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Effects of annealing on the physico-chemical structure and permeation performance of novel hybrid membranes of poly(vinyl alcohol)/γ-aminopropyl-triethoxysilane

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Abstract

Novel organic–inorganic hybrid membranes of poly(vinyl alcohol) (PVA)/γ-aminopropyl-triethoxysilane (APTEOS) were prepared through a sol–gel approach in this study. The PVA/APTEOS hybrid membranes were characterized by a wide angle X-ray diffractometer (WXRD), scanning electronic microscope (SEM), themogravimetric analysis (TGA) and a contact angle meter to elucidate the effect of annealing temperature and time on the structure of the hybrid membranes. The swelling of the annealed hybrid membranes in an aqueous ethanol solution was investigated, and permeation performance of the annealed hybrid membranes was studied by pervaporation (PV) of 85 wt% ethanol aqueous solution. With annealing temperature or time increasing, both the swelling degree and the permeation flux of the hybrid membranes decreased, while water permselectivity increased. The interaction parameter of water with the membrane χ_{13}, and ethanol with the membrane χ_{23} increased with annealing temperature and time increasing. The relation of the free volume with the permeation properties of the annealed hybrid membranes was studied by positron annihilation lifetime spectroscopy (PALS). And the diffusion behavior of water and ethanol in an aqueous ethanol solution through the hybrid membranes was analyzed by Maxwell–Stefan equation.
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1. Introduction

Organic–inorganic hybrid materials, which are attractive for the purpose of creating new materials with new or enhanced properties compared with the single organic or inorganic material, have been recognized in various fields [1–3]. In the membrane separation processes, the organic–inorganic hybrid materials are viewed as the next generation membrane materials. Since the possibility of combining the film-forming property of a polymer and the stability of an inorganic compound, the hybrid materials offer consistent and unique opportunities to combine the specific transport properties of organic and inorganic materials in order to produce a highly permselective membrane [2,4,5].

Organic–inorganic hybrid membranes, which was applied in gas separation, pervaporation, reverse osmosis and ion exchange [2,4]; have been researched broadly by many researchers who devote their attention to materials and chemical engineering fields. Polyimides have been widely regarded as gas separation membrane materials because of their good physical properties and the tunable chemical composition of this category of polymer. In order to improve the permeability and selectivity of these membranes, several authors had prepared polyimide/silica hybrid materials which improved separation performances over polyimides [6–11]. Villamo et al. synthesized hybrid

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siloxane membranes containing fixed sulphide and amino binding sites by a sol–gel process, they were permselective towards silver, and have higher separation factor for silver to copper [12]. Microbial biofouling is one of the major obstacles for reaching the ultimate goal to realize a high permeability over a prolonged period of reverse osmosis operation. In order to reduce membrane biofouling, Kim et al. devised a hybrid thin-film-composite membrane consisting of self-assembly of TiO_2 nanoparticles with photocatalytic destructive capability on microorganisms [13,14]. In PV processes, researchers have prepared organic–inorganic hybrid PV membranes, such as chitosan/γ-glycidyloxypropyltrimethoxysilane (GPTMS) [15,16], chitosan/silica [17], quaternized chitosan/tetraethoxysilane (TEOS)[18], PVA/GPTMS[5,19], PVA/TEOS [3,20,21], polyurethane/TEOS [22], poly(methyl methacrylate-*co*-vinyltriethoxysilane)/TEOS and poly(butyl methacrylate-*co*-vinyltriethoxysilane)/TEOS [23], which have film-forming property, chemical and physical stability and high permselectivity.

Organic–inorganic hybrid materials are usually prepared using two approaches, one is by inorganic particles filling, and the other is by chemical synthesis, such as a sol–gel reaction. In the second approach, the hybrid materials is obtained at the molecular level or nanocomposite, in which covalent bonding exists between the organic and inorganic parts [2,4]. And the annealing effect on the structure and permeation performance of the hybrid membrane is remarkable in the preparing process. Uragami et al. prepared PVA/TEOS and poly(vinyl alcohol-*co*-acrylic acid)(P(VA-*co*-AA))/TEOS organic–inorganic hybrid membranes used in PV separation of an aqueous ethanol solution. When the hybrid membranes were annealed, water permselectivity increased with annealing temperature and time increasing. The annealing process promoted the dehydration–condensation reaction between PVA or P(VA-*co*-AA) and TEOS, and leaded to an enhanced water permselectivity of the hybrid membrane [3,24]. Hibshman et al. found that the annealing process increased gas permeation of polyimide/organosilicate hybrid membranes by 200 – 500% [10]. Peng et al. investigated the annealing effect on PV properties of PVA/GPTMS hybrid membranes through PALS, and concluded that the annealing temperature and time strongly affected the permeation properties of PVA-GPTMS hybrid membranes in PV of benzene/cyclohexane mixtures, the free volume fraction of the hybrid membrane decreased with the annealing temperature and time increasing [25].

In the previous work, we successfully prepared novel PVA/APTEOS organic–inorganic hybrid membranes by a sol–gel reaction. The incorporation of APTEOS into the PVA matrix can effectively change the physico-chemical structure of the hybrid membranes. And the hybrid membranes showed a significant improvement in the permeation performance in PV of water/ethanol (or isopropanol) mixtures [26,27]. And the hybrid membranes broke the trade-off between the permeation flux and water permselectivity in PV of an aqueous solution. In this work, we focus on the relationship among the annealing conditions, physico-chemical properties and permeation performances of the hybrid membranes. The annealing effect on the performances of the hybrid membranes in PV of water/ethanol mixture were studied, and the relation of the free volume and permeation properties of the annealed hybrid membranes was investigated by PALS.

2. Experimental section

2.1. Materials

Poly (vinyl alcohol), polymerization degree of 1750 ± 50 and degree of hydrolysis of 98%, was supplied by Sinophatm Chemical Reagent Co. Ltd. (China). γ-Aminopropyl-triethoxysilane (APTEOS), was purchased from Shanghai Yaohua Chemical Plant (China). All other solvents and reagents, of analytical grade and used without further purification, were purchased from Sinophatm Chemical Reagent Co. Ltd.

2.2. Preparation of PVA/APTEOS hybrid membranes

The PVA/APTEOS hybrid membrane with different APTEOS content was prepared by the approach described in the previous studies [26,27]. The obtained membranes were transparent, thickness about 18 μm. The mass ratio of APTEOS to PVA was varied at 0, 2.5, 5, 7.5 and 10, and the resulted homogenous hybrid membranes were designated PA*X*, where *X* represent the mass ratio of APTEOS to PVA.

In order to investigate the effects of annealing temperature and time on the physico-chemical properties and permeation performance of the hybrid membranes, the hybrid membranes were annealed from 80 to 160 °C at intervals of 20 °C for 6 h under vacuum, or annealed at 120 °C for 6, 12, 24 h, respectively.

2.3. Membrane characterization

The physical structure of the PVA and hybrid membranes was studied at room temperature using CAD4 – PDP11/44 X-ray diffractometer (Enraf – Nonious Co. Holland). The dried membrane with thickness of 10 μm was mounted on the microscope slides; the membrane sample was scanned in the reflection mode at an angle 2θ in a range from 5° to 35° at a speed of 8°/min. The surface morphology and element analysis of the hybrid membrane was observed using a Philips LEO1530 scanning electronic microscope equipped with energy-dispersive X-ray spectroscopy (EDX) of ISIS300 (Oxford). Thermal behavior of the hybrid membranes was determined by themogravimetric analysis (TGA) on a NETZSCH STA 409EP analyzer under nitrogen atmosphere, with a heating rate of 10 °C/min. The contact angles for water on the surface of the PVA and hybrid membranes were measured using a contact angle meter (SL200B, Shanghai Solon Tech Inc Ltd.) at 25 °C. And the density of the hybrid membranes

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