Chemical Engineering Science 160 (2017) 236–244

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Thin poly(ether-block-amide)/attapulgite composite membranes with improved CO_2 permeance and selectivity for CO_2/N_2 and CO_2/CH_4

Long Xiang[a], Yichang Pan[a,*], Jinlong Jiang[b], Ye Chen[c], Jing Chen[b], Lixiong Zhang[a], Chongqing Wang[a,*]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China
[b] Jiangsu Provincial Key Laboratory of Palygorskite Science and Applied Technology, Huaiyin Institute of Technology, Huaian 223003, PR China
[c] State Key Laboratory for Modification of Fiber Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, PR China

ARTICLE INFO

Keywords:
Mixed matrix membrane
Gas separation
Carbon dioxide separation
Attapulgite

ABSTRACT

Composite membrane with a thin selective layer on porous polymer substrate is more attractive than the asymmetric polymer membrane. In this study, a thin layer of attapulgite-poly(ether-block-amide) (ATP-Pebax) hybrid material was successfully deposited on a porous polyacrylonitrile (PAN) support to form a composite membrane. The poly[1-(trimethylsilyl)-1-propyne] (PTMSP) gutter layer plays the crucial role in decreasing the thickness of ATP-Pebax selective layer due to its superior hydrophobicity. A contact 2 wt% ATP-Pebax selective layer (~700 nm) was successfully deposited on the PAN support. The CO_2 permeance on the composite membrane was significantly improved from 2.6 to 108 GPU, compared with the 2 wt% ATP-Pebax freestanding membrane. The ideal selectivity for CO_2/N_2 and CO_2/CH_4 were also enhanced by 35% and 16%, respectively. The gas permeability in ATP fillers were achieved by adsorptive measurements and validated by the generalized Maxwell model for ATP-Pebax hybrid materials. The effect of the feeding pressure and permeating temperature on both single and mixed gas permeation were examined. The separation performance on the composite membranes under dry and humidified-state feeding were also compared. The optimized separating performance of the thin ATP-Pebax composite membrane are attractive for potential applications like natural gas sweetening or biogas purification.

1. Introduction

Membrane-based CO_2 separation is considered as a promising alternative in terms of energy consumption and cost effectiveness (Merkel et al., 2010; Kim and Nair, 2013; Rezakazemi et al., 2014; Seoane et al., 2015). Polymeric membranes have already been successfully demonstrated in natural gas sweetening and oil recovery, but are always subject to a trade-off between permeability and selectivity, which is well known as Robeson's upper bound (Robeson, 1991, 2008). To overcome this, mixed matrix membranes (MMMs) integrating appropriate polymer and filler materials is considered as an effective alternative for improvement of CO_2 membrane separation (Moore et al., 2004; Chung et al., 2007; Kim et al., 2013; Dong et al., 2013).

Although the permeation results of inherently rigid polyimides with aromatic structure are close to or above the upper-bound curve, the complex synthesis procedure and low yield always limit their extensive application as polymer matrix for MMMs (Robeson, 2008; Freeman, 1999; Buonomenna et al., 2012). On the contrary, Poly(ether-block-amide) polymer (Pebax), a commercial rubbery copolymer material, is considered as an ideal candidate for CO_2-based MMMs (Bondar et al., 2000). The rubbery property of Pebax endows the well integration of inorganic fillers compared with the glassy polymer, and their polyethylene oxide (PEO) and polyamide (PA) segments inside the Pebax matrix can separately provide high CO_2 permeability and robust mechanical strength to the membrane. As a result, Pebax matrices have been blended by various fillers, including zeolites (Surya Murali et al., 2014), graphene oxide (Shen et al., 2015), carbon nanotubes (Zhao et al., 2014), mesoporous silica (Kim and Lee, 2001; Wu et al., 2014) and metal-organic frameworks (Li et al., 2013; Nafisi and Hägg, 2014), by virtue of the special transport mechanism and preferential CO_2 transporting on above fillers (Wijmans and Baker, 1995; Pandey and Chauhan, 2001). The resulting MMMs exhibited enhanced either permeability or selectivity (or sometimes both), compared with the pristine Pebax membrane.

Recently, we also first demonstrated that a natural clay attapulgite (ATP) can be used as effective filler to improve both CO_2 permeability

* Corresponding authors.
E-mail addresses: panyc@njtech.edu.cn (Y. Pan), cqw@njtech.edu.cn (C. Wang).

http://dx.doi.org/10.1016/j.ces.2016.11.037
Received 15 September 2016; Received in revised form 12 November 2016; Accepted 21 November 2016
Available online 23 November 2016

Nomenclature

P	Permeability coefficient (Barrer)
D	Diffusion coefficient (cm^2/s)
S	Solution coefficient ($cm^3/(cm^3\ cmHg)$)
A	Membrane area (cm^2)
m_t/m_∞	The fractional adsorption uptake
t	Time (s)
r_c	The length of ATP fillers (cm)
Δp_i	Partial pressure difference of component i across the membrane (cmHg)
N_i	Flux through the membrane of penetrant component i (cm^3/s)
L	Membrane thickness (cm)
J_i	Permeance for penetrant component i (GPU)
α	The selectivity of membrane
C	The concentration for adsorbed component (cm^3 (STP)/ cm^3 (ATP))
p	The adsorbate gas pressure at equilibrium (cmHg)
P_{MMM}	Effective permeability of the mixed matrix membrane (Barrer)
G	Geometric factor
$\varnothing_d$	The volume fraction of dispersed ATP in the membrane
w_d	The weight fraction of the ATP nanorods
ρ_c	Density of the pebax 1657 polymer (g/cm^3)
ρ_d	Density of the ATP nanorods (g/cm^3)

and CO_2/N_2 selectivity of pristine Pebax membrane (Xiang et al., 2016). Incorporation of a small amount of dispersed ATP fillers with nano-rod morphology possibly disrupt the polymer chains to increase of accessible free volume in the Pebax matrices and hence, an increase of gas permeability in the resulting MMMs. In addition, their tunnel-like rectangular microspores (3.7×6.0 Å) is responsible for distinguishing CO_2 (3.30 Å) from N_2 (3.64 Å) based on the kinetic separation principle, leading to a slight increase of the CO_2/N_2 selectivity in the MMMs. Besides the satisfied separating stability, the low-cost and high-availability of the both ATP and Pebax also suggests their promising potential application in CO_2 membrane separation. However, the bulk freestanding ATP/Pebax MMMs with larger thickness only exhibit very low CO_2 permeance (2–3 GPU), which is far away from the requirement for large-scale membrane application. To this end, composite membrane with very thin selective layers (typically the thickness in the range of 0.1–2 μm), which is deposited on the low-cost porous polymer support, is more attractive than the asymmetric polymer membranes (Sullivan and Bruening, 2003; Peter and Peinemann, 2009; Li et al., 2015). In this study, a thin ATP-Pebax selective layer deposited on a porous polyacrylonitrile (PAN) support was proposed in this study to improve CO_2 permeance. Besides CO_2/N_2 system, the separating performance of CO_2/CH_4 on the thin film composite membrane is also expected to improve, because the pore dimension of ATP fillers is just between kinetic diameter of CO_2 (3.3 Å) and CH_4 (3.8 Å). The gas permeability in ATP fillers are achieved by adsorptive measurements, and validated through the generalized Maxwell model. The effect of feeding pressure and permeating temperature on both single and mixed gas permeation were also examined. The separating performance of the thin ATP-Pebax composite membrane are attractive for potential applications like natural gas sweetening or biogas purification.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. Pebax® 1657 composited of 60 wt% PEO and 40 wt% PA6 was purchased from Arkema Inc. (France). PTMSP was purchased from ABCR. Attapulgite was obtained from Xuyi, Jiangsu, China. The porous PAN support was obtained from GMT Membrantechnik GmbH (Rheinfelden). Pure gas (CO_2, N_2, CH_4) and mixed gas (CO_2/CH_4 50/50 vol% and CO_2/N_2 25/75 vol%) were all supplied by Nanjing Sanle group Co., Ltd. Analytical grade ethanol was supplied from Sinopharm Chemical Reagent Co., Ltd. The water used in all experiments was treated by the Millipore Milli-Q purification system.

2.2. Preparation of thin ATP-Pebax composite membranes

The fabricating procedure for ATP-Pebax composite membranes is illustrated in Fig. 1. Prior to the casting of ATP-Pebax selective layer, a PTMSP gutter layer was firstly deposited on the porous PAN support by either spin-coating or doctor-blade casting method. The PTMSP casting solution was prepared by dissolving 1 wt% PTMSP in toluene. After depositing, the PAN support with PTMSP gutter layer was dried at room temperature for 24 h. Secondly, the ATP-Pebax solution was deposited on the PTMSP gutter layer in tandem with the PAN support by either doctor-blade casting or spin-coating method. The ATP-Pebax solution was prepared by the standard 'priming' technique, which can be seen elsewhere (Xiang et al., 2016). Finally, the as-synthesized composite membranes were dried in a vacuum oven at 60 °C for 24 h. The composite membranes were mainly fabricated by the spin-coating technique unless otherwise specified. As a comparison, pristine Pebax composite membranes were also fabricated from pure Pebax solution on the PAN support through the same casting and drying processes. The rotation speed and time of the spin-coating method for both PTMSP gutter layer and ATP-Pebax selective layer were optimized as 3000 rpm and 20 s, respectively, and the thickness of the ATP-Pebax

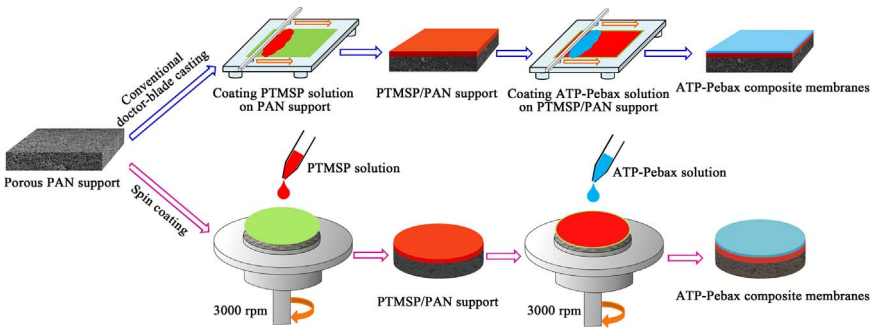

Fig. 1. Illustration of the fabricating procedure for ATP-Pebax composite membranes through the spin-coating or conventional doctor-blade casting technique.