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Novel ploy(vinyl alcohol)/carbon nanotube hybrid membranes for pervaporation separation of benzene/cyclohexane mixtures

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Abstract

Novel ploy(vinyl alcohol)/carbon nanotube hybrid membranes were prepared and carbon nanotube was dispersed by using β-cyclodextrin (β-CD). These hybrid membranes were characterized by TEM, SEM and DMA. Both pure PVA and β-CD-CNT/PVA hybrid membranes are uniform and these hybrid membranes exhibited significant improvement in Young's modulus and thermal stability as compared to pure PVA and β-CD/PVA membranes. These membranes were applied to pervaporation separation of benzene/cyclohexane mixtures, and showed excellent pervaporation properties. The permeation flux of benzene could be 61.0 g/(m^2 h) and separation factor could be 41.2, which are above the upper bound trade-off curve summarized by Lue and Peng. The effects of β-CD-CNT content, operating temperature and feed flow rate on pervaporation properties also were investigated.

Keywords: Pervaporation; Poly(vinyl alcohol); Carbon nanotube; Hybrid membrane; β-Cyclodextrin

1. Introduction

Organic mixtures have conventionally been separated by extractive distillation, extraction and adsorption processes; but there are high capital investment and energy consumption for these separation technologies. Recently, pervaporation, as an environment-benign and energy-saving technology, has gained much attention to separate organic mixtures due to its high separation efficiencies coupled with energy savings, especially for the close boiling point and azeotropic mixtures [1,2]. Pervaporation is a very promising membrane technology for separation of organic/organic mixtures, among which separating benzene/cyclohexane mixture is one of the most important and most difficult processes.

Organic–inorganic hybrid membranes have attracted considerable recent attention as potential "next generation" membrane materials [3–5]. Such hybrid membranes are typically composed of polymeric and inorganic materials, and have both membrane-forming properties of a polymer and physicochemical stability of an inorganics [6,7]. Inorganic particles in organic–inorganic hybrid membrane are usually silica, zeolite, metal oxide nanoparticle, nanotube and so on. More recently, there has been growing interest in exploring new applications of porous carbons because of their ability to interact with molecules not only at their surfaces but also within the bulk of the material [8]. In our previous paper, we had reported PDMS-carbon molecular sieve (CMS) [9], poly(vinyl alcohol) (PVA)–CMS [10], and PVA–graphite composite or hybrid membranes [2,11] for removal of benzene from aqueous solution and separation of benzene/cyclohexane mixtures.

Poly(vinyl alcohol) (PVA) is polar and hydrophilic, and is an ideal membrane material to separate benzene/cyclohexane mixture [12] due to the distinct preferential adsorption/solution of PVA toward benzene over cyclohexane since the solubility of benzene in water (1.8 g/L, 298 K [13]) is one order of magnitude larger than that of cyclohexane (0.0561 g/L, 298 K [20]). But because of the big difference of solubility parameters between benzene/cyclohexane and PVA, PVA often showed lower permeability to benzene and cyclohexane. Considering the superior

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properties such as high flexibility, low mass density, plus the effective π–π stacking interaction between carbon nanotube and aromatic compounds [14,15], carbon nanotube (CNT) is speculated to be excellent candidate for substituting or complementing conventional nanofillers in the fabrication of organic–inorganic hybrid pervaporation membrane [16–19].

To fully explore the potential of CNT, the serious aggregation of CNTs leads to difficulties in their manipulation and incorporation into polymeric matrixes [20]. The dispersion and solubility behavior of CNT can be remarkably improved through incorporation of cyclodextrin [21,22]. In our previous study, we have found that incorporation of β-CD into PVA matrix could considerably enhance the pervaporation performance of benzene and cyclohexane mixtures [23].

In this study, the pervaporation properties of poly(vinyl alcohol) (PVA) membranes filled with carbon nanotubes (CNT) dispersed by β-CD for separation of benzene/cyclohexane mixtures were studied. The membrane structure and properties were characterized by TEM, SEM and DMA. The effects of β-CD-CNT content, operating temperature and feed flow rate on the pervaporation properties of these membranes were investigated.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (the degree of polymerization was 1750 ± 50, degree of hydrolysis was 95%) was supplied by Tianjin Yuanli Chemical Company (Tianjin, China), benzene and cyclohexane were purchased from Tianjin Jiangtian Chemicals Ltd., Tianjin, China. Multi-wall carbon nanotube was purchased from Tsinghua University, China. β-CD was purchased from Sigma Co. All the chemicals were of analytical grade and were used without further purification. Double distilled water was used throughout the study.

2.2. Membrane preparation

The CNT was dispersed by β-CD, and the preparation procedure was in accordance with that outlined by Chen et al. [22] in which a mixture of β-CD and CNT (in a 30:1 ratio) was ground in an agate mortar and pestle for approximately 2 h with the dropwise addition of ethanol (1 mL) over the first 10 min, then dried for 24 h at 348 K. This procedure resulted in a fine homogeneous black powder (β-CD-CNT).

Poly(vinyl alcohol) (5 g) was dissolved in 45 g distilled water at 363 K. The hot solution was filtered and to the filtrate, a certain amount carbon nanotube dispersed by β-CD and 2 mL cross-linker glutaraldehyde (25 wt.% aqueous solution) as well as 1 mL of concentrated HCl catalyst were added to initiate the cross-linking reaction. The solution was gently stirred for about 4 h at room temperature and the resulting homogeneous solution was cast onto a glass plate with the casting knife. The membranes were allowed to dry at room temperature for 1–2 days and the completely dried membranes were subsequently peeled off. Then, the membranes were heat-treated at 393 K for 1–3 h, and the membrane thickness was about 80 μm. The mass ratio of β-CD-CNT to PVA was varied as 0.02, 0.04, 0.06, 0.08, 0.10, 0.20 and 0.30.

2.3. Membrane characterization

The structures of the pristiline carbon nanotubes and carbon nanotubes dispersed by β-CD were examined by a JEOL-JEM-100CX α transmission electron microscopy (TEM) with an acceleration voltage of 1.0×10^5 V. The cross-section morphologies of the membranes were investigated by scanning electron microscopy (SEM) (XL30ESEM, PHILIPS). The membrane samples were fractured in liquid nitrogen and then coated with gold. Dynamic mechanical data were obtained with a Perkin-Elmer DMA instrument. All samples were tested within the temperature range of 298–500 K at a heating rate of 5 K/min, and a frequency of 1 Hz was selected for all the experiments.

2.4. Pervaporation experiment

Pervaporation experiment apparatus is shown in Fig. 1. Pervaporation experiments were performed on the P-28 membrane module (CM-Celfa AG Company, Switzerland). The effective surface area of the membrane in contact with the feed mixture is 28.0 cm^2. The vacuum in the downstream side of the apparatus was maintained (1 kPa) using a vacuum pump. After a steady state (about 2 h) was attained, the permeate liquid was collected in cold traps immersed in the liquid nitrogen. The compositions of benzene and cyclohexane were estimated by gas chromatography (Agilent 6820, USA). The results from the permeation of benzene/cyclohexane mixtures during the pervaporation were reproducible, and the errors inherent in the pervaporation measurements were in the order of a few percent. From the pervaporation data, separation performances of the membranes can be assessed in terms of total flux (J) and separation factor (α_{PV}), and they were calculated, respectively, using the following equations:

$$J = \frac{W}{At} \tag{1}$$

$$\alpha_{PV} = \frac{P_B/P_C}{F_B/F_C} \tag{2}$$

Here W is the mass of permeate (g), A the area of the membrane in contact with the feed mixture (m^2), t the permeation time (h), P_B and P_C the weight fractions of benzene and cyclohexane in the permeate, respectively, and F_B and F_C are the respective weight fractions of benzene and cyclohexane in the feed. In this study, benzene/cyclohexane (50/50 wt.%) mixtures were used.

3. Results and discussion

3.1. Membrane characterization

3.1.1. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was used to directly view the structure of the pristiline carbon nanotubes and