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Enhanced CO_2 separation properties by incorporating poly(ethylene glycol)-containing polymeric submicrospheres into polyimide membrane

Shaofei Wang [a,b], Zhizhang Tian [a,b], Jiangyan Feng [b], Hong Wu [a,b], Yifan Li [a,b], Ye Liu [a,b], Xueqin Li [a,b], Qingping Xin [a,b], Zhongyi Jiang [a,b,*]

[a] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China*
[b] *Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China*

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ABSTRACT

Poly(ethylene glycol)-containing polymeric submicrospheres (PEGSS) were synthesized via distillation precipitation polymerization and incorporated into polyimide (PI) matrix to prepare hybrid membranes. The PEGSS and hybrid membranes were characterized by Fourier transform infrared (FTIR) spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Single gas permeabilities of N_2, CH_4 and CO_2 were measured by using the time-lag method. The hybrid membranes showed enhanced CO_2 permeability and CO_2/N_2, CO_2/CH_4 selectivities at low PEGSS loadings. The favorable affinity between PEGSS and CO_2 greatly enhanced CO_2 solubility and thus CO_2 permeability. Whereas, N_2 and CH_4 permeabilities both decreased for the tortuous gas transport pathways by PEGSS incorporation. Particularly, PI–PEGSS(20) membrane, with 20 wt% PEGSS loading, showed 35% of increase in CO_2 permeability and 104% of increase in CO_2/N_2 selectivity compared with those of pristine polyimide membrane.

1. Introduction

Energy-efficient and scalable carbon capture from large emission sources, e.g. flue gas, syngas and natural gas, stands as one of the greatest challenges [1]. Among various separation technologies, membrane gas separation has evolved as a green and affordable alternative [2] owing to its intrinsic advantages such as small footprint, low capital and operating costs [3]. Currently, polymers with good mechanical stability and scale-up simplicity constitute the most promising candidates for large-scale applications [4].

Polyimides are a family of glassy polymers synthesized via polymerization of various diamine and dianhydride monomers. In recent years, polyimides have attracted considerable attention due to their excellent CO_2 separation performance, high chemical resistance, superior thermal stability and mechanical strength [5,6]. However, gas permeation properties of the existing polyimide materials need continuous exploitation to better meet the requirements for practical applications [7]. Great deal of strategies have been put forward to enhance the performance of polyimide membrane. Specific tailoring of the polyimide molecular structure to suppress polymer chain packing and increase fractional free volume has been demonstrated a commonly applied method [8,9]. Another facile and promising alternative is fabricating hybrid membranes.

Hybrid membranes, comprising a polymer bulk phase and a dispersed filler phase, offer an approach to synergistically combine the favorable properties of two moieties and may open up additional opportunities for better exploration of the existing polyimides [10,11]. Therefore, a broad range of porous fillers with good size sieving ability (e.g. metal organic frameworks (MOFs) [12–14], zeolites [15], carbon molecular sieves [16]) have been attempted to endow the membranes with enhanced diffusivity and diffusivity selectivity. Meanwhile, incorporating fillers with polar groups that favorably interacted with CO_2 may confer the membrane with enhanced CO_2 solubility and thus permeability [5,17,18]. This approach may be more effective for glassy polymers with high intrinsic diffusivity selectivity. For instance, MCM-41 was functionalized with $–SO_3H$ and incorporated into Matrimid to fabricate hybrid membranes. The resultant membranes showed up to 31% increase in CO_2 permeability and 14% increase in CO_2/CH_4 selectivity partially because of the polar $–SO_3H$ groups, which increased the affinity of fillers towards CO_2 molecules [19]. Since

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[*] Correspondence to: Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, 92# Weijin Road, District Nankai, Tianjin 300072, China. Tel./fax: +86 22 23500086.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

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CO_2 with double bond may react reversibly with transition metal ions to form a π-bonded complex, novel POSS–Matrimid–Zn^{2+} hybrid membranes were prepared and an obvious increase of CO_2 solubility was verified by CO_2 sorption tests [20]. However, functional groups with strong polarity in membranes may increase polymer chain rigidity and decrease fractional free volume of membranes, which is detrimental to gas diffusivity [18].

Low molecular weight poly(ethylene glycol) (PEG) with abundant polar ether groups could produce dipole–quadrupole interactions with CO_2 and has been recognized as an effective polymer to achieve high CO_2 permeability and CO_2/other gas selectivity [18,21,22]. Numerous efforts have been devoted to explore PEG-containing blend membranes [23], copolymer membranes [24] and hybrid membranes [25,26] for efficient CO_2 separation. Considering the moderate polarity of PEG and the favorable affinity between PEG and CO_2, rationally designed PEG-containing fillers may act as solubility promoter without causing polymer chain rigidification in membranes. However, rare efforts have been devoted to employ PEG-containing filler in hybrid membranes, especially in glassy polymer matrix [27,28].

Therefore, in this study, PEG-containing polymeric submicrospheres (PEGSS) were synthesized as fillers to prepare hybrid membranes. Matrimid 5218 was utilized as the polymer matrix for its excellent mechanical stability and commercial availability. PEGSS with low molecular weight PEG are designed to tune the interaction between the filler and polymer matrix and may produce desirable polymer–filler interface morphology. Fourier transform infrared (FTIR) spectra, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements were conducted to acquire an in-depth insight of chemical structure and thermal properties of the hybrid membranes. N_2, CH_4 and CO_2 diffusivities, solubilities and permeabilities of hybrid membranes with different filler loadings were measured to investigate the relevant transport property in these membranes. Moreover, effect of operating temperature on gas permeability was studied.

2. Experimental

2.1. Materials

Matrimid 5218 (PI), poly(ethylene glycol) methacrylate (PEGMA) and ethylene glycol dimethacrylate (EGDMA) with an average of 8.3 ethylene glycol units were purchased from Alfa Aesar China Co., Ltd. Methacrylic acid (MAA), 2, 2′-Azoisobutyronitrile (AIBN), N,N-dimethylformamide (DMF) and ethanol were purchased from Tianjin Guangfu Fine Chemical Engineering Institute. Acetonitrile was purchased from Tianjin Kewei Co., Ltd. Chemical structures of EGDMA, MAA and PEGMA are shown in Fig. 1.

2.2. Synthesis of PEGSS

The PEGSS, a block copolymer named poly{[poly(ethylene glycol) methyl etheracrylate]-co-(acrylic acid)}, were synthesized by applying the precipitation polymerization method reported by Dai et al. [29]. In a typical synthesis, 600 μL PEGMA, 400 μL MAA, 600 μL EGDMA and 0.036 g AIBN were added to a 100 ml flask with 80 ml acetonitrile. Then the mixtures were heated to boiling state and reacted for 60 min. Subsequently, the products were separated and purified by centrifugation at 8000 rpm for 10 min. Afterwards, the PEGSS were dried in a vacuum oven at 40 °C for 2 days before use.

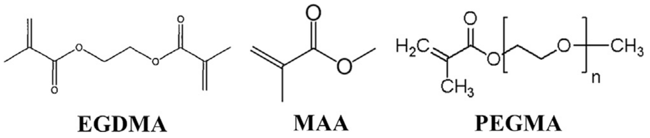

Fig. 1. Chemical structures of EGDMA, MAA and PEGMA.

2.3. Preparation of hybrid membranes

Pristine PI and hybrid membranes were prepared by a solution casting method. To be specific, certain amount of as-synthesized PEGSS was first added into DMF solvent and sonicated for 1 h (10 KHz, below 30 °C) to get a homogeneous dispersion of PEGSS. Then PI powder was added to the suspension and stirred for 5 h. After sonication for one more hour, the suspension was cast onto a glass mold placed in an oven. The solvent evaporation process was conducted at 50 °C for 12 h. Afterwards, the membranes were treated for 12 h at 80 °C and another 48 h at 120 °C. The resultant membranes with 55 ± 4 μm thickness were denoted as PI–PEGSS (*X*), where *X* (5, 10, 20, 30) represents the mass percentage of PEGSS to PI. The densities of PEGSS and hybrid membranes were calculated based on the Archimedean principles after measuring the weight of the membranes in air and in ethanol by using a density meter.

2.4. Characterization of PEGSS and membranes

2.4.1. Transmission electron microscopy (TEM)

The size as well as morphology of the synthesized PEGSS was observed by a JEOL, Tecnai G2 F20 transmission electron microscope.

2.4.2. Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra for PEGSS, pristine PI and hybrid membranes were obtained by using a BRUKER Vertex 70 Fourier transform infrared spectrometer with scan range of 4000–400 cm^{-1} and resolution of 1.93 cm^{-1}. The hybrid membranes were measured directly whereas the PEGSS were prepared in KBr pellets.

2.4.3. Field emission scanning electron microscope (FESEM)

Membrane cross-sectional morphology and dispersion of PEGSS in hybrid membranes were examined with a Nanosem 430 field emission scanning electron microscope operated at 10 kV. Before analyzing, membranes were cryogenically fractured in liquid nitrogen and then sputter-coated with a thin layer of gold.

2.4.4. X-ray diffraction (XRD)

The crystal structure of the membranes were recorded on a Rigaku D/max 2500 v/pc X-ray diffractiometer (XRD) in the range of 5–50° at the scan rate of 3 °/min. The X-rays of 1.5406 Å wavelength were generated by a Cu Kα source.

2.4.5. Differential scanning calorimeter (DSC) measurements

Glass transition temperatures (T_g) of the membranes were analyzed by a Netzsch DSC 200F3 calorimeter. The measurements were performed from 50 to 400 °C at a heating rate of 10 °C/min. Nitrogen was used as a purge gas with a flow rate of 20 ml/min. T_g was determined as the midpoint temperature of the transition in the DSC curve.

2.5. Gas permeation experiments

A custom-built apparatus based on the well-established constant volume/variable pressure method was utilized [26] to