Journal of Membrane Science 338 (2009) 153–160

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Substrate resistance in composite membranes for organic vapour/gas separations

Li Liu, Nan Jiang, Charles M. Burns, Amit Chakma, Xianshe Feng*

Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, Ontario, Canada N2L 3G1

ARTICLE INFO

Article history:
Received 2 March 2009
Received in revised form 7 April 2009
Accepted 10 April 2009
Available online 18 April 2009

Keywords:
Composite membrane
Gas and vapour separation
Substrate resistance
Poly(ether block amide)
Poly(dimethyl siloxane)
Resistance model
Hollow fiber

ABSTRACT

Composite membranes with a rubbery polymer skin layer are promising for the separation of organic vapours (e.g., light olefins and volatile organic compounds (VOCs)) from nitrogen for emission control and recovery of valuable components. Because of the high flux of composite membranes, the resistance of the substrate becomes increasingly important to the overall permeation. The effect of substrate resistance on gas permeation was studied using flat poly(ether block amide)/polysulfone (PEBA/PSf) and poly(dimethyl siloxane)/polyetherimide (PDMS/PEI) hollow fiber composite membranes. It was found that for a given substrate, the selectivity of the PEBA/PSf membrane for the separation of binary methanol/N_2 and ethanol/N_2 mixtures decreased as the PEBA skin layer thickness was reduced. The selectivity of the PDMS/PEI composite membrane to C_2H_4/N_2 and C_3H_6/N_2 was much lower than the intrinsic selectivity of PDMS. This is attributed to the substrate resistance that represents a significant contribution to the overall mass transport resistance for the permeation of highly permeable components (e.g., VOCs), while the skin layer may still dominate the permeation of slow permeant (e.g., N_2). Depending on the magnitude of the substrate resistance relative to the skin layer, the membrane permselectivity can be compromised substantially. In the development of advanced composite membranes, when the skin thickness is reduced, the substrate structure should be optimized so as to minimize the effect of the substrate resistance.

1. Introduction

Commercial success of membrane gas and vapour separation is, to a large extent, attributed to the development of defect-free high flux membranes with thin skins supported on microporous substrate. Integrally asymmetric and thin film composite membranes are now used extensively in industrial gas separations in order to achieve high fluxes. In these structurally asymmetric membranes, the thin skin layer is responsible for separation, and the porous substrate acts as a mechanical support. The pore size and porosity of the substrate should be sufficiently large so as to minimize its resistance to mass transport as long as the mechanical strength is satisfied and the skin layer is defect-free. The gas permeation through these membranes can be characterized by two morphological aspects of the skin layer: the skin layer thickness and the skin integrity. Membrane separation is a rate-controlled process. The thinner the selective layer is, the higher the permeation flux will be, with no or little effect on the membrane selectivity. However, when the flux is high, the relative contribution of the substrate to the overall mass transfer resistance will no longer be negligible. As such, the substrate resistance will become increasingly important for high flux membranes. This is believed to be especially the case when vacuum is applied to the permeate side to provide the driving force for permeation. In the separation of condensable gases and vapours (e.g., gas dehydration, monomer recovery from polyolefin off-gas, volatile organic vapour recovery from waste streams), vacuum is often used on the permeate side of the membrane to remove the vaporous permeate. For a given porous substrate, a viscous flow that would occur under a super-atmospheric pressure could shift into the Knudsen flow regime under vacuum due to the increased mean free path of gas molecules. In this case, the substrate resistance may prevail as Knudsen flow offers much larger resistance than viscous flow.

It is therefore important to study how the substrate influences the flux through composite membranes so as to optimize its performance and establish appropriate operating conditions. Gales et al. [1] reported the removal of organic vapours of acetone, ethyl acetate and ethanol from air using three composite membranes consisting of a poly(dimethyl siloxane) (PDMS) skin layer and a polyetherimide substrate with different thicknesses of the PDMS skin layers. The apparent permeabilities of the vapours through the membrane were shown to vary substantially with the thickness of the PDMS layer, while the permeabilities of N_2 and O_2 remained almost the same for the three membranes. This indicates that the substrate resistance to the vapour permeation cannot be neglected. Clausi et al. [2] demonstrated the substructure resistance of asymmetric membranes based on gas permeation at a constant transmembrane

---

* Corresponding author. Fax: +1 519 746 4979.
E-mail address: xfeng@uwaterloo.ca (X. Feng).

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.04.019

pressure while varying the average gas pressure within the membrane. Liu et al. [3] reported water vapour permeation through a PDMS/polysulfone composite membrane with vacuum applied on the permeate side. It was found that the microporous substrate dominates the mass transport resistance over the skin layer of the asymmetric membrane. In a study of trichloroethylene vapour separation from nitrogen using a thin film composite membrane, a significant mass transfer resistance of the support layer was also observed [4,5]. Huang and Feng [6] used a resistance model approach to analyze the selectivity of asymmetric membranes for pervaporation, and showed that the selectivity is influenced not only by the relative resistance of the skin layer and the substrate but also by the relative resistance of the polymer matrix and the pores in the substrate. Therefore, the development of high flux membranes should be directed towards not only producing a thin skin layer but also reducing the substrate resistance.

The removal and recovery of volatile organic compounds (VOCs) and olefin monomers from waste streams by membranes have attracted significant attention because of the economic values of the organic compounds and the increasingly stringent environmental emission regulations. Suitable membranes for such applications are mainly fabricated from rubbery polymers to exploit the high solubility of the organic permeant in the polymers. Their permselectivity is primarily derived from the solubility–selectivity, and their permeability can be 2–3 orders of magnitude higher than the permeability of glassy polymers. Recently, membranes based on poly(dimethyl siloxane) and poly(ether block amide) have been used extensively for various applications, including the recovery of gasoline vapour and other volatile organic compounds from nitrogen or air, olefin monomers recovery from the degassing off-gas during polyolefin manufacture [7–11]. These membranes in general exhibit a high permeation rate and selectivity for separation of organic compounds from permanent gases such as air or nitrogen. However, in our studies it has been observed that the membrane performance is lower than that expected on the basis of the selective layer, and that the deviation appears to be more remarkable for the organic permeant with a higher permeability. When tested with oxygen and nitrogen, which are the slow gases of interest in our studies, the membrane permeability and selectivity are very close to the intrinsic properties of the active layer. This appears to be caused by the substrate resistance.

In order to have a better understanding on the importance of the substrate resistance, thin film poly(ether block amide) (PEBA)/polysulfone (PSf) composite membranes were used in this study for the separation of gaseous methanol/nitrogen and ethanol/nitrogen mixtures. The composite membranes were fabricated by laminating a thin PBEA layer onto a microporous PSf substrate. This would allow us to evaluate the skin layer and the substrate separately. Methanol and ethanol were chosen as the representative VOCs because of their permeabilities in PEBA as well as their relatively high vapour pressures [9], which offers a broad range of process conditions for investigation. In addition, poly(dimethyl siloxane) (PDMS)/polyetherimide (PEI) hollow fiber composite membranes for the separation of olefin monomers (i.e., ethylene and propylene) from N_2 were also investigated. This study thus covers both modes of operation: evacuation of permeate for VOC/N_2 separation where the feed is at an atmospheric pressure, and positive pressure operation for olefin recovery where the feed gas is available at super-atmospheric pressures.

2. Experiments

2.1. Materials

PEBA (type 2533) was supplied by Arkema Inc. in the form of elliptic pellets. Isopropanol (from EM Science) and *n*-butanol (from Fisher Scientific) were used as the solvent to prepare PEBA solutions. Microporous PSf membrane from Pall Corporation was used as the substrate for PEBA membranes. Methanol and ethanol were supplied by Sigma–Aldrich. PDMS (RTV 655) prepolymer was provided by GE Silicones, and *n*-hexane (from EM Science) was used as solvent for preparing PDMS solutions. Polyetherimide (Ultem-1000) was supplied by General Electric, and *N*-methyl-2-pyrrolidone and γ-butyrolactone were supplied by Sigma–Aldrich. They were used to fabricate microporous hollow fiber substrates for PDMS membranes. All solvents were of reagent grade and used as received. All gases (i.e., propylene, ethylene, nitrogen and oxygen) used in the permeation experiments were of research grade (99.8–99.999% pure) and they were obtained from Praxair Specialty Gases and Equipment.

2.2. Membrane preparation

The general procedure for the fabrication of PEBA/PSf thin film composite membranes has been described previously [12]. Basically, a predetermined amount of PEBA 2533 was dissolved in a mixed solvent of isopropanol and *n*-butanol (mass ratio 3:1) at 80 °C to form a homogenous solution containing 7 wt% of the polymer. One or two drops (ca. 0.01–0.03 g) of the polymer solution were dripped gently onto the surface of de-ionized water, and the polymer solution spread quickly and spontaneously, during which process the solvent exchanged with non-solvent water, forming a very thin PEBA film floating on water surface. The thin films were laminated on the microporous polysulfone substrate as a mechanical support, thereby forming thin film composite membranes. In order to determine the intrinsic permselectivity of the PEBA membrane without interference of the support layer, homogenous membranes with a thickness of about 25 μm were also prepared by solution casting followed by solvent evaporation using the same PEBA solution.

The PDMS/PEI hollow fiber composite membranes were prepared by dip-coating the external surface of PEI hollow fiber substrate with a PDMS solution followed by a curing and drying process. The hollow fiber substrate membranes were extruded using a homogeneous dope solution containing 25 wt% PEI, 55 wt% NMP, and 20 wt% γ-butyrolactone. De-ionized water was used as both the internal and external coagulant. The details of the hollow fiber spinning can be found in our previous reports [13,14]. The inside and outside diameters of the hollow fibers were 450 and 700 μm, respectively. The PEI fibers were pre-wetted with hexane and then dip-coated with a PDMS solution for 15 min at room temperature. Hexane was used as the solvent for preparing the PDMS solutions. After coating, the fibers were dried in a fume hood at room temperature for 20 min followed by thermal treatment at 75 °C for 3.5 h to complete crosslinking and to remove the residual solvent. Dense PDMS and PEI films were also prepared by the solution casting and solvent evaporation technique for measurements of their intrinsic permeabilities; the dry membrane thickness was 90 and 25 μm for PDMS and PEI, respectively.

2.3. Gas permeation and separation

Fig. 1 shows the experimental set up for methanol/N_2 and ethanol/N_2 separations with PEBA/PSf composite membranes. The flat membrane was mounted into the permeation cell, with an effective membrane area of 13.85 cm^2. The binary VOC/N_2 gas mixtures were generated by bubbling nitrogen at a given pressure through a solvent tank. Then the gas mixture was admitted to the membrane cell. Throughout the experiments, the feed mixture was kept at atmospheric pressure, and vacuum (<1 kPa abs.) was applied to the permeate side. The VOCs permeated through the membrane were collected in a cold trap, and the VOC permeation rate was