Journal of Membrane Science 348 (2010) 383–388

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Pervaporation characteristics of pore-filling PDMS/PMHS membranes for recovery of ethylacetate from aqueous solution

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ARTICLE INFO

Article history:
Received 14 October 2009
Received in revised form
12 November 2009
Accepted 14 November 2009
Available online 6 December 2009

Keywords:
Hydrophobic membrane
Pore-filling-type membrane
Cross-linking
Pervaporation
Organic/water separation

ABSTRACT

Hydrophobic organic–inorganic composite membranes with cross-linked poly(dimethyl siloxane)–poly(methyl hydrogen siloxane) (PDMS/PMHS) were prepared on a porous alumina tubular support. The PDMS/PMHS polymer penetrated into and plugged the pores of the γ-alumina support. The membrane had an approximately 3.5-μm-thick polymer/alumina composite layer. The alumina matrix inhibited the swelling of the PDMS/PMHS membrane. The pervaporation separation of an ethylacetate/water mixture with low percentages of ethylacetate was carried out with these composite membranes. The effect of the thermal treatment of the PDMS/PMHS membrane on the existence of silanol and methyl groups, and the flux and separation factor were investigated. The flux and separation factor were varied depending on the temperature of thermal treatment of the PDMS/PMHS membranes.

1. Introduction

Pervaporation is a promising technique with significant potential in a wide range of applications, such as dehydration of organic compounds, recovery of organic compounds from water, separation of azeotropic mixtures, and separation of thermally degradable organic mixtures, because of its many advantages: easy process design, high selectivity, low energy consumption, and moderate cost-to-performance ratio. Pervaporation with hydrophilic membranes are appropriate to separate water from water/organic mixtures with a low water concentration [1–4]. Hydrophobic membranes are suitable for separation of volatile organic components (VOCs) from organic/water mixtures with low organic concentrations [5–17].

Poly(dimethyl siloxane) (PDMS) is a widely used membrane material that has a hydrophobic surface and repels the passage of water molecules, while it allows larger organic molecules to pass through [6,10,12–16]. However, some aspects of the pervaporation performance such as permeation flux and selectivity are still insufficient. To optimize the membrane performance, it is important to control membrane swelling and thickness. Polymeric membranes have been modified with various chemical and physical methods, including filling [4,7–11,15], grafting [13], and copolymerization [14,16]. In general, filling methods can be classified into two types. One method is the introduction of inorganic particles into the polymer matrix [9]. The concept of an inorganic-filled membrane has been proposed for controlling adsorption and membrane swelling. In this method, silica [4], zeolite [9,10], activated carbon [11], and carbon black [15] are used as fillers. Another method is the immobilization of polymer membranes into the pores of the porous support [7,8]. The concept of a pore-filling-type membrane has been proposed for controlling membrane swelling. The development of robust inorganic porous supports of controlled pore size triggered the preparation of pore-filling-type polymer membranes in which a polymer layer influences the separation performance, while the inorganic support provides mechanical strength.

On the other hand, the utilization of cross-linked polymeric materials improves membrane stability. Bueso et al. have prepared hydrophobic composite membranes from a mixture of PDMS and poly(methyl hydrogen siloxane) (PMHS) [14,16]. A cross-linking reaction occurs in which the Si–H bonds of the PMHS react with the hydroxyl groups of PDMS, liberating hydrogen.

In this study, the active layer was prepared using PDMS and PMHS in the pores of an alumina tubular support of 5 nm average pore size. Esters are numerically the largest group of aromas as VOCs. Ethylacetate was chosen as a model VOC in this study. The separation performance of the resulting PDMS/PMHS membranes was investigated for the pervaporation separation of ethylac-

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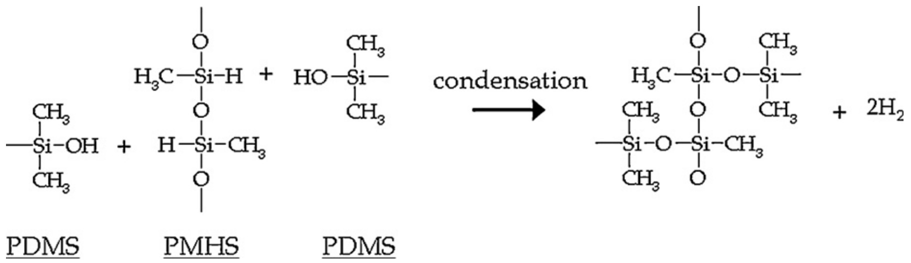
doi:10.1016/j.memsci.2009.11.033



Scheme 1. Cross-linking mechanism of PDMS and PMHS.

etate/water mixtures. The effect of thermal treatment of the PDMS/PMHS membrane on the existence of silanol and methyl groups, and the flux and separation factor were investigated.

2. Experimental

2.1. Materials

PDMS (Mw = ca. 35,000) and PMHS (Mw = ca. 1900) were purchased from Sigma-Aldrich Chemical Co. and Alfa Aesar, respectively, and used without further purification. α-Alumina porous tubular supports (outer diameter: 10 mm; inner diameter: 7 mm; length: 450 mm; average porosity: 35%; average pore size: 0.1 μm) were purchased from Noritake Co. Ltd. and cut into 35 mm long pieces. The pore size of the α-alumina tubular supports was lowered to the 5 nm range by applying a thin γ-alumina layer. The γ-alumina layer was prepared by dip-coating using a boehmite (γ-AlOOH) sol according to the reference procedure [18].

2.2. Preparation of PDMS/PMHS membranes

A cross-linked PDMS/PMHS layer was coated on the γ-alumina layer as follows. A coating solution was prepared from PDMS, PMHS, hexane, and NaOH. NaOH was used as a catalyst for the cross-linking reaction of PMHS and PDMS. Only the PDMS/PMHS weight ratio was changed with the total amount of siloxanes held constant. In a typical synthesis, 2.6 g PDMS and 2.6 g PMHS were dissolved in 15 ml hexane. Then, 0.05 g NaOH was added to the above solution, and sonicated at room temperature for 20 min. Scheme 1 shows the cross-linking reaction of PMHS and PDMS. Membranes were prepared by dip-coating the alumina supports in the coating solutions at a withdrawal rate of 1.2 mm/s and heated at 85–420 °C for 3 h.

2.3. Characterization

Fourier-transform infrared spectroscopy (FTIR) spectra of the samples were recorded in the 500–3500 cm^{-1} range using a JIR-7000 spectrometer (JEOL) at 4 cm^{-1} resolution. Thermogravimetric analysis (TGA) was performed on a DTG-60H apparatus (Shimadzu) at a heating rate of 2 °C/min. FTIR and TGA measurements were performed with a powdery sample, which was prepared on a non-porous silicon substrate and peeled from the substrate. The composition and thickness of the membranes were measured by scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis on a VE-8800 microscope (Keyence).

Contact angles were measured at room temperature. A 2 μl portion of the 5 wt% ethylacetate/water mixture was dropped onto the sample surface at different locations. The average of the measured contact angles was taken as the contact angle of the sample.

The dried membranes with alumina support were immersed into an aqueous solution of 5 wt% ethylacetate at 30 °C. The membranes were then taken out, wiped quickly with a filter paper, and weighed. The degree of swelling of the membrane, S, was determined by

$$S = \frac{w_s - w_d}{w_d}, \tag{1}$$

where w_d and w_s represent the weight of the dry and swollen membranes without support, respectively. The degree of swelling of the dried membranes on the non-porous silicon substrate was measured similarly, for reference.

Permeation of pure gases through the membranes was performed at 293 K. In the permeation test, the total pressure on the feed side was maintained at 0.15–0.20 MPa and that on the permeate side was maintained at atmospheric pressure. The permeate streams were measured with a soap meter.

2.4. Pervaporation

Pervaporation experiments using ethylacetate/water mixtures were conducted. In the experimental apparatus, the downstream compartment was evacuated, and the permeate was collected in a vacuum trap condenser cooled using liquid nitrogen. The permeation flux, J, at a steady state is defined by

$$J = \frac{Q}{At}, \tag{2}$$

where Q is the weight of the collected permeate during the experimental time interval, t, and A is the effective membrane surface area. The feed and permeate concentrations were determined by Karl Fisher titration. The separation factor, α_{EA}, is defined by

$$\alpha_{EA} = \frac{y_{EA}/y_w}{x_{EA}/x_w}, \tag{3}$$

where y_{EA} and y_w are the mole fractions of ethylacetate and water in the permeate, respectively, and x_{EA} and x_w are their corresponding mole fractions in the feed.

3. Results and discussion

3.1. Effect of PDMS/PMHS ratio

Fig. 1 shows the variation in the separation performance as a function of the PDMS/PMHS weight ratio. With PMHS, the only siloxane precursor, the membrane had a relatively high separation factor of over 100. However, the flux of ethylacetate through the PMHS membrane was lower than 1.0 kg/m^2 h. In contrast, when only PDMS was used, the flux of ethylacetate through the PDMS membrane was higher than 1.0 kg/m^2 h, and that of water was also relatively high. Thus, the separation factor was less than 100. It is conjectured that the relatively high flux of water is attributed to surface hydrophilicity due to the presence of silanol groups in PDMS. From these results, it was hypothesized that by combining PMHS and PDMS at various ratios, a high separation factor and flux of ethylacetate could be obtained. At a PDMS/PMHS weight ratio of 1, the PDMS/PMHS membrane had the highest separation