Preparation and Pervaporation Performances of Fumed-Silica-Filled Polydimethylsiloxane–Polyamide (PA) Composite Membranes

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ABSTRACT: Fumed-silica-filled polydimethylsiloxane (PDMS)–polyamide (PA) composite membranes were prepared by the introduction of hydrophobic fumed silica into a PDMS skin layer. The cross-sectional morphology of these filled composite membranes was observed with scanning electron microscopy. Their pervaporation performances were tested with aqueous ethanol solutions at 30, 35, and 40°C. Increasing the amount of the fumed silica resulted in significantly enhanced ethanol permeability of the membranes. When the content of the fumed silica in the PDMS skin layer was 20 wt %, the ethanol permeability increased to nearly twice that of the unfilled PDMS–PA composite membrane. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3132–3137, 2007

Key words: membranes; polysiloxanes; silicas

INTRODUCTION

Polydimethylsiloxane (PDMS) membranes and their pervaporation applications to organic separation from organic/water mixtures have been attracting more and more attention because of their preferential permeation for volatile organic compounds, extremely low glass-transition temperature, and high thermal stability over a wide range of temperatures.[1–4] In particular, there has been growing research interest in the application of PDMS membranes to biochemical engineering areas such as the recovery of ethanol from fermentation broths for fuel ethanol production.[5–8] However, the pervaporation performances, including the permeation flux and selectivity, are still insufficient for practical applications. To improve the pervaporation performances, PDMS membranes have been modified with various physical and chemical methods, including filling, grafting, copolymerization, blending,[9] and organofunction.[10] Filling a polymer membrane with a particulate material is a physical modification examined in a number of studies. Active carbon, carbon black, zeolite, silicalite, carbon molecular sieves (CMSs), and other sorption agents are usually used as fillers. For the filling modification of PDMS membranes, carbon black, silicalite, and CMSs are the prevalent choices. Netke et al.[11] used a silicalite-filled PDMS membrane to separate acetic acid from water. As a result, the selectivity of the membrane for acetic acid increased with increasing silicalite content in the membrane and hydrophobicity of the silicalite, but the flux of acetic acid decreased. Adnadjević et al.[12] determined the pervaporation properties of PDMS membranes filled with several kinds of hydrophobic zeolites. An increase in the zeolite content resulted in an increase in both the membrane permeability and selectivity, but the flux was still lower. The physicochemical properties, including the hydrophobic degree of the zeolites, significantly influenced the membrane pervaporation properties. Ye et al.[13] studied the pervaporation for aqueous ethanol solutions of carbon black filled PDMS membranes. They found the permeation rate increased with the carbon black content in the membranes, whereas the selectivity of the filled membranes for ethanol was almost consistent with that of pure PDMS membranes. However, the carbon black content was less than 5 wt % with respect to PDMS, and the permeation rate of the membrane decreased dramatically with N330-type carbon black when the filler content was more than 3 wt %. Xiao et al.[14] found that the incorporation of a CMS enhanced simultaneously the permeation flux and separation factor of PDMS membranes for an acetic acid/water system if the filler content was up to 20 wt %, but the improvement of the permeation flux was not enough. Peng et al.[15] used a CMS-filled PDMS pervaporation membrane for removing benzene from an aqueous solution. The results showed that the CMS increased the separation factor of the membrane and decreased the permeation flux slightly. However, the membrane was too thick to obtain considerable flux.
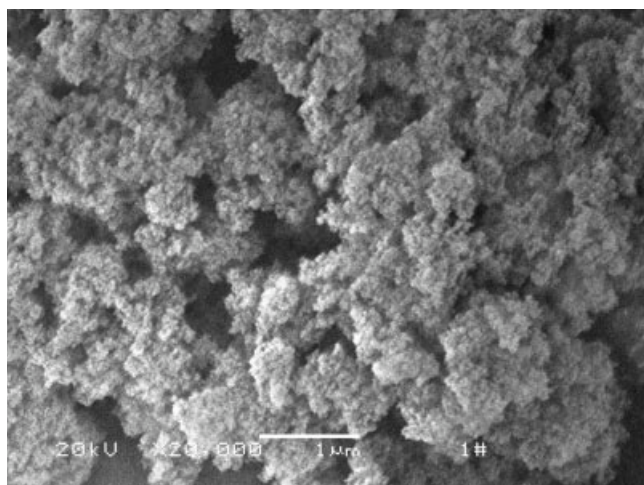
Figure 1 SEM photograph of hydrophobic fumed silica.

Fumed silica, consisting of spherical nanoscale particles and produced by the flame hydrolysis of chlorosilanes, is commonly used for the reinforcement of polymer materials such as silicone rubber.[16] Fumed silica always exists in the form of aggregates whose particle size (nanograde) is smaller than that of the traditional silica particles, and the aggregates tend to agglomerate into big particles, as shown in Figure 1. There has been much research about the effects of fumed silica on the mechanical[17] and rheological properties of polymers[18] and the configuration of polymer–filler interfaces.[19] In contrast, there have been few studies on the influence of fumed silica on the separation performances of polymer membranes. However, the applications of fumed silica to membrane separation have been intriguing since Merkel et al.[20] and Gomes et al.[21] found a significant increase in the permeability of nanocomposite membranes based on glassy polymers with high free volumes through the addition of nonporous fumed silica to the polymer matrix. The results were attributed to the capacity of these fillers to disrupt polymer chain packing and to increase the system free volume.[20,21]

In this work, we introduced hydrophobic fumed silica into the PDMS skin layer of PDMS–PA composite membranes to prepare silica-filled PDMS–PA composite membranes and experimentally evaluated their pervaporation performances for ethanol/water mixtures to develop a kind of multilayer PDMS composite membrane of high performance.

EXPERIMENTAL

Materials

A hydroxyl-terminated PDMS base polymer (107#RTV), with a viscosity of 10,000 mPa s, was purchased from the Chengguang Chemical Institute (Chengdu,

China). Normal heptane (reagent-grade) was selected as the solvent of PDMS. Tetraethoxysilane (TEOS; reagent-grade) and dibutyltin laurate (DBTOL; reagent-grade) were used as the crosslinker and initiator (catalyzer) in the polycondensation reaction of the PDMS base polymer, respectively. The filler was hydrophobic fumed silica, with a particle size of 10–40 nm, as shown in Figure 1.

PA support layer

The PA support layer was a blend of polyamide and polysulfonamide that was prepared by solvent evaporation. The pore size of the prepared PA membranes was 0.4–0.8 μm (bubble point). Before being coated with PDMS, the microporous PA support layer was treated with an organic solvent including N-methylpyrrolidone.

Preparation of the unfilled PDMS–PA composite membranes

The PDMS–PA composite membranes were prepared on the basis of the literature[3] by the polycondensation of the PDMS base polymer. At first, the base polymer, crosslinker, and solvent were added to a beaker in given proportions to obtain a 2 wt % PDMS solution. The solution was agitated by a magnetic mixer for an hour at room temperature, and then the initiator was introduced. After further mixing for 10 min, the solution was cast onto the PA support layer, which was suspended on water. After vulcanizing for several hours at room temperature, the PDMS–PA membrane was cured in a vacuum oven for 6 h at 60°C. Thus, an approximately 5-μm-thick PDMS skin layer was formed on the support layer, and the PDMS–PA composite membranes were achieved. Figure 2 shows the polycondensation of the PDMS base polymer.

Preparation of the fumed-silica-filled PDMS–PA composite membranes

The PDMS prepolymer was first dissolved in the solvent normal heptane in the same percentage as in the previous section. After being treated for an hour
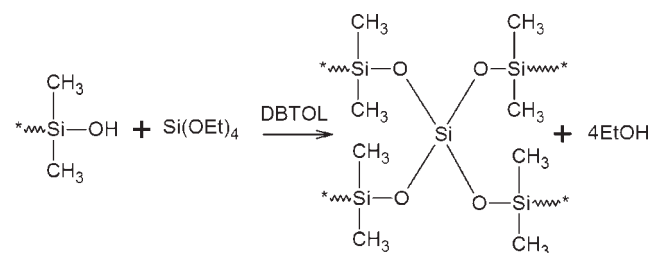

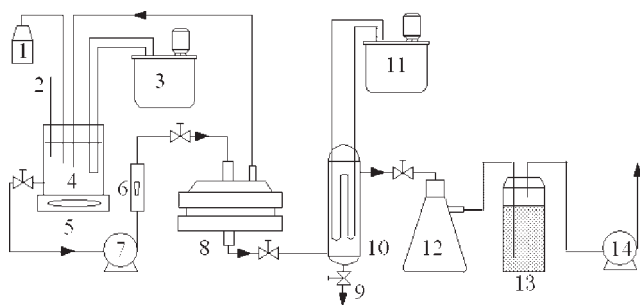**Figure 2** Crosslinking mechanism of the PDMS membrane.

Figure 3 Schematic representation of pervaporation equipment: (1) sampling tube, (2) thermometer, (3) thermostat, (4) feed reservoir, (5) magnetic mixer, (6) rotameter, (7) circular bump, (8) membrane module, (9) permeate outlet, (10) cold trap, (11) low-temperature thermostat, (12) buffer flask, (13) dehumidifying bottle, and (14) vacuum bump.

in an oven at 110°C, the fumed silica was added to the PDMS solution in given proportions. After further stirring for several minutes on the magnetic mixer, the solution was treated by an ultrasonic agitator for 10 min at 30°C for better dispersion of the fumed silica. Then, the crosslinker TEOS was added to the solution, which was continuously agitated for an hour on the magnetic mixer. After the initiator DBTOL was introduced, the remaining operation steps were the same as those in the previous section for the preparation of the unfilled PDMS–PA composite membrane. Finally, the fumed-silica-filled PDMS–PA composite membranes were achieved with

filler contents of 5, 10, 15, and 20 wt % (based on the weight of PDMS).

Pervaporation tests

The pervaporation apparatus is shown in Figure 3. Pervaporation experiments were carried out with the unfilled membrane and the membranes filled with 5, 10, 15, and 20 wt % fumed silica. The effective membrane area was 254 cm^2. The test temperatures were 30, 35, and 40°C, and the absolute pressure in the downstream of the membrane was held at 10 mmHg. The feed solution was an ethanol/water mixture of 8 wt % ethanol. The flow rate through the membranes was kept at 110 L/h. The pervaporation performances of these membranes were characterized by the flux, selectivity, and ethanol permeability ($Q_{ethanol}$). $Q_{ethanol}$ of the membranes, derived from a transport equation for the pervaporation process in the solution-diffusion model, is written as follows:

$$Q_{ethanol} = \frac{J_{ethanol}}{p_{ethanol,feed}^{vapor} - n_{ethanol,permeate}\, p_{permeate}} \quad (1)$$

where $J_{ethanol}$ is the permeate flux of ethanol, $p_{ethanol,feed}^{vapor}$ is the equilibrium partial vapor pressure of ethanol in the feed, $n_{ethanol,permeate}$ is the molar fraction of ethanol in the permeate, and $p_{permeate}$ is the permeate pressure. The selectivity of the membranes is expressed by separation factor α, which is defined
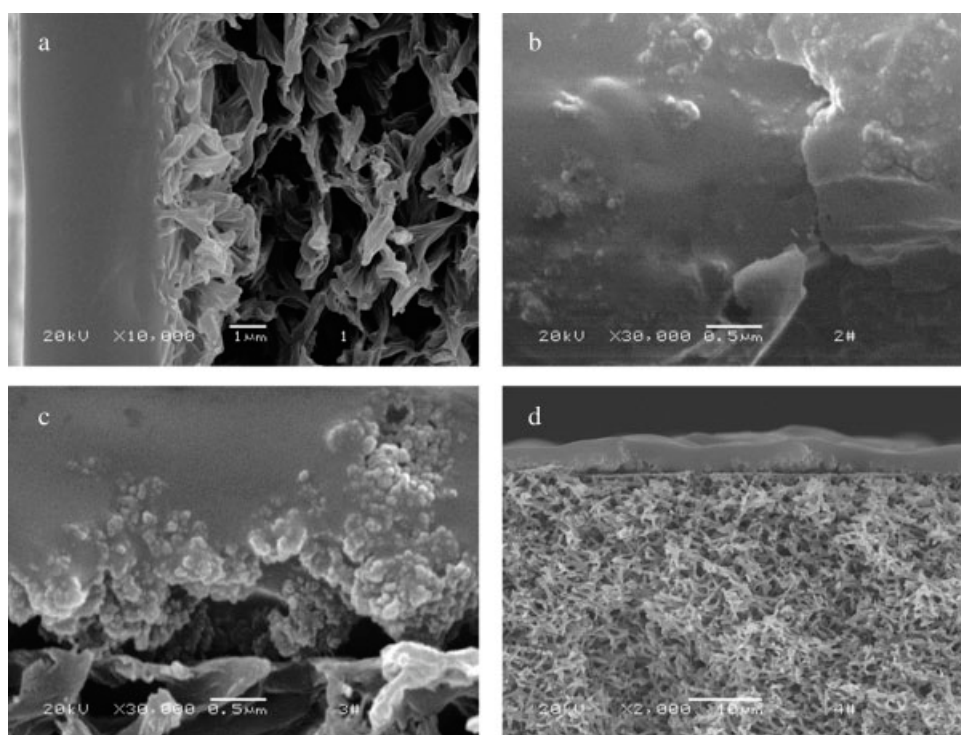

Figure 4 Cross-sectional SEM pictures of PDMS–PA composite membranes: (a) unfilled PDMS–PA, (b) 5% fumed silica filled PDMS–PA, (c) 10% fumed silica filled PDMS–PA, and (d) 15% fumed silica filled PDMS–PA.

as follows:

$$\alpha = \frac{c_{ethanol}^{permeate} \Big/ c_{water}^{permeate}}{c_{ethanol}^{feed} \Big/ c_{water}^{feed}} \qquad (2)$$

where c is the weight fraction of ethanol. The content measurements for the retentate and permeate were carried out with a density meter (DMA 4500, Anton Paar, Graz, Austria).

RESULTS AND DISCUSSION

Cross-sectional morphology of the membranes

The cross-sectional pictures of the prepared membranes by scanning electron microscopy (SEM) are shown in Figure 4. Figure 4(a) indicates that, for the unfilled membrane, PDMS intruded lightly into the pores and obtained good adhesion with the porous support layer. Figure 4(c,d) shows that, for the filled membrane, the fumed silica particles were deposited near the interface of the PDMS skin layer and porous support layer, and the aggregate size was around 100 nm according to Figure 4(c) when the filler amount was up to 15 wt %. Comparing Figure 4(c,d) and Figure 4(a), we find that the silica-filled PDMS skin layer did not intrude into the pores of the support layer, and thus the adhesion between the two layers was not so good.

Effect of the fumed silica content in PDMS on $Q_{ethanol}$

The dependence of $Q_{ethanol}$ on the fumed silica content in the PDMS skin layer and the feed concentra-
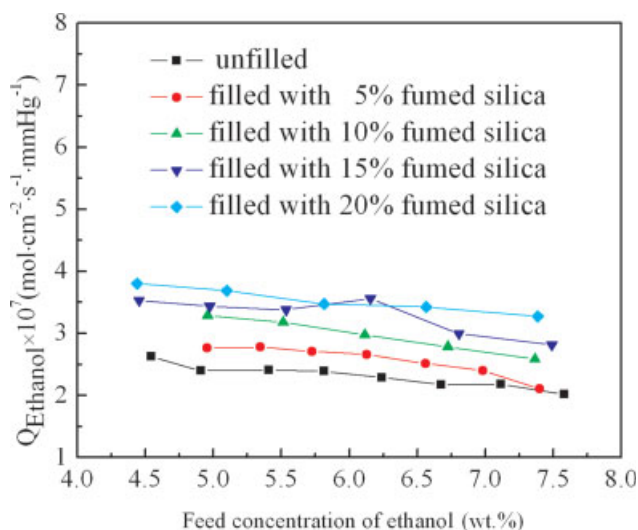
Figure 6 Dependence of $Q_{ethanol}$ on the feed concentration of ethanol with different amounts of fumed silica at 40°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
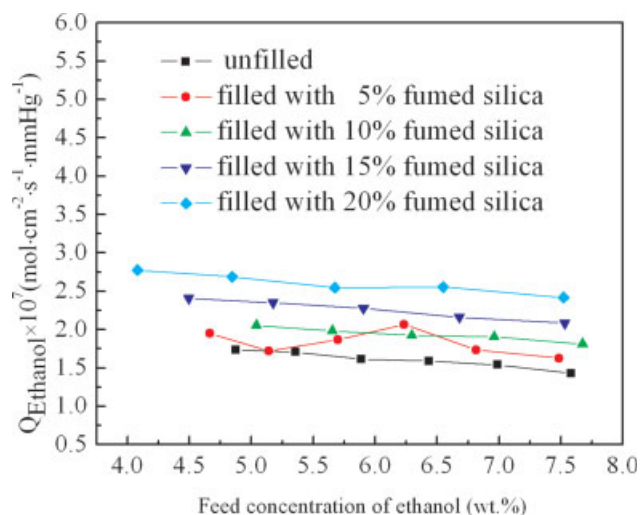
tion at different temperatures is shown in Figures 5 and 6. $Q_{ethanol}$ of the silica-filled membranes increased with increasing silica content in the skin layer of the membrane. When the filler content was 20 wt %, $Q_{ethanol}$ was almost twice that of the unfilled PDMS–PA composite membrane. This may be attributed to the disruption of PDMS chain packing by the introduced fumed silica, which led to an increase in the free volume of PDMS, as reported in the literature.[20] The increase in the free volume elevated the diffusion coefficient of molecules through PDMS and hence enhanced the permeation of organic molecules. With increasing fumed silica con-
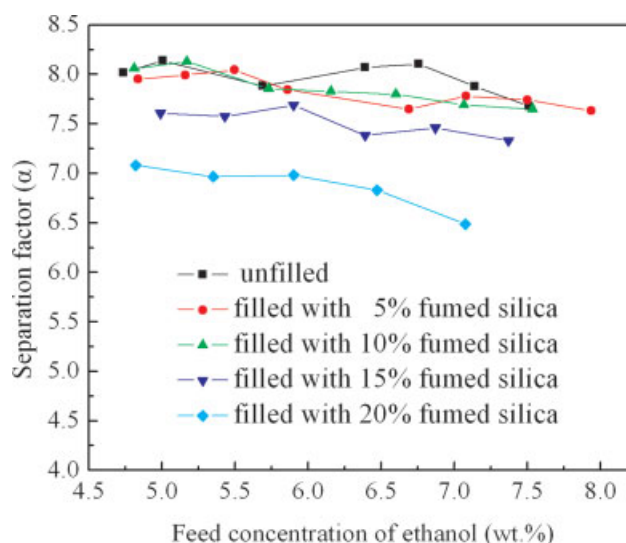
Figure 5 Dependence of $Q_{ethanol}$ on the feed concentration of ethanol with different amounts of fumed silica at 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Dependence of α on the feed concentration of ethanol with different amounts of fumed silica at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tent in the PDMS skin layer, the disruption chance of PDMS chain packing by the fillers increased, as explained in the literature.[20,21]

Effect of the concentration of ethanol on $Q_{ethanol}$

$Q_{ethanol}$ hardly changes with the concentration of ethanol from Figures 5 and 6. This is consistent with general observations about pervaporation. With the decreasing feed concentration of ethanol, the transport driving force decreased. The decreased transport driving force decreased the ethanol flux, and hence $Q_{ethanol}$ hardly varied.

Effect of the fumed silica content in PDMS on the selectivity

Figures 7–9 indicate that the selectivity decreased with an increase in the fumed silica content. This may be attributed to the imperfect adhesion of PDMS to the fumed silica and the aggregation of the fumed silica particles. The bigger aggregation of the fumed silica in PDMS might have resulted in some defects (cavities) penetrating the skin layer. The defects affected the permeation of both organics and water to some extent. The increasing filler content led to more and bigger aggregation and thus more defects, as shown in Figure 4(b,c). Meanwhile, because of the imperfect adhesion of PDMS and hydrophobic fumed silica, some defects existed between PDMS and fumed silica particles. A smaller water molecule could move through the defects more easily than a larger ethanol molecule. Therefore, the selectivity of the filled PDMS–PA composite
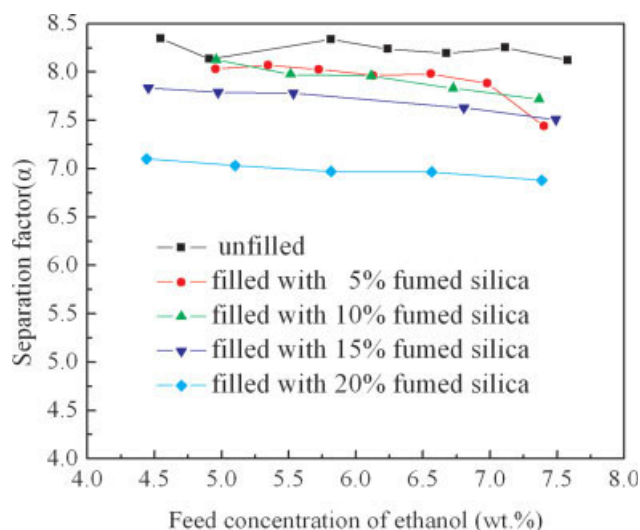

Figure 8 Dependence of α on the feed concentration of ethanol with different amounts of fumed silica at 35°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 9 Dependence of α on the feed concentration of ethanol with different amounts of fumed silica at 40°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
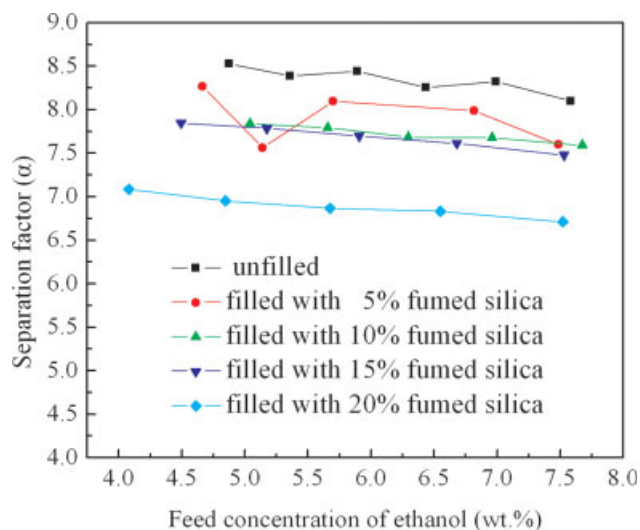
membranes was slightly lower than that of the unfilled membrane and decreased lightly with the increasing filler content.

Effect of the feed temperature and feed concentration of ethanol on the selectivity

Figures 7–9 show that the temperature had little effect on the selectivity of these membranes. Moreover, the selectivity decreased slightly with the increase in the feed concentration. The swelling of the membranes weakened the interaction between PDMS chains and partially increased the free volume of the polymer, and this made the smaller water molecules permeate more quickly than the ethanol molecules.

CONCLUSIONS

A new type of filled PDMS–PA composite membrane was prepared by the introduction of hydrophobic nanofumed silica into the PDMS skin layer. SEM pictures showed that the fumed silica particles that filled PDMS were deposited near the interface of the skin layer and porous support layer and did not aggregate seriously because the aggregate size was around 100 nm. The filler silica had a greatly positive effect on the pervaporation performance of the membranes. $Q_{ethanol}$ of the silica-filled membranes increased greatly with increasing silica content in the PDMS skin layer of the membrane. For instance, $Q_{ethanol}$ of a PDMS–PA composite membrane filled with 20 wt % fumed silica was up to 2.66×10^{-7} mol·cm^{-2}·s^{-1}·mmHg^{-1} in a pervaporation experiment at 40°C with an ethanol/water mix-

ture of 5 wt %, which was almost twice that of the unfilled PDMS–PA composite membrane. This may be attributed to the disruption of PDMS chain packing by the introduced fumed silica and the interaction between PDMS and fumed silica, which led to an increase in the free volume of PDMS. Furthermore, although the silica particles produced more defects in the skin layer, the selectivity did not decline significantly. This should be attributed to the hydrophobic features of the fumed silica used.

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