7,8] have been made to not only improve the gas selectivity but also to keep the gas permeability. Lai et al. [9] had added a nonsolvent, dimethylformamide, together with $CuCl_2$ to a polycarbonate membrane. The gas permeability was greatly improved. They [10] also used wet inversion method to form a cobalt chelated asymmetric membrane to improve the gas permeability.

In order to improve the gas selectivity and to maintain the gas permeability, this study attempted to form a thin cobalt chelating layer on top of PU membranes. Hydroxyl terminated polybutadiene (HTPB) based PU was used as the substrate. HTPB allowed the membrane to be easily modified. The HTPB based PU membrane was treated with low power ethylenediamine (EA) plasma. A high nitrogen containing thin layer was formed for cobalt chelating. The cobalt chelated membrane was prepared by immersing the plasma treated membrane into a cobalt(II)/formamide solution. The gas permeabilities and O_2/N_2 selectivities of all three membranes, untreated, EA plasma treated, and cobalt chelated membranes, were compared. The permeabilities and selectivities of the top layers of EA plasma treated and cobalt chelated membranes could be calculated from a series model for composite membranes. Therefore, the transport properties of the top layers were also compared.

2. Experimental

2.1. Material

Chemicals used for PU synthesis were 4,4-dicyclohexylmethane diisocyanate (HMDI) from Mobay and hydroxyl terminated polybutadiene (HTPB) (average functionality=2.3, M.W.=2000) from ACROS Organics. 1,4-Butanediol (1,4-BD) and dibutyltin diaurate (DBTDL) from Merck were used as the chain extender and the catalyst, respectively. Tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) from Merck were used as solvents. The two stage PU polymerization method was employed. A –NCO terminated prepolymer was first synthesized and then chain extended with 1,4-BD. The reaction process was the same as that described by Huang et al. [3].

2.2. The modification of PU membrane by plasma treatment

The PU membrane was treated by plasma in a tubular type reactor with a pair of copper electrodes separated by 10 cm. The RF generator (Model RFG-300) purchased from Samco was used to produce plasma. The PU membrane was located in the center of two electrodes. After the system was evacuated to a pressure of 10^{-3} torr, the ethylenediamine vapor was introduced to the system to a predetermined pressure of 1 torr. Finally, The RF power was switched on and the plasma treatment started. The plasma power was controlled at 10 W for 30 min.

2.3. The preparation of cobalt chelated PU membrane

The plasma treated membranes were immersed into cobalt solution ($CoCl_2{\cdot}6H_2O$/formamide$=1.67\times10^{-3}$(mole ratio)) at 110°C for 1, 2, 3, 4, or 5 h. After that, the chelated membrane was washed by formamide and then dried in vacuum oven for 12 h at 25°C.

2.4. Gas permeation measurement

The apparatus and experimental procedure for gas permeability measurements have been described in a previous report [12]. The gas flux was determined by the following equation:

$$P = \frac{1}{p_1 - p_2}\left(\frac{q/t}{A}\right)$$

where P denotes the gas permeability [cm^3(STP)/cm^2 s cmHg], q/t is the volumetric flow rate of gas permeation [cm^3(STP)/s], p_1 and p_2 are the pressures (cmHg) on the high and low pressure sides of the membrane, respectively, and A is the effective membrane area (cm^2). The gas permeation fluxes are reported in gas permeation units, GPU (GPU=1× 10^{-6} cm^3(STP)/cm^2 s cmHg).

2.5. FTIR

A Shimadzu FT8000 FTIR/ATR spectrometer was used for the FTIR–ATR analysis.

2.6. SEM

The membrane structures were examined by a Hitachi (ModelS570) scanning electron microscope (SEM). In SEM studies, membrane samples were fractured in liquid nitrogen and coated with gold to 150 Å.

2.7. ESCA

The ESCA analysis was performed with a Perkin-Elmer PHI 590AM spectrometer using Mg anode ($h\nu$=1253.6 eV). The take-off angle α=45.

2.8. Series model for gas diffusion through a composite membrane

The flux of gas A through a simple membrane, which is shown in Fig. 1, can be described as

$$j_{\mathrm{A}} = k(A_1 - A_1') \tag{1}$$

where k is the mass transfer coefficient of gas A; A_0 and A_2 denote the upstream and downstream concentrations; A_1 and A_1' denote the concentration of A at the front and the end sides of the membrane, respectively. If we define the solubility of gas A in the membrane as $S = A_1/A_0 = A_1'/A_2$, then Eq. (1) can be expressed as

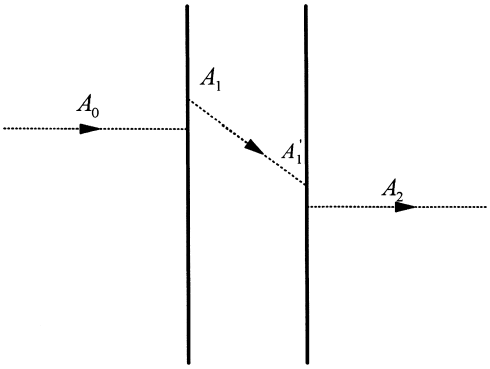

Fig. 1. Gas transport through a simple membrane.

$$j_{\mathrm{A}} = k(SA_0 - SA_2) = kS(A_0 - A_2) \tag{2}$$

When the downstream pressure is low, the above equation can be simplified as

$$j_{\mathrm{A}} = kSA_0 = PA_0 \tag{3}$$

where P is the permeability.

The flux of gas A through a two-layered composite membrane, which is shown in Fig. 2, can be described as

$$j_{\mathrm{A}} = k_1(A_1 - A_1') = k_2(A_2 - A_2') \tag{4}$$

where k_1 and k_2 are the mass transfer coefficients of the upper and the bottom layers of the membrane. A_1 and A_1' denote the concentration of A at the front and the end sides of the first layer of the membrane, respectively. A_2 and A_2' denote the concentration of A at the front and the end sides of the second layer of the membrane, respectively. If the solubility of gas A in the first layer is defined as $S_1 = A_1/A_0$, the solubility in the second layer is defined as $S_2 = A_2'/A_3$, and the partition coefficient between the first and second layers is defined as $S_{1/2} = A_1'/A_2$. Eq. (4) can then be expressed as

$$j_{\mathrm{A}} = k_1(S_1A_0 - A_1') = k_2(A_1'/S_{1/2} - S_2A_3) \tag{5}$$

When the downstream pressure is low, the above equation can be simplified as

$$j_{\mathrm{A}} = k_1(S_1A_0 - A_1') = k_2A_1'/S_{1/2} \tag{6}$$

A_1' can therefore be expressed as $j_{\mathrm{A}}S_{1/2}/P_2$. The final expression for the flux j_{A} is

$$j_{\mathrm{A}} = \frac{k_1S_1A_0}{1 + \frac{k_1}{k_2}S_{1/2}} \tag{7}$$

The effective permeability of gas A through the composite membrane is

$$P_{eff} = \frac{k_1S_1}{1 + \frac{k_1}{k_2}S_{1/2}} = \frac{k_1S_1}{1 + \frac{k_1S_1}{k_2S_2}} = \frac{P_1}{1 + \frac{P_1}{P_2}} \tag{8}$$

since $S_{1/2}$ is approximately equal to S_1/S_2.

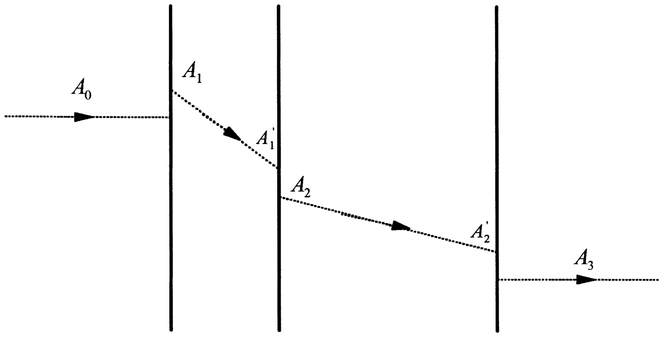

Fig. 2. Gas transport through a composite membrane.

3. Results and discussion

3.1. Characterization of ethylenediamine plasma treated HTPB based PU membranes

The untreated PU and plasma-treated PU membranes were examined by FTIR-ATR for verifying the existence of grafted EA on the surface of PU membranes. As shown in Fig. 3, new peaks appeared in the FTIR-ATR spectra of plasma treated PU membrane at 3278 cm^{-1} and 1658 cm^{-1}, which was expectively contributed by the N–H and C=N stretching absorbency. The appearance of N–H and C=N stretching on the surface of membranes indicated that ethylenediamine was grafted onto the PU membrane by plasma treatment.

The EA grafting can be further verified by the appearance of the emitted electrons from nitrogen atoms shown in the ESCA spectra. As shown in Fig. 4. The emission of 401.5 eV in the spectra was attributed to the emission of electrons from N_{1s}.

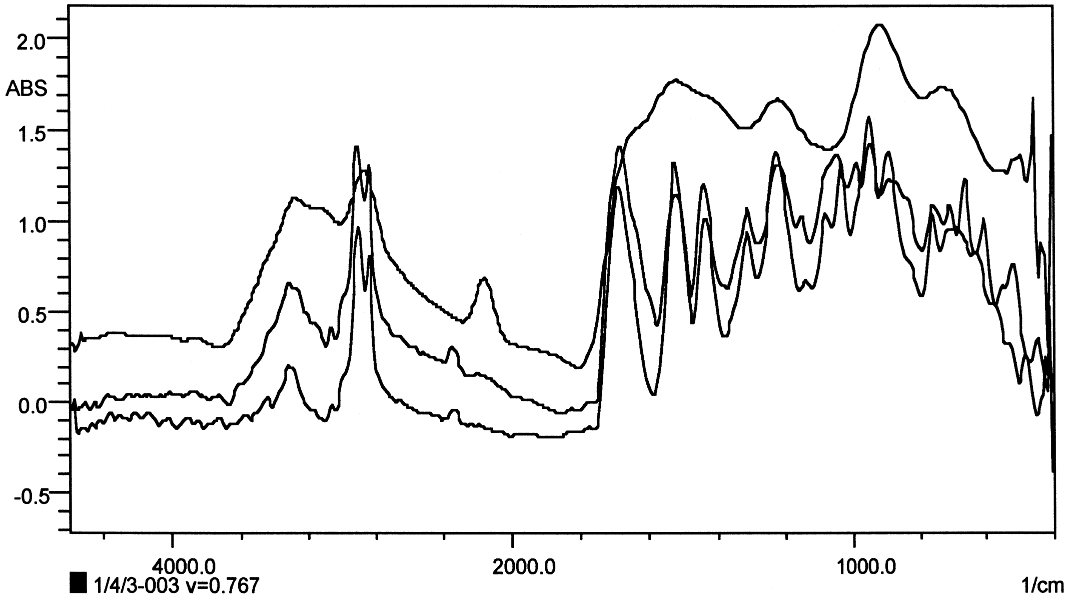

Fig. 3. The FTIR-ATR analysis of the modified membrane. (a) Untreated PU membrane. (b) Plasma treated PU membrane.

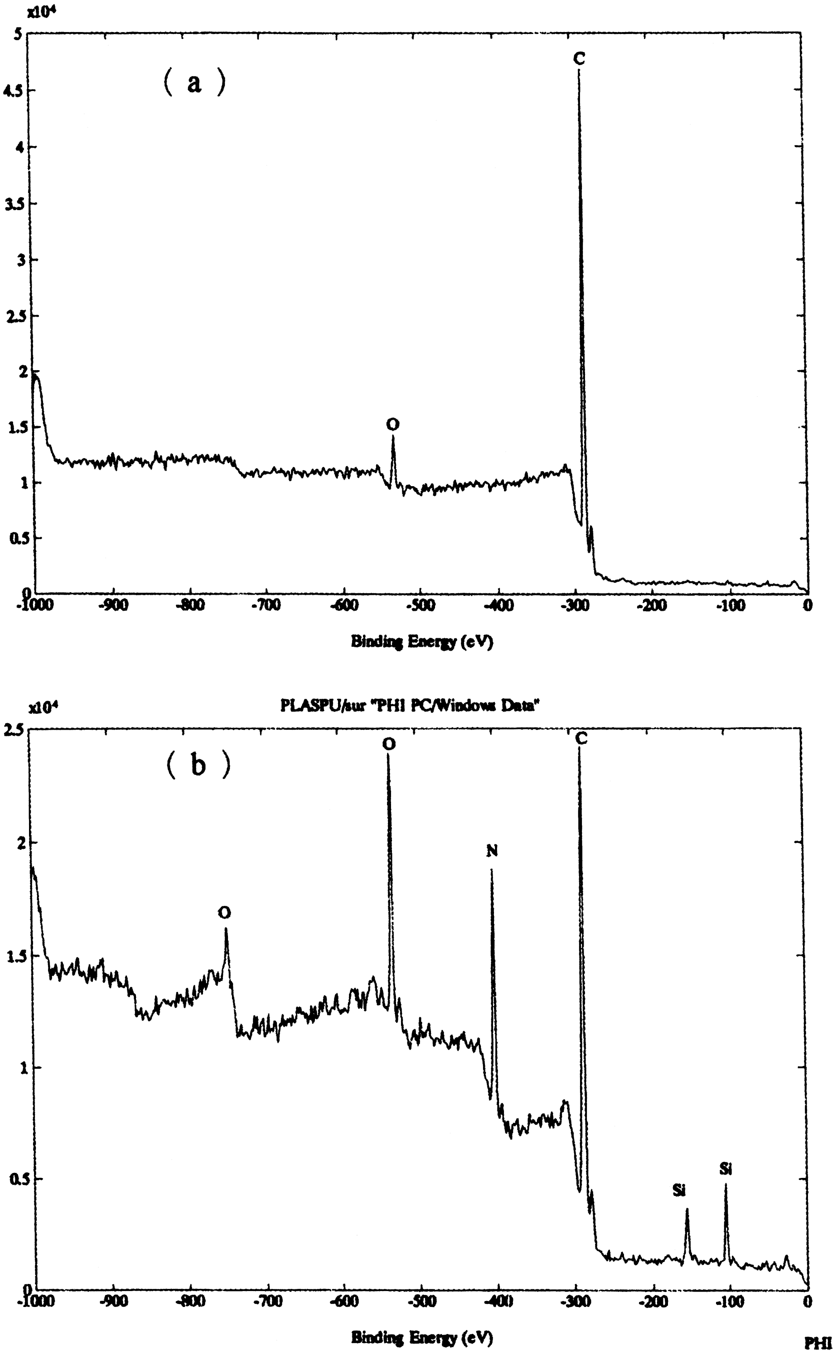

Fig. 4. The ESCA spectra of the N_{1s} region of the plasma treated PU membrane.

Table 1
The selectivities and permeabilities of the untreated and the surface modified PU membranes

	Selectivity (O_2/N_2)	Permeability (GPU) (Oxygen)
Untreated PU	2.6	0.88
PU plasma treated	3.1	0.35
PU-Co chelate*	4.4	0.23

* Reaction time: 1 h.

3.2. Gas transport properties of the plasma treated and the cobalt chelated membranes

The oxygen and nitrogen transport properties of the plasma treated and the cobalt chelated membranes were listed in Table 1. The oxygen permeability of the untreated PU membrane was 0.875 GPU and the O_2/N_2 selectivity was 2.6. After EA plasma treatment, the gas permeability decreased to 0.375 GPU and the O_2/N_2 selectivity increased to 3.1. The decrease in gas permeability was probably attributed to the cross-linking effect on the treated surface. Cross-linking may result in free volume reduction and a decrease in the flexibility of polymer chains. Subsequently, the gas permeability was reduced. Based on the concept of solution–diffusion model, there might be two possible reasons for the increase in membrane selectivity. One possible reason was the size-sieving effect caused by the surface cross-linking. The other was the increase in oxygen solubility caused by the incorporation of ethylenediamine.

The cobalt chelated membrane was prepared by immersing the plasma treated membrane into a cobalt(II) formamide solution at 110°C for 1 h. Cobalt(II) would chelate with the amine groups on the surface of plasma treated PU membrane. It was found that the gas selectivity increased from 3.1 to 4.4 but the permeability decreased to 0.21 GPU, which are shown in Table 1.

There were many investigations [11–13] about the oxygen enrichment by cobalt chelating. Those studies indicated that oxygen/nitrogen selectivity could be enhanced by the affinity between oxygen molecules and chelated cobalt(II) ions. According to the data shown in Table 1, apparently, the chelated cobalt enhanced the O_2/N_2 selectivity. But whether the selectivity enhancement was caused by the affinity between oxygen and chelated cobalt(II) ions required further investigations.

3.3. Effect of immersing time on gas transport properties of PU-chelated membranes

The previous mentioned Co(II) chelated membranes were prepared by immersing plasma treated membrane into a cobalt (II) formamide solution at 110°C for 1 h. The effect of immersing time on the cobalt chelation on the surface was also under investigation. According to ESCA analysis shown in Fig. 5, the increase in immersing time resulted in an increase in the cobalt/carbon ratio on the surface. However, the increase in surface cobalt content did not necessarily enhance the O_2/N_2 separation. As shown in Fig. 6, the oxygen to nitrogen selectivity did increase after 1 h of cobalt immersion. But the selectivity gradually decreased when the immersing time was longer than 1 h. As the increase of immersing time, gas permeability first decreased and then gradually increased. The increase in gas permeability was always accompanied by a decrease in O_2/N_2 selectivity and vice versa. The effect of immersing time on the gas permeability can be explained by the competing processes of cobalt complexation and membrane swelling. For a short time immersion, cobalt complexed with the amine groups on the membrane surface. The cobalt complexation, which resulted in a highly dense skin layer, caused the decrease in gas permeability. After prolong immersion, although the amount of cobalt complexation increased, the effect of membrane swelling gradually overpowered the cobalt complexation, the gas permeability gradually increased.

3.4. The transport properties of untreated PU and plasma treated PU after solvent immersion

To understand the swelling effect on the gas transport properties, the gas transport properties of the untreated and plasma treated membranes were measured after they were immersed in formamide for various periods of time. As shown in Fig. 7, the gas permeability of the untreated membrane increased only slightly with the increase in immersing time. But the swelling effect caused by formamide was apparent on the plasma treated membrane. As shown in Fig. 8, the swelling effect was clearly observed by

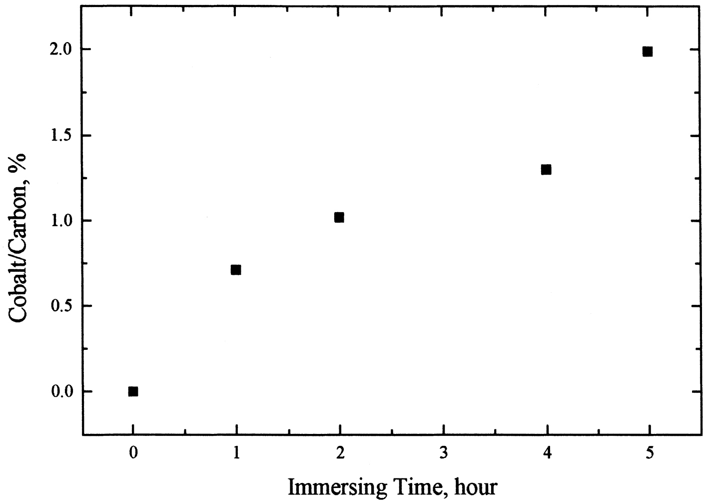

Fig. 5. Effect of immersing time on the Co/C ratio by ESCA analysis.

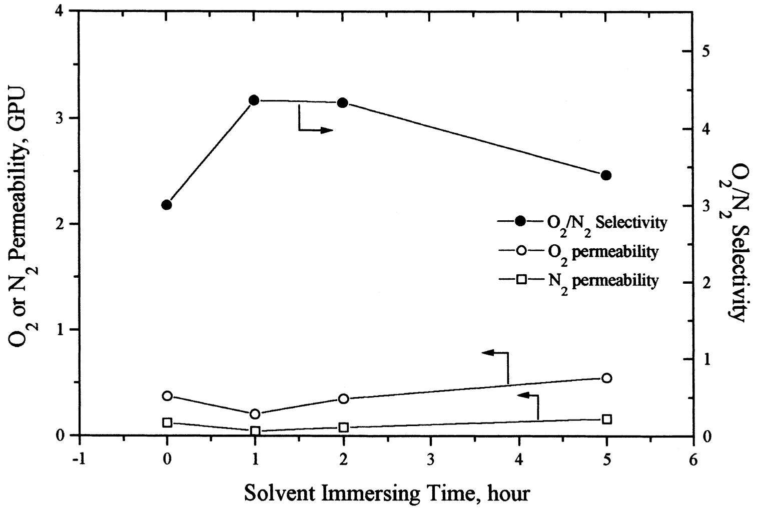

Fig. 6. Effect of the $CoCl_2{\cdot}6H_2O$/formamide immersing time on the selectivity and permeability of the cobalt chelated membrane.

the continuous increase in gas permeability with respect to solvent immersing time. This result lead us to believe that the increase in gas permeabilities and the decrease in O_2/N_2 selectivities of the cobalt chelated membranes were caused by the swelling effect by formamide.

Interestingly, it was found that the O_2/N_2 selectivities of the untreated and plasma treated membranes, shown in Figs. 7 and 8, were almost unaffected by the membrane swelling. It was interesting to know why the swelling had no effect on the selectivity of plasma treated membrane but had advert effect on cobalt chelated one.

3.5. The swelling effect on the top layer of the modified membranes

If we can regard the behavior of untreated PU the same as the bottom substrate of plasma treated and cobalt chelated membranes, the gas permeability

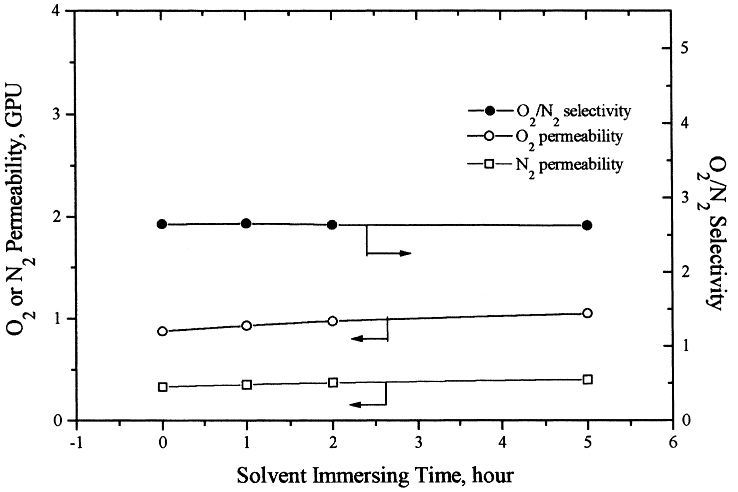

Fig. 7. Effect of the formamide immersing time on the selectivity and permeability of the untreated PU membrane.

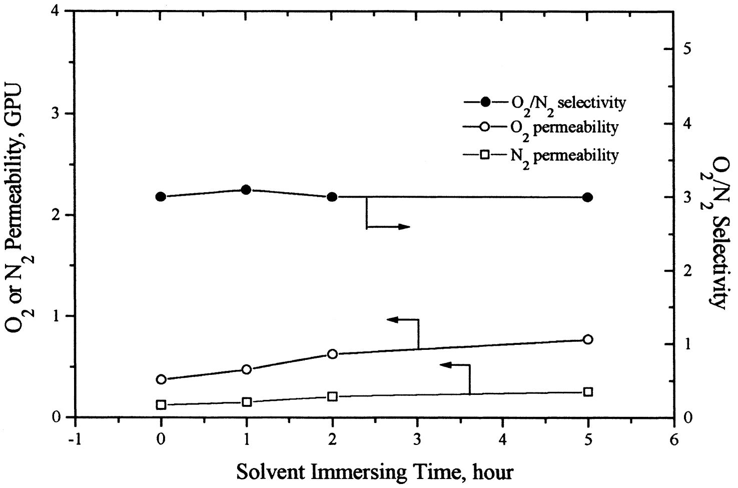

Fig. 8. Effect of the formamide immersing time on the selectivity and permeability of the plasma treated PU membrane.

obtained from the untreated PU was approximately equal to those of the substrate layer. Therefore, the permeability of the top layers could be calculated according to Eq. (8). The effect of solvent immersing time on the permeability of the top layer can now be elucidated.

The swelling effect on the top layer of plasma treated membrane is shown in Fig. 9. Unlike the bottom substrate, the top layer gas permeability increased significantly along with solvent immersing time. Comparing the swelling of the plasma treated and untreated PU membranes, formamide obviously had stronger swelling effect on the plasma treated top layer than the bottom substrate. Interestingly, the O_2/N_2 selectivity of the top layer did not fall off because of swelling. On the contrary, the O_2/N_2 selectivity increased slightly after swelling. This result indicated that the O_2/N_2 separation by the top layer was mainly contributed by the oxygen affinity of the grafted EA rather than the size sieving effect. The swelling by

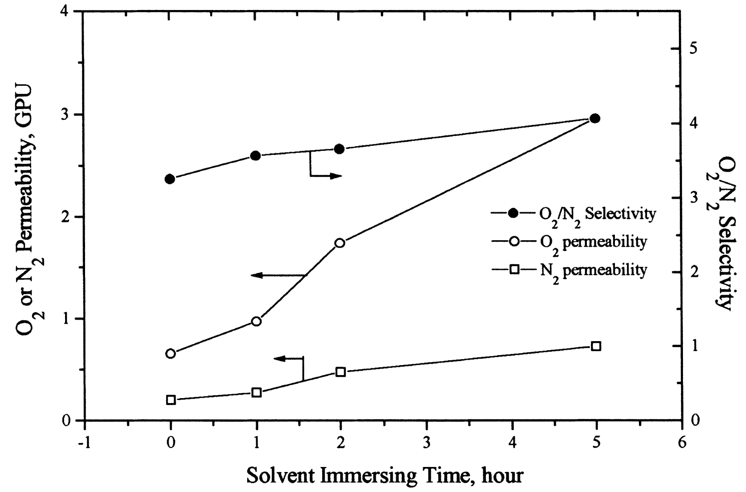

Fig. 9. Effect of solvent immersing time on the transport properties of the top layer of the plasma treated membrane.

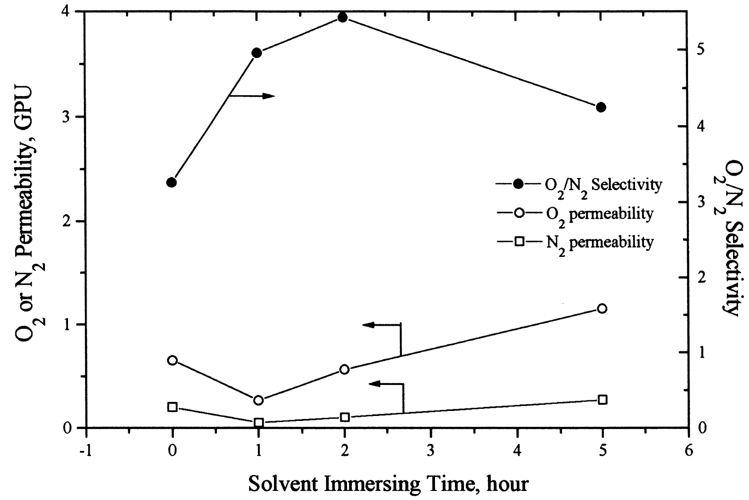

Fig. 10. Effect of solvent immersing time on the transport properties of the top layer of the cobalt complexed membrane.

formamide, which increased the polymer chain flexibility, might increase the chance for oxygen–EA interaction.

The swelling effect on the top layer of the cobalt complexed membrane is shown in Fig. 10. This result was similar to that of the whole cobalt complexed membrane shown in Fig. 6. Both processes, cobalt chelating and solvent swelling, happened simultaneously during solvent immersion. The cobalt chelation caused a decrease in gas permeability and an abrupt increase in O_2/N_2 selectivity. The selectivity did not fall off immediately after the top layer swelled. Instead, the highest selectivity of the top layer occurred after the membrane had been immersed in cobalt/formamide solution for 2 h, when the swelling effect began to overcome the restriction by cobalt complexation. Further swelling caused a decrease in O_2/N_2 selectivity. After 5 h immersion, the top layer selectivity of cobalt complexed membrane was 4.25. Comparing the gas transport behaviors of the plasma treated and the cobalt chelated membranes after 5 h immersion, the O_2/N_2 selectivities of both membranes were similar, but the gas permeability of plasma treated membrane was much higher. This comparison led us to suspect that the contribution of chelated cobalt was mainly on decreasing the pore size on the membrane surface. The selectivity enhancement caused by cobalt chelating was largely contributed by the size sieving effect rather than the well known cobalt–oxygen interaction (The dynamic diameter of oxygen is 357 pm, which is smaller than that of nitrogen, 374 pm.).

4. Conclusion

The cobalt chelated membranes can be obtained by immersing an EA plasma treated PU membrane in a cobalt(II)/formamide solution. It was found that cobalt chelating enhanced the O_2/N_2 selectivity but reduced the gas permeability. The swelling of cobalt chelated membrane had advert effect on the O_2/N_2 selectivity. Solvent swelling and cobalt chelating resulted in a maximum O_2/N_2 selectivity occurring when the membrane had been immersed in cobalt(II)/formamide solution for 2 h. Interestingly, the solvent swelling did not reduced the O_2/N_2 selectivity of plasma treated membrane. The transport properties of the modified top layer can be calculated from a series model for a composite membrane. It was found that the swelling of EA grafted top layer not only increased the oxygen permeability but also increased the O_2/N_2 selectivity. But the swelling of the cobalt chelated top layer reduced its O_2/N_2 selectivity. This led us suspect that the EA grafting enhanced the O_2/N_2 selectivity by increasing its oxygen affinity, but the cobalt chelating increased the O_2/N_2 selectivity by enhancing the size sieving effect. There were numerous studies reporting the possible interaction between Co(II) and oxygen. Whether the enhancement of O_2/N_2 selectivity is due to size sieving or Co–O_2 interaction requires more studies for verification.

Acknowledgements

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