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Interfacially polymerized polyetheramine thin film composite membranes with PDMS inter-layer for CO_2 separation

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ABSTRACT

Polyether based thin film composite (TFC) membranes were developed by interfacial polymerization (IP) on polysuylfone (PSf) ultra-filtration membrane with poly (dimethylsiloxane) (PDMS) inter-layer. Polyetheramine (PEA) and Trimesoyl Chloride (TMC) were selected as aqueous monomer and organic monomer, respectively. The thickness of the PDMS inter-layer was 550 nm, while IP separation layer was only 100 nm. The effects of the PDMS inter-layer and the PEA molecular weight on the TFC membrane performance were investigated. The gas permeation results show that the TFC membrane with PDMS inter-layer exhibits higher CO_2/N_2 selectivity compared to the membranes without PDMS inter-layer. PDMS inter-layer is able to eliminate the defects on the support membrane and diminish the TMC hydrolysis as well. Among the membranes prepared with three different molecular weight PEAs (ED-600, ED-900 and ED-2003), the membrane of ED-900 exhibits the best performance with an impressive CO_2 permeance of 360 GPU and CO_2/N_2 selectivity of 67.2 for a mixture CO_2/N_2 (20/80 by volume), while for a mixture of CO_2/CH_4 (10/90 by volume) it demonstrates CO_2 permeance of 275 GPU and CO_2/CH_4 selectivity of 31.6.

1. Introduction

Due to the “green house” effect, the removal of CO_2 from flue gas and natural gas has attracted considerable attention. A wide variety of technologies have been proposed to capture CO_2 such as absorption, adsorption, and membrane technology. Among the CO_2 separation methods, membrane technology is extremely attractive for its energy efficiency, simplicity and compact modular structure. Recent efforts have focused on improving membrane performance for CO_2 separation.

Polymers containing ether groups, especially poly (ethylene oxide) (PEO) based polymeric materials, are attractive for CO_2 removal due to the strong affinity between CO_2 and ether groups. The strong affinity to CO_2 can increase CO_2 solubility in the membrane and provide high CO_2 permeability and CO_2/light gas selectivity [1–6]. Due to high ether group content, PEO has been regarded as a very promising membrane material for CO_2 separation. However, PEO suffers from high crystallinity and weak mechanical properties. The formation of crystal is generally deleterious, since it acts as impermeable obstacle to gas molecular transport. Unlike polyimide and cellulose acetate membranes, PEO cannot be used to prepare asymmetric membrane with an ultra-thin separation layer due to weak mechanical properties.

To overcome the inherent drawbacks of PEO, several studies have focused on the PEO-based block copolymers and cross-linked PEO membranes [7–10,30,31]. Freeman [7] reported four kinds of phase-separated polyether-b-polyamide segmented block copolymer membranes with thickness of 25–36 μm. These membranes demonstrated CO_2 permeabilities of 66–221 Barrers (1 Barrer $= 7.5 \times 10^{-15}$ m^3(STP) m/m^2 s KPa) and CO_2/N_2 selectivities of 23.4–56.4. Liu et al. [8] prepared poly(ether block amide)/polysulfone (PEBA/PSf) composite hollow fiber membrane for CO_2/N_2 separation with CO_2 permeability of 260 Barrer and CO_2/N_2 selectivity of 32. Car et al. [9,30] prepared poly(ethylene oxide)-poly (butylene terephthalate) segmented copolymer (PEO-PBT) membranes with CO_2 permeability of 122–750 Barrer and CO_2/N_2 selectivity of 40–51.5. Ijzer [10] and Reijerkerk [11] randomly incorporated poly(propylene oxide) (PPO) with PEO in segmented block copolymer membranes, in which ploymer crytallinity was completely suppressed. In these membranes, the polyamide and polyester domains provide the mechanical strength, whereas the polyether domains offer the membrane high CO_2 permselectvity.

Besides the block copolymers containing PEO segments, the cross-linked PEO membrane is another kind of PEO-based membranes. Freeman and coworkers [2,12–15] prepared a series of crosslinked PEO membranes. In these studies the effects of chemical composition and cross-linking density on the gas permselectivity were investigated; the

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crosslinked PEO membranes displayed CO_2 permeabilities of 145–300 Barrer and CO_2/N_2 selectivities of 41–66. Patel [16] prepared crosslinked PEG membrane incorporated with fume silica nanoparticles (PEGda/FS). The membrane displayed CO_2 permeability of 70 Barrer and CO_2/N_2 selectivity of 60–70. Enick [32] reported cross-linked polytetramethylene ether glycol (PTMEG) membrane with a CO_2 permeability of 329 Barrer and a CO_2/H_2 selectivity of 5.6.

Both block copolymer membranes with segmented PEO segments and crosslinked PEO membranes are able to suppress the crytallinity of the PEO, and thereby these membranes are able to display high CO_2 permeability. However, due to the difficulty in the preparation of PEO-based thin film membranes, most of the PEO based membranes have a relatively low CO_2 permeance. Recently, Liu et al. [17] prepared an ultrathin poly (ether block amide) membrane based on spontaneous spreading of block copolymer solution on water surface. Yave [6] reported a nanometric thin composite membrane by dip-coating the polymer solution on polyacrylonitrile support with PDMS inter-layer. Ren et al. [31] prepared PEI/PDMS/PEBA/PDMS multi-layer composite membrane with a PEBA layer thickness of 0.5 μm. The membrane displayed a CO_2 permeance of 157GPU and CO_2/N_2 selectivity of 64.

As for crosslinked PEO membrane, the preparation of thin film membrane is more difficult. For example, the crosslinked PEO membrane is prepared by mixing low molecular weight monomer and crosslinker together, and then mixture is casted on quartz plates to form a homogenous film [15]. The thickness of the crosslinked membrane in the literature is about 20–600 μm [15,16]. Due to the membrane thickness, the reported cross-linked PEO membranes showed a very low CO_2 permeance. There are several methods to crosslink PEO-based polymers such as photo crosslinking [5,12–14], free radical crosslinking [16,24], and thermal crosslinking [32]. Recently, Wang [18] prepared a cross-linked PEO membrane with an ultra-thin selective layer using interfacial polymerization (IP) technology. The results showed that the membrane demonstrated a high CO_2 permeance.

On the basis of the studies mentioned, in this study a cross-linked polyether thin film composite (TFC) membrane was developed by interfacial polymerization on a polysulfone (PSf) support. Commercially available polyether diamines, polyetheramine, were selected as water soluble monomers. Trimesoyl chloride (TMC) was used as monomer of organic phase. Polyetheramine has repeated ether groups in the chain and amino groups on the end of chain. The ether groups in polyetheramine enable the membrane to achieve high CO_2 permselectivity due to the strong affinity between ether group and CO_2. The amino groups on the end of polyetheramine chain react with TMC to form cross-linked network in the interfacial polymerization process. To minimize the defects on the membrane and the hydrolysis of TMC, a PDMS inter-layer was introduced into the TFC membrane. The developed membranes have a very thin separation layer (100 nm).

2. Materials and methods

2.1. Materials

The polysulfone (PSf) ultra-filtration membrane with an average cut-off molecular weight of 6000 Da was supplied by Vontron Technology Co., Ltd. (China). Polyetheramines (PEA) with different molecular weights (ED-600, ED-900 and ED-2003) were supplied by Huntsman International LLC. (USA). Trimesoyl chloride (TMC) purity (99.5%) used as an active monomer in organic solution was supplied by Qingdao Benzo Chemical Co. Ltd. (China). Polydimethylsiloxane (PDMS) was obtained from Shin-Etsu Chemical Co., Ltd. (Japan). Tetraethyl orthosilicate (TEOS), ditin butyl dilautate (DBD) and Na_2CO_3 were of analytical grade and purchased from Aladdin Industrial Inc. (China). All chemicals were used without further purification.

2.2. Membrane preparation

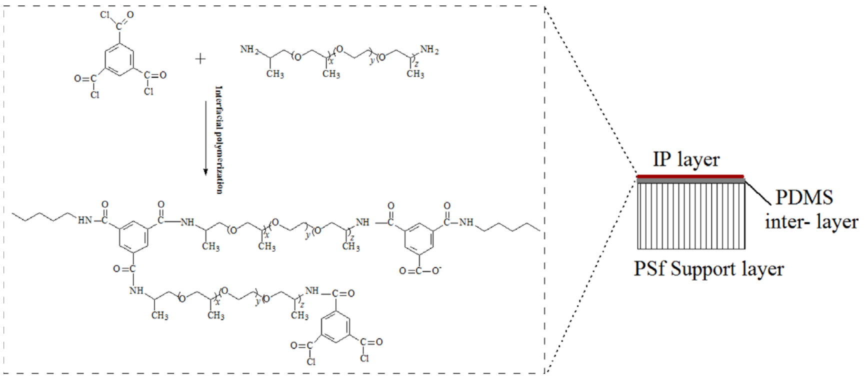
The basic scheme of the TMC-PEA/PDMS/PSf membrane structure is presented in Scheme 1.

PSf support with PDMS inter-layer was prepared by following process:

1. PDMS, DBD and PEOS (in the ratio 3:1:1 by weight) were dissolved in heptane to obtain a colorless solution with PDMS concentration of 3 wt%. Then the PDMS solution was degassed for 30 min before casting.
2. This bubble free solution was casted on the PSf support and dried at room temperature for 5 h and then placed in an oven at 75 °C for 48 h.

TMC-PEA/PDMS/PSf membrane was prepared by interfacial polymerization.

1. TMC was dissolved in hexane to form TMC solution (0.015 mol/L). The PDMS modified PSf support was immersed into TMC solution for 10 min. Then the excess solution was removed



ED-600 $y \approx 9,\ (x+z) \approx 3.6$

ED-900 $y \approx 12.5,\ (x+z) \approx 6$

ED-2003 $y \approx 39,\ (x+z) \approx 6$

Scheme 1. Structure of polyether based membrane prepared by interfacial polymerization.