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Molecular interaction, gas transport properties and plasticization behavior of cPIM-1/Torlon blend membranes

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ABSTRACT

Polymers of intrinsic microporosity, specifically PIM-1, have emerged as promising materials for gas separation due their high gas permeability. However, its insolubility in common polar aprotic solvents like N-Methyl-2-pyrrolidone (NMP) limits its full potential and possible industrial applications. In this study, the solubility of PIM-1 in such solvents has been modified by carboxylation via hydrolysis reaction in a short period of 1 h. The success of carboxylation was verified by nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR) and water contact angles. The carboxylated PIM-1 (cPIM-1) was subsequently blended with Torlon to enhance the intrinsic permeability of Torlon rich membranes and the intrinsic selectivity of cPIM-1 rich membranes. The additions of 5, 10 and 30 wt% cPIM-1 into Torlon increase its CO_2 permeability by 26%, 128% and 791%, respectively, from the original value of 0.541–0.682, 1.233 and 4.822 (1 Barrer=1 $\times$ 10^{-10} $cm^3(STP)\ cm/cm^2\ s\ cmHg = 3.348 \times 10^{-19}$ kmol m/m^2 s Pa) with minor sacrifices in CO_2/CH_4 selectivity. These permeability improvements are attributed to the formation of hydrogen bonding and charge transfer complexes (CTC) between cPIM-1 and Torlon, which promotes better interactions in the blends. In addition, all the cPIM-1/Torlon membranes exhibit a great plasticization resistance up to 30 atm. This is ascribed to the incorporation of the rigid Torlon that may lead to restricting chain mobility in CO_2 environments. The overall separation performance has been driven closer to the Robeson upper bound for O_2/N_2, CO_2/CH_4, CO_2/N_2 and H_2/N_2 separations. Therefore, the newly developed membranes may have great potential for energy development and industrial applications.

1. Introduction

Anthropogenic CO_2 emissions arise from forest burning, industrial manufacturing and power plants. According to the IPCC Climate Change 2007 report, the CO_2 emission from energy sectors is predicted to increase from 40% to 110% between 2000 and 2030 [1]. A recent study by Yamasaki stated that CO_2 contributes about 60% of global warming as compared to other greenhouse gases [2]. To mitigate the global warming, CO_2 capture has been discussed aggressively. The main purpose of CO_2 capture is to concentrate CO_2 before it can be transported to CO_2 storage sites [3,4]. Among all the available technologies, the polymer-based membrane separation process has played a significant role in CO_2 capture because of its environmentally benign nature, easy processability, simple operation, small footprint and cost competitiveness [5–10]. Compared to existing polymer materials, polyimide emerges as a promising polymer because it exhibits high selectivity in major gas pairs (e.g., CO_2/CH_4 and O_2/N_2), high thermal stability and reasonable mechanical strength [11–15].

Nevertheless, polyimide membranes generally have the plasticization issue when the separation involves a highly condensable gas (e.g., CO_2) or is operated in aggressive conditions (e.g., high pressure and temperature). Plasticization happens with an increase in CO_2 pressure that causes certain structure dissolution within the polymer matrix [11,12,16]. As a result, the inherent selectivity of polymer chains deteriorates. To enhance the membrane stability against the CO_2-induced plasticization, many researchers have modified their membranes through cross-linking [12,13,17–19]. However, the cross-linked membranes yield a high selectivity but a reduced permeability in most cases.

Other than cross-linking, polyimide polymers with an intrinsic high anti-plasticization property such as Torlon have been utilized. Torlon is a type of polyamide-imide that dissolves in polar aprotic solvents such as N-Methyl-2-pyrrolidone (NMP) and N,N-dimethylformamide (DMF). It has an impressive plasticization pressure up to 30–40 atm [20]. However, this polymer has a very low permeability which makes it impractical for industrial CO_2 capture. Attempts have been made to modify Torlon by blending it with other polymers such as Matrimid and PBI [21]. Miscible

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blends were formed owing to the existence of hydrogen bonding between polymers, but no gas permeability of these blends was reported.

Compared to Torlon, PIM-1 is a type of polymer of intrinsic microporosity well recognized for its superior gas permeability recently [22–29]. However, blending PIM-1 with Torlon is not feasible because PIM-1 only dissolves in dichloromethane (DCM), tetrahydrofuran (THF), chloroform ($CHCl_3$), while Torlon dissolves in NMP or DMF. In the recent work of Du et al.'s group, PIM-1 was chemically modified to replace nitrile groups by carboxylic groups through hydrolysis [30–32]. With the aid of carboxylic groups, the carboxylated PIM-1 (cPIM-1) became soluble in polar aprotic solvents. The resultant cPIM-1 membrane (treated at 120 °C for 5 h) showed an increase in CO_2/N_2 selectivity of about 136% (from the initial value of 11 to 26) but a decrease in CO_2 permeability of approximately 93% (from the initial value of 8310 Barrer to 620 Barrer) [28].

Since Torlon has superior gas-pair selectivity and plasticization resistance while PIM-1 has outstanding gas permeability, we aim to explore a simple and novel method in this paper to combine their strengths by blending Torlon and the modified PIM-1 as new materials for gas separation membranes with enhanced gas transport properties and plasticization resistance. Different from Du et al.'s work, PIM-1 powders instead of PIM-1 membranes would be used for the chemical modification. Therefore, the objectives of this work are to: (1) molecularly tailor cPIM-1/Torlon membranes with synergistic separation efficiency and anti-plasticization property, (2) fundamentally understand the properties and interactions of the polymer blends and (3) investigate the effects of blend ratio on separation performance and plasticization behavior. To our best knowledge, this is the first paper investigating the polymer blends of cPIM-1 and polyamide-imide for gas separation with enhanced separation performance and superior anti-plasticization behavior.

2. Experimental

2.1. Materials

A PIM-1 polymer with the weight-average molar mass (M_w) of 108,500 was synthesized in our lab while Torlon 4000TF powders were supplied by Solvay Advanced Polymers. Torlon was dried overnight under vacuum at 120 °C before use. N-methyl-2-pyrrolidone (NMP, > 99.5%) from Merck was further purified via vacuum distillation before usage. Anhydrous potassium carbonate (K_2CO_3, > 99.5%) and sodium hydroxide (NaOH, ≥ 98%) from Sigma Aldrich were used as received. Methanol (MEOH, ≥ 99.9%) and N,N-dimethylformamide (DMF, > 99.5%) from Merck were utilized without further purification. Hydrochloric acid (HCl, 37.5%), ethanol (EtOH, ≥ 99.9%), dichloromethane (DCM, 99.99%) and tetrahydrofuran (THF, 99.99%) from Fisher Scientific were used as received. The chemical structures of PIM-1 and Torlon are depicted in Fig. 1.

2.2. Modification of PIM-1 to cPIM-1

The cPIM-1 was formed by the hydrolysis of the nitrile group of PIM-1 [30–32]. PIM-1 powders were first immersed in a 20 wt% NaOH solution with the ratio of ethanol/water of 1:1 at 120 °C for 1 h. After that, the polymer was filtered from the solution and then boiled in deionized water with the addition of HCl (pH 4–5) for 1 h. The product was then filtered, rinsed with deionized water and washed again with MEOH to remove the HCl residue. The cPIM-1 powders were dried at 70 °C under vacuum for 24 h prior to use. The modification mechanism of PIM-1 to cPIM-1 is depicted in Fig. 2. The molecular weight of cPIM-1 was analyzed by gel permeation chromatography (GPC). The GPC system comprises a Waters 1515 iscoratic HPLC pump, a Waters 717 plus autosampler and a Waters 2414 refractive index detector. Polystyrene standards were used for calibration. DMF was used as the solvent at a flow rate of 1 mL/min with the testing temperature of 35 °C. The concentration of PIM-1 powders dissolved in DMF was 0.005 wt%. The GPC results showed the weight-average molar mass (M_w) of 193,500. The apparent surface areas of cPIM-1 were characterized from Brunauer–Emmett–Teller (BET) using a BET model NOVA4200e. The apparent surface area of cPIM-1 was 486 $m^2\ g^{-1}$.

2.3. Membrane fabrication

Dense films with different ratios of cPIM-1/Torlon were prepared via the solution casting method. Torlon was first dissolved in NMP and stirred overnight at 65 °C. Subsequently, cPIM-1 was added into the solution and stirred overnight. The final solution containing 2 wt% cPIM-1/Torlon was then filtered through a 1 μm PTFE filter and cast onto a silicon wafer at ambient temperature. The polymer solution was heated under vacuum at 40 °C for 12 h and then increased to 75 °C for 24 h. The formed dense films were peeled off from the silicon wafer and dried under vacuum with a temperature ramp of 25 °C/30 min to 250 °C and held for 12 h. The resultant dense films were labeled as "cPIM-1/Torlon (weight composition ratio)", for example, cPIM-1/Torlon (5:95). The

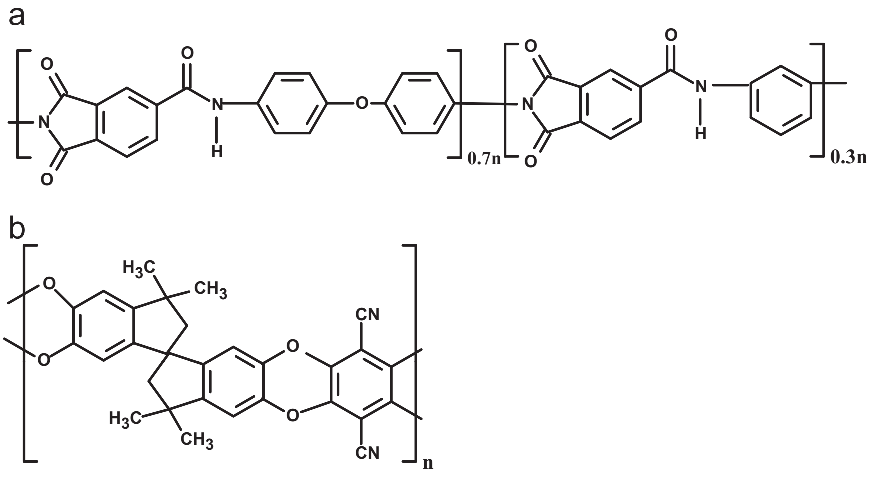

Fig. 1. Chemical structures of (a) Torlon and (b) PIM-1.