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Poly(amide-6-*b*-ethylene oxide)/[Bmim][Tf_2N] blend membranes for carbon dioxide separation☆

Yongtao Qiu[a,b], Jizhong Ren[a,*], Dan Zhao[a,b], Hui Li[a], Maicun Deng[a]

[a] *National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

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ABSTRACT

Poly(amide-6-*b*-ethylene oxide) (Pebax1657)/1-butyl-3-methylimidazo-lium bis[trifluoromethyl)sulfonyl]-imide ([Bmim][Tf_2N]) blend membranes with different [Bmim][Tf_2N] contents were prepared via solution casting and solvent evaporation method. The permeation properties of the blend membranes for CO_2, N_2, CH_4 and H_2 were studied, and the physical properties were characterized by differential scanning calorimeter (DSC) and X-ray diffraction (XRD). Results showed that [Bmim][Tf_2N] was dispersed as amorphous phase in the blend membranes, which caused the decrease of T_g (PE) and crystallinity (PA). With the addition of [Bmim][Tf_2N], the CO_2 permeability increased and reached up to approximately 286 Barrer at 40 wt% [Bmim][Tf_2N], which was nearly double that of pristine Pebax1657 membrane. The increase of CO_2 permeability may be attributed to high intrinsic permeability of [Bmim][Tf_2N], the increase of fractional free of volume (FFV) and plasticization effect. However, the CO_2 permeability reduced firstly when the [Bmim][Tf_2N] content was below 10 wt%, which may be due to that the small ions of [Bmim][Tf_2N] in the gap of polymer chain inhibited the flexibility of polymer chain; the interaction between Pebax1657 and [Bmim][Tf_2N] decreased the content of EO units available for CO_2 transport and led to a more compact structure. For Pebax1657/[Bmim][Tf_2N] blend membranes, the permeabilities of N_2, H_2 and CH_4 decreased with the increase of feed pressure due to the hydrostatic pressure effect, while CO_2 permeability increased with the increase of feed pressure for that the CO_2-induced plasticization effect was stronger than hydrostatic pressure effect.

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1. Introduction

Global warming has been one of the most severe challenges, which induced the changes of climate, the rise of sea levels and the reduction of crop yields. CO_2, derived from the combustion of fossil fuel (petroleum, coal and natural gas), is considered to be the main factor for these great changes. CO_2 capture and storage (CCS), could be a potential method to reduce CO_2 emissions [1]. As CO_2 separation is the most power-wasting step, improving current technologies or developing new approaches for CO_2 separation are urgent for CCS. Compared with chemical absorption, pressure swing adsorption and cryogenic separation [2–4], membrane separation technology possesses much lower energy consumption, and numerous additional inherent advantages, for example, easy to scale up and small footprint [5]. These superiorities also promote the implementation of membranes in industrial processes, such as the enrichment of oxygen from air, the purification of hydrogen [6,7] and the removal of acid gas from flue gas or natural gas stream [8,9].

However, the trade-off limitation between permeability and selectivity expressed as the upper bound curves, proposed by Robeson [10], is one of the main obstacles limiting the implementation of polymer membranes in gas separation. Therefore, a considerable amount of researchers are dedicated to synthesizing new membrane materials or modifying commonly used materials to improve the separation efficiency. The membrane modification includes chemical method, such as blocking, grafting and cross-linking [11–13], and physical method, such as blending [14,15]. By taking the advantage of different materials, polymer blending is believed to be an attractive way to optimize membrane material to improve its mechanical property and gas separation performance. Meanwhile, compared with blocking or cross-linking, polymer blending is simple, reproducible and feasible.

Lin and Freeman [16] have reported a review on membrane material selection for CO_2 separation and found that ethylene oxide (EO) units contributed to the permeation of CO_2 due to the quadrupole–dipole interactions between CO_2 and polar ether

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* Corresponding author. Tel: +86 411 84379961; Fax: +86 411 84379613.
E-mail address: renjizhong@dicp.ac.cn (J. Ren).

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segments (EO units), which was consistent with the fact that the permeability of polyether-block-polyamide (Pebax) membrane was obviously improved with the increase of PE content in the copolymer [17]. Pebax is a thermoplastic elastomer consisting of rigid polyamide (PA) segments that provide mechanical strength support and flexible polyether (PE) segments which offer the transport way for gas molecule. Meanwhile, Pebax exhibited high thermal stability. Bondar et al. [18] studied the permeation of CO_2, H_2, and CH_4 through Pebax membranes and found that Pebax exhibited high CO_2 permeability and CO_2/non-polar gas (N_2 and H_2) selectivities, which proved that Pebax was a promising membrane material for CO_2 separation.

Ionic liquids (ILs) are a broad category of organic salts in liquid state at the room temperature composed of a bulky organic cation and either an inorganic or organic anion in general. Due to their unique properties such as high thermal stability, high solubility, negligible vapor pressure, adjustable structure and properties defined by multitudinous feasible cation–anion combinations, ILs have drawn great attentions in various applications such as chemical synthesis, catalysis, solvent extraction, and electrochemistry [19–23]. Blanchard et al. [24] firstly found the high solubility of CO_2 in ILs in 1999. Subsequent studies interpreted a fact that ILs containing fluoroalkyl groups exhibited high CO_2 solubility [25]. It was reported that CO_2 solubility of ILs containing imidazolium cation was higher than that of ILs containing ammonium cation or phosphonium cation, and that CO_2 solubility of ILs with fluoroalkyl anion was higher than that of ILs with chloride anion $[Cl]^-$ or cyanamide anion $[dca]^-$.

As promising materials, ILs have been applied in membrane separation process in manner of supported ionic liquid membranes (SILMs) [26,27], polymeric room temperature ionic liquids membranes (Poly(RTILs)) [28–30] and blend membranes [31,32]. However, the drawbacks, such as the instability of SILMs due to the loss of membrane liquid, are still the severe issues for SILMs. SILMs cannot withstand higher pressure required in many industrial gas separation processes [33,34], which could be further exacerbated with increasing temperature due to the decrease of liquid viscosities. Similarly, Poly(RTILs) also have some shortcomings, such as small free volume and less mobility, which result in low gas permeabilities [35]. Blend membranes could be a promising method to overcome these problems. With the simplicity and commercial feasibility, blend membrane possesses considerable superiorities. Nancarrow [36] fabricated Polybenzimidazole/$[C_4mim][Tf_2N]$ and Polyimide/$[C_4mim][Tf_2N]$ composite membranes, and found that the gas permeabilities were improved with the increase of $[C_4mim][Tf_2N]$. When the content of $[Bmim][Tf_2N]$ was 40 wt%, the CO_2 permeability was reached to 7 Barrer compared to 2.5 Barrer in pure Polybenzimidazole. Friess [31] fabricated poly(vinylidene fluoridecohexafluoropropylene)/[Emim][TFSI] gel membrane, gas permeabilities significantly increased in the presence of [Emim][TFSI], the CO_2 permeability was about 533 Barrer at 80 wt% [Emim][TFSI] content. Jansen et al. [37] investigated the permeabilities of CO_2, CH_4, H_2 and N_2 for Pebax/[Bmim][OTf] blend membranes, found that [Bmim][OTf] greatly increased the gas permeabilities, the CO_2 permeability was reached to approximately 150 Barrer (25 °C) at 40 wt% [Bmim][OTf] content, while the gas selectivities slightly decreased. Therefore, ILs were interesting membrane materials for the academic research and industrial application of CO_2 separation.

In this work, Pebax1657/$[Bmim][Tf_2N]$ blend membranes, were prepared to achieve high CO_2 permeability. The thermal and structure properties of Pebax1657/$[Bmim][Tf_2N]$ blend membranes were characterized by DSC and XRD. The effect of $[Bmim][Tf_2N]$ content on the permeation properties of Pebax1657/$[Bmim][Tf_2N]$ blend membranes was evaluated. The influences of operation pressure and temperature on gas permeabilities were also discussed, and Maxwell model was used to describe gas transport process.

2. Theory

The gas permeability of dense polymeric films is generally expressed as the product of the gas solubility in the polymeric material and its diffusivity according to solution–diffusion model, just as shown in the following formula:

$$P = D \times S \tag{1}$$

where P is the permeability, D refers to the diffusion coefficient and S stands for the solubility coefficient of gas under steady-state.

Separation factor $\alpha_{A/B}$ for gas (A) over gas (B) is defined as the ratio of their permeability:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A}{S_B} \times \frac{D_A}{D_B} \tag{2}$$

The volume fraction of dispersed phase ϕ_D is obtained from the follow equation:

$$\phi_D = \frac{M_D/\rho_D}{M_D/\rho_D + (1 - M_D)/\rho_C} \tag{3}$$

where M_D is the mass fraction of dispersed phase, and ρ is the density; the subscripts C and D represent the continuous phase and the dispersed phase.

3. Experimental

3.1. Material selection

It was reported [38] that the CO_2 permeability in the imidazolium-based ILs was significantly more than the respective value for ammonium-based ILs and phosphonium-based ILs. It has been also reported that ILs containing $[Tf_2N]^-$ showed high CO_2-solubility in comparison to $[CF_3SO_3]^-$, $[dca]^-$ and $[Cl]^-$ [39]. Therefore, $[Bmim][Tf_2N]$ was chosen as the filler to improve gas transport properties of Pebax1657 by preparing Pebax1657/$[Bmim][Tf_2N]$ blend membranes.

Table 1 displays the Hildebrand solubility parameters δ of $[Bmim][Tf_2N]$, Pebax1657 and 1-butanol. The calculated δ_{ave} of $[Bmim][Tf_2N]$ was 23.1 $MPa^{0.5}$ which was approximate to the values of Pebax1657. It was proved that $[Bmim][Tf_2N]$ could be well compatible with Pebax1657. Meanwhile, 1-butanol was used as solvent to fabricate Pebax1657/$[Bmim][Tf_2N]$ blend membranes due to its similar Hildebrand solubility parameter to $[Bmim][Tf_2N]$ and Pebax1657.

3.2. Materials

Pebax1657 (ρ = 1.14 g/cm^3) was purchased from ARKEMA. Its structure was given in Fig. 1. The Ionic liquid used in this paper was 1-butyl-3-methylimidazolium bis[(trifluoromethyl)-sulfonyl]imide (>98%, Shanghai Chengjie Chemical Co. LTD), and its structure and properties were shown in Fig. 1 and Table 2, respectively.

1-Butanol (99.5%, Tianjin Bodi Chemical Engineering Co. Ltd.) was used as solvent. The gases for permeation test (N_2, H_2, CH_4 and CO_2, all with purity of 99.9+%) were supplied by Dalian Gases Company. All the materials and gases were used as received.

3.3. Membrane preparation

Pebax1657/$[Bmim][Tf_2N]$ blend membranes were prepared by solution casting and solvent evaporation method. Pebax1657 was dissolved in 1-butanol with continuous stirring under reflux conditions at least 8 h until a clear homogeneous solution with concentration of 5 wt% was obtained. Different amounts of $[Bmim][Tf_2N]$ were added into Pebax1657 solution. Then, the Pebax1657/$[Bmim][Tf_2N]$ solution

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