Journal of Membrane Science 443 (2013) 156–169

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

High performance PIM-1/Matrimid hollow fiber membranes for CO_2/CH_4, O_2/N_2 and CO_2/N_2 separation

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ARTICLE INFO

Article history:
Received 13 March 2013
Received in revised form
10 April 2013
Accepted 12 April 2013
Available online 2 May 2013

Keywords:
Gas separation
Polymer blends
Hollow fibers
PIM-1
Matrimid

ABSTRACT

Polymers of intrinsic microporosity (PIM-1) have received worldwide attention but most PIM-1 researches have been conducted on dense flat membranes. For the first time, we have fabricated PIM-1/Matrimid membranes in a useful form of hollow fibers with synergistic separation performance. The newly developed hollow fibers comprising 5–15 wt% of highly permeable PIM-1 not only possess much higher gas-pair selectivity than PIM-1 but also have much greater permeance than pure Matrimid fibers. Data from positron annihilation lifetime spectroscopy (PALS), field emission scanning electron microscopy (FESEM) and apparent dense layer thickness indicate that the blend membranes have an ultrathin dense layer thickness of less than 70 nm. PIM-1 and Matrimid are partially miscible. The effect of partial miscibility on dense selective layer was studied. Defect-free hollow fibers with gas pair selectivity more than 90% of the intrinsic value can be spun directly from dopes containing 5 wt% PIM-1 with proper spinning conditions, while post annealing and additional silicone rubber coating are needed for membranes containing 10 and 15 wt% PIM-1, respectively. Comparing to Matrimid, the CO_2 permeance of as-spun fibers containing 5 and 10 wt% PIM-1 increases 78% and 146%, respectively (e.g., from original 86.3 GPU ($1\ \text{GPU} = 1 \times 10^{-6}\ \text{cm}^3\ (\text{STP})/\text{cm}^2\ \text{s cmHg} = 7.5005 \times 10^{-12}\ \text{m s}^{-1}\ \text{Pa}^{-1}$) to 153.4 GPU and 212.4 GPU) without compromising CO_2/CH_4 selectivity. The CO_2 permeance of the fiber containing 15 wt% PIM-1 improves to 243.2 GPU with a CO_2/CH_4 selectivity of 34.3 after silicon rubber coating. Under mixed gas tests of 50/50 CO_2/CH_4, this fiber shows a CO_2 permeance of 188.9 GPU and a CO_2/CH_4 selectivity of 28.8. The same fiber also has an impressive O_2 permeance of 3.5 folds higher than the pristine Matrimid (e.g., from original 16.9 GPU to 59.9 GPU) with an O_2/N_2 selectivity of 6.1. The newly developed membranes may have great potential to be used for natural gas purification, air separation and CO_2 capture.

1. Introduction

A recent data reveals that the CO_2 concentration has reached 394 ppm in the atmosphere [1] which is far beyond the upper safety limit of 350 ppm [2]. With current energy demand, experts predicted that the CO_2 concentration in the atmosphere would further increase by 50% to reach 570 ppm in the year of 2100 [2]. In 2011, the U.S. Department of Energy announced their investment of $41 million over a 3-year period for the development of post-combustion technologies for CO_2 from coal-fired power plants [3]. Amine absorption and cryogenic separations are the conventional technologies for CO_2 capture [4]. However, the high energy and solvent consumptions as well as environmental concerns are the main bottlenecks of these technologies. In order to treat the huge volume of natural gas and flue gas in reducing CO_2 release directly to atmosphere, a high performance and environmentally friendly technology for CO_2 capture is desperately required.

Membrane technology has been demonstrated to possess properties of energy savings and environmental friendliness with small footprints for CO_2 capture in the integrated gasification combined cycle (IGCC) coal-fire power plant [5]. Additionally, due to the ease of processing and cost competitiveness, polymeric membranes have been widely used in both research and development and industrial applications for gas separation [4–6]. Polymeric hollow fiber membranes are favorable for industrial gas separation owing to their high surface over volume ratio, good flexibility, self-mechanical support and ease of handling during large scale module fabrication [7–11]. Typically, hollow fiber membrane has an asymmetric structure that comes with a selective layer overlaying on top of a porous support.

In the past decades, commercially available polyimide, Matrimid has been widely studied as the material for both flat sheet and

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http://dx.doi.org/10.1016/j.memsci.2013.04.037

hollow fiber membrane because of its high thermal stability and good processibility [12–16]. According to the literature, the pristine Matrimid exhibits prominent gas-pair selectivity of about 30–40 for CO_2/CH_4 and 6–6.6 for O_2/N_2 [12–16]. However, it possesses relatively low gas permeability. Clausi and Koros [14] were the first to develop defect-free Matrimid hollow fiber membranes with an ultra-thin selective layer of around 100 nm. They obtained a high O_2 permeance of 33.7 GPU and O_2/N_2 selectivity of 6.0 when the fibers were spun with an air-gap of 2.5 cm. When the air-gap was increased to 18.5 cm, fibers had an enhanced O_2/N_2 selectivity of 6.8 but a relatively lower O_2 permeance of 11.2 GPU. Jiang et al. [15] studied the Matrimid/ polyethersulfone (PES) dual-layer hollow fiber membranes by using Matrimid as the outer selective layer and PES as the inner supportive layer. The use of dual-layer co-extrusion is one of the strategies to reduce the manufacturing cost since the costly Matrimid is only used in the outer layer. They developed the dual-layer fibers with an O_2/N_2 selectivity of 6.26 in pure gas tests and a CO_2/CH_4 selectivity of 40 in a binary 40/60 mol% CO_2/CH_4 mixture. Besides, Dong et al. [16] carried out a detailed study to examine the effects of spinning conditions on Matrimid hollow fibers. Their fibers had a CO_2 permeance of about 11 and a CO_2/CH_4 selectivity of 47–67. Recently, David et al. [17] also spun Matrimid hollow fibers for hydrogen separation from multicomponent gas mixtures. However, most of the aforementioned hollow fiber membranes have relatively low gas permeance. The permeance must be further improved for disruptive industrial applications.

In addition to synthesizing totally new materials [6,18–27], modifications of existing materials [6,28–34] have been extensively employed to design new membranes with enhanced performance. Among various modification approaches, polymer blend is one of the most cost- and time-effective routes as it combines the advantages of different materials into a new compound with unique and synergetic properties that are often difficult to be obtained by other synthesis means [35,36]. As a consequence of superior thermal stability and separation performance, polyimide blended hollow fiber membranes have been broadly studied [37–40]. Matrimid blended with polybenzimidazole (PBI) [37], PES [38,39] and (BTDA-TDI/MDI) P84 [39] as hollow fiber membranes for gas separation have been explored by different research groups. Hosseini et al. [37] developed dual-layer hollow fiber membranes consisting of Matrimid/PBI as an outer selective layer and polysulfone (PSF) as the inner supportive layer. The addition of PBI significantly enhanced the membranes to be H_2 selective with a H_2 permeance of 29.26 GPU and a H_2/CO_2 selectivity of 11.11. Kapantaidakis and Koops [38] showed that the incorporation of Matrimid into PES hollow fiber membranes increased permeance significantly if comparing with the pristine PES. The CO_2 permeance was about 31–60 GPU with a CO_2/N_2 selectivity of 35–40 after a silicon rubber coating.

In the work of Visser et al. [39], the introduction of P84 in Matrimid resulted in higher O_2/N_2 and CO_2/CH_4 selectivity. In addition, P84/Matrimid fibers showed strong resistance to plasticization for CO_2 feed concentrations below 80 vol%. On the other hand, the addition of PES into Matrimid increased plasticization resistance but resulted in a lower gas-pair selectivity comparing to the pristine Matrimid. Other than Matrimid-based blends, PBI and polyetherimide (PEI) hollow fiber membranes had been reported [40]. The incorporation of 0–30 wt% PBI into PEI formed miscible blends due to strong hydrogen bonding between them. However, the gas permeance decreased significantly with an increase in PBI concentration. Nevertheless, the addition of PBI successfully tuned the pristine PEI properties towards high H_2/N_2 selectivity.

In one of our previous studies, we had explored the blend compatibility between Matrimid and polymers of intrinsic microporosity (PIMs) and studied their synergistic gas permeability [34]. PIMs were chosen because not only they are a class of novel polymers but also possess extremely high free volume and large surface area due to the kinked ladder-type backbone structure [34,41–47]. Our results showed that the incorporation of 5 and 10 wt% of PIM-1 into Matrimid induces the permeability increments of 25% and 77%, respectively, from the original 9.6 to 12 and 17 Barrer (1 Barrer $= 1 \times 10^{-10}$ cm^3 (STP) cm/cm^2 s cmHg) without much compromises in CO_2/CH_4 selectivity. Clearly, blending Matrimid and PIM-1 is a new strategy to molecularly design Matrimid based hollow fiber membranes with an enhanced flux and to simultaneously retain the high selectivity of the original Matrimid.

Among all the PIMs synthesized, PIM-1 is one of the most recognized types [30,34,44–47]. Briefly, PIM-1 has a superior CO_2 permeability of around 3000–8000 Barrer and a CO_2/CH_4 selectivity of 9–16 depending on synthesis and post-treatment conditions [30,34,44–47]. Moreover, the O_2 permeability of PIM-1 is about 700–1700 Barrer with an O_2/N_2 selectivity of 2.2–4.3 [30,34,44–47]. To the best of our knowledge, no prior work has been reported on PIM-1 related hollow fiber membranes in the literature possibly due to its unimpressive gas pair selectivity. Modifications of PIM-1 with a high selectivity have received worldwide attention [41–43].

Therefore, the purposes of this work are (1) to molecularly construct novel PIM-1/Matrimid blend hollow fiber membranes with synergistic separation performance by combining characteristics of high gas pair selectivity from Matrimid and high permeability from PIM-1, (2) to fundamentally understand the science and engineering for the formation of PIM-1/Matrimid hollow fiber membranes, and (3) to fabricate high-performance defect-free PIM-1/Matrimid blend hollow fiber membranes with an ultrathin dense-selective layer. The effects of spinning parameters such as dope formulation, bore fluid composition, take-up speed, PIM-1 concentration, and post-treatment conditions on gas separation performance will be systematically investigated. The miscibility and glass transition temperature (T_g) of blends will be also investigated by a polarized light microscope (PLM) and differential scanning calorimetry (DSC). It is envisioned that the fundamentals and knowledge gained throughout this study may create greater opportunities for further enhancements in polymeric hollow fiber membranes for gas separation applications.

2. Experimental

2.1. Materials

The monomers 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (TTSBI, 97%) and 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN, 99%) were purchased from Alfa Aesar and Matrix Scientific, respectively. TTSBI was purified by re-crystallization in methanol, while TFTPN was sublimated under vacuum prior to use. Matrimid powder was supplied by Huntsman Advanced Materials. It was dried overnight at 120 °C under vacuum before use. N-methyl-2-pyrrolidone (NMP, $>99.5\%$) from Merck was further purified via vacuum distillation before use. Anhydrous potassium carbonate (K_2CO_3, $>99.5\%$) from Sigma Aldrich and methanol (MEOH, ≥99.9%) from Merck were used without further purification. Dichloromethane (DCM, 99.99%), hydrochloric acid (HCl, 37.5%), tetrahydrofuran (THF, 99.99%) and *n*-hexane (≥99.9%) from Fisher Scientific were used as received.

2.2. Synthesis and characterizations of PIM-1

The synthesis of PIM-1 was carried out by the traditional polycondensation reaction between TTSBI and TFTPN under