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Preparation of poly(vinylidene fluoride) hollow fiber membranes for microfiltration using modified TIPS process

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Abstract

The porous PVDF hollow fiber membranes with the particulate morphology were successfully prepared through the modified TIPS process and the addition of solvent into non-solvent in the coagulation bath. The structures of formed membranes were investigated using differential scanning calorimetry, X-ray diffraction measurement, and scanning electron microscopy together with the corresponding microfiltration performances such as water flux, rejection rate, and elongational strength. Initially, the asymmetric membranes having spherical particles formed due to crystallization of PVDF transformed to skinless porous structure, leading to the change of crystalline structure from α to β-form crystallines PVDF with increasing solvent into a coagulant bath. Thereby, water flux and mean pore size increased at the expense of reduction of rejection rate and mechanical strength.

Keywords: Poly(vinylidene fluoride); Hollow fiber membrane; Microfiltration; Morphology; Membrane characterization; Crystal structure

1. Introduction

Recently, the attention of polymeric microfiltration (MF) membranes has increased for practical and potential applications in the fields of wastewater treatment and water purification [1]. The MF membrane is a size exclusive barrier to reject suspended solids and microorganisms in the feed stream, whereby all particles larger than the pores are retained on the feed side of the membrane. For the formation of such microporous membranes, one of the most well-known fabrication methods is so-called immersion precipitation (IP) process, wherein liquid–liquid demixing and/or crystallization by the exchange of solvent for non-solvent phase is used to give porous structured membranes with pore sizes ranging from the nano- to micro-scales [2]. In a practical and academic view point, this approach is particularly valuable since membrane morphology can simply be controlled by changing the casting or spinning conditions such as temperature, additives, and concentration [3,4]. A variety of polymers including poly(sulfone), poly(acrylonitrile), poly(amide), and cellulose acetate have been applied for membrane formation through the IP process in order to prepare membranes with the enhanced separation properties accompanied with the controlled porous structures [5–10].

Among such membrane forming polymers, semicrystalline poly(vinylidene fluoride) (PVDF) has attracted much attention owing to its good mechanical properties, the feasibility to form membranes, as well as its intrinsic exceptional chemical stability [11]. The PVDF membranes with various pore structures were produced by IP and their filtration performances as well as structural properties were investigated depending on preparation conditions such as solvent used, concentration, and temperature [12,13]. However, the PVDF membranes fabricated by the conventional IP often show asymmetric structures consisted of a dense skinned layer and a fragile macroporous substructure together with a restricted pore size range and porosity [14,15]. This asymmetric structure is unfavorable since membranes for microfiltration generally require the skinless porous structures to minimize the resistance against water flux.

As an alternative to IP, the thermally-induced phase separation (TIPS) process has been introduced to prepare microporous membranes. Due to its intrinsic advantages over IP process, the TIPS process has been applied to a wide range of polymers and more details of membrane formation using TIPS process were reported elsewhere [16,17]. The preparation of membrane from TIPS system generally requires a binary mixture consisted of polymer and diluent and high temperature above melting tem-

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perature of polymer. Although the preparation of membranes from this approach is particularly favorable due to less control parameters than those in IP process, the widely use of TIPS process may be limited by the choice of diluent and high process temperature. Thus, it is believed that the use of solvent with wide solubility at relatively low temperature is quite desirable to take advantage of TIPS process to produce MF membranes with balanced permeation and rejection properties.

In this study, the modified TIPS process was employed to explore the possibility of structural control of the membranes prepared from PVDF/γ-butyrolactone (γ-BL) system. Such process was consisted of both high temperature spinning and the exchange between solvent and non-solvent. The microfiltration properties as well as structures of the membranes were further controlled and tailored by use of soft coagulant, where the solvent is added to the coagulant for optimizing membrane structure. Although many studies about the formation of porous PVDF membranes have previously reported, both preparation and characterization of PVDF hollow fibers by use of the modified TIPS process is still rare, which is the main objective of the present study.

2. Experimental

2.1. Materials

PVDF (KF 1300) was purchased from Kureha Chemical Industry Co. As all reagent grades, γ-butyrolactone, dimethylacetamide (DMAc), and ethylene glycol (EG) were obtained from Samchun Chemicals. All chemicals and materials were used without further purification.

2.2. Preparation of hollow fiber membranes

PVDF in pelletized form was dissolved in γ-BL solvent to prepare a 40 wt% solution. A clear and homogeneous dope solution was achieved at 140 °C. For the spinning after degasification, the dope solution was transported to a spinning nozzle by a gear pump. The jacket type pump head and nozzle were also maintained at 140 °C. Subsequently, spinning into each coagulation bath composed of varying DMAc and EG proportions, maintained at 20 °C was performed. The EG/DMAc weight ratios in the bath were set at 70/30, 60/40, 50/50, and 40/60, respectively. As an inner coagulant, EG/DMAc mixtures of 50/50 was used for all the spinning conditions with a fixed air gap of 10 cm. After the mutual exchange between the solvent and non-solvent phases, the as-spun hollow fiber membranes were rolled to a take-up machine and further washed in tap water for 120 h to remove residual solvent. For comparison, the hollow fiber membranes were prepared using a pure EG as inner and outer coagulant. For the module preparation, the wet fibers were immersed into 50 wt% glycerin aqueous solution for 24 h before drying in ambient conditions to prevent the collapse of porous structure. A test module containing six fibres with an effective length of 9 cm was made using an acryl tube with a diameter of 10 mm and poly(urethane) as a potting material.

2.3. Sol–gel transition temperature

To determine the spinning temperature of PVDF/γ-BL systems that show thermoreversible gelation behavior, sol–gel transition temperatures for the varying polymer concentrations was determined. The sol–gel transition temperature was recorded as the temperature that the sample did not flow, by observing the status of the tilted solution after the homogeneous solutions were kept for 24 h in the convection oven at a desirable temperature, as reported previously [18,19].

2.4. X-ray diffraction study

X-ray diffraction experiments were performed on a PANalytical (X'Pert-Pro) multi-purpose diffractometer using Cu Kα radiation (1.54×10^{-10} m) for the outer surface of hollow fiber samples. A rotating anode generator with a copper target was operated at 40 kV of the acceleration voltage with 30 mA of supplying current. All Samples were analyzed in continuous scan mode (counting 0.5 s per 0.020° 2θ) between 5° and 60° 2θ. Data were collected using X'Pert Industry and analyzed using Highscore software packages (PANalytical Ltd.).

2.5. FT-IR measurement

FT-IR measurements were performed on a Varian 2000 FTIR spectrometer in mode of the attenuated total reflectance (ATR-FTIR) using a Ge crystal detector with an incident angle of 45°. For each sample, 16 scans were signal-averaged at a resolution of 4 cm^{-1}. Baseline corrected infrared spectra were obtained for all fibers in absorbance mode at room temperature.

2.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (Hitachi model S-3500N) was employed to investigate the outer surface and cross-sectional morphologies of the hollow fibers. The membranes were fractured into small pieces in liquid nitrogen and fixed on a sample holder to analyze the membrane structure. In order to minimize the fiber damage due to the electron beam and also to obtain clear images, platinum palladium alloy was sputtered onto the fiber samples.

2.7. Determination of mean pore size

The mean pore size of the membranes were determined using a capillary flow porometer (Porous Materials Inc., model CFP-1200-AE), which gives information about the constricted part of the through pore diameters in the 0.033–500 μm range. The analysis is based upon a three-curve graph: dry curve, wet curve and half-dry curve. To get the dry curve, a dry hollow fiber membrane was put into the test module containing three fibers, nitrogen gas pressure was increased on the inner side of the sample, and the flow rate and gas pressure were measured. To attain the wet curve, the same membrane was saturated with a wetting fluid with known surface tension (Galwick; 15.9×10^{-5} N/cm) and gas pressure was increased on one side of the sample. The