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High solvent resistance PTFPMS/PEI hollow fiber composite membrane for gas separation

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ABSTRACT

Poly(fluoropropylmethylsiloxane) (PTFPMS), which had different properties with polydimethylsiloxane (PDMS) due to C—F bond. The limitation for PTFPMS membrane to achieve industrial-scale applications was the forms of membrane modules. Thus, PTSPMS/polyetherimide (PEI) hollow fiber composite membranes have been prepared. Effects of PTFPMS concentration, coating method, selective layer thickness, operating pressure and temperature on the separation performance of the composite membranes have been investigated. PTFPMS can form a top dense layer on PEI substrate under a suitable concentration. The gas permeation rates decrease in the following order: $CO_2 > C_3H_6 > H_2 > O_2 > CH_4 > N_2$. Permeation rates of CO_2 and C_3H_6 change significantly with the increase of operating pressure. Based on pure gas permeation rates, the selectivities range from 16.03 to 18.80 for CO_2/N_2 and 11.75–19.76 for C_3H_6/N_2 under operating pressure ranging from 0.1 to 0.5 MPa. Operating temperature has significant impact on permeation rates of CO_2, CH_4, O_2, H_2 and N_2. PTFPMS/PEI hollow fiber composite membrane exhibits stable separation performance after immersed in i-octane and petroleum ether. The selectivity decreases ratio of PTFPMS/PEI hollow fiber composite membranes varies in the range of 1.56–10.70%, much lower than those of PDMS/PEI membranes of 8.02–21.34%.

1. Introduction

Membrane separation processes have been used successfully in the industrial separation because of many advantages, such as environmental benignity, low operation cost, ease of operation and small footprint over conventional separation techniques [1–3]. Currently, gas separation membrane has been employed in air separation (oxygen enrichment) [4–6], H_2 separation [7–9], CO_2 separation [10–16] and volatile organic compounds (VOCs) separation [17]. There are two types of polymers, glassy and rubbery, are used in gas separation. Glassy polymer such as polyetherimide (PEI) [18,19] and polysulfone (PSf) [20] were widely used in industrial gas separation in the early years. In the recent years, polyimide (PI) [21–23] has been got more attention because of its excellent separation performance. In glassy polymer, gas penetrants are separated by molecular size, so diffusion selectivity plays an important role in the separation process. Herein, H_2 can permeate through the membrane firstly owing to its small molecular size in H_2 separation process (e.g. H_2/N_2, H_2/CO_2 and H_2/CH_4). Usually, glassy polymer membrane has high selectivity, whereas low permeability.

Compared with glassy polymer, rubbery polymers are usually soft and flexible [24]. So rubbery materials cannot be used alone in gas membrane separation. Thus, rubbery polymers as coating materials are prepared to form composite membrane. Composite membrane composed of selective layer and support layer has been widely applied in gas separation [19,25] and water purification [26]. Poly(dimethylsiloxane) (PDMS), as a typical rubbery polymeric material, is used to be the selective layer of composite membrane. PDMS composite membrane has a large amount of applications in O_2/N_2 [2], H_2/N_2 [19,27] and VOCs separation [17] processes. However, PDMS, like most rubbery polymer, has a tendency to swell in organic solvents [28].

Recently, fluorinated silicone rubbers (FSRs) have attracted more attention as materials for gas separations owing to their excellent properties by the introduction of fluorine-containing groups into the side chain of silicone rubbers. Poly(fluoropropylmethylsiloxane) (PTFPMS), as one of the most commonly used FSRs, has different properties with PDMS. Due to C—F bond, PTFPMS has high thermal and chemical stability, resistance to swelling by condensable gases or vapor and good membrane-forming ability [29]. It is reported that PTFPMS dense

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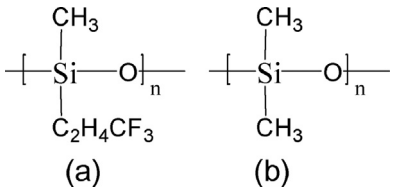

Fig. 1. Repeat unit structure of PTFPMS (a) and PDMS (b).

membrane possesses He, O_2, CO_2 and CH_4 permeability of 247, 217, 1388 and 201 barrer (1 barrer = 10^{-10} cm^3 (STP)/cm^2 s cmHg), respectively [30]. PTFPMS also has good membrane-forming ability, so it can be deposited on the surface of porous support layer and forms a selective layer. Zhang et al. [19] reported a kind of PTFPMS/PEI resistance composite membrane for H_2/N_2 and O_2/N_2 separation. Low molecular weight PTFPMS as a thin sealing layer was deposited on surface of asymmetric PEI flat sheet membrane to plug the defects. Nie et al. [25] reported a kind of PTFPMS-polyethylene glycol (PEG)/PEI blend composite membrane for CO_2 separation. PEG was introduced as a promoting material to improve CO_2 separation. The N_2 permeation rate of the PTFPMS-PEG blend composite membrane is 2.11 GPU (1 GPU = 10^{-6} cm^3/cm^2 s cmHg), combined with CO_2/N_2 selectivity was 26.67. The limitation for PTFPMS dense and flat sheet composite membrane to achieve industrial-scale applications is the forms of membrane modules.

In this work, high solvent resistance PTFPMS/PEI hollow fiber composite membrane for gas separation was prepared. First of all, the effects of PTFPMS concentration and coating method on separation performance of composite membrane have been investigated. Secondly, gas permeation performance of composite membrane was measured under different operating pressure and temperature. Finally, in order to prove the solvent resistance property, gas separation performance of the PTFPMS/PEI hollow fiber composite membrane was measured before and after immersed in i-octane and petroleum ether and compared with PDMS/PEI hollow fiber composite membrane.

2. Experimental

2.1. Materials

PEI (Ultem® 1000) was purchased from GE Plastics (USA), and dried in a vacuum oven at 105 °C for 24 h prior to be used. PTFPMS and PDMS with number average molecular weight about 1,000,000 g mol^{-1} were obtained from Shanghai 3F new materials Co., Ltd. (China) and Wacker Chemicals South Asia Pte Ltd. (Germany), respectively. The chemical structures of PTFPMS and PDMS are shown in Fig. 1(a) and (b). The polysiloxane containing SiH functional groups used as the cross-linker and platinum divinyl-tetramethylsiloxane complex used as the catalyst were provided by Shenzhen Kejunchi Co. Ltd. (China). Ethyl acetate (>99.5%) was purchased from Tianjin Fuyu Chemical Reagents Co. Ltd. (China). N,N-dimethyl acetamide (DMAc, Reagent grade), i-octane (Reagent grade) and 1,4-butyrolactone (GBL, Reagent grade) were purchased from Shanghai Jinshan Jingwei Chemicals Co. Ltd. (China), Tianjin Fuchen Chemical Reagents Co. Ltd. (China) and Research Center of Tianjin Guangfu Fine Chemicals (China), respectively. H_2, N_2, O_2, CO_2, CH_4 and C_3H_6 of research grade were supplied by Dalian Institute of Chemistry and Physics (China). All gases and chemicals were used as received.

Table 1
Spinning conditions of PEI hollow fiber asymmetric membrane.

Spinning parameters	Value
Dope solution composition	24/22/54 (PEI/GBL/DMAc, wt.%)
Length of air gap	5.0 cm
Injection rate of dope solution	4.8 mL/min
Injection rate of bore liquid	3.0 mL/min
Bore liquid composition	Deionized water
External coagulant	Deionized water
Winding speed	0 m/min
Temperature	25 ± 1 °C

2.2. Membranes preparation

2.2.1. PEI hollow fiber substrate membrane

PEI hollow fiber substrates used in this study were prepared by dry–wet phase inversion method [31]. The spinning conditions for the preparation of PEI substrate were listed in Table 1. After spinning, PEI fibers were soaked in deionized water.

2.2.2. PTFPMS/PEI hollow fiber composite membrane

PTFPMS coating solution was prepared by dissolving the PTFPMS polymer resin, cross-linking agent and catalyst with a weight ratio of 50:10:1 (w/w/w) in ethyl acetate at room temperature to obtain a homogeneous solution. Air bubble was removed by ultrasonic oscillator (AS5150B, Tianjin Automatic Science Instrument Co., Ltd., China). Wet membrane coating method and dry membrane coating method were employed:

(1) In the wet membrane dip-coating method (wet method), the water of PEI substrates surface was removed by filter paper. The wet membrane was submerged in PTFPMS coating solution with different concentrations, and then the membrane was withdrawn and additional solution was dripped off.
(2) In the dry membrane dip-coating method (dry method), the PEI substrates were dried in a vacuum oven at 105 °C for 12 h to remove the solvent and water completely. The dry membrane was coated by PTFPMS as the same as the wet dip-coating solution.

Composite membranes prepared by two methods were cured in an oven for 2 h at 85 °C to complete PTFPMS cross-linking.

2.2.3. PDMS/PEI hollow fiber composite membrane

PDMS/PEI hollow fiber composite membrane was prepared by wet membrane dip-coating method in order to compare solvent resistance performance. Coating solution was prepared by PDMS, cross-linking agent and catalyst with a weight ratio of 80:10:1 (w/w/w) in i-octane at room temperature. The preparation process of PDMS/PEI composite membrane was the same to that of PTFPMS composite membrane as the above.

2.2.4. PTFPMS dense membrane

PTFPMS dense membrane was prepared by pouring the coating solution on Teflon® plate directly for comparing with composite membrane to characterize FT-IR and XPS. The cross-linking condition was the same to PTFPMS/PEI composite membrane.

2.3. Characterizations and measurements

2.3.1. Viscosity

The viscosity of PTFPMS coating solution was measured with Brookfield LVT DV-III viscometer (Brookfield, USA) at 25 ± 0.5 °C controlled by water bath.