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Reorganization of the surface geometry of hollow-fiber membranes using dip-coating and vapor-induced phase separation

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ABSTRACT

Phase separation is one of the major methods to prepare a hollow-fiber membrane in industry. Despite the strong demands for the control of the inner membrane structure and surface geometry, it is still difficult to obtain the desired membrane structure and surface geometry simply by phase separation. In this work, we employed thermally induced phase separation, dip-coating and vapor-induced phase separation to prepare a hollow-fiber membrane with the controlled surface geometry and homogeneous inner structure, which led to high water permeability and high mechanical strength. First a poly(vinylidene fluoride) (PVDF) hollow-fiber membrane was prepared via thermally induced phase separation (TIPS) and then the outer surface of a membrane was dip-coated with another PVDF solution, followed by vapor induced phase separation (VIPS) to reorganize the outer surface of the membrane. The dip-coating and the VIPS treatment produced a highly porous mesh-like layer on the membrane surface. Filtration experiments using nanospheres and protein solutions revealed that the newly-formed layer served as a “separation layer” to determine the separation properties. The membrane pore-size was controlled to some extent by the conditions for the dip-coating and the VIPS treatment. The surface-reorganized membrane kept its intrinsic high water permeability and mechanical strength. In addition, the membrane exhibited improved low-fouling properties in the filtration of humic acid and protein solutions.

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1. Introduction

Microfiltration (MF) using hollow-fiber membranes is widely used for removing contaminants or recovering valuable constituents from wastewater without intensive chemical treatments or secondary pollution. It is also used in prefiltration for sea water before desalination processes using reverse osmosis membranes [1,2]. The progress of biotechnology and medical technology has expanded potential applications of MF [3,4]. There are still increasing demands for membranes with high separation performance: precise control of the pore-size, low-fouling property and high mechanical strength etc.

Phase separation of a polymer solution is a powerful approach to prepare a polymeric porous hollow-fiber membrane. Nonsolvent-induced phase separation (NIPS) is the major approach to commercially prepare polymeric membranes. It easily produces a porous membrane with macrovoids and with relative low mechanical

strength [5]. Thermally induced phase separation (TIPS) is another approach to prepare a porous membrane without a macrovoid. The membrane without a macrovoid has a relatively homogeneous structure of an inner membrane matrix, which contributes to mechanical strength of a membrane and the high water permeability. In many cases, a hollow-fiber membrane prepared via TIPS has a dense layer on its outer-surface and the dense layer is supposed to determine the separation characteristics of a membrane. The rapid solidification in the TIPS process usually provides the membrane high mechanical strength and high productivity. However, the TIPS method has disadvantages too. It is generally difficult to control the dense layer geometry by the TIPS method, because the dense layer is mandatorily produced by the evaporation of a solvent at high temperature before a polymer solution entering a quenching bath [6,7]. Crystalline structures are often formed in a solid-liquid TIPS process for a crystalline polymer (depending on the kinds of a polymer and the solvent), which results in a heterogeneous membrane surface and a decline in the porosity of a membrane surface [6]. These mean the difficulties of the pore-size control and of the surface geometry control in the TIPS method. The surface geometry of a hollow-fiber membrane can be controlled by the preparation conditions to a limited extent. The control of the

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pore-size by changing experimental conditions in TIPS process often accompanies the porosity of the membrane, resulting in the drastic change in the permeability. It would be of great importance to prepare a hollow-fiber membrane having a controlled surface geometry and a homogeneous inner membrane matrix.

Vapor-induced phase separation (VIPS) is classified as a NIPS process. In a VIPS process, the non-solvent is introduced as a gas phase and the non-solvent sorption to a polymer solution leads to the phase separation. VIPS is a very slow process compared with other phase separation processes due to the slow mass-transfer rate of a non-solvent vapor to a polymer solution. There were only a limited number of reports describing membrane preparation via VIPS, although VIPS can produce membranes with highly porous and ordered surface pattern or attractive surface properties [8–10], membranes without macrovoid defects [11], and polymeric microsieves [12]. Several polymer systems involving VIPS were reported in literatures [13–16]. These reports described mainly the preparation of flat membranes via VIPS. VIPS sometimes plays an assistant role in the preparation of hollow-fiber membranes via NIPS [8,17]. Before a polymer solution extruded enters into a coagulation bath to induce the phase separation, controlled water vapor in an air gap (the space between an extruder spinneret and a coagulation bath) induces the partial phase separation of a polymer solution to help the formation of a membrane surface. However, the control of the surface geometry at the air gap was very limited due to the too short time for VIPS in the air gap.

Herein, we employed TIPS, dip-coating and VIPS to prepare a hollow-fiber membrane with controlled surface geometry and with a homogeneous inner membrane matrix, which led to high membrane performances. A PVDF hollow-fiber membrane was prepared by the TIPS method, and the membrane was then dip-coated with another PVDF solution, followed by a VIPS treatment. A VIPS treatment produced a reorganized outer surface of the membrane with a controlled geometry, which facilitated as a new separation layer for a hollow-fiber membrane.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF) (type 6020, MW 322 kDa) was purchased from Solvay Soieixis K.K (Tokyo, Japan). Methyl methacrylate (MMA), 2-aminoethyl methacrylate hydrochloride (AEMA-HCl), fluorescein isothiocyanate (FITC) and humic acid were purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Triethanolamine-HCl and 2,2'-azodiisobutyronitrile (AIBN) were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Polystyrene nanospheres were purchased from Thermo Scientific (Fremont, CA, USA). All the other chemicals were purchased from Wako Pure Chemical Industries (Osaka, Japan). The water used was high-quality deionized water (DI water, $> 15 \text{ M}\Omega \text{ cm}^{-1}$) produced by an Elix-5 system (Millipore, Molsheim, France).

2.2. Membrane preparation (TIPS) and surface reorganization using dip-coating and VIPS

A model PVDF hollow-fiber membrane was prepared using a batch-type extruder (BA-0, Imoto Machinery Co., Kyoto, Japan) by the thermally-induced phase separation (TIPS) method. A homogeneous PVDF solution (PVDF/diethyl phthalate (DEP)=25/75 wt%) at 190 °C was extruded through a spinneret with an inner lumen made by a bore solution (DEP) into a water bath (20 °C, quenching bath) to induce phase separation and solidification. The gap between the spinneret and the bath was 5 mm, and the membrane was wound on a take-up winder at approx. 0.26 m/s. Finally, the residual solvent in

the prepared membrane was extracted using excess amounts of ethanol and DI water. The membranes were stored in DI water until use. The outer diameter of the membrane was approx. 1.0 mm and the inner diameter was approx. 0.6 mm. The detail experimental methods were described previously in [18].

For the reorganization of a surface of a PVDF hollow-fiber membrane, another PVDF solution was prepared for dip-coating. Dip-coating solutions were prepared by dissolving weighted PVDF (or other polymers) into a mixture of an organic solvent and nonsolvent (for PVDF). A dimethylacetamide (DMAc)/ethanol (65/35 vol%) mixture was used for a dip-coating solution. The PVDF solutions were stirred at 80 °C for 2 h.

A PVDF hollow-fiber membrane of approx. 25 cm in length, whose both ends were tied up not to allow a dip-coating solution to enter into the lumen, was dipped in a dip-coating solution for approx. 10 s and was slowly taken up by hand. The dip-coated membrane was set in a closed chamber with a three-neck cover saturated with a water vapor (relative humidity 100%) at controlled given temperature to induce VIPS of the dip-coated layer (Fig. 1). The transfer time between coating and putting a membrane in a chamber was kept less than 15 s. After the VIPS treatment, the membrane was immersed into DI water for several minutes to thoroughly solidify the surface. The water was then kept stirring for several hours for extracting organic solvents from the membrane.

To investigate the effects of relative humidity (RH) in VIPS on the membrane properties, the RH was controlled by placing water or a saturated magnesium chloride solution at 80 °C in the chamber (Fig. 1) [19]. The RH was measured using a thermo-hygrometer (HN-CHT, Chino Co., Tokyo, Japan), which was set in the chamber through one of the side necks of the chamber cover. The RH of $70 \pm 2\%$ was obtained by stirring the saturated MgCl_2 solution at 150 rpm. The RH of $50 \pm 5\%$ was obtained by stirring the saturated MgCl_2 solution at 300 rpm at approx. 0.06 MPa using a vacuum pump (MDA-015, ULVAC, Inc., Chigasaki, Japan) and the RH of $30 \pm 10\%$ was obtained by stirring the saturated MgCl_2 solution at 50 rpm at approx. 0.01 MPa.

2.3. Characterization of surface-reorganized membranes

DI water filtration was performed with a laboratory-scale apparatus developed in our laboratory at room temperature to determine the pure water permeability of a membrane [20]. The apparatus consisted of a minimodule device that contained a single hollow-fiber membrane, 10.6 cm in length, with an outer diameter of approx. 1.0 mm and an inner diameter of approx. 0.6 mm. DI water was permeated from the outside to the inside of a hollow-fiber membrane at a flow rate of 15 ml/min at a transmembrane pressure of 0.5 bar (Fig. 2a). The transmembrane pressure was controlled by nitrogen gas. Pure water permeability was measured after 5 min filtration of DI water.

The pore-size of the membrane was evaluated by filtrating solutions containing standard polystyrene nanospheres with diameters of 80 nm, 100 nm, 200 nm and 300 nm. The feed solutions containing polystyrene nanospheres were prepared by dispersing standard nanospheres stock solutions into buffer solutions containing Triton-X (0.1 wt%). The polystyrene nanospheres with the diameter above 100 nm were dispersed at the stock solution/buffer ratio of 1/300 vol%. The polystyrene nanospheres with the diameter less than 100 nm were dispersed at the ratio of 1/100 vol%.

An aqueous solution containing styrene nanospheres was filtered through a membrane from the outside to the inside at 15 ml/min at 0.5 bar. Each filtration experiment was carried out for 20 min to reach a stable permeation state. The rejection of the nanospheres, R_{np} , by a membrane was determined by measuring the absorbance at 380 nm in the permeate solution using a UV

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