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Improving CO_2 permeation and separation performance of CO_2-philic polymer membrane by blending CO_2 absorbents

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ABSTRACT

To research effects of CO_2 absorption capacity and type of CO_2 absorbent on the CO_2 separation and free-volume properties of facilitated transport membranes, two types of CO_2 absorbents, namely monoethanolamine (MEA) and ionic liquids (ILs:[P_{66614}][Triz] and [P_{66614}][2-Op]), were adopted. The CO_2 absorption capacities of MEA, [P_{66614}][Triz] and [P_{66614}][2-Op] were about 0.561 mol CO_2 per mol, 0.95 mol CO_2 per mol and 1.60 mol CO_2 per mol, respectively. All mean free-volume hole radiuses of membranes decreased after blending CO_2 absorbents. After polymer membrane blended with two ILs, number of free-volume hole increased, resulting in modest increase of the fractional free volume. Both CO_2 permeability and selectivity increased after blending MEA and ILs. The increasing range of CO_2 permeability corresponded with CO_2 absorption capacity of CO_2 absorbents, and membrane blending with [P_{66614}][2-Op] showed the highest CO_2 permeability of 672.1 Barrers at 25 °C. Pebax/PEGDME membrane blending with MEA obtained the highest CO_2/H_2 and CO_2/CH_4 selectivity at 17.8 and 20.5, respectively.

1. Introduction

Biomass energy, as a renewable energy with zero CO_2 emission, will be further developed and used in the future. Among the utilization patterns of biomass energy, the fermentation process of hydrogen and methane cogeneration shows great potential [1,2]. Two products of the fermentation process, namely, biohydrogen and biomethane, contain approximately 40 vol% CO_2. The existence of a large number of CO_2 degrades the calorific values of biohydrogen and biomethane and results in inefficient direct utilization [3]. Thus, the CO_2 separation from biohydrogen and biomethane is imperative. In comparison with solvent– and sorbent–CO_2 separations, membrane-based gas separation technologies present several advantages, such as lower operating costs, smaller carbon footprint, and ease of operation [4,5]. Among all gas separation membranes, CO_2-philic polymer membranes show two great advantages. First, CO_2 can be separated from small gas molecules (such as H_2) by this kind of membranes. Therefore, H_2 recompression and loss can be minimized [6]. Second, the trade-off limitation between CO_2 permeability and CO_2/H_2 selectivity does not apply to CO_2-philic polymer membranes [7]. As such, the selection and optimization of CO_2-philic polymer membrane materials are vital. Pebax/polyethylene glycol (PEG) (hybrid material poly (amide-b-ethylene oxide) and PEG-based polymers) composite membranes exhibit good CO_2 permeability and selectivity because they contain a large number of ethylene oxide units, which are identified as the optimal chemical group for CO_2 separation [6,8–11]. However, the performances of such membranes, especially their permeability, are not satisfactory to meet the requirements of industrial application [7]. Therefore, the further improvement of such membranes is imperative.

To improve the performance of CO_2-philic membranes, many materials were adopted to blend into the membrane, such as polymers with special characteristics, CO_2 absorbents, porous materials (including MOFs, silicas and zeolites) [10,12–14]. Meanwhile, three component based membranes, in which ILs and porous materials (SAPO 34, ZIF 8, etc.) were simultaneously blended in, were also prepared and researched [15–18]. Fixing CO_2 absorbent into polymer materials is an effective way to enhance the CO_2 permeability of CO_2-philic membranes. Through a reversible reaction with the targeted gas CO_2, the CO_2 absorbent (e.g., amine groups and ionic liquid (IL)) can facilitate CO_2 transport in the membrane, and

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Abbreviations: Pebax, poly (amide-b-ethylene oxide); PEGDME, polyethylene glycol dimethyl ether; MEA, monoethanolamine; PEG, polyethylene glycol; RTIL, room-temperature ionic liquid; PVAm, polyvinylamine; p(VDF-HFP), poly(vinylidene fluoride-co-hexafluoropropylene); PALS, positron annihilation lifetime spectroscopy; *FFV*, the fractional free volume; FTIR, fourier transform infrared; DSC, differential scanning calorimeter; Ps, positronium; AFM, atomic force microscope; *P*, permeability; *D*, diffusivity; *S*, solubility.

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the resulted membranes were called facilitated transport membranes [13]. Qiao et al. adopted small molecular amines to modify polyvinylamine (PVAm) membrane, and both the CO_2 permeability and selectivity were enhanced [7]. Blending monoethanolamine (MEA), in particular, increased the CO_2 permeability nearly twice. However, such experiments required a humid environment. Also, different types of IL were blended in the CO_2-philic polymer materials, and the performances of the membranes were improved. Jansen et al. [19] prepared p(VDF-HFP)/[EMIM][TFSI] blending membranes, and the CO_2 permeability increased to approximately 600 Barrer (1 Barrer = 1×10^{-10} cm^3 (STP) μm/cm^2 s cmHg, where STP is the standard temperature and pressure). They also researched the effect of adding IL ([BMIM][OTf]) on the performance of Pebax® 1657 and Pebax® 2533 membranes and found that the CO_2 permeability increased after blending IL into Pebax® 1657 membrane [20]. However, most of studies researched one type of CO_2 absorbents and CO_2 absorption capacities of most of them were too low. Therefore, the comparison between blending different types of CO_2 absorbents with a range of CO_2 absorption capacities was not explicitly discussed before. Also, the change of free-volume properties after CO_2 absorbents mixed into polymer chains was little researched.

In this work, To research effects of CO_2 absorption capacity and type of CO_2 absorbent on CO_2-philic polymer membrane, two different types of CO_2 absorbents, namely MEA and two ILs ([P_{66614}][Triz] and [P_{66614}][2-Op]), were adopted to blend into a CO_2-philic polymer. [P_{66614}][2-Op] showed one of the highest CO_2 absorption capacities up to 1.6 mol CO_2 per mol, followed by CO_2 absorption capacity of [P_{66614}][Triz] at 0.95 mol CO_2 per mol IL [21,22]. For CO_2 absorption capacity of MEA, one of reported highest values reached up to 0.561 mol CO_2 per mol MEA [23,24]. The composite of Pebax and polyethylene glycol dimethyl ether (PEGDME), which had shown good CO_2 permeation and separation performance in several studies, was adopted as polymer material, and film membranes were prepared [9,10]. The chemical structures of ILs, MEA, Pebax and PEGDME were shown in Fig. 1. Modified performances (such as free-volume parameters, membrane density, CO_2 permeability and selectivity) were researched and compared with each other. Also, α-Al_2O_3 ceramic hollow fiber-supported composite membranes were prepared. Ceramic hollow fiber-supported membrane structure not only has advantages of hollow fiber membrane (such as easy assembling and large surface area per unit volume of membrane material), but also obtain good mechanical and thermal stabilities of ceramic. In this study, surface morphology, CO_2 permeation rates, CO_2/H_2 and CO_2/CH_4 selectivity of α-Al_2O_3 ceramic hollow fiber-supported Pebax/PEGDME/[P_{66614}][2-Op], Pebax/PEGDME/[P_{66614}][Triz] and Pebax/PEGDME/MEA membranes were researched. Meanwhile, time effect on CO_2/H_2 separation performance of α-Al_2O_3 ceramic hollow fiber-supported composite membranes was studied.

2. Experimental

2.1. Materials

Pebax® MH 1657 was provided by Arkema Company. PEGDME (average M.W. ~500) was obtained from Sigma–Aldrich Company. [P_{66614}][Triz] (density: 0.933 g/ml) and [P_{66614}][2-Op] (density: 0.907 g/ml) were provided by the Department of Chemistry, ZJU-NHU United R&D Center at Zhejiang University, China. MEA (density: 1.020 g/ml) was purchased from Aladdin Company. Asymmetric α-Al_2O_3 ceramic hollow fibers (the internal diameter was approximately 1 mm, the external diameter was approximately 1.4 mm, the average pore size of the outside layer was 200 nm, and the porosity was approximately 60%) were provided by the State Key Laboratory of Chemical Engineering at Zhejiang University, China.

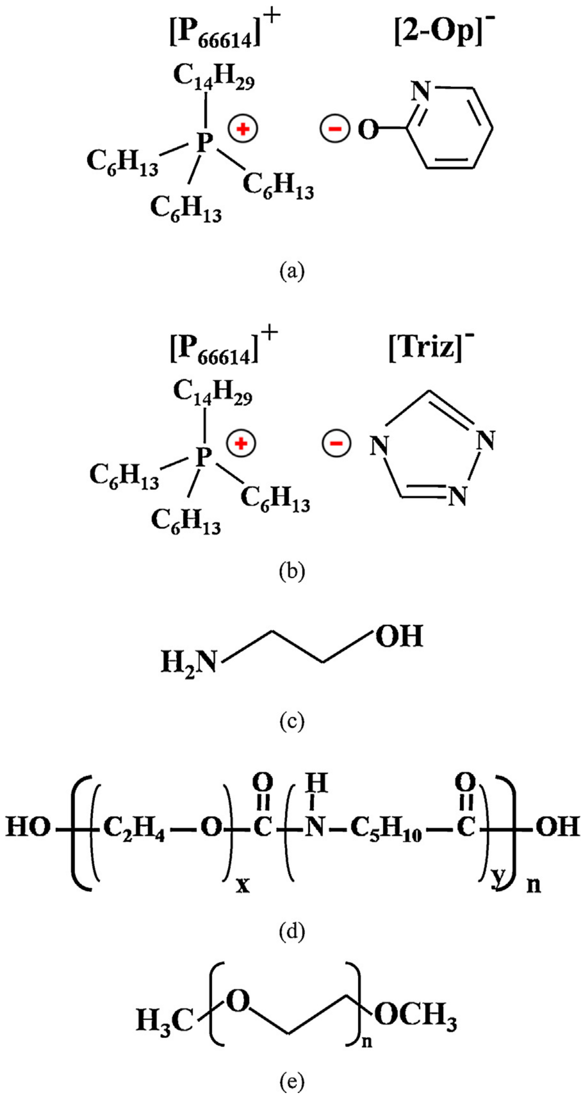

Fig. 1. Chemical structures of [P_{66614}][2-Op] (a), [P_{66614}][Triz] (b), MEA (c), Pebax (d) and PEGDME (e).

2.2. Preparation of Pebax/PEGDME solutions blended with different CO_2 absorbents

Pebax/PEGDME homogeneous solution was primarily prepared using a method described in a previous study [25]. Approximately 2 g of Pebax MH 1657 pellets were dissolved in 38 g of ethanol/water solvent (70/30, weight ratio). Under reflux at 80 °C, the polymer solution was stirred for more than 2 h. After cooling to room temperature, the solution was added with 2 g of PEGDME and then stirred for about 40 min at room temperature. The obtained homogeneous solution was filtered through a stainless steel filter with a pore size of 32 μm and was designated as the Pebax/PEGDME coating solution. The Pebax/PEGDME solution was divided into three parts with same quality. Then, three CO_2 absorbents, namely [P_{66614}][2-Op], [P_{66614}][Triz] and MEA, were respectively added into one part of the solution. The mass ratio of CO_2 absorbent/the (Pebax/PEGDME) solution was 1/210. Solutions were stirred for 0.5 h at room temperature, placed in a microwave bath, and vibrated for other 15 min to ensure that the CO_2 absorbent