Glycopolymer-filled microporous polypropylene membranes for pervaporation dehydration

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ABSTRACT

Natural polysaccharides such as chitosan have been widely used to prepare polymer membranes for pervaporation dehydration. As their synthetic analogues, glycopolymers are also promising materials for the same purpose due to their high affinity interactions with water. In this work, glycopolymer-filled composite membranes were prepared by a pore-filling strategy from microporous polypropylene membrane using ultraviolet-initiated in situ copolymerization of acrylic acid (AA) and D-gluconamidoethyl methacrylate (GAMA). The morphologies and chemical structures of the fabricated membranes were characterized and the dense pore-filled structure was evaluated. Swelling experiments in water, isopropanol and their mixture revealed that the sorption selectivity of the GAMA units in the glycopolymer with water was higher than that of the AA units. Pervaporation on isopropanol/water mixture containing 10 wt% water was carried out and the membranes showed separation selectivity on water with high normalized flux. Investigation on sorption selectivity and diffusion selectivity indicated that the sorption selectivity of the GAMA units on water was the determining factor for the separation property of the glycopolymer-filled composite membranes. These membranes showed fine structural and performance stability during a ten-day operation.

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1. Introduction

In the past few decades, pervaporation has been developed as a promising membrane technology for the dehydration of organic solvents. This membrane process is regarded to possess characteristics of high efficiency, low energy consumption and ability to break azeotrope without entrainers [1,2]. Many efforts have been devoted on the development of new membranes with high separation performance and reliability. These studies result in a wide range of pervaporation membranes, from various polymers such as poly(vinyl alcohol) [3], polyimide [4,5], poly(acrylonitrile) [6,7], polyamide [8], polyaniline [9,10] and polyelectrolyte [11], to typical inorganic materials (zeolite [12], for example). Organic–inorganic hybrid membranes have also been investigated extensively [13]. Among those polymeric materials for pervaporation membranes, polysaccharides including chitosan [14–17], cellulose [15], alginate [18,19] and their derivatives have received much attention due to their good separation selectivity and high flux for the dehydration of organic solvents. The dehydration ability of polysaccharide-based membranes can be attributed to the amounts of hydroxyl groups in the saccharide residues, which provide both high affinity

to water molecules by polarity interactions and hydrogen bonds [20], and a dense network structure by the inter-chain and intra-chain hydrogen bonds [21].

Inspired by the chemical and physical structures of natural polysaccharides, glycopolymers have been synthesized and widely studied in the past 35 years [22,23]. However, few reports have been published on the application of glycopolymers for pervaporation dehydration. With saccharide residues as side groups, glycopolymers inherit the high hydrophilicity of natural polysaccharides [23], which makes them potential candidates for the preparation of pervaporation dehydration membranes. On the other hand, unlike natural polysaccharides with complex structures and compositions, glycopolymers are synthetic materials prepared from highly purified monomers, and therefore with molecular structures more easily to be evaluated and designed. This will open the door for creating a family of glycopolymer-based pervaporation membranes with various saccharide residues and chain structures, targeting at the purification of specific solvents. The structure–performance relationship of the glycopolymer-based membranes can thus be revealed and membranes with better performance can be achieved.

However, the weakness of over-swelling by water and the lack of mechanical stability are two obstacles for the practical application of glycopolymer-based membranes in pervaporation dehydration [24]. A common solution to these problems is to

fabricate the glycopolymers into composite membranes. Compared with the natural polysaccharides, glycopolymers are considered to be more versatile for the preparation of various composite membranes. In this work, therefore, pore-filling strategy [25–27] was adopted to fabricate robust, high-performance membranes with good anti-swelling property from glycopolymers for the first time. The glycopolymer-filled membranes were prepared by the ultraviolet (UV)-initiated in situ copolymerization of D-gluconamidoethyl methacrylate (GAMA) and acrylic acid (AA) in microporous polypropylene membrane (MPPM). To test the pervaporation performance of the fabricated composite membranes, isopropanol was selected as a model solvent, which is an important industrial solvent but forms azeotrope at 87.5 wt% in aqueous solution [28]. The overall objective of this work is to show the availability of glycopolymers as a new type of pervaporation membranes for the dehydration of organic solvents.

2. Experimental

2.1. Materials

Commercial MPPM (Membrana GmbH, Germany) used in this work was prepared by a thermally induced phase separation (TIPS) method with an average pore size of 0.20 μm, a porosity of 75%, and a membrane thickness of 160 μm. This membrane was cut into squares of 3 cm × 3 cm and washed in acetone for 0.5 h to remove the impurities on the membrane surface. Following that the membrane samples were dried under reduced pressure at 40 °C to constant weight and then stored in a desiccator for further use. GAMA was synthesized according to literature [29]. AA and ethyleneglycol dimethacrylate (EGDMA) were purified by vacuum distillation before use. Azobisisobutyronitrile (AIBN) was purified by recrystallization. Methanol and isopropanol were of analytical grade and used without further purification. Water used in all experiments was deionized and ultrafiltrated to 18 MΩ using an ELGA Lab Water system.

2.2. Membranes preparation

The composite membranes were fabricated by in situ copolymerization in the pores of MPPM substrates. A monomer solution was prepared with GAMA, AA and EGDMA dissolved in the mixture of water/methanol (volume ratio 1:1). The mass of EGDMA was 5 wt% of the total monomers. 0.33 wt% of AIBN was added as photo-initiator. A MPPM substrate was immersed in 5 mL monomer solution for 20 min to allow sufficient entering of the monomer solution into the membrane pores. The impregnated substrate was then fixed between two pieces of filter papers (No. 593, Schleicher & Schuell, saturated with the monomer solution) in a Petri dish, and the in situ copolymerization was initiated by UV irradiation. After that the membrane sample was taken out and washed with water and methanol alternatively for 48 h to remove unreacted monomers and initiator, and then dried under reduced pressure at room temperature to constant weight. To study the anti-swelling property of the membranes, bulky glycopolymer samples were also prepared in a similar way except that no MPPM substrate was presented.

2.3. Membrane characterization

The morphologies of the membrane surfaces and cross-sections were characterized by a field emission scanning electron microscope (FESEM, HITACHI S-4800, Japan) at the acceleration voltage of 5.00 kV after coating with a gold layer. The roughness of the membrane surface was analyzed using an atomic force microscope (AFM, Seiko SPI3800N, Japan). The AFM system was operated in

tapping mode at 25 °C in air and silicon tips (NSG10, NT-MDT) with a resonance frequency of about 300 kHz were used. The chemical structure of the membranes was studied by attenuated total reflectance Fourier transform infrared spectroscopy (ATR/FT-IR). The measurement was carried out on a Nicolet FT-IR/Nexus 470 spectrometer equipped with an ATR accessory (ZnSe crystal, 45°). Thirty-two scans were taken for each spectrum at a nominal resolution of 2 cm^{-1}.

A DropMeter A-200 contact angle system (MAIST Vision Inspection & Measurement Ltd Co., China) was employed to determine the water contact angle (WCA) on the membrane surface at room temperature. WCA was measured by the sessile drop method as described in literature [30]. First, a water drop (~2 μL) was dropped onto the dry membrane surface with a microsyringe and the images of the droplet were recorded by a CCD camera system at a certain rate. The contact angles were calculated from these images with the software named as "Dropmeter". Values of WCA were taken at 6 s after the contacting of the drop with the membrane surface and each reported value was averaged from eight parallel experiments.

2.4. Sorption and desorption experiments

The swelling behavior of the glycopolymer-filled membranes was studied in terms of liquid uptake and sorption selectivity. Water, isopropanol and their mixture (with water content of 10 wt%, the same as the pervaporation feed) were used. The sorption experiments were carried out by firstly soaking a membrane sample in 50 mL liquid in a sealed tube on a vibrator at room temperature (25 °C) for a certain time. The swelled sample was then taken out and quickly blotted by tissue papers to remove the liquids on the surface for gravimetrical measurement. Liquid uptake was calculated by Eq. (1)

$$\text{Liquid uptake} = (M_s - M_d)/M_d \times 100\% \tag{1}$$

where M_d is the mass of the dry membrane, and M_s is the mass of the swelled membrane.

Desorption experiment was conducted by putting the swelled membrane sample into a sealed flask in a water bath of 70 °C. The flask was then connected with a vacuum pump and desorbed vapor was condensed by liquid nitrogen and analyzed on an Abbe refractometer (Type WAY-2W, Shanghai Precision & Scientific Instrument Co., Ltd.). The sorption selectivity α_s was calculated by Eq. (2):

$$\alpha_s = (C_i/C_w) \times (C'_w/C'_i) \tag{2}$$

where C_w and C'_w are the mass fractions of water in liquid mixture and membrane, and C_i and C'_i are the mass fractions of isopropanol in liquid mixture and membrane, respectively.

2.5. Pervaporation evaluation

The pervaporation evaluation was carried out on a home-built setup. The effective membrane area was 3.90 cm^2. Temperature of the feed was controlled by a water bath connected with a thermostat. Downstream pressure was kept at about 500 Pa using a vacuum pump. After the establishment of equilibrium for about 2 h, the permeate was collected in cold traps by liquid nitrogen, weighed and then analyzed by the Abbe refractometer. The flux, J (kg m^{-2} h^{-1}) and the separation factor, α, were calculated respectively by Eqs. (3) and (4):

$$J = M/(A \times t) \tag{3}$$

$$\alpha = (P_w/P_i) \times (F_i/F_w) \tag{4}$$

where M (kg), A (m^2) and t (h) are the weight of the permeate, the effective membrane area, and the collecting time, respectively.