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Bioinspired fabrication of composite pervaporation membranes with high permeation flux and structural stability

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ABSTRACT

The properties of composite membrane depend immensely on the quality of the interaction between the support layer and the active layer. This work describes the facile method to improve the interfacial adhesion of the chitosan (CS)/polyethersulfone (PES) composite membranes mediated by dopamine. A thin adherent poly-dopamine film was formed through the spontaneous deposition on top of the PES support layer, and acted as a transition layer. The CS active layer was subsequently coated on dopamine transition layer. The optimal recipe and procedure for CS/PES composite membrane preparation was as follows: PES support layer was treated with 4 mg ml^{-1} dopamine solution (pH 9.47, dipping time 48 h), fully dried and then coated with crosslinked chitosan. The resulting CS active layer was about 10 μm thick. The as-prepared CS/PES composite membrane exhibited high pervaporation flux of 2.28 kg m^{-2} h^{-1} for 90 wt.% aqueous alcohol solution in the feed at 80 °C. It could be derived that dopamine mediation would be an effective method for preparing composite membranes with stable structural and high pervaporation flux.

1. Introduction

The key to the success of pervaporation process is fabrication of suitable membranes yielding high permeability, good selectivity and sufficient mechanical strength. For the purpose of improving the pervaporation performance especially for permeation flux of polymeric membranes, much effort has been devoted to fabricate the well-structured composite membrane comprising support layer and active layer which could be optimized individually [1,2].

Apart from the selectivity and productivity, attention should also be paid to the structural integrity of the composite membrane [3]. Since majority of the active layer of composite membranes were made of hydrophilic materials, whereas the support layers were mostly made of hydrophobic materials [7], the significant differences of surface tension between these two materials cause the segregation of these two layers under swollen conditions. Additionally, to acquire the high permeation flux, the active layer should be made as thin as possible, however, this often resulted in serious structural defects of the composite membrane. Some methods have been developed to enhance the structural stability of the composite membrane, including the crosslinking of the top layer [4–6], the multi-layer structure strategy [7,8], and the integrally skinned structure approach [9]. One solution was to construct a transition layer which was compatible with both layers to firmly anchor the active layer onto the support layer. Transition layer frequently employed some highly reactive chemical reagents represented by chemical coupling agent, which brought complicated processes and rigorous conditions in membrane preparation [7]. In recent years, mussel adhesive proteins (MAPs) excreted by marine mussels have attracted much attention for their ability to form strong adhesive interaction with various substrates in wet environment [10]. In fact, the adhesive proteins used by one of nature's most prolific fouling organisms have provided a rich source of inspiration for endowing sufficient interfacial binding [11]. It has been found that mussels and other marine organisms secrete remarkable protein-based adhesive materials for very tight adherence to the substrates upon which they reside. Lee and Messersmith reported a method to form multifunctional polymer coatings through simple dip-coating of objects in an aqueous solution of dopamine, a kind of low-molecular weight catecholamine mimics of the adhesive protein. Dopamine self-polymerization was delicately utilized to form thin, surface-adherent poly-dopamine films onto a wide range of inorganic and organic materials, including noble metals, oxides, polymers, semiconductors, and ceramics [12]. Inspired by their pioneering work, versatile and facile approaches for fabricating composite membranes with stable structure can be envisioned by employing dopamine as starting material for transition layer construction.

Recently, many investigations [13–15] have been directed to chitosan (CS) as a pervaporation membrane material due to its extremely high affinity to water, good film forming properties, functional groups which are easy to modify, and superior mechan-

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ical and chemical stability. Polyethersulfone (PES) is one of the most common ultrafiltration (UF) materials, which has excellent chemical, mechanical and biological stability. It seems that for composite membrane preparation, chitosan as active layer material and PES as support layer materials should be a suitable match according to the previous reports [26,27]. However, the structural stability of such-made composite membrane is often poor because of the incompatibility of these two materials. In this study, poly-dopamine acted as transition layer was intervened to decrease the surface tension and enhance the interfacial adhesion of the CS active layer and the PES support layer.

The composite membranes comprising PES support layer, poly-dopamine transition layer and crosslinked CS active layer were fabricated and their pervaporation performance for the separation of aqueous ethanol mixtures were assessed. The effects of concentration, value of pH, dipping time of dopamine aqueous solution on the pervaporation performance of the resulting composite membranes were investigated in detail.

2. Experimental

2.1. Materials

Chitosan (the degree of deacetylation is 90.2%) was purchased from Jinan Haidebei Marine Bioengineering Co. Ltd. (Jinan, China). Dopamine hydrochloride was purchased from Wuhan Yuancheng Tech. Development Co., Ltd. PES ultrafiltration membranes were purchased from Shanghai MegaVision Membrane Engineering & Technology Co., Ltd. (Shanghai, China). The PES ultrafiltration membranes (molecular weight cutoff of 50,000) are of asymmetric structure supported by nonwoven polyester fabric. Ethanol, glutaraldehyde (50%) and acetic acid were from Tianjin Kewei Ltd. (Tianjin, China). 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 PES ultrafiltration membranes (the area of 10 cm × 10 cm) were soaked in double distilled water for 2 days to remove glycerin and then fully dried to be employed as the support layer of the composite membrane. The PES support layer was dipped in aqueous dopamine solution with different concentrations and pH for a certain time, and then dried. The transition layer was formed through the spontaneous deposition of a thin adherent poly-dopamine film on top of the support layer.

The construction of active layer by glutaraldehyde crosslinked CS (CS-GA) was performed according to a reported method [16,17]. Chitosan was dissolved in dilute acetic acid solution and stirred at 80 °C for 1 h to obtain 2 wt.% chitosan solutions. After filtration, a certain amount of GA (based on CS) was added with stirring for 30 min. The dried PES with poly-dopamine layer were dipped into the resultant casting solution for several minutes and then taken out to dry. The membranes were placed with a certain inclination angle when they were under drying. All the membranes are dried at room temperature for 24 h.

2.3. Membrane characterization

FT-IR spectra were recorded on a Nicolet-560, 5DX instrument equipped with both horizontal attenuated total reflectance (HATR) accessories. Thirty-two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum. X-ray photoelectron spectra (XPS) were acquired with a PHI-1600 (PE USA) spectrometer equipped with an Mg Kα ($h\nu$ = 1486.6 eV) as radiation source.

The thickness of active layer and poly-dopamine layer was detected by Dektat 6 Stylus Profiler. The static contact angles of the membranes were measured at room temperature by a contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China). The microstructures of membranes were examined by scanning electron microscope (SEM) using a Philips XL30ESEM instrument.

2.4. Pervaporation measurements

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 (1.0 kPa) using a vacuum pump and the feed flow rate was about 60 l/h. After a steady state (about 2 h) was obtained, the permeate liquid was collected in cold traps immersed in the liquid nitrogen. The compositions of ethanol and water were estimated by gas chromatography (Agilent 4890, USA). The results from the permeation during the pervaporation were reproducible, and the errors, marked in the date figures, 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 permeate flux (J) and separation factor (α), and they were calculated, respectively, using the following equations:

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

$$\alpha = \frac{P_W/P_E}{F_W/F_E} \tag{2}$$

where Q is the mass of permeate (g); A the effective area of the membrane in contact with the feed (m^2); t the permeation time (h); P_W and P_E are the weight fractions of water and ethanol in permeate, respectively; F_W and F_E are the weight fractions of water and ethanol in feed, respectively.

3. Results and discussion

3.1. Membrane characterization

3.1.1. FT-IR

The thorough coating of poly-dopamine onto PES support layer could be demonstrated by the appearance of characteristic peak of dopamine at 1610 cm^{-1} was assigned to the overlap of C=C resonance vibration in aromatic ring and N–H bending as shown in Fig. 1. The N–H shearing vibration of the amide group was observed at 1520 cm^{-1}. The phenolic C–OH bending and stretching vibration existed at 1390 and 1290 cm^{-1}. Meanwhile, it was observed that the characteristic peak of PES disappeared, which meant that the support layer was fully covered by dopamine layer. In addition, evident absorption peak of –OH and characteristic peak of chitosan has been detected in the spectrum of “CS/PES” and “CS/D-PES” membranes around 3300 cm^{-1}, 1500 cm^{-1}, 1050 cm^{-1}, 1400 cm^{-1}, which indicated that the surface of the composite membranes was completely covered by chitosan.

3.1.2. XPS

XPS analysis has been applied to confirm the chemical composition of this poly-dopamine layer of uncoated PES and coated PES samples, and the results were shown in Fig. 2(a). The N/C molar ratio for the composite membranes approached the theoretical value of pure dopamine (0.125), indicating that the coating should be derived from the in situ self-polymerization of dopamine. The notably eliminated peak of sulfur (167.0 eV, Fig. 2(a)) shows that the thorough deposition of poly-dopamine layer on the substrate,