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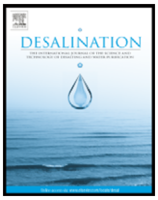

Preparation and characterization of poly(vinyl butyral) hollow fiber membrane via thermally induced phase separation with diluent polyethylene glycol 200

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ABSTRACT

Hydrophilic poly(vinyl butyral) (PVB) microporous hollow fiber membranes were prepared via thermally induced phase separation (TIPS), polyethylene glycol with molecular weight 200(PEG200) was used as diluent. The phase diagram of PVB/PEG200 system indicated L–L phase separation. The effects of preparation condition such as take-up speed, bore liquid flow rate, air-gap, and water bath temperature on the properties of the membrane were investigated. The results showed that PVB hollow fiber membrane prepared at air-gap 5 mm had a little greater tensile strength, breaking strength and elongation than those prepared at air-gap zero, and the former had a little greater rejection but smaller water permeate. The increase of the take-up speed led to the decrease of inner diameters and thickness, the increase of the bore liquid flow rate led to the increase of inner diameter and outer diameter, but the decrease of thickness.

1. Introduction

Thermally induced phase separation (TIPS) method is one of the most useful techniques to prepare the porous membranes [1–6]. In the membrane preparation via TIPS, a polymer is dissolved in a diluent at high temperature and the homogeneous polymer solution is cooled to induce phase separation. After the polymer is solidified by crystallization or glass transition, the diluent is removed. TIPS method has some advantages over the conventional membrane preparation technique, such as low tendency for defect formation, and effective control of the final pore size [7]. Moreover, TIPS can be applied to a wide range of polymers, including those that cannot be formed into membranes because of poor solubility [8].

Some researchers have reported the membrane formation via TIPS from the basic standpoint of thermodynamics and kinetics [1–6,9–15]. Lloyd et al. studied the solid–liquid [1] and liquid–liquid [2] phase separation of porous polypropylene membranes prepared via TIPS and investigated the effects of thermodynamic interactions, crystallization kinetics and properties of diluent on the structures of membranes [3–6]. Many homopolar crystalline polymers such as polyethylene(PE) and polypropylene(PP) are suitable for making hydrophobic polymer membranes via TIPS [16–19].

However, due to solute adsorption and pore blocking, especially in the case of protein separation, the fouling that causes flux decline is easily suffered for hydrophobic membranes. This fouling makes frequent cleaning necessary, accordingly increase maintenance and operating costs [20]. There are some methods to reduce fouling, and the use of hydrophilic membrane is one useful method. Generally, proteins adsorb more strongly at hydrophobic surfaces and are less readily removed than at hydrophilic surfaces. Thus, hydrophilic polymer membranes are desirable for lessening the fouling of the membrane.

Poly(vinyl butyral) (PVB) is a product of the reaction between poly (vinyl alcohol) (PVA) and butyl aldehyde in the presence of an acid catalyst, the final structure can be considered to be a random terpolymer of vinyl butyral, vinyl alcohol and vinyl acetate [21], its structural formula is shown in Fig. 1.

Being an innocuous and tasteless polymeric material, PVB can endure the low temperature, light, change in humidity, bacteria, microorganism, alkali and diluent acid [22]. Moreover, it seems to be regarded that PVB molecular will provide with some hydrophilicity because of its hydroxyl groups. Therefore, PVB seems to be an attractive material for preparing the membrane [23]. F. Shen et al. [23] prepared PVB-based ultrafiltration membranes by immersion–precipitation in water coagulation bath, the increase of PVB in the components can increase the hydrophilicity of the membrane. However, there are very few reports on the preparation of PVB hollow fiber membrane. In our previous work [24], we have explored the effects of diluent molecular weight on the properties of PVB hollow fiber membrane using three kinds of polyethylene glycols (PEG) with the molecular weights of 200, 400 and 600. However, as the molecular weight of diluent increase, the viscosity of the polymer solution also increases, and more additional pressure of N_2 upon the polymer solution is needed for the extrusion of suitable amount of

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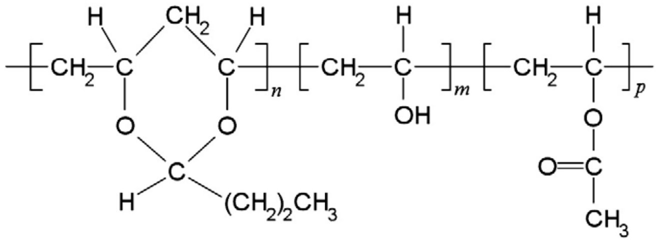

Fig. 1. Structural formula of poly(vinyl butyral).

polymer solution. Furthermore, the residual diluent in the hollow fiber membrane is not so easy to clean through the washing bath if the greater molecular weight of diluent is used due to the increase of viscosity and decrease of diffusion coefficient. Thus, it is necessary to further investigate the preparation and properties of PVB hollow fiber membrane prepared with a relative small molecular weight of diluent PEG200.

In this work, hydrophilic PVB hollow fiber membranes were prepared using PEG200 as diluent via TIPS, and the effects of take-up speed, bath temperature, air-gap, and bore liquid flow rate on the properties of the hollow fiber membrane were investigated extensively.

2. Experiment

2.1. Materials

Copolymer poly(vinyl butyral) (the average polymerization degree = 2400) was purchased from Denka Co. (Japan). Vinyl butyral and vinyl alcohol parts of the copolymer are 81 wt.% and 17 wt.%, respectively, the residual vinyl acetate part is 2 wt.%. Polyethylene glycol with the molecular weight of 200(PEG200) used as diluent were purchased from Wako Pure Chemical Industries. All the chemicals used in this study were not purified further.

2.2. Phase diagram

Cloud point was measured as follows. Homogeneous polymer–diluent samples were prepared by an IMC-119D mixer with a twin-blade (Imoto Co., Japan) [25]. Forty gram mixture of polymer and diluent was put into the vessel, heated to a certain temperature and then mixed for 10 min at 50 rpm of rotating speed. The obtained homogeneous sample was cut into small pieces and placed between a pair of microscope slides, while a 100 μm-thick Teflon film with a square opening in the center was inserted between the slides. The sample was heated on a hot stage (Linkam, LK-600 PH, UK) up to 180 °C for 3 min and then cooled to 25 °C at a controlled rate of 10 °C/min. The cloud point temperature T_{cloud} was visually determined by observing the appearance of turbidity under an optical microscope (Olympus, BX50, Japan). Every T_{cloud} was measured for 3 times, and the average temperature was obtained as the cloud point.

A Perkin-Elmer DSC-7 was used to determine the dynamic glass transition temperature T_g. The solid polymer–diluent samples were sealed in an aluminum differential scanning calorimetry (DSC) pan, melted at 180 °C for 5 min, then cooled at 10 °C/min to 25 °C, and immediately heated to 180 °C at 10 °C/min again. Thermograms in the second heating were used to determine T_g.

2.3. Light scattering measurement

The light scattering measurement was carried out to obtain the structure growth data with a polymer dynamics analyzer (Otsuka Electronics Co., DYNA-3000) [25]. The hot stage was located between a He–Ne laser (5 mW) and a detector. The sample was sealed with two cover slips, placed on the stage and heated at 180 °C. Then it was cooled to 25 °C at the cooling rate of 40 °C/min. The structure growth behavior during the cooling with constant cooling rate was monitored by the light scattering measurement at the time interval of 0.2 s.

2.4. Hollow fiber membrane preparation

Hollow fiber membranes were prepared by a batch-type extruder (Imoto Co., BA-0, Japan). Measured amounts of PVB and PEG200 were fed to the vessel, heated to 180 °C, and then mixed for 30 min. The PVB concentration was fixed at 20 wt.%. A short twin-screw was employed in the vessel to ensure the complete mixing by scraping the wall of the vessel. After holding at this high temperature for 1 h, the homogeneous polymer solution was fed to a spinneret by a screw pump under the pressure of nitrogen. The spinneret consists of outer and inner tubes, and their diameters are 1.58 and 0.83 mm, respectively. The temperature of the spinneret was controlled at 160 °C. PEG200 was introduced into the inner orifice to make a lumen of the hollow fiber, the temperature was 140 °C. The hollow fiber was extruded at a certain extrusion rate from the spinneret and wound on a take-up winder after entering into a water bath to induce the phase separation and solidify the membrane. The variables in the spinning process were, the take-up speed, the air-gap distance, and the bore liquid flow rate, and water bath temperature.

2.5. Characterization of the hollow fiber membrane

2.5.1. SEM observation

To obtain the dry membrane, the prepared membranes were immersed into water to extract the remaining diluent, and freeze-dried with a freeze dryer (EYELA, FD-1000, Japan). The dry hollow fiber membranes were fractured in liquid nitrogen and treated with Au/Pd sputtering. The cross-sections and the surfaces of the hollow fiber membranes were examined using a scanning electron microscope (SEM, JSM-5610LVS, Hitachi Co., Japan) with an accelerating voltage of 20 kV.

2.5.2. Water permeability

Pure water was forced to permeate from the inside to the outside of the hollow fiber membrane. The transmembrane pressure could be applied by adjusting the pressure valve close to the release side, and the pressure was averaged from the readings of the inlet pressure gauge and outlet one, and the pressure was ranged from 0.05 to 0.10 MPa. Water permeability was calculated on the basis of the inner surface area of the hollow fiber membrane. The permeability of each type of hollow fiber was the averaged value of two batches, and each batch of hollow fiber was measured for 3 times.

2.5.3. Particle rejection

The filtration experiment was performed using the same apparatus as that used in the water permeation experiment. The particles used were mono-dispersed polystyrene latex particles with diameter of 102 nm (Duke Scientific Co., CA). The feed suspension was prepared by dispersing the latex particles in an aqueous nonionic surfactant (0.1 wt.% Triton X-100). The particle concentration in the permeate and feed suspension were measured with an U-2000 UV spectrophotometer (Hitachi Co., Japan) under the wavelength of 385 nm.

2.5.4. Tensile strength and elongation

The tensile strength and elongation of the hollow fiber membrane was measured with a tensile tester (AGS-J, Shimadzu Co., Japan). The membrane was fixed vertically between two pairs of tweezers with the length of 50 mm. Then the membrane was extended at a constant elongation rate of 50 mm/min until it was broken. The tensile strengths were calculated on the basis of the cross-sectional areas of hollow fiber membrane. The average of the three membranes was