Poly(amide-12-b-ethylene oxide)/glycerol triacetate blend membranes for CO_2 separation

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ABSTRACT

In this paper, CO_2-philic membranes are prepared with poly(amide-12-b-ethylene oxide) (Pebax1074) and glycerol triacetate (GTA) by polymer blending, which show excellent compatibility for different GTA compositions. The additive GTA into Pebax1074 matrix can improve the chain mobility, induce high CO_2-philicity and decrease membrane crystallinity. With the increase of GTA mass content from 0 to 80 wt%, CO_2 permeability increases from ~135 to ~1800 Barrer, and CO_2/H_2 ideal selectivity also increases from 10 to 19. For Pebax1074/GTA blend membranes, the threshold mass content of GTA (C^*) which corresponds to the rapid increase of gas permeability is about 40 wt%. When GTA mass content is not more than C^* (40 wt%), the gas permeation properties are mainly dominated by Pebax1074. But for Pebax1074/GTA blend membranes with GTA mass content above C^* (40 wt%), their gas permeabilities and CO_2/light gas selectivities both change dramatically, which are mainly influenced by GTA. These membranes show excellent separation performance for CO_2/N_2 and CO_2/H_2, especially for CO_2/H_2 separation.

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1. Introduction

Recently, concerns about CO_2 emission into the atmosphere based on fossil fuel usage have been growing greatly, because the CO_2 concentration in the atmosphere increases significantly from a pre-industrial value of about 280 ppm in 1750 to 367 ppm in 1999 and to 393 ppm in 2012 (Luis et al., 2012; NOAA, 2012). The continuous increase of CO_2 concentration in the atmosphere will lead to climate change and serious environmental issue (Luis et al., 2012). Therefore, it is extremely important to develop high efficient approaches for carbon capture and storage (CCS). A large number of CO_2 capture processes have been developed, and they are being proposed into the main strategies: post-combustion capture (CO_2/N_2), pre-combustion capture (CO_2/H_2), natural gas treatment (CO_2/CH_4) and so on (Favre, 2011; Ghoniem, 2011; Luis et al., 2012; Scholes et al., 2012; Sridhar et al., 2007). Currently, the main technologies for CO_2 separation include absorption, adsorption, cryogenic separation and membrane separation (Lin and Freeman, 2005). Compared with other separation processes, membrane separation has attracted a number of attentions both in academia and industry due to its high energy efficiency, enhanced space efficiency, absence of moving parts, and low operating costs (Brunetti et al., 2010).

Conventional gas separation membrane materials are usually made from glassy polymers which are based on the solution-diffusion mechanism, such as cellulose acetate, polyimides, polysulfones and perfluoro-polymers (Favre, 2011; Powell and Qiao, 2006; Scholes et al., 2012). Generally, glassy polymer membranes have excellent thermal and mechanical stability, but relatively low CO_2 permeability (Xia et al., 2011). In practical application, it is difficult to meet the required separation demands especially when the CO_2 concentration in gas mixtures is high, because the plasticization induced by CO_2 can significantly decrease gas permselectivity (Lo et al., 2010). In the case of CO_2/H_2 separation, these membranes are more permeable to H_2 than CO_2, resulting in low pressure H_2 product which requires additional recompression (Reijerkerk et al., 2011a). Therefore, in order to improve CO_2 permeation performance, some new rubbery polymers, which usually contain CO_2-philic groups, such as carbonyl, ether, acetate groups, have been developed as membrane materials recently aiming to increase CO_2 solubility and CO_2 solubility selectivity. Generally, CO_2-philic groups are classified as hard bases by Pearson's hard and soft acid–base principles (Pearson, 1963, 1968), and they can interact with the hard acid CO_2 which has a large quadrupole moment (Kauffman, 2001). As is known, the solubility of penetrant gas mainly depends on gas physical properties (condensability) and its interactions with the polymer matrix. Therefore, these functional groups will make polymers CO_2-philic and increase CO_2 solubility.

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Poly(ether-block-amide) (under the trade name Pebax®) is a family of copolymers, consisting of an aliphatic polyamide (PA) as the hard block, a polyether (PE) as the soft block and a diacid serving as the joint between the two blocks (Liu et al., 2004; Yang and Tsai, 2006), where PA is an aliphatic polyamide "hard" block (i.e., nylon 6 [PA6], or nylon 12 [PA12]), and PE is a polyether "soft" block, either poly(ethylene oxide) [PEO] or poly-(tetramethylene oxide) [PTMEO] (Bondar et al., 1999; Mandal and Bhattacharya, 2006). The hard crystalline polyamide block as an impermeable phase provides mechanical strength, and the soft polyether block acts as the permeable phase due to its high chain mobility (Bondar et al., 1999, 2000; Kim et al., 2001). So Pebax is an alternative membrane material for CO_2 separation due to its excellent chemical, mechanical and thermal stabilities as well as good permselectivity (Sampranpiboon et al., 2000). Bondar and Kim reported the gas separation performance for polar (CO_2)/nonpolar $(H_2, N_2,$ and $CH_4)$ gases with different Pebax grades (Bondar et al., 2000; Kim et al., 2001). Because of the strong affinity between ethylene oxide (EO) units and CO_2, the selectivity of CO_2/H_2 for poly(amide-12-b-ethylene oxide) (Pebax1074) can be up to 9.8 (10 atm, 35 °C) and the selectivity of CO_2/N_2 for poly(amide-6-b-ethylene oxide) (Pebax1657) is about 71 (3 atm, 25 °C) (Bondar et al., 2000; Kim et al., 2001). But in order to improve their competitiveness with other separation processes, CO_2 permeability should be improved. Glycerol triacetate (GTA), a nontoxic solvent and plasticizer (Mathew et al., 2005), is a CO_2-philic compound due to its structure analogous to a trimer of polyvinyl acetate (PVAc), which is considered as the most CO_2-philic oxygenated hydrocarbon-based polymer up to date (Miller et al., 2010). It is reported that CO_2 solubility in GTA is about 5 and 6 times as much as that in water and Diesel oil (Redemann et al., 1960), respectively, which could be comparable to CO_2 solvent used in the Selexol process (Miller et al., 2010). Barillas prepared supported liquid membrane using GTA and found that CO_2 permeability and CO_2/H_2 mixed gas selectivity were 1844 Barrer and 8.7 at 37 °C and 0.2 atm, respectively (Barillas et al., 2011). However, the performance of GTA supported liquid membrane can degrade seriously due to the evaporation and 'wash-out' of GTA.

In order to overcome the shortcoming of one single polymer, some efforts have focused on the optimization of membrane materials by tailoring the existing polymers due to the smaller time and lower cost involved than those necessary to obtain new polymers (Hosseini et al., 2008; Kim et al., 1999; Lin and Freeman, 2005; Sridhar et al., 2007). Because of its simplicity, reproducibility and commercial feasibility, polymer blending is considered as an ideal technique to obtain the tailor-made polymeric membrane (Ben Hamouda et al., 2010; Kim et al., 1997; Patrício et al., 2006). Furthermore, the membrane prepared with blended polymers shows better membrane-forming ability, improved mechanical properties and gas performance, which makes polymer blending essential for membrane technology (Ben Hamouda et al., 2010).

In this paper, block copolymer Pebax1074 and GTA are firstly used to prepare CO_2-philic Pebax1074/GTA blend membranes. For the prepared Pebax1074/GTA blend membranes, their physical properties are characterized by DSC, FT-IR, XRD and SEM firstly, and the composition-dependent glass transition temperature (T_g) is analyzed. Then the gas permeation characteristics of CO_2, N_2, H_2 and CH_4 are investigated for Pebax1074/GTA blend membranes with different GTA mass content. The threshold mass content of GTA (C^*) corresponding to the rapid increase of gas permeabilities is obtained. And gas transport processes are described in two different zones according to C^*. Finally, the ideal selectivities of CO_2/N_2 and CO_2/H_2 versus CO_2 permeability are discussed with the literature data.

2. Experimental

2.1. Materials

Pebax® MV 1074 (Pebax1074), in the form of elliptic pellets, was supplied by Arkema. Glycerol triacetate (GTA) was obtained from Acros and used without further purification. 1-Butanol was bought from Tianjin Bodi Chemical Engineering Co., Ltd. All gases used for gas permeation test were of research grade (>99.9% pure), and they were supplied from Dalian Gas Company. All gases and solvents were used as received.

2.2. Membrane preparation

1-Butanol was used as the solvent to prepare 5 wt% of Pebax1074 polymer solution with continuous stirring under reflux at 80 °C. After a homogenous solution was obtained, different amounts of GTA were added ranging from 20 to 80 wt% relative to the total amount of GTA and Pebax1074, and the solution was kept stirring at 80 °C continuously. After the homogenous solution was obtained again, it was kept still at 80 °C for at least 24 h to remove gas bubbles. And then the bubble-free solution was cast on a Teflon ring mold. The generated membranes were dried at about 50 °C for 15 h to evaporate the solvent. Subsequently, homogeneous dense membranes were stripped from the Teflon ring mold and further dried in a vacuum oven at room temperature for at least 3 days to remove residual solvent. Although mechanical strength measurements were not conducted on the membranes, it was obvious from handling the membranes that the membrane strength diminishes with increasing GTA content.

2.3. Membrane characterization

Thermal properties of samples were characterized in the temperature range from −100 to 200 °C using Q2000 DSC (TA, USA). Measurements were performed at the scan rate of 10 K/min.

FT-IR spectra characterizations of the membrane samples were obtained in ATR (attenuated total reflectance) mode on Nicolet 6700 (ThermoFisher) instrument and the scanning range was from 4000 to 650 cm^{-1}.

A wide-angle X-ray diffractometer (PANalytical B.V. X'pert) was utilized to determine the structures of the membranes at room temperature. The angle (2θ) of diffraction was varied from 5° to 70° to identify the crystal structure.

The dried membrane samples were sputtered with a thin layer of gold using Quorum Q150T Sputtering Device. The surface and cross-sectional morphologies of the prepared membranes were studied by FEI SEM using a NOVA Nanosem 450 microscope.

The gas permeabilities for prepared membranes were determined using a constant volume/variable pressure method. Generally, the feed pressure was controlled from 0.2 MPa to 1.0 MPa (Bondar et al., 2000; Chen et al., 2010; Muñoz et al., 2008; Reijerkerk et al., 2010). So in this paper, the feed pressure was set to 0.5 MPa for all gases. The permeation cell was a stainless steel holder with an area of 7.07 cm^2. It should be careful to mount the membrane composed of 80 wt% GTA into the permeation cell due to its frail property. Before testing, both upstream and downstream volumes were exposed to vacuum overnight for degassing.

Gas permeability was calculated from the steady-state rate of pressure increase in a fixed downstream volume, the equation was as follows:

$$P = \frac{1}{760} \cdot \frac{V}{A} \cdot \frac{273.15}{T} \cdot \frac{l}{\Delta p} \cdot \frac{dp}{dt} \tag{1}$$

where P is the gas permeability $(cm^3(STP) cm cm^{-2} s^{-1} cmHg^{-1})$, and it is usually characterized using unit of Barrer