Journal of Membrane Science 385–386 (2011) 40–48

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Polyetheramine–polyhedral oligomeric silsesquioxane organic–inorganic hybrid membranes for CO_2/H_2 and CO_2/N_2 separation

Mei Ling Chua [a], Lu Shao [b], Bee Ting Low [a], Youchang Xiao [a], Tai-Shung Chung [a],*

[a] *Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 119260, Singapore*
[b] *Department of Polymer Science and Engineering, Harbin Institute of Technology, 150001, China*

ARTICLE INFO

Article history:
Received 13 May 2011
Received in revised form 2 September 2011
Accepted 6 September 2011
Available online 28 September 2011

Keywords:
Carbon capture
CO_2-selective membrane
PEA
PEO
POSS

ABSTRACT

In this study, composite polyetheramine (PEA)–polyhedral oligomeric silsesquioxane (POSS) membranes were successfully fabricated for carbon dioxide/hydrogen (CO_2/H_2) and carbon/nitrogen (CO_2/N_2) separation. The organic functional groups on the POSS cage and its small particle size enhanced its compatibility with PEA. With the optimized conditions for membrane fabrication, a uniform distribution of POSS particles across the membranes could be observed from the SEM–EDX analysis. With the weight ratio of PEA:POSS 50:50, the crystallinity of the membranes is significantly suppressed as observed in the reduction of the melting point to 2.6 °C, compared with the original PEA melting point of 37.4 °C. In addition, the mechanical strength of the soft PEA is enhanced. A high CO_2 permeability of 380 Barrer with a moderate CO_2/N_2 selectivity of 39.1 and a CO_2/H_2 selectivity of 7.0 are achieved at 35 °C and 1 bar for PEA:POSS 50:50 membrane. The relationship between gas transport properties and membrane composition is elucidated in terms of PEA/gas interaction and nanohybrid structure. Fundamental study on the effect of temperature and pressure on the performance of the membranes were also carried out. The gas permeability through the membrane is found to increase at the expense of selectivity with the increase in temperature. At higher upstream gas pressure during permeation tests, improvements are observed in both CO_2 permeability and ideal CO_2/H_2 and CO_2/N_2 selectivity due to the plasticization effect of CO_2. The CO_2/N_2 selectivity of the membrane is found to decrease considerably under the binary mixture because of competitive sorption between CO_2 and N_2 in the membranes.

1. Introduction

The typical separation of carbon dioxide from gas mixtures using amine absorption is an energy-intensive process and it involves the need to regenerate the solvent. Membrane technology offers an attractive alternative to amine absorption due to its higher energy efficiency, small footprint and environmental friendliness feature [1]. A suitable candidate for fabricating gas separation membranes is polymeric materials as the cost is low and it can be easily processed into different configurations [2]. However, the relatively low performance of commercial polymers and the sensitivity towards harsh process conditions of gas streams (pressure, temperature, high flow rates) are some of the drawbacks of polymeric membranes [3,4]. This drives the researchers to develop membrane materials that exhibit better performance and that are robust enough for long-term operations.

Over the last few years, poly(ethylene oxide) (PEO), a semi-crystalline polymer, has gained interests as a feasible material to fabricate carbon dioxide-selective membranes for carbon dioxide/hydrogen (CO_2/H_2) and carbon dioxide/nitrogen (CO_2/N_2) separations [5–14]. Its strong affinity to carbon dioxide due to the polar ether groups present allows preferential removal of carbon dioxide. However, its shortcomings such as tendency to crystallize due to its semi-crystalline nature and weak mechanical strength have restricted its applications [5]. Incorporating PEO with other monomers as copolymers or as polymer blends or crosslinking it are some of the strategies done to overcome the drawbacks of PEO and improve the gas separation performance. Okamoto and co-workers fabricated PEO-segmented copolymers with various hard segments [6]. Peinemann's group blended different low molecular weights of poly(ethylene glycol) (PEG) with synthesized PEO-PBT (poly(butylene terephthalate)) and commercial Pebax® respectively [7,8]. Enhancement in the gas separation performance of the membranes was observed. CO_2 permeability increased by eight-fold to more than 850 Barrer for the Pebax membrane blended with 50 wt% of PEG-dimethyl ether. The CO_2/N_2 selectivity was 31. Reijerkerk et al. also attempted to blend an additive, PDMS (poly(dimethyl siloxane))–PEG, into Pebax with the aim to enhance the membrane performance with the aid of highly permeable and flexible PDMS and highly selective PEO [9]. CO_2 permeability was

---

* Corresponding author. Tel.: +65 65166645; fax: +65 67791936.
E-mail address: chencts@nus.edu.sg (T.-S. Chung).

0376-7388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2011.09.008

improved by five times to 530 Barrer at 50 wt% of PDMS–PEG. The increase in permeability was mainly ascribed to the increase in diffusivity due to the incorporation of PDMS. Freeman's group applied ultraviolet light to crosslink different ratios of PEG diacrylate (PEGDA) and PEG methyl ethyl acrylate (PEGMEA) [10]. The resultant structure had a hyperbranched network in which crystallization of PEO was restricted. Siloxane-based monomers were incorporated with PEO acrylates with the intention to increase permeability [11,12]. The CO_2 permeability was enhanced while the selectivity decreased. Shao and Chung also explored the addition of silane as a crosslinking agent to form PEO-based membranes. This strategy hindered the formation of crystals which in turn increased the permeability of PEO [13]. Further studies by grafting PEG methacrylate (PEGMA) and blending PEG into the polymer matrix had improved the performance of the membranes significantly by 5 folds and 2.5 folds, respectively [14,15]. Thus, combining with highly permeable groups and fabricating it as an organic–inorganic hybrid network seems to be a promising strategy to enhance the inherent properties of CO_2-selective PEO.

Polyhedral oligomeric silsesquioxane (POSS), a molecule with cage-like rigid structure of particle size ranging from 1 to 3 nm, may be another suitable candidate to crosslink PEO to attain high performance gas separation membranes. The functional side groups available on the POSS cage structure allow POSS molecules to possess good chemical reactivity and compatibility with many polymer systems [16]. Furthermore, the small particle size of POSS enables it to have better dispersion at molecular level in the membranes [17,18]. The formation of a crosslinked network may disrupt the PEO crystals arrangement and potentially reduce the crystallinity. In addition, the bulky POSS molecules may aid to increase free volume and the cage may provide a possible pathway for gas transport. Simulation results showed that the distance between two diametrical opposite silicon atoms in each face was approximately 4.442 Å, which is larger than the kinetic diameter of carbon dioxide and nitrogen [19]. An attempt by Dominguez et al. to exploit the above-mentioned advantages of POSS molecules has demonstrated that the permeability of oxygen and nitrogen increased with the inclusion of POSS with polystyrene as copolymers [20]. This rise in permeability could be attributed to the increase in free volume contributed by the bulky POSS molecules.

In this study, we aim to explore the feasibility of fabricating an organic–inorganic hybrid membrane combining the various advantages of a polyetheramine (PEA), which contains predominately PEO backbone, and POSS for CO_2/H_2 and CO_2/N_2 separation, which are the major components in the pre-combustion and post-combustion capture of carbon dioxide respectively. Different compositions of PEA and POSS are fabricated. The physiochemical and mechanical properties of the membranes are characterized and the effects of varying POSS composition, testing pressure and temperature on gas performance of the membranes are evaluated.

2. Experimental

2.1. Materials and membrane fabrication procedure

Poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) (PEA) with M_n 2000 g/mole (approximately 85 wt% of PEO) was purchased from Sigma–Aldrich and was chosen as the source for PEO due to its low cost and widespread availability. Glycidyl polyhedral oligomeric silsesquioxane (POSS®) cage mixture, acquired from Hybrid Plastics, Inc, was selected to react with PEA to form epoxy-amine crosslinked organic–inorganic hybrid membranes. Tetrahydrofuran (THF), obtained from Merck, was used as the solvent to dissolve PEA and POSS. All the chemicals were used as received. The respective chemical structure of the starting materials is illustrated in Fig. 1. To fabricate the membrane, PEA and POSS were dissolved in THF at various compositions to prepare a homogeneous solution containing 2 wt% solid concentration. The solution was then heated under reflux at 60 °C for 3 h to initiate the reaction between the epoxy groups in POSS and the amino groups in PEA [13]. After sonicating for 10 min to remove the trapped gases, the solution was slowly casted onto a Telfon dish and placed in the oven at 40 °C. A glass plate was used to cover the Telfon dish to allow slow evaporation of the solvent. The dried membrane was peeled off and further annealed under vacuum at 120 °C for 12 h. The membrane preparation procedure is depicted in Fig. 2. All the membrane samples were kept in the dry box after fabrication. The ratio of PEA to POSS is represented by PEA:POSS *X*:*Y* in the subsequent figures, where *X* and *Y* are the weight ratio of PEA and POSS, respectively.

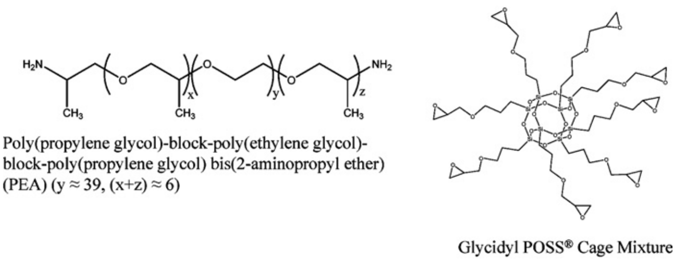

Fig. 1. Chemical structure of the starting materials for fabricating the hybrid membranes.

2.2. Membrane characterizations

Analytical tools were employed to verify the structure and characterize the physical properties of the fabricated membranes. The bond vibration of the various groups of atoms in the polymer matrix was detected by a Perkin-Elmer Fourier Transform Infrared spectrometer (FTIR-ATR) (Spectrum 2000). The wavenumber domain obtained ranged from 4000 cm^{-1} to 600 cm^{-1}. Scanning electron microscope and electron dispersive X-ray analysis (JEOL JSM-6360LA) was employed to examine the distribution of POSS in the membranes (SEM–EDX). The density of the crosslinked network was measured using a gas pycnometer (Quantachrome Ultrapyc 1200e) where helium was used to determine the volume of the samples. The inter-chain spacing (d-space) and the crystallinity of the membranes were analyzed at room temperature by an X-ray diffractometer (Bruker D8 advanced diffractometer). The X-ray source used was Ni-filtered Cu Kα rays at the wavelength of $\lambda = 1.54$ Å. The dimension spacing between diffracting planes (d-space) can be computed based on the Bragg's law.

$$n\lambda = 2d\ \sin\theta \tag{1}$$

where *n* is an integer, λ is the wavelength of the X-ray source and θ is the diffraction angle.

The thermal properties of the membranes were analyzed by using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA). The membranes were tested under N_2 environment (100 ml/min) using DSC822^e (Mettler Toledo) at temperatures ranging from −100 °C to 100 °C. The ramping rate was set at 10 °C/min. The first cycle of ramping and cooling of the sample was to eliminate any thermal history. The second heating curve was used for further analysis. TGA was performed on Perkin-Elmer TGA 7. The temperature was ramped at 10 °C/min from 25 °C to 800 °C. N_2 was used as the purging gas and the flow rate was maintained at 100 ml/min.

The mechanical strength of the membranes was tested using a nano-indentor (Agilent Nanoindentor XP). A 5 mN load was placed