Pervaporation of ethanol aqueous solution by polydimethylsiloxane/polyphosphazene nanotube nanocomposite membranes

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ABSTRACT

Polyphosphazene nanotubes (PZSNTs) were incorporated into polydimethylsiloxane (PDMS) membranes to form nanocomposite membranes. SEM characterization showed that PZSNTs were well dispersed in PDMS. The nanocomposite membranes exhibited higher separation factor for water–ethanol mixture compared with PDMS membranes. As PZSNT content increased, the selectivity increased and permeation flux increased at first to a maximum value and then almost kept the same. The decrease of nanotube diameter caused an increase of permeation flux and separation factor. The effects of temperature and feed solution concentration on pervaporation properties were also investigated. Sorption measurements explained the pervaporation results well.

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1. Introduction

The pervaporation (PV) is considered to be a promising alternative to conventional energy intensive technologies such as extractive or azeotropic distillation in liquid mixture separation. There has been growing research interest in the application of pervaporation to biotechnology in areas such as recovery of ethanol from fermentation broths [1–3]. Success of PV for ethanol–water separation depends on the development of a membrane material that has high permeability, high permselectivity and good film forming properties. The polymers that have been used for ethanol-permselective membranes [3] include polydimethylsiloxane (PDMS) [4–7] and poly[1-(trimethylsilyl)-1-propyne] (PTMSP) [8,9]. Polyorganophosphazenes are important organic–inorganic hybrid polymers and are potential membrane materials for this application owing to its flexible mainchain and good tailoring property of chemical and physical properties.

Polymer systems containing dispersed nanoparticles represent a class of materials with a combination of properties generally not obtainable in conventional polymers. For the pervaporation technique, incorporated mixed matrix membranes have been considered as innovative and attractive membranes. In previous work [10–18], various nanocomposite membranes have been pre-

pared for pervaporation. Recently, carbon nanotube (CNT)–polymer hybrid membranes have been much attractive. Peng et al. [10,11] focused their work on the pervaporation performance of PVA-carbon nanotube membrane for benzene/cyclohexane. The results showed that the permeation flux and separation factor both increased. However, to the best of our knowledge, the pervaporation performance of CNT–polymer hybrid membrane for ethanol/water and other volatile organic compound (VOC)/water mixture was not studied, possibly due to the small affinity between CNT and general VOCs. Besides, the bad dispersibility in solvents and polymers causes some inconvenience in membrane preparation. The cost of CNT is high which also limit their application.

Polyphosphazene nanotube (PZSNT) [19] is a novel type of nanotube which can be prepared by the reaction between hexachlorocyclotriphosphazene (HCCP) and 4,4′-sulfonyldiphenol (BPS). PZSNT is a highly crosslinked polymer, resulting in high stability in solvent. Compared with CNT, PZSNT has following merits. Preparation of PZSNT is easy and convenient and sizes of PZSNT can be easily tailored by changing preparation conditions. Polyphosphazene microspheres (PZSMS) having the same chemical structure with PZSNT can also be easily prepared. Therefore, it is convenient to study the relationship between morphology of fillers and pervaporation performance. PZSNT is organic–inorganic hybrid polymer and can be well dispersed in most general solvents. It was possibly due to that the organic components could provide some degree of affinity to organic molecule and polymers. In addition, there are nanopores on the wall of PZSNT [20] which may reduce diffusion resistance.

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In this study, the PZSNTs were incorporated in polydimethylsiloxane (PDMS) to form PDMS/PZSNT nanocomposite membranes. The morphology of membranes was studied by SEM. The sorption of solvents in the composite membranes was measured. The pervaporation performance of the composite membranes with different contents and sizes of PZSNT, concentration and temperature was also discussed. In addition, the pervaporation performance of PDMS/PZSMS and polyphosphazene heteropolymer $(NP(OC_6H_4C_3H_5)_{0.12}(OC_6H_5)_{0.56}(OCH_2CF_3)_{0.32})_n)$/PZSNT (2CF/PZSNT) was measured to compare with PDMS/PZSNT, in order to investigate the influence of filler and polymer.

2. Experimental

2.1. Materials

Methanol, ethanol, toluene, phenol, tetrabutylammonium bromide, tetraethylorthosilicate (TEOS), dibutyltin dilaurate and petroleum ether were purchased from Shanghai Chemical Reagents Corp. and were used without further purification. 2,2,2-Trifluoroethanol and 2-allylphenol was purchased from Aldrich Corp. Sodium hydride (60% dispersion in minseral oil) was purchased from Rohm-Haas Corp. Prepolymer α,ω-dihydroxylpolydimethylsiloxane with average molecular weight of 16,000 was kindly provided by DowCorning Corp. Tetrahydrofuran (THF, Shanghai Chemical Reagents Corp.) was treated with sodium to remove residue water and was then distilled before used. Benzoyl peroxide (Shanghai Chemical Reagents Corp.) was purified by several times of precipitation from THF solution to methanol. PZSNT and PZSMS were prepared by the method, respectively, described in report [19] and [21]. Nylon microporous membrane (diameter 100 mm, pore size 0.22 μm, thickness 140 μm) was provided by Shanghai Yadong Heji Resin Limited Company.

2.2. Preparation of 2CF

Poly(dichlorophosphazene) $(PNCl_2)_n$ was synthesized by one step method as described by Carriedo and co-workers [22]. The preparation route of 2CF was shown in Scheme 1. The synthesis procedure was carried out as follows. A solution of $(PNCl_2)_n$ (4.46 g, 0.038 mol) was prepared with THF (50 ml) in a 250 ml three-neck flask. Three solutions for substituting, i.e. the solutions of sodium 2-allylphenoxide, sodium phenoxide and sodium trifluoroethoxide, were sequentially added to the $(PNCl_2)_n$ solution and stirred at 60 °C, respectively, for 6, 24, and 24 h. The solution of 2-allylphenoxide was made by the addition of sodium hydride (0.286 g, 7.15 mmol) to a solution of 2-allylphenol (1.03 g, 7.72 mmol) in 50 ml of THF. The 2-allylphenoxide solution was

stirred at room temperature until the sodium hydride was completely consumed, approximately 5 min. The solution of phenoxide was prepared using phenol (3.95 g, 0.042 mol) and sodium hydride (1.58 g, 0.040 mol) in 50 ml of THF. The solution of trifluoroethoxide was prepared using trifluoroethanol (1.56 g, 0.034 mol) and sodium hydride (1.27 g, 0.032 mol) in 50 ml THF and the resulting solution was stirred at 40 °C for 10 min to ensure complete consumption of the sodium hydride. Isolation of the polymer was accomplished through precipitation into water and petroleum ether, respectively. The solid polymer was finally dried in vacuum. 2.42 g of a transparent brown elastomer was isolated in 48% yield. ^1H NMR $(CDCl_3)$ characterization data: δ (ppm) 7.0 (brs), 5.7(brs), 4.8 (brs), 4.1 (brs), 3.2 (brs). FTIR data: C=C (allyl) 1641 cm^{-1}; P=N 1285, 1255 cm^{-1}; P–O–Ar 1199, 930 cm^{-1}; CH=CH$_2$ 995, 904 cm^{-1}. P–O–C 1419, 1048, 962 cm^{-1}; C–F 1172 cm^{-1}.

2.3. Preparation of PDMS casting solution

PDMS solutions were prepared by following method: prepolymer α,ω-dihydroxylpolydimethylsiloxane (PDMS) with average molecular weight of 16,000, crosslinking agent tetraethylorthosilicate (TEOS) and catalyst dibutyltin dilaurate were mixed according to 10:1:0.1 weight ratio in toluene. This solution was treated at 40 °C for 36 h to form a viscous solution.

2.4. Membrane preparation

PDMS and 2CF nanocomposite membranes were prepared by casting method. Casting solutions were prepared by mixing two solutions: polymer solutions and filler solutions. 2CF solutions were made from toluene with 5 wt.% 2CF and 0.3 wt.% BPO. Filler solutions were made from toluene with 5 wt.% PZSNT or PZSMS and then sonicated for 30 min. These solutions were mixed and stirred at 25 °C for 1 h. The formed solution was cast on nylon support. Before use, the nylon support was soaked in water and then placed on a glass plate. Excess water on the nylon support surface was wiped off with a filter paper. Afterwards, a glass ring (50 mm diameter, 3 mm thickness) was placed on the nylon support to hold the solutions and the solution was covered by a hood. The toluene solvent was allowed to evaporate completely at ambient temperature leaving defect free thin dense films as discrete layers on the nylon support. The crosslinking of PDMS and 2CF nanocomposite membranes was, respectively, accomplished by treatment at ambient temperature for 24 h and at 110 °C for 1 h. Finally, the membranes were dried under vacuum at 50 °C for 12 h. The membrane thicknesses were around 25 μm (±2 μm).

2.5. Analytical equipments and techniques

The morphology of composite membrane was characterized by Field emission scanning electron microscope (SEM, JEOL JSM 7401F) and transmission electron microscopy (TEM, JEOL JEM-100CX). The samples for SEM measurements of surface morphology were mounted on copper studs using conductive adhesive and sputter coated with gold before analysis. The samples for SEM measurements of cross-sectional morphology were prepared by liquid nitrogen fracture. The fractured section was also mounted on copper studs and coated with a layer of sputtered gold. For TEM characterization, the samples were dispersed on reticular copper coated with carbon support film.

2.6. Sorption determinations

Determination of sorption for membrane was performed through immersion of pre-weighed samples of membrane, respectively, in water and ethanol at 40 °C for 2 days. The membranes were
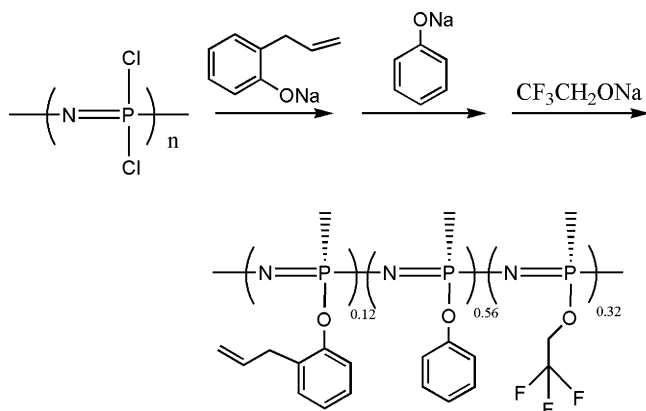
Scheme 1. Preparation route of 2CF.