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Preparation and characterization of microporous poly(vinyl butyral) membranes by supercritical CO_2-induced phase separation

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Abstract

Microporous poly(vinyl butyral) (PVB) membranes were successfully prepared by supercritical CO_2-induced phase separation. The obtained membrane structures were characterized by scanning electron microscope. The results indicated that the process parameters, such as PVB concentration in casting solution, CO_2 pressure, temperature and depressurization time, had significant effects on the membrane structure. The increase of PVB concentration led to a decrease of the mean pore size. With the increase of temperature and CO_2 pressure, the top surface of the membrane became dense, the pore size of cross-section increased and the asymmetry became more pronounced. With the increase of the depressurization time, the top surface became porous and the pore size of cross-section increased. Macrovoids occurred at a certain distance from the skin layer of the membrane prepared under the pressure of 15 MPa or at the PVB concentration of 19% (w/w). The crystallinity and thermal stability of membranes were characterized by wide-angle X-ray diffraction, differential scanning calorimeter and thermogravimetric analysis. The relations between the membrane characteristics and the process parameters were extensively discussed.

Keywords: Microporous membrane; Preparation technique; Supercritical CO_2; Phase separation; Poly(vinyl butyral)

1. Introduction

Poly(vinyl butyral) (PVB) is a member of the class of poly(vinyl acetal) resins. It is manufactured from poly(vinyl alcohol) by polymerizing butyl aldehyde in the presence of a strong acid. PVB is characterized by high adhesion to glass, toughness, light stability, clarity as well as excellent mechanical strength and impact resistance. It is therefore extensively used as an adhesive interlayer between glass plates in the manufacture of laminated safety glass bullet-proof composition [1]. In addition, being an innocuous and inodorous polymeric material, PVB can withstand some special conditions, such as low temperature, bacteria, microorganism, alkali and diluent acid [2]. These properties of PVB make it an attractive membrane material used in membrane bioreactor (MBR). It was reported that porous PVB membranes had been used for the urease immobilization [3] and for the adsorption of heavy-metal ions [4]. Recently, it was reported that PVB-based ultrafiltration membranes had been prepared by the conventional wet phase inversion [5].

The wet phase inversion is a method widely used for the microporous polymer membrane preparation. In this process a viscous solution is first cast on a suitable support, and then immersed in a nonsolvent bath. The membrane is formed by polymer precipitation, which occurs as a consequence of concentration variations following diffusive interchange between the solvent and the nonsolvent. However, this liquid separation process involves the use of organic solvents that must be expensively removed from the membrane with post-treatments, especially in the case of biomedical application. An alternative technique, using supercritical CO_2 ($ScCO_2$) as the nonsolvent to induce the phase separation, has been recently proposed. The advantages of this technique over the wet phase inversion method are: $ScCO_2$ can dry the polymer membrane rapidly without collapse of the structure due to the absence of a liquid–vapor interface; the dry membrane can be obtained without the post-treatment and the solvent dissolved in $ScCO_2$ can be easily removed and recovered. The technique has attracted a lot of attention and been used for the preparation of some typical polymeric membranes [6–19]. However, the effects of some operating parameters on the

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morphology and structure of the polymeric membranes prepared with various materials by this technique may be completely different. For example, the effect of depressurization time on polylactide (PLA) membrane obtained by Xu et al. [13] showed that the mean pore size increased and the pore density decreased with the increase of depressurization time; however, the effect of depressurization time on polysulfone (PSF) membrane investigated by Temtem et al. [15] indicated that fast depressurization tended to increase the surface porosity and to produce larger pores.

The main purpose of this work is to study the feasibility of preparing PVB membranes by ScCO$_2$-induced phase separation process and to systematically investigate the effects of operating parameters, such as PVB concentration in casting solution, CO$_2$ pressure, temperature and depressurization time, on the morphology and structure of PVB membranes. In addition, a comparison is made with the morphologies of the membranes prepared by this technique and by the wet phase inversion. The crystallinity and thermal property of PVB material and its membranes are evaluated by wide-angle X-ray diffraction, differential scanning calorimeter and thermogravimetric analysis.

2. Experimental

2.1. Materials

PVB (45–49% of butyl aldehyde group; $T_g = 70–80\,°C$) was supplied by Sinopharm Chemical Reagent Co. Ltd. Dimethyl acetamide (DMAC) (purity > 99.5%) was supplied by Tianjin Bodi Chemicals Co. Ltd. CO$_2$ (purity, 99%) was obtained from School of Chemical Engineering, Dalian University of Technology. All materials were used as received.

2.2. Membrane preparation

The experimental setup is schematically shown in Fig. 1. PVB powders were dissolved in DMAC with mechanical stirring to form a homogenous casting solution. After removing air bubbles, the solution was cast onto a clean metal dish with a diameter of 40 mm using a doctor's blade with a 200 μm gap. Then, the metal dish with the solution film was immediately (less than 30 s) put inside the membrane formation cell to avoid the evaporation of solvent. Valve 2 (see Fig. 1) was opened and CO$_2$ compressed by membrane compressor was introduced into the cell which was placed in an isothermal water bath. When the pressure in the membrane formation cell reached a desired value, it was hold for 40 min. Then, valve 3 was opened to sweep the cell with fresh compressed CO$_2$ and dry the membrane at the constant pressure for 30 min. At the end of the experiment, the cell was slowly depressurized at the experimental temperature. The depressurization time was 1 h unless otherwise specified.

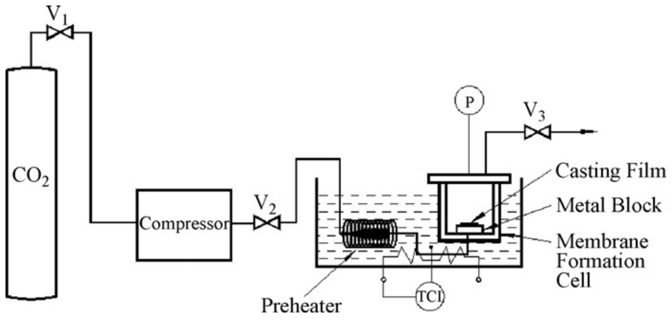

Fig. 1. Schematic presentation of the experimental setup used for the formation of PVB membranes by ScCO$_2$-induced phase separation process. V: valve; P: pressure gauge; TCI: temperature control indicator.

2.3. Membrane characterization

For an observation of the cross-section, the PVB membrane prepared by the ScCO$_2$-induced phase separation process was freeze-fractured in liquid nitrogen and sputter coated with gold. A scanning electron microscope (SEM; KYKY-2800B) at an accelerating voltage of 25 kV was used to determine the membrane characteristics of top surface and cross-section. KYKY-SemImage software was used to analyze the mean diameter and the diameter distribution of pores. Approximately 200 pores were analyzed for each examined membrane.

The wide-angle X-ray diffraction (WAXD) patterns were recorded by the reflection scan with nickel-filtered Cu Kα radiation using an X-ray diffractometer (D/Max-3A, RIGAKU Co.). The X-ray generator was run at 40 kV and 100 mA. All the WAXD measurements were performed at 2θ between 5° and 60°. The scan speed and scan step were 6°/min and 0.02°, respectively.

The melting endotherms of polymer powder and the formed membranes were determined by differential scanning calorimeter (DSC) (DSC822, Mettler, USA) under a nitrogen atmosphere at a heating rate of 10 °C/min over the range of 40–180 °C. The flow rate of nitrogen gas was 20 ml/min. The sample weight was in the range of 5–10 mg.

The thermal stability of membranes was monitored by thermogravimetric analysis (TGA) (SDTA851, Mettler, USA). The TGA measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min over the range of 50–600 °C.

3. Results and discussion

3.1. Effect of PVB concentration

A first set of experiments with the polymer concentrations ranging from 10 to 19% (w/w) in DMAC were performed at temperature of 35 °C and CO$_2$ pressure of 10 MPa to evaluate the effect of the initial polymer concentration. Different membrane structures of top surface and cross-section were obtained as shown in Fig. 2. Under these operating conditions, a porous skin layer and a sponge-structured sublayer were observed in all cases. With the increase of the initial PVB concentration, both the size and the density of the pores on the top surface decrease gradually. The diameter distributions of the pores on the cross-sections are shown in Fig. 3. It can be seen that all distributions are asymmetric. Moreover, with the increase of the PVB con-