Facilitated Oxygen Transport in a Novel Silicone Polymer Membrane Containing Carboxylic Cobalt Groups

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ABSTRACT: A novel silicone polymer membrane with facilitated oxygen transport properties was prepared by using 11-alkene acid cobalt, a silicone rubber containing vinyl groups of 5 mol %, a hydrogen-containing silicon oil, and chlorine platinum acid. The solution casting and the vulcanization were carried out simultaneously at room temperature. Investigation showed that P_{O_2} increased and P_{N_2} did not change with decreasing gas pressure difference. This facilitated oxygen transport behavior was contributed by a polymeric cobalt complex formed from carboxylic groups and cobaltous ions in the membrane to result in the simultaneous increase of both P_{O_2} and α_{O_2/N_2} under lower gas pressure difference. For example, the P_{O_2} and α_{O_2/N_2} of the membrane containing 11-alkene acid cobalt of 2.5 wt% were 750 Barrer and 3.09 under a gas pressure difference of 0.05 mPa. As much as 5 wt% 11-alkene acid cobalt could be added to the membranes; P_{O_2} and α_{O_2/N_2} increased to 802 Barrer and 3.34 respectively when the membrane contained 11-alkene acid cobalt of 5 wt %. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1038–1044, 2003

Key words: gas separation membrane; silicone rubber; facilitated oxygen transport, 11-alkene acid cobalt

INTRODUCTION

For many years polydimethylsiloxane (PDMS) has received considerable attention as a potential membrane material for gas separation because of its high intrinsic permeability to gases.[1–2] Therefore, PDMS became one of the most important oxygen permselective membranes among commercially available polymers. PDMS membranes have an excellent oxygen permeability coefficient (P_{O_2} = 600 Barrer), which is attributed to its large free volume from the flexibility of the siloxane (—SiO—) linkages. However, its oxygen/nitrogen separation factor is very low (α_{O_2/N_2} = 2), and its membrane-forming ability is so poor that it limits its direct applications.

Various modifications of PDMS membranes have focused on enhancement of their membrane-forming ability and permselectivity. For this purpose, different functional groups were introduced into the backbone or side chains of PDMS. Stern et al.[3] systematically investigated the substitution effects of increasingly bulkier functional groups in the backbone chains or side chains of PDMS on the relationship between gas permeability and selectivity. The results showed the usual inverse relationship between selectivity and permeability. The higher selectivity was, the lower the permeability was when bulkier and stiffer functional groups were substituted in PDMS.

Some investigations have been involved in block, graft, and alternating copolymerizations of PDMS. Ward et al.[4] synthesized PDMS-*block*-polycarbonate, and this copolymer membrane showed an oxygen permeability of P_{O_2} = 200 Barrer and α_{O_2/N_2} = 2. Asakawa et al.[5] prepared polyvinylphenol membranes crosslinked by PDMS segments, which had an oxygen permeability of P_{O_2} = 340 Barrer and α_{O_2/N_2} = 2.1. These results with no change in $\alpha_{O_2/N2}$ and a decrease in P_{O_2}, occurred because the gas molecules permeate only through the PDMS domains formed by microphase separation, resulting in a lessening in the permeable area. Nakajina et al.[6] synthesized a triblock copolymer of PDMS and poly (amino acid) showing a P_{O_2} of 23 Barrer and α_{O_2/N_2} of 3. Kawakami et al.[7–8] synthesized a comb-shaped polymer with short oligodimethylsiloxane chains as grafts. The membranes showed permeation properties of P_{O_2} = 10–100 Barrer and α_{O_2/N_2} = 2.4–4.4 when DMS content was 60–70 wt %. Nagase et al.[9–10] synthesized different main chain graft copolymers containing a smaller number of longer siloxane graft chains. When the main chains were polysulfone or polyimide and DMS content was 60–65 wt %, P_{O_2} and α_{O_2/N_2} were 115 and 163 Barrer and 2.66 and 2.45, respectively. Yang et al.[11] synthesized acrylic acid (AA)–grafted silicone polymer and

found that the membrane with 86% AA–grafted showed a P_{O_2} of 239 Barrer and α_{O_2/N_2} of 1.75, whereas the control was 601 Barrer and 1.69. Kiyotsukuri et al.[12] reported that an alternating polyamide was synthesized from 1,3-bis(aminopropyl) disiloxane and aliphatic dicarboxylic acid and showed the oxygen-enriching properties of P_{O_2} = 20.4 Barrer and α_{O_2/N_2} = 2.73 when DMS content was 35.5 wt %. All the above modification results showed that the membrane-forming abilities of copolymers were somewhat improved and α_{O_2/N_2} increased to a certain extent (not over 3.0 generally), but P_{O_2} decreased significantly, and the synthesis methods were not simple.

Gas permeability is closely concerned with the chain and aggregation structures, as well as the gas transport mechanism, for a polymeric membrane. Crosslinking is a simple and effective way to change the membrane structure and to improve selectivity. The crosslinking methods include covalent bond crosslinking and metal ion bond crosslinking, from which an ionomer can be formed.[13–14] Blending or attaching an oxygen carrier into a polymeric membrane is another important approach for improving selectivity as a result of introducing a facilitated transport mechanism. Facilitated oxygen transport behavior, which exhibits a distinct improvement in selectivity, can be observed by a reversible absorbtion of the carrier for oxygen.[15–19] Only a few studies have reported on silicone polymer membranes containing an oxygen carrier, whereas their influence on modifiying selectivity has not been obvious.[20–21]

We previously reported on the preparation and oxygen-enriching properties of a rubbery cobalt-neutralized sulfonated EPDM membrane, with an interesting finding that the ionomer membrane exhibited a facilitated transport property for oxygen.[22–23] Based on this consideration, PDMS with a high vinyl content, such as 5 mol %, was selected as a polymer membrane material to prepare a novel PDMS-crosslinked membrane containing carboxylic groups and cobaltous ions. The process of membrane formation and the crosslinked reactions could be carried out simultaneously. It was found that this simple modification method improved membrane-forming ability and enhanced α_{O_2/N_2}, while P_{O_2} did not decrease under a lower pressure difference.

EXPERIMENTAL

Materials

Silicone rubber was obtained from the Research Center of Organic Silicone of Chengdu. The number-average molecular weight was 50,000, and the vinyl content was 5 wt %. Hydrogen-containing silicone oil (number-average molecular weight of 7000 and hydrogen-containing content was of 1.6 wt %) and chlo-

rine platinum acid solution (as a catalyst) were obtained from Fine Chemical Institute of Silicone and Fluoride of Guangzhou. Cobalt acetate, 11-alkene acid, and tetrahydrofuran (from Shanghai Chemical Reagent Co.) were used as received.

Preparation of 11-alkene acid cobalt

To 10 mL of a saturated solution of cobaltous acetate 5 g of 11-alkene acid was added which was stirred for 2 h at 40°C. The product was poured into a tap funnel to settle. The superstratum in the funnel, which was a dark red solution, was separated. The 11-alkene acid cobalt was obtained by further drying under vacuum.

Preparation of modified PDMS membranes

Silicone rubber with a vinyl content of 5 mol % (1.0 g) was dissolved in 10 mL of THF to form a solution. The hydrogen-containing silicone oil (0.06 g) and chlorine platinum acid solution (0.006 g), as well as different amounts of 11-alkene acid cobalt (Table III were added into the above solution and stirred to form a uniform solution. The membranes were prepared by casting from the solution on a PET sheet at room temperature. The resulting membranes were easily stripped and then dried in a vacuum. Light red and flexible rubbery membranes were obtained. The membranes were approximately 100 μm thick, average calculated by determining thickness of more than five locations on any membrane.

Measurement of gas permselectivity

Oxygen and nitrogen permeability coefficients [cm² (STP) cm/cm² · s · cmHg] of the membranes were measured according to the variable-volume method of Stern et al.[24] The operation process has been described elsewhere.[20–21] P_{O_2}, P_{N_2}, and α_{O_2/N_2} can be calculated using the following equations:

$$P = \frac{(\Delta V / \Delta t) l}{\Delta p(A)}$$

$$\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}}$$

where ΔV and Δt are the changes in volume for the permeated gas and in time, respectively; A and l are the effective area and the thickness of the membrane, respectively; and Δp is the gas pressure difference across the membrane. The measurement conditions included: testing temperatures from 20 to 50°C; gas pressure differences across the membranes from 0.05 to 0.40 mPa; A was 3.94 cm²; each value of Δt was

TABLE I
Oxygen-Enriching Properties of Various Modification Silicone Rubber Membranes

Number	PDMS-modified membranes	P_{O_2} (Barrer)	α_{O_2/N_2}	Reference
1	PDMS-*b*-PC	200	2	4
2	Poly (viny/phenol) crosslinked by PDMS	340	2.1	5
3	Triblock copolymer of PDMS and poly (amino acid) (DMS content: 54 mo (%))	23	3	6
4	Comb-shaped polymer with oligodimethyloxane (DMS content: 60–70%)	10–100	2.4–4.4	7,8
5	PDMS-*g*-Polysulfone (DMS content: 60–65%)	115	2.66	9
6	PDMS-*g*-Polyimide (DMS content: 60–65%)	163	2.45	10
7	Acrylic-*g*-PDMS (86% AA-grafted)	239 (601)[a]	1.75 (1.69)[a]	11
8	Polyamide from 1,3-bis(aminopropyl)disiloxane and aliphatic dicarboxylic acid (DMS content: 35.5%)	20.4	2.73	12
9	PDMS containing 11-alkene acid cobalt of 2.5 wt % (at 20°C, under pressure difference of 0.05 mPa)	750	3.09	

[a] The values in the bracket are data of PDMS as a control.

obtained by determining it at least three times. Data are shown in Table I.

Spectroscopic measurement

The oxygen-binding property of the membranes was monitored by electron spin resonance (ESR) spectroscopy (Bruker ECS-106). The sample tube, containing some fragments of the membranes, was exhausted and filled with nitrogen alternately and repeatedly and then was measured on the X-band at 0°C. After the sample was exposed to air for several minutes, the same operation was repeated.

RESULT AND DISCUSSION

Crosslinking reactions and membrane-forming ability

The vinyl content of silicone rubber typically is less than 1 mol %. To introduce more carboxylic acid groups and cobaltous ions into the membranes and to crosslink more fully, a silicone rubber with a vinyl content of 5 mol % was selected as a membrane matrix material. Under catalysis by chlorine platinum acid, the active hydrogen atoms of the hydrogen-containing silicone oil reacted with the vinyl groups of the silicone rubber and 11-alkene acid cobalt to form a possible crosslinked network structure, as shown in Figure 1:

The crosslinked membranes were in a light red and flexible rubbery state at room temperature and had enough mechanical strength to measure gas permeability. The preparation process and vulcanization reactions of the crosslinking membranes were completed simultaneously. This modification method is not only simpler than those adopted in the above-mentioned literature, but also favors coating applications to porous membranes. Membrane-forming ability was also improved in comparison with the usual

silicone rubber membranes. This may be because carboxylic groups were introduced into the crosslinked network structures to increase polarity of the silicone rubber molecular chains. There are two types of crosslinks—the covalent bonds and metal ion bonds—in the membrane. Although the crosslink extent of the membranes was larger, they did not exhibit fragility. These properties can be attributed to the oligomer structures of the hydrogen-containing silicone oil as a crosslinking agent.

Oxygen-enriching properties

The effect of the gas pressure difference (Δp) on the permeability coefficients (P_{O_2}, P_{N_2}) and oxygen/nitrogen separation factor (α_{O_2/N_2}) of a membrane containing 11-alkene acid cobalt of 2.5 wt % is shown in Figures 2 and 3. Figure 2 indicates that the P_{O_2} of the membrane increased with a decrease in the oxygen pressure difference ($\Delta p(O_2)$). For example, P_{O_2} increased from 501 to 750 Barrer, when $\Delta p(O_2)$ decreased from 0.40 to 0.05 mPa at 20°C. By contrast, the
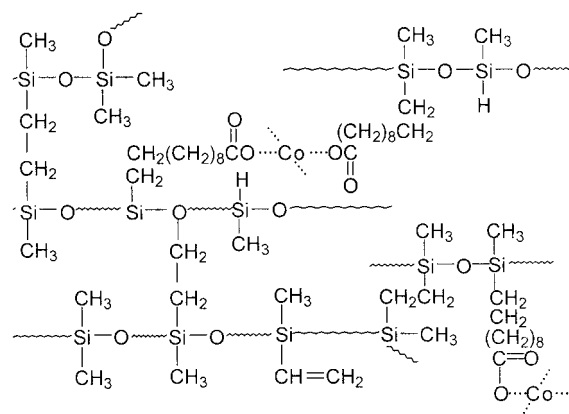

Figure 1 Schematic crosslinked structures of the silicone rubber membranes containing 11-alkene acid cobalt.
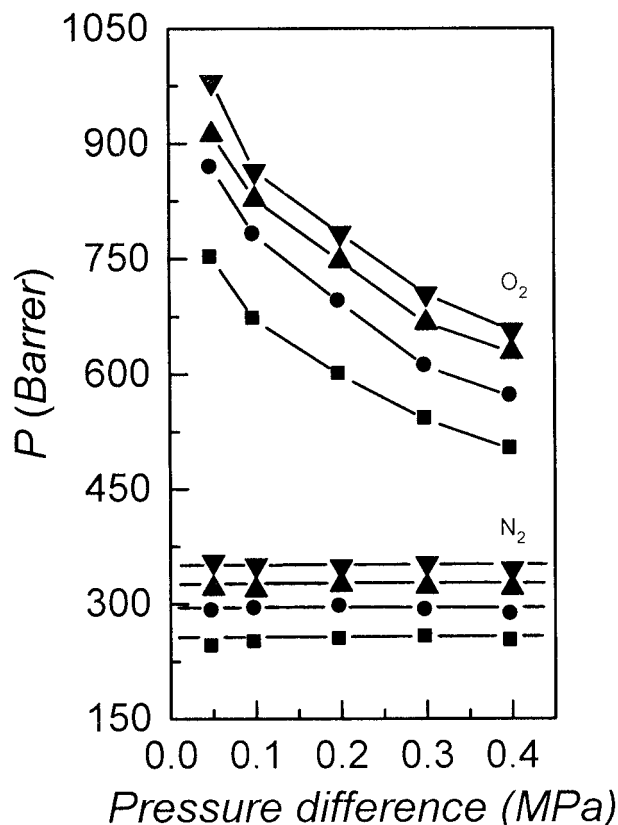
Figure 2 Effect of the gas pressure difference on P_{O_2} and P_{N_2} for the silicone rubber membrane containing 11-alkene acid cobalt of 2.5 wt%: at 20°C (■); 30°C (●); 40°C (▲); 50°C (▼).

Figure 3 Effect of the gas pressure difference on α_{O_2}/N_2 for the silicone rubber membrane containing 11-alkene acid cobalt of 2.5 wt%: at 20°C (■); 30°C (●); 40°C (▲); 50°C (▼).

P_{N_2} of the membrane was independent of the nitrogen pressure difference [$\Delta p(N_2)$], and the P_{N_2} - $\Delta p(N_2)$ curves exhibited horizontal lines. The different influences of Δp on P_{O_2} and P_{N_2} resulted in a distinct increase in α_{O_2}/N_2. This changing tendency is clearly shown in Figure 3. Under the above conditions, α_{O_2}/N_2 increased from 2.0 to 3.09. Oxygen permeability data of various modified silicone rubber membranes are summarized in Table I, and which shows that the oxygen-enriching properties of the membranes were higher than the data reported in the above-mentioned literature. Table II lists additional values of P_{O_2}, P_{N_2}, and α_{O_2}/N_2 of the membranes with Δp varied at 20°C. It can be seen that a synchronous enhancement behavior in both P_{O_2} and α_{O_2}/N_2 occurs under a lower Δp, showing an obvious difference from other modification results.

A simultaneous increase in both P_{O_2} and α_{O_2}/N_2, with a decrease in Δp, exhibited a typical characteristic of the facilitated transport membranes with fixed oxygen carriers. Apparently, the improvement in the oxygen-enriching properties of the membrane should be attributed to ionomer structures formed from incorporating carboxylic cobalt groups. In our previous study, a rubbery cobalt-neutralized sulfonated EPDM
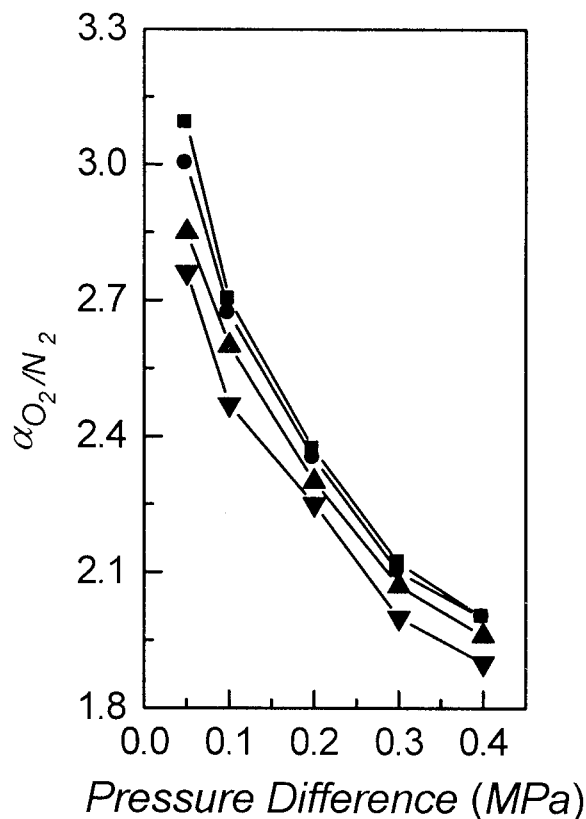
ionomer membrane was prepared, and a facilitated transport behavior for oxygen was observed, suggesting that a polymer cobalt complex could be formed. The carboxylic easily groups as a ligand, in fact, to form a polymeric coordinate complex with cobaltous ions, in comparison with the sulfonic groups. In fact, the silicone rubber membranes containing cobaltous ions were turned into an ionomer with a crosslinked structure when 11-alkene acid cobalt was incorporated into the polymeric network structures. There has been some controversies in ionomer investigations about the morphologies of ion aggregates. The FTIR studies of Han et al.[25] proved that ionomers containing carboxylic groups and transitional metal ions tended to

TABLE II
Oxygen-Enriching Data of Silicone Rubber Membrane Containing 11-Alkene acid Cobalt of 2.5 wt % at Room Temperature Under Various Gas Pressure Differences

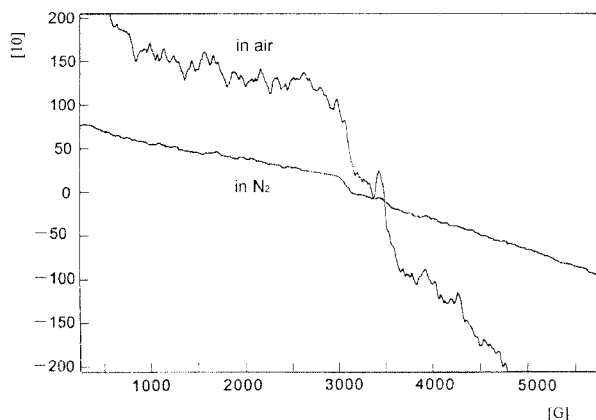| Pressure difference (mPa)	P_{O_2} (Barrer)	P_{N_2} (Barrer)	α_{O_2}/N_2
0.40	501	250	2.00
0.30	540	255	2.12
0.20	598	252	2.34
0.10	670	248	2.70
0.05	750	243	3.09

Figure 4 Reversible ESR spectral changes of the silicone rubber containing 11-alkene acid cobalt of 2.5 wt%.

form a polymeric complex, which was based on poly-(ethylene-*co*-methacrylic acid). The silicone rubber membranes containing carboxylic cobalt, in another point of view, also validate the above result because, only when polymeric cobalt complexes were formed, could facilitated oxygen transport characteristics be exhibited.

The reversible oxygen-binding properties of the polymeric cobalt complexes can be further detected by electron spin resonance (ESR) spectroscopy (as shown in Fig. 4). A sample tube containing some fragments of the membrane was exhausted and filled with N_2 alternately and repeatedly and then was measured by ESR spectroscopy in the X-band at 0°C. The results showed a nearly horizontal line, indicating that there was little signal in the vicinity of $g = 2.0$ (see the curve in N_2). A strong signal occurred under the same conditions after the sample in the tube was exposed from N_2 to air for several minutes. This signal was assigned to the cobalt–oxygen adduct in the literature.[15–17] The agreement between the cyclic experiments and the above results shows that the oxygen-binding equilibrium process was reversible.

Effect of 11-alkene acid cobalt content

To enhance the oxygen-enriching property of the membranes, larger amounts of the 11-alkene acid cobalt were incorporated into the membranes. The uniformity and flexibility of the membranes, however, lessened when increasing 11-alkene acid cobalt content. The appearance of the membranes was obviously less uniform, and they became more friable when the 11-alkene acid cobalt content was increased to more than 5 wt % in the membranes. Hence, the uppermost 11-alkene acid cobalt content incorporated into the membranes was 5 wt %. Figure 5 and Table III show the effect and oxygen-enriching data of various 11-alkene acid cobalt contents in the membranes at 20°C
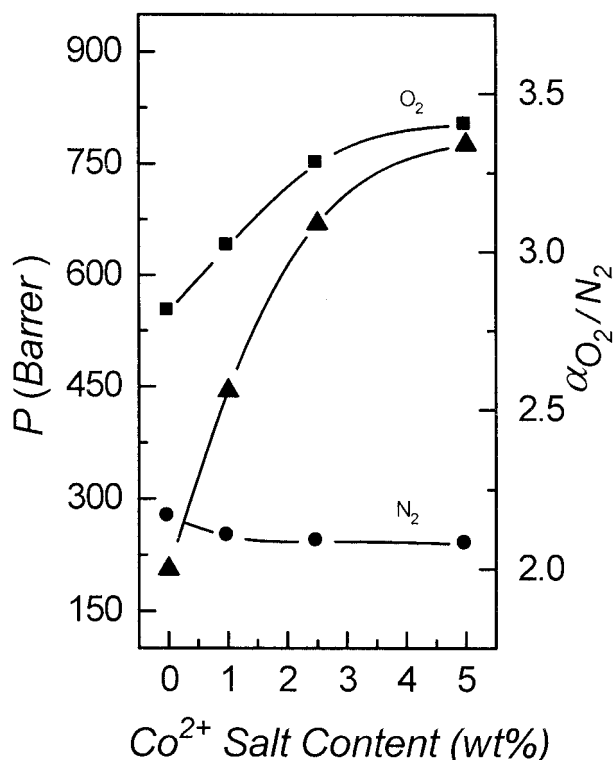

Figure 5 Effect of the 11-alkene acid cobalt content on P_{O_2}, P_{N_2} and α_{O_2/N_2} for the silicone rubber membranes.

under a Δp of 0.05 mPa, showing an obvious increase in P_{O_2} and a slight decrease in P_{N_2} which led to a rise in α_{O_2/N_2}; for example, P_{O_2} and α_{N_2/N_2} were 802 Barrers and 3.34, respectively, when the 11-alkene acid cobalt content was 5 wt % in the membrane. Such data could be seen as a fairly satisfactory result for the silicone rubber membranes modified by means of a simple method. Stern suggested in 1994 that a potential method of increasing gas selectivity on silicone polymers, without significantly decreasing their permeability, was to incorporate function groups that induce specific interactions to the desired penetration by gases.[1] The membranes containing carboxylic cobalt groups as the functional groups should be beneficial for oxygen transport.

Incorporating the cobaltous ions into the membranes, in the form of an 11-alkene acid salt, is the key

TABLE III
11-Alkene Acid Cobalt Content in Silicone Rubber Membranes and Oxygen-Enriching Properties at 20°C Under Pressure Difference of 0.05 mPa

11-Alkene acid cobalt (wt %)	P_{O_2} (Barrer)	P_{N_2} (Barrer)	α_{O_2/N_2}
0	551	276	2.00
1.0	639	250	2.56
2.5	750	243	3.09
5.0	802	240	3.34

vestigated structure–permeability relationships for different silicone polymers. The diffusion coefficient always increased with increasing temperature, whereas for the solubility coefficient it was generally the opposite. The significant increase in both Po_2 and P_{N_2}, as shown in Figure 6, indicates that the enhanced extent of the diffusion coefficient should be much higher than the reduced extent of the solubility coefficient with temperature. In other words, the gas permeability enhancement was basically a result of the increase in the diffusion ability of the gases in the membrane when the temperature was raised. Hence, the solubility behavior of the gas for the membrane became an important control factor for the gas permeation process here. In conclusion, the effect of temperature on oxygen-enriching properties of the membranes was in accord with the general role of gas separation membranes.

CONCLUSIONS

To enhance O_2/N_2 selectivity without a significant loss in the permeability to O_2, a novel PDMS membrane was prepared by a simple modification method that incorporated a reversible adsorbing O_2 carrier, namely, 11-alkene acid cobalt. The preparation process and vulcanization reactions of the modified membranes were completed simultaneously at room temperature. The incorporation of carboxylic cobalt groups into crosslinked network structures played an important role in modifying the properties of the PDMS membranes. It not only increased the polarity of the macromolecular chains to improve the membrane-forming ability of the PDMS but also formed a polymeric cobalt complex to enhance the O_2/N_2 selectivity of the membranes. The modified membranes exhibited a characteristic facilitated oxygen transport behavior with increased values of both Po_2 and $\alpha O_2/N_2$ with decreasing $\Delta p(O_2)$. Also, the values of both Po_2 and $\alpha O_2/N_2$ of the modified membranes increased with an increasing amount of 11-alkene acid cobalt content incorporated into the membranes. For example, the values of Po_2 and $\alpha O_2/N_2$ increased from 750 Barrers and 3.09 to 802 Barrers and 3.34, when 11-alkene acid cobalt contents in the membranes increased from 2.5 to 5.0 wt % under a gas pressure difference of 0.05 mPa. Only up to 5 wt % of 11-alkene acid cobalt, however, could be incorporated into the membranes because the membranes became less uniform and more friable with a further increase in 11-alkene acid cobalt content. More studies on the selection of an alkene acid with a shorter carbon chain and on a way of incorporating more amount of alkene acid cobalt into PDMS membranes are being carried out.

Figure 6 Effect of temperature on Po_2, P_{N_2} and $\alpha O_2/N_2$ for the silicone rubber membrane containing 11-alkene acid cobalt of 2.5 wt%.

to the modification. In fact, the cobalt ions play two important roles in improving the selectivity of the membranes: the formation of crosslinked networks and the polymeric cobalt complex. The more carboxylic cobalt content in the membrane, the more polymeric cobalt complexes like the oxygen carriers are formed. Strongly facilitated oxygen transport certainly leads to a distinct increase in both Po_2 and $\alpha O_2/N_2$. Moreover, for nitrogen permeation, the increase in both the polarity and the extent ion-crosslinking of the membrane causes a slight decrease in P_{N_2}.

Effect of testing temperature

Figure 6 presents the relationships between Po_2, P_{N_2}, and $\alpha O_2/N_2$, as well as temperatures under a low-pressure difference of 0.05 mPa for the membrane containing 11-alkene acid cobalt of 2.5 wt %. Here "inverse" permeability/selectivity behavior was observed—Po_2 increased and $\alpha O_2/N_2$ decreased with increasing temperature. The results showed that Po_2 increased from 750 to 980 Barrers and $\alpha O_2/N_2$ decreased from 3.09 to 2.76 when the temperature rose from 20°C to 50°C. Even so, the value of $\alpha O_2/N_2$ at 50°C was still higher than those reported in the above literature at room temperature. Stern et al.[3] demonstrated that the effects of temperature on permeability coefficients depended on changes in the diffusion coefficient and the solubility coefficient when they in-

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