

Hydrophobic composite membranes for separating of water–alcohol mixture by pervaporation at high temperature

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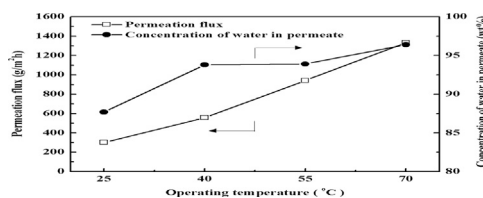
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KEY HIGHLIGHTS

- Hydrophobic composite membrane used to separate a mixture of 90 wt% alcohol–water.
- The performance of hydrophobic membrane surpassed that of hydrophilic membranes.
- The membrane suited for applications at high temperature.
- For higher water content feed, the membrane performance was further enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrophobic composite membranes for dehydrating aqueous alcohol mixtures by pervaporation were investigated. It was suited for applications at high temperatures and for feed mixtures of water and alcohols with high number of carbon atoms. With increasing operating temperatures, pervaporation data indicated simultaneous increase in permeation flux and concentration of water in permeate. At 70 °C and for a feed mixture of 10 wt% water and 90 wt% ethanol, the composite poly(2,6-dimethyl-1,4-phenylene oxide) membrane delivered a high flux of 1333 g/(m²h) and a high permeate content of 96.4 wt% H₂O. For a feed with higher water content, the membrane performance was further enhanced. The microstructure of the selective layer was probed with positron annihilation lifetime spectroscopy at varying temperatures. A bimodal free volume distribution was obtained, which described different shifts of free volume as temperature increased: a shift of smaller free volume to a region of much smaller free volume and a shift of bigger free volume to a region of much bigger free volume.

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1. Introduction

Pervaporation is a membrane separation process with vapor pressure difference as the driving force. It is considered as an attractive alternative to conventional techniques for the separation of azeotropic mixtures or aqueous and organic mixtures having

similar physical and chemical properties (Bowen et al., 2007; Lee and Oh, 1995; Li et al., 2004; Svang-Ariyaskul et al., 2006; Zhou and Koros, 2006). Pervaporation has been receiving increased attention because of its higher separation efficiency and energy savings (O'Brien et al., 2000; Shao and Huang, 2007; Vane, 2005) compared to conventional distillation.

It is well known that pervaporation has found viable applications in the following three areas: (1) dehydration of organic solvents, (2) removal of organic compounds from dilute aqueous streams, and (3) separation of organic–organic mixtures (Smitha

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et al., 2004). Of these three, the first area has been the subject of numerous and intense investigations. Membrane properties dictate the type of separation achieved in pervaporation applications. In general terms, the hydrophobic membranes used in PV, mainly for the separation of alcohols from water, are rubber types. For a rubbery hydrophobic membrane, organic compounds preferentially permeate through the membrane, so the permeate will be enriched with the organic compounds. Based on solution–diffusion, the sorption and swelling of material play a dominant role in the separation. However, the swelling has a very low influence on separation for glassy polymers, such as Poly(2,6-dimethyl-1,4-phenylene oxide). For a hydrophilic membrane, the organic feed mixture will be dehydrated, and the permeate will be rich in the water component.

The solution–diffusion theory is the generally accepted mechanism of mass transport through non-porous membranes (Blume et al., 1990; Sharma et al., 2004). This theory states that an ideal polymeric membrane for pervaporation should have a solubility parameter close to that of the component to be selectively permeated, so that the sorption of this component is high. Because of this idea of preferential sorption, the choice of hydrophilic membranes for purposes of dehydration of mixtures is a common concept in the field of pervaporation. Earlier research has used natural polymers, e.g. cellulose and its derivatives (Bhat and Pangarkar, 2000; Neel, 1991; Song and Hong, 1997). Afterward, several other hydrophilic materials have been studied, which include polyethyleneimine, poly(acrylic acid), poly(vinyl alcohol), sodium alginate, chitosan, and synthetic zeolites (Jafar and Budd, 1997; Lee et al., 2000; Rao et al., 2007; Toti and Aminabhavi, 2004; Upadhyay and Bhat, 2004; Zhang et al., 2006).

High permeability, good selectivity and robust stability are important factors for choosing suitable pervaporation membranes. Hydrophilic polymers have high permeability and good selectivity for the dehydration of organic solvents, but they lack stability in aqueous solutions (Finch, 1973; Xiao et al., 2006). Many researchers have improved the membrane stability by cross-linking and blending. Cross-linking limits the mobility of polymer chains, and thus excessive membrane swelling can be suppressed (Tsai et al., 2008; Urugami et al., 2002; Zhang et al., 2006). However, the extent of cross-linking should be controlled; otherwise, membranes will lose too much of their permeability. Blending of hydrophilic polymers with other polymers can increase both the mechanical strength and the stability of the membrane in aqueous solutions (Kalyani et al., 2006; Shieh and Huang, 1998; Rao et al., 2006).

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a glassy polymer at room temperature. It has high permeability to gases because of the absence of polar groups in the polymer backbone. In addition, it possesses excellent mechanical and thermal properties, and is resistant to several chemicals, including acids, bases, and alcohols. These properties of the PPO membrane make it a good candidate for the pervaporation separation of organic–organic mixtures. Pervaporation separation of methanol from its mixture with ethylene glycol has been devoted to the use of dense flat-sheet PPO membrane (Khayet et al., 2004). It was found that methanol permeated preferentially through the membrane, with a separation factor less than 15 and permeation flux lower than 200 g/m² h at a feed methanol concentration of 70 wt%. The pervaporation application of PPO membrane to the dehydration of organic solvents has few reported, because of its hydrophobic nature that results in low permeability and selectivity. An observation from previous research showed that the permeation flux and separation factor of dense PPO membrane in pervaporation of 10 wt% water/ethanol mixture at 25 °C was 210 g/m² h and 146, respectively (Shih et al., 2007).

The present work investigated on the performance of hydrophobic composite membranes for the pervaporation separation of

alcohol–water mixtures. We prepared a composite membrane consisting of a porous support layer with a thin dense hydrophobic layer on top of it. Its pervaporation performance surpassed that of hydrophilic membranes. Its free volume properties were probed with positron annihilation lifetime spectroscopy to confirm the outstanding pervaporation performance of hydrophobic membrane. In addition, we prepared another hydrophobic composite membrane for checking the reproducibility of the pervaporation performance.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (Mw=50,000) and polyimide (Matrimid[®]) were purchased from Aldrich Chemical Co. and Alfa Aesar Chemical Co., respectively. Polyacrylonitrile (PAN), as support layer in composite membranes, was supplied by Tong-Hua Synthesis Fiber Co. Ltd. (Taiwan). Reagent grade N-methyl-2-pyrrolidone (NMP), chloroform, and dichloromethane were used as solvents without further purification. Alcohols employed in the different aqueous mixtures, namely methanol, ethanol, n-propanol, and n-butanol, for swelling and pervaporation measurements were obtained from TEDIA Co., Inc.

2.2. Membrane preparation

A flat porous membrane support was prepared by casting a 15 wt% PAN-NMP solution onto a nonwoven polyester fabric with the use of a 200- μ m gap casting knife. The cast solution was precipitated by immersion in a bath of water. The resulting porous PAN membrane was washed in water overnight and then dried at room temperature.

In preparing a composite membrane of PPO or of polyimide, a 2 wt% PPO in chloroform or a 4 wt% polyimide in dichloromethane was cast onto the porous PAN membrane, which was fixed on a glass plate. The solvent was then allowed to evaporate slowly at ambient conditions for 24 h. A layer of PPO or of polyimide on the resulting composite membrane had a thickness of about 9 μ m.

For swelling and sorption tests, a freestanding membrane of PPO was also prepared. A casting solution of the polymer was poured in a Petri dish. Then, the solvent was evaporated by exposing it to the atmosphere for 24 h. The resulting membrane was dried in a vacuum oven at 50 °C for 24 h to remove traces of the solvent.

2.3. Swelling test

Samples of dry freestanding membranes of known weight were immersed in a mixture of 90 wt% alcohol–water and were allowed to equilibrate for 72 h. The swollen membranes were taken out and wiped with a tissue paper to remove the adhering aqueous mixture. Then they were weighed. The swelling ratio was calculated using the following equation (Anilkumar et al., 2008):

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

where W_d denotes the weight of the dry membrane and W_s refers to the weight of the swollen membrane.

2.4. Sorption test

Freestanding membranes were immersed in a mixture of 90 wt% ethanol–water at 25 °C for 24 h. They were subsequently blotted between tissue papers to remove the excess mixture and placed in

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