Preparation and oxygen-enriching properties of PDMS/TMS−MC composite membrane based on polyetherimide as supporting layer

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Abstract

Cellulose and its derivatives, which used as the membrane separation materials, are a type of abundance and environment friendly nature polymers. Based on polydimethylsiloxane containing vinyl groups (PDMS) and trimethylsilyl methylcellulose (TMS−MC) as matrix materials, PDMS/TMS-MC composite membrane was prepared by using porous polyetherimide as supporting layer and solution-casting method. Effects of TMS−MC content, temperature and difference pressures on oxygen-enriching properties of the composite membranes were discussed. The results showed that the composite membranes had better oxygen-enriching properties. For example, when TMS-MC content was 5 wt.%, the separation factor for oxygen and nitrogen is 3.85. The oxygen-enriching properties of the composite membranes may be attributed to the introduction of TMS-MC and polyetherimide supporting layer.

Keywords

Oxygen-enriching properties; polydimethylsiloxane; trimethylsilyl methylcellulose; polyether imide.

1. Introduction

Polydimethylsiloxane (PDMS) has been long utilized industrially as one of the most important polymeric membrane materials for oxygen/nitrogen separation from air due to extremely high intrinsic permeability [1]. However, its oxygen/nitrogen separation factor is very low (only about 2.0) and the membrane-forming ability is also unsatisfactory to limit its further effective applications in a way. Therefore, various modification studies on PDMS membranes have focused on enhancing both permselectivity and membrane-forming ability. For example, cross-linking including covalent bonds and metal ion bonds is very effective in reinforcing polymeric membrane materials and improving oxygen-enriching properties [2-4].

Cellulose and its derivatives are long-known biopolymers and are well-established membrane materials [5-7]. The growing interest of this polymer for membrane technology lies on its abundant availability, low cost, excellent hydrophilicity, biocompatibility and its solvent resistance [8]. Puspasari reported a new synthetic route of fabricating regenerated cellulose nanofiltration membranes with a thin selective layer of cellulose, which was prepared by regeneration of trimethylsilyl cellulose membrane followed by crosslinking [8].

In the paper, porous polyetherimide (PEI) possessing good membrane -forming performance and low cost was selectes as supporting membrane materials. PDMS membranes containing cobalt were first prepared through addition reaction and then a novel composite membrane was also prepared by using polydimethylsiloxane containing vinyl groups (PDMS) and trimethylsilyl methylcellulose (TMS−MC) as matrix materials,

2. Experimental Procedure

2.1 Materials

Polydimethylsiloxane (PDMS) and a chloroplatinic acid solution ($H_2PtCl_6 \cdot 6H_2O$) were purchased from the Research Center of Organic Silicone of Chengdu, China. The number-average molecular weight of PDMS was 500,000, and the vinyl content was 10 % (molar percentage). 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) was obtained from Fine Chemical Institute of Silicone and Fluoride of Guangzhou, China. Methylcellulose (DS =1.8) and hexamethyldisilazane (HMDS) was provided by Tianjin Kemiou Chemical Reagent Co., Ltd. Porous polyetherimide (PEI) membrane was purchased from GE company. Vinyl acetic acid was obtained from Aldrich agent. Cobalt hydroxide, dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Guangzhou Chemical Agent Company, China. All other chemicals were of analytical grad and used without further purification. Pure gases, O_2 and N_2 were purchased from Guangzhou Gas Ltd., China. All the gases used had minimum purity of 99.9%.

2.2 Preparation of vinyl acetic acid cobalt

Cobalt hydroxide and vinyl acetic acid were mixed by molar ratio of 1 to 2. The mixture was added into proper THF and was stirred for 1 h. A fuchsia and transparent solution was obtain. The solution was put into vacuum dryer to eliminate THF and water. The fuchsia vinyl acetic acid cobalt was prepared.

2.3 Synthesis of TMS-MC

1 g methyl cellulose (MC) was dissolved in 10 ml DMF under nitrogen system. 3 ml hexamethyldisilazane (HMDS) was added slowly into the solution at 80℃ and then reacted for 3 h. The product was cooled to room temperature and precipitated by using a large amount of distilled water. The precipitation was dissolved by using THF and then precipitated by using distilled water. Finally, the purified product was dried for 48 h and TMS-MC was obtained.

2.4 Preparation of PDMS/TMS-MC composite membrane

PDMS (1.0 g) was dissolved in proper THF to form PDMS solution. 0.1 g vinyl acetic acid cobalt and 0.2 g were dissolved into PDMS solution. The even solutions were obtained after string 0.5 h at 70℃. 0.16g D_4^H and proper $H_2PtCl_6 \cdot 6H_2O$ solutions were added slowly into the above solution at room temperature. After an addition reaction for 40 min, the solution were casted on porous PEI membranes at room temperature. The resulting PDMS/TMS−MC composite membranes were easily stripped and then dried in a vacuum dryer at 60℃ for 24 h to remove any residual solvent.

2.5 Measurement of oxygen-enriching properties

Oxygen and nitrogen permeability coefficients of the composite membranes were measured according to the variable-volume method of Stern [9]. The apparatus and experimental procedure employed for the gas permeability measurements had been described in the previous literatures [10]. Permeability coefficient for oxygen (P_{O_2}) and permeability coefficient for nitrogen (P_{N_2}) and separation factor (α_{O_2/N_2}) could be calculated using the following equations:

$$P = \frac{\Delta V \bullet l}{A \bullet \Delta p \bullet \Delta t} \tag{1}$$

$$\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \tag{2}$$

Where ΔV and Δt were the changes in volume for the permeated gas and in time, respectively. A and l were the effective area and thickness of the membrane, respectively. Δp was the gas pressure difference across the membrane. The standard deviation was within ca. ±5%.

3. Results and disscussion

Effects of TMS-MC content, temperature and difference pressures on oxygen-enriching properties of the PDMS/TMS-MC composite membranes were investigated and showed in Table 1.

Table 1 Oxygen-enriching properties of the PDMS/TMS−MC composite membranes

TMS-MC content (wt%)	difference pressures(MPa)	Permeability coefficient for O_2 (10^{-5} cm^3/cm^2 s cmHg)				separation factor for O_2/N_2 (10^{-5} cm^3/cm^2 s cmHg)			
		20℃	30℃	40℃	50℃	20℃	30℃	40℃	50℃
1	0.05	2.157	2.196	2.224	2.236	3.45	3.28	3.18	3.10
	0.1	1.920	2.002	2.002	2.050	3.09	3.00	2.87	2.85
	0.2	1.751	1.825	1.858	1.858	2.82	2.74	2.67	2.59
	0.3	1.640	1.739	1.785	1.785	2.65	2.63	2.59	2.50
	0.4	1.574	1.625	1.688	1.756	2.56	2.50	2.48	2.47
3	0.05	2.014	2.060	2.083	2.108	3.58	3.44	3.33	3.23
	0.1	1.806	1.861	1.878	1.920	3.21	3.11	3.02	2.95
	0.2	1.656	1.721	1.721	1.751	2.96	2.89	2.78	2.71
	0.3	1.558	1.640	1.640	1.688	2.80	2.75	2.65	2.61
	0.4	1.468	1.519	1.574	1.625	2.65	2.57	2.56	2.53
5	0.05	1.805	1.841	1.870	1.909	3.83	3.69	3.58	3.51
	0.1	1.627	1.688	1.719	1.769	3.47	3.40	3.30	3.26
	0.2	1.493	1.546	1.599	1.629	3.20	3.12	3.09	3.02
	0.3	1.412	1.446	1.484	1.484	3.02	2.95	2.88	2.76
	0.4	1.339	1.381	1.426	1.468	2.88	2.82	2.79	2.74

3.1 Effect of TMS−MC content on oxygen-enriching properties

Effects of different TMS-MC contents (1%, 3%, 5%) on oxygen-enriching properties were present in Fig.1 and Fig.2 at the same temperature and difference pressures. Obviously, permeability coefficients for oxygen were decreased and but separation factors for oxygen and nitrogen were increased with an increasing of TMS-MC contents. For example, at 20℃ and under pressure difference of 0.05 MPa, the permeability coefficients for oxygen was 6.25×10^{-6} $cm^3/(cm^2$ s cmHg) and separation factors for oxygen and nitrogen was 3.45 when TMS-MC content was 1 wt.%. However, permeability coefficient for oxygen was 4.71×10^{-6} $cm^3/(cm^2$ s cmHg) and separation factors for oxygen and nitrogen was 3.83 when TMS-MC content was 5 wt.%.

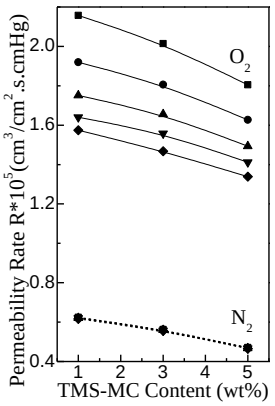

Fig. 1 Effect of TMS-MC contents on permeability (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

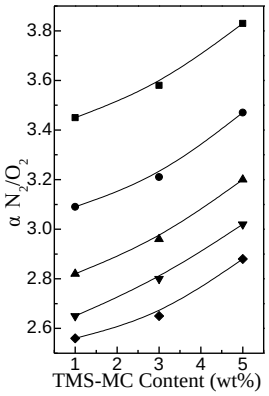

Fig. 2 Effect of TMS-MC contents on separation factor (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

3.2 Effect of pressure differences on oxygen-enriching properties

Fig. 3 and Fig. 4 showed the effect of pressure differences on permeation coefficient and separation factor of the composite membrane (5 wt.% TMS-MC content), respectivily. It revealed that permeation coefficient for oxygen and separation factor for oxygen and nitrogen were decreased gradually with an increasing of the pressure differences. The effect of pressure differences on permeation coefficient and separation factor was more distinctly at lower pressure difference.

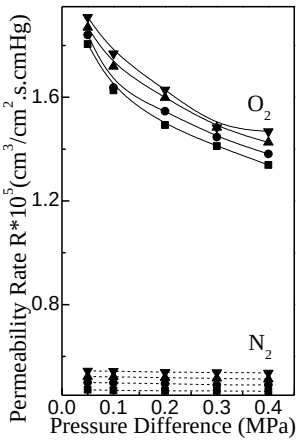

Fig. 3 Effect of the pressure difference on permeability (■:20℃, ●:30℃, ▲:40℃, ▼:50℃)

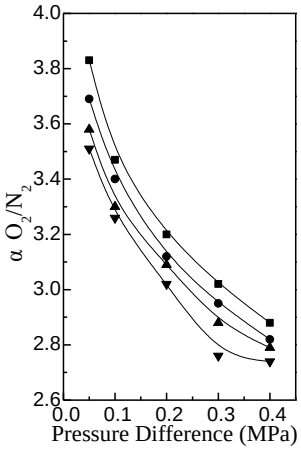

Fig. 4 Effect of the pressure difference on separation factor (■:20℃, ●:30℃, ▲:40℃, ▼:50℃)

3.3 Effect of testing temperature on oxygen-enriching properties

Fig. 5 and Fig. 6 showed the effect of temperature on permeation coefficient and separation factor of the composite membrane (5 wt.% TMS-MC content), respectivily. It could be seen from the figures and Table 1 that permeation coefficients were increased with an increase of temperature under the same pressure difference. However, separation factors of the composite membrane were decreased with an increase of temperature. The effect of testing temperature on gas separation properties of the composite membrane is in accord with the general role of gas separation membrane.

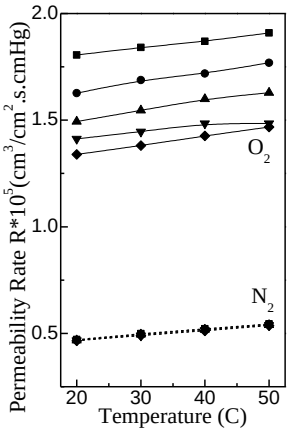

Fig. 5 Effect of temperature on permeability(■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

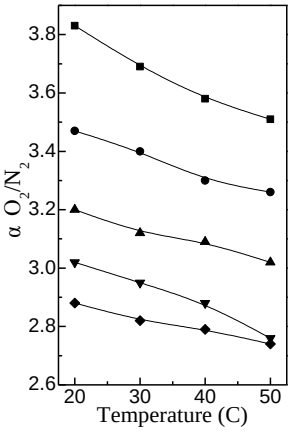

Fig. 6 Effect of temperature on separation factor (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

Arrhenius curves for the composite membranes under different pressure differences were obtained by drawing a figure of ln toward 1/T (as shown in Fig. 7). It could be seen from the figure, Arrhenius curves was a linear relationship, and smaller differential pressure was, higher Arrhenius curve was. The results showed that smaller pressure difference was, lower permeability activation energy was, easier gas penetration was.

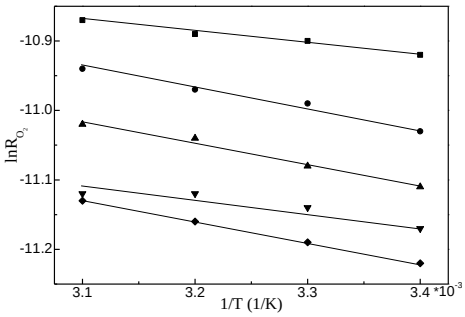

Fig.7 Arrhenius curves of O2 at different pressure difference (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

4. Conclusion

PDMS/TMS-MC composite membrane had better oxygen-enriching properties and membrane-forming properties than non-modified PDMS membrane. Incorporating the environment friendly TMS-MC into the composite membranes is the key to the modification for PDMS. In addition, the porous PEI used as supporting layer is benefit to improve the gas separation properties of the composite membranes. Therefore, the oxygen-enriching properties of the composite membranes may be attributed to the introduction of TMS-MC and PEI supporting layer.

Acknowledgements

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