Preparation and gas separation properties of PDMS composite membrane materials

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Abstract

The key and desiderate problem of polymeric gas separation membranes is to increase simultaneously permeability and premselectivity. Based on polydimethylsiloxane containing vinyl groups (PDMS) and vinyl acetic acid cobalt as matrix materials, tetramethylcyclotetra siloxane as crosslinking agent, PDMS crosslinked membrane containing cobalt was first prepared by hydrosilylation reaction at room temperature. A novel PDMS composite membrane was also prepared by using porous polyetherimide as supporting layer and solution-casting method. Effects of some factors (such as cobalt content, testing temperature and difference pressures) on the gas separation properties of the composite membranes were investigated. The results show that the composite membranes possess excellent gas separation properties and their permeability and premselectivity can be increased simultaneously. For example, permeability coefficient for oxygen is 2.181×10-5 cm3/(cm2•s•cmHg) and the separation factor for oxygen and nitrogen is 3.41 at 20℃ and the pressure difference of 0.05 MPa. The excellent gas separation properties of the composite membranes may be attributed to the formation of the cobalt complex structure and polyetherimide supporting layer.

Keywords

Gas separation; polyetherimide; polymeric membrane; gas separation properties; silicone rubber.

1. Introduction

Gas separation membranes are widely applied in the field of industry because of low energy consumption, simple operation and compacted device. The separation and enrichment of oxygen from air for the separation membranes is an important field for polymeric gas separation membrane [1,2]. Oxygen-enriching can be directly used in respiratory diseases and oxygen environment complement for oxygen need, increasing combustion efficiency and promoting chemical reaction [3,4]. Because the molecular diameter of oxygen and nitrogen is very close, the researchers often face a problem: polymers with high permeability usually have low selectivity, and others with high selectivity have low permeability [5,6]. And the "inverse" permeability/selectivity relationship is not supported by the any theoretical considerations. For example, polyimide membranes possess good gas premselectivity but bad permeability. On the contrary, silicone rubber possesses good permeability but bad gas premselectivity [7,8]. polydimethylsiloxane (PDMS) has received considerable attention as a special membrane material for gas separation owing to its intrinsically high permeation rate. However, its oxygen/nitrogen ideal separation factor is very low, and its membrane-forming ability is so poor that direct applications are limited [9,10]. Therefore, to improve simultaneously gas premselectivity and permeability or mainly increase premselectivity under high permeability has become a new trend and a pressing problem for developing new separation membranes or modified membrane materials.

Incorporating an oxygen carrier into separation membranes is a simple and effective way to change the membrane structure and to improve selectivity [10-12]. Gas permeation through the membranes often follows not only dissolution-diffusion mechanism but also reversible complex mechanism, which is benefit to improve simultaneously gas premselectivity and permeability [13,14]. For example, PDMS membranes by introducing unsaturated carboxylic acid cobalt into PDMS had facilitated oxygen transport and gas premselectivity and permeability were improved simultaneously due to the formation of crosslinked networks and the polymeric cobalt complex [10].

Porous polyetherimide (PEI) membrane is a kind of polymeric support membrane materials and widely used in water treatment and the preparation of ultrafiltration membrane. However, the research and application in field of gas separation are barely reported. PEI possessing good film-forming performance and low cost may make it have a good application prospect in the field of gas separation membrane. In the paper, PDMS membranes containing cobalt are first prepared through addition reaction and then a novel PDMS composite membrane with excellent gas separation performance is also prepared through solution-casting method by using porous PEI as supporting membrane materials. In addition, the effect of preparation parameters and testing condition on gas separation properties of the PDMS composite membranes are also investigated.

2. Experimental Procedure

2.1 Materials

Polydimethylsiloxane (PDMS) and a chloroplatinic acid solution ($H_2PtCl_6\ 6H_2O$) 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. Porous polyetherimide (PEI) membrane was purchased from GE company. Vinyl acetic acid was obtained from Aldrich agent. Cobalt hydroxide and tetrahydrofuran (THF) was obtained from chemical agent of Guangzhou, 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 Preparation of the composite membrane

PDMS (1.0 g) was dissolved in proper THF to form PDMS solution. The prepared vinyl acetic acid cobalt with different different mass percentage (0%, 2.5%, 5%, 7.5% and 10%) was dissolved respectively into the PDMS solution. The even solutions were obtained after string 0.5 h at 70℃. 0.16g D_4^H and proper $H_2PtCl_6\ 6H_2O$ 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 composite membranes were easily stripped and then dried in a vacuum dryer at 60℃ for 24 h to remove any residual solvent.

2.4 Measurement of gas permselectivity

Oxygen and nitrogen permeability coefficients of the composite membranes were measured according to the variable-volume method of Stern [15]. The apparatus and experimental procedure employed for the gas permeability measurements had been described in the previous literatures [16,17]. Permeability coefficient for oxygen (P_{O_2}) and permeability coefficient for nitrogen (P_{N_2}) and ideal separation factor (α_{O_2/N_2}) could be calculated using the following equations:

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

$$\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \quad (2)$$

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%.

2.5 Morphology Analysis of the composite membrane

The standard samples were prepared for 20 mm (length) ×80 μm (thick) ×16 mm (width). The substrate-facing surface and the fracture surface of the composite membranes were coated with gold and observed by using a Field Emission Scanning Electron Microscopy (ZEISS, ULTRA 55 FE-SEM, Germany), respectively. The morphologies of the membranes were inspected using at 15 kV accelerating voltage and were viewed at different magnifications.

3. Results and disscussion

3.1 Preparation process of the composite membrane

PDMS has received considerable attention as gas separation membrane because of its high intrinsic permeability to gases. And PDMS membranes have an excellent oxygen permeability coefficient, which is attributed to its large free volume from the flexibility of the siloxane (–SiO–) linkages. However, because the flexibility of the chains and the hinder of asymmetric side-base methyl for the polymer chain segment results in low cohesive energy density and the formation of amorphous gap area for the polymer membrane, oxygen/nitrogen separation factor for the unmodified PDMS membrane is very low and its membrane-forming ability is poor. Therefore, PDMS containing vinyl groups and vinyl acetic acid cobalt as matrix materials, tetramethylcyclotetra siloxane as crosslinking agent, PDMS crosslinked membrane containing cobalt is first prepared by using hydrosilylation reaction in the paper. The cobalt ion is incorporated into the crosslinked network structure of the PDMS membranes and used as a oxygen carrier which is benefit to oxygen transport for polymeric membranes. In addition, the novel PDMS composite membrane is also prepared by using porous polyetherimide as supporting layer. The crosslinked reaction and structure for the composite membranes was shown in Fig.1.

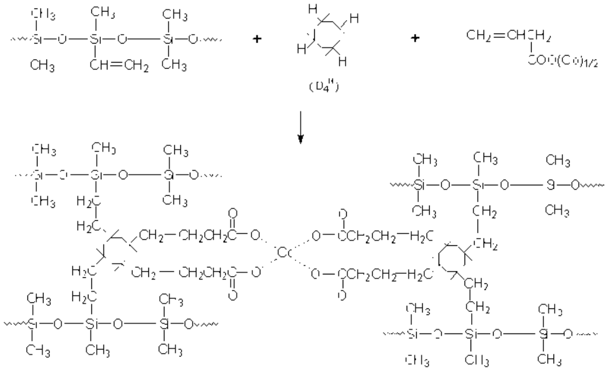

Fig. 1 Scheme of crosslinked reaction and structure for the composite membranes

3.2 Effect of membrane thickness on gas separation properties

The membrane thickness of the composite membrane can be adjusted by changing the cover rate of cobalt. Effect of membrane thickness on gas separation properties of the composite membrane was shown in Fig.2 under different pressure differences. It can be seen from the figure that the permeability coefficients for oxygen or nitrogen are decreased and separation factors are unchanged with increasing of the cover rate and the membrane thickness. For example, at testing temperature of 20℃ and under pressure difference of 0.05 MPa, the permeability coefficients for oxygen is 2.181×10^{-5} $cm^3/(cm^2 \cdot s \cdot cmHg)$ and separation factor for oxygen and nitrogen is 3.42 when the cover rate is 0.127 kg/m^2. The permeability coefficients is 1.870×10^{-5} $cm^3/(cm^2 \cdot s \cdot cmHg)$ and separation factor for oxygen and nitrogen is 3.41 when the cover rate is 0.153 kg/m^2.

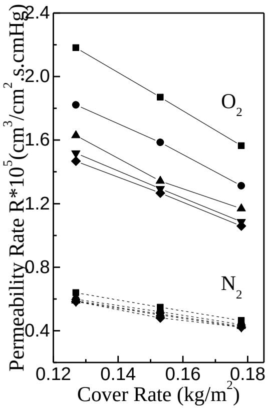

Fig. 2 Effect of membrane thickness on gas separation properties (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

3.3 Effect of cobalt content on gas separation properties

Effects of different cobalt contents (0%, 2.5%, 5%, 7.5% and 10%) on gas separation properties were present in Fig.3 and Fig.4 when the cover rate was 0.127 kg/m2. Obviously, increase in permeability coefficient for oxygen but slight decrease in permeability coefficientare nitrogen obtained to exhibit two lines with decreasing pressure difference, resulting in an increasing in separation factor for oxygen and nitrogen. For example, at testing temperature of 20℃ and under pressure difference of 0.05 MPa, the permeability coefficients for oxygen is 1.939×10^{-5} cm^3/(cm^2 s cmHg) when the cobalt content is 5%. The permeability coefficients for oxygen is 2.181×10^{-5} cm^3/(cm^2 s cmHg) when the cobalt content is 10% and exhits manimum value.

Apparently, the improvement in the gas separation properties of the composite membrane should be attributed to ionomer structures formed incorporating carboxylic cobalt groups. The special behavior of oxygen permeation through the composite membrane corresponded to membranes containing cobalt complexes as a fixed oxygen carrier. The results showed that cobalt ion was benefit for gas separation property of PDMS membrane.

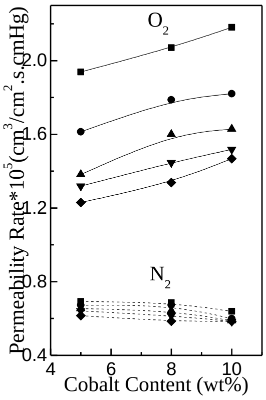

Fig. 3 Effect of cobalt contents on permeability (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

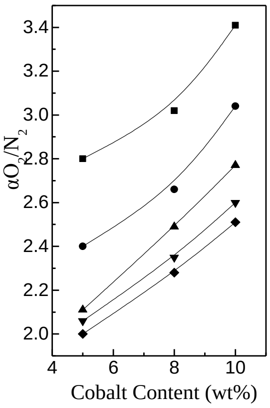

Fig. 4 Effect of cobalt contents on separation factor (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

3.4 Effect of pressure differences on gas separation properties

Fig. 5 and Fig. 6 showed the effect of pressure difference on permeation coefficient and separation factor of the composite membrane (10% cobalt content), respectivily. It revealed that a gradual decrease for permeation coefficient for oxygen with an increase of pressure difference was observed at the same temperature. The effect of pressure difference on permeation coefficient for oxygen was more distinctly at lower pressure difference. In addition, gas difference pressures had also affect obviously on separation factor for oxygen and nitrogen.

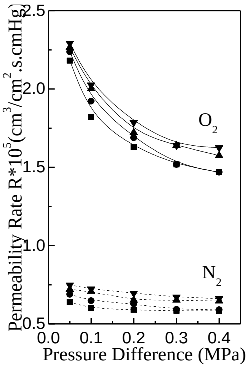

Fig. 5 Effect of the pressure difference on permeability (■:20℃, ●:30℃, ▲:40℃, ▼:50℃)

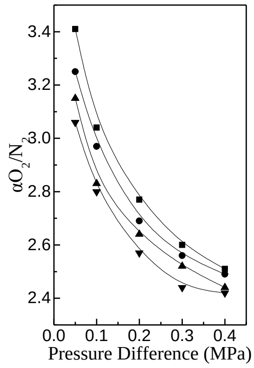

Fig. 6 Effect of the pressure difference on separation factor (■:20℃, ●:30℃, ▲:40℃, ▼:50℃)

3.5 Effect of testing temperature on gas separation properties

Fig. 7 and Fig. 8 showed the effect of testing temperature on permeation coefficient and separation factor of the composite membrane (10% cobalt content), respectivily. It could be seen from Fig. 7 that permeation coefficient were increased with an increase of testing temperature under the same pressure difference. However, separation factors of the composite membrane were decreased with an increase of testing 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.

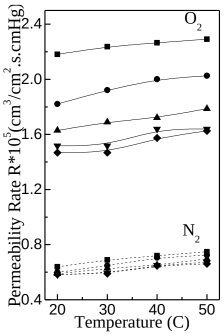

Fig. 7 Effect of temperature on permeability(■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

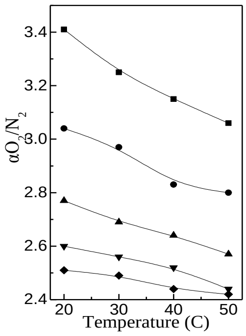

Fig. 8 Effect of temperature on separation factor (■:0.05, ●:0.1, ▲:0.2, ▼:0.3, ◆:0.4 MPa)

3.6 Morphology of the composite membrane

The samples for the composite membrane were observed by scanning electron microphotography (SEM). Fig. 9 shows the SEM photographs offor the the composite membrane (cobalt content: 10%). It can be seen that the composite membranes show dense, sleek and even appearances either SFS or FS. In addition, much denser cross-linked morphology in their inside could be also observed.

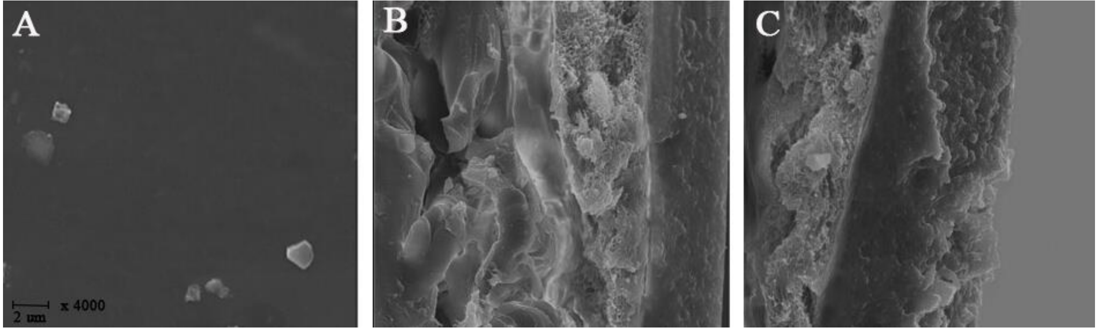

Fig. 9 The SEM figures of the composite membranes (A: the substrate-facing surface, B: the fracture surface)

4. Conclusion

Incorporating the cobalt ions into the composite membranes is the key to the modification for PDMS. In fact, the cobalt ions play two important roles in improving the gas separation properties of the composite 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. In addition, the porous polyetherimide used as supporting layer is benefit to improve the gas separation properties of the composite membranes.

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References

[1] B. Bouchra, L.M. Yann, H. Hayato, et al. Energy efficiency of oxygen enriched air production technologies: cryogeny vs membranes, Energy Procedia, vol. 63 (2014), 497-503.

[2] Z.L. Xin, J.G. Zhao, D.Q. Zhang, et al. Progress on research and application for oxygen enriching membrane materials, Science & Technology in Chemical Industry, vol. 17 (2009), 45-49.

[3] Y.H. Zhang, Y. Xiong, X. Liu, et al. Operating performance of oxygen-enriched membrane module based on application to vehicle engine on highland, Journal of Logistical Engineering University, vol. 25 (2010), 51-55.

[4] A. Meriläinen, A. Seppälä, P. Kauranen. Minimizing specific energy consumption of oxygen enrichment in polymeric hollow fiber membrane modules, Applied Energy, vol. 94 (2012), 285-294.

[5] L.M. Robeson. The upper bound revisited, Journal of Membrane Science, vol. 320 (2008), 390-400.

[6] T. Suzuki, Y. Yamada. Physical and gas transport properties of novel hyperbranched polyimide-silica hybrid membranes, Polymer Bulletin, vol. 53 (2005), 139-146.

[7] I. Kammakakam, H.W. Yoon, S.Y. Nam, et al. Novel piperazinium-mediated crosslinked polyimide membranes for high performance CO_2 separation, Journal of Membrane Science, vol. 487 (2015), 90-98.

[8] B.D. Freeman. Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, Macromolecules, vol. 32 (1999), 375-380.

[9] T.H. Zhu, S.H. Chen, J.Z. Lou, et al. Preparation and separation performance of silicone-based composite membrane for oxygen enrichment, Modern Chemical Industry, vol. 34 (2014), 89-92.

[10] Z.Y. Zhang. Facilitated oxygen transport in a novel silicone polymer membrane containing carboxylic cobalt groups, Journal of Applied Polymer Science, vol. 90 (2003), 1038-1044.

[11] Z.H. Liu, Z.Y. Zhang. Advance on polymer gas separation membrane containing low molecular weight additives, Polymer Bulletin, vol. 4 (2001), 61-68.

[12] Y. He, H.S. Li, P.C. Huang, et al. The effect of oxygen carriers on gas transport through polysiloxane and ethylcellulose membranes, Polymer, vol. 39 (1998), 3393-3397.

[13] H.X. Rao, F.N. Liu, Z.Y. Zhang. Oxygen-enriching properties of silicone rubber crosslinked membrane containing cobalt, Journal of membrane science, vol. 296 (2007), 15-20.

[14] M. Shoji, H. Nishide. Fluorophilic cobalt phthalocyanine-containing Nafion membrane: high oxygen permeability and proton conductivity in the membrane, Polymers for Advanced Technologies, vol. 21 (2010), 646-650.

[15] S.A. Stern, T.F. Sinclair, P.A. Gareis. An improved permeability apparatus of the variable-volume type, Journal of Modern Plastic, Vol. 42 (1964), 154-158.

[16] P. Roman. New apparatus for gas permeability, diffusivity and solubility assessing in dense polymeric membranes, Journal of Membrane Science, vol. 369 (2011), 466-473.

[17] Y. Song, P. Sun, L. L. Henry, et al. Menchanisms of structure and performance controlled thin film composite membrane formation via interfacial polymerization process, Journal of Membrane Science, vol. 251 (2005), 67-79.