



Effect of additives on the morphology and properties of poly(vinylidene fluoride) blend hollow fiber membrane prepared by the thermally induced phase separation method

Saeid Rajabzadeh, Cui Liang, Yoshikage Ohmukai, Tatsuo Maruyama, Hideto Matsuyama*

Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan

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ABSTRACT

The effects of poly(vinylpyrrolidone) (PVP) and poly(methyl methacrylate) (PMMA) additives on poly(vinylidene fluoride) (PVDF) hollow fiber membranes fabricated via the thermally induced phase separation process were studied. The addition of PVP showed a significant effect on the membrane structure, while addition of PMMA had little effect. In the PVDF/PVP blend membrane, the growth of spherulites was effectively inhibited due to the low compatibility between PVDF and PVP. An asymmetric structure consisting of a dense skin layer near the outer surface and a spherulite structure inside the membrane was obtained in this blend membrane. Measurements of tensile strength and water contact angle were also carried out. In contrast to the addition of PMMA, the addition of PVP significantly improved the maximum stress, elongation and hydrophilicity of membranes. Filtration experiments with BSA solution showed that PVDF/PVP membranes had much better fouling resistance than PVDF/PMMA and plain PVDF membranes.

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1. Introduction

As global demand for water increases, water purification using hollow fiber membranes has attracted increasing attention, because of their multiple advantages, including superior water product quality, simple control of operation, low cost and easy maintenance. One promising polymeric membrane material, poly(vinylidene fluoride) (PVDF), has gained considerable attention due to its excellent properties, including high mechanical strength, excellent resistance against corrosive chemicals, and good thermal stability [1,2]. PVDF also possesses better processability than other materials. Because of these superior properties, PVDF has been considered for use in various membrane-based filtrations (e.g., micro/nano/ultra-filtration) [3–5], membrane distillation [6–9], pervaporation [10], and membrane gas absorption [11,12]. However, there are still a number of problems that limit the further development and applications of PVDF membranes, especially in the areas of purification and separation of aqueous solution systems. The low surface energy of PVDF results in poor wettability and strong hydrophobicity. The strongly hydrophobic nature of PVDF leads to serious membrane fouling during filtration, caused by various types of hydrophobic solutes and colloids (termed foulants), such as natural organic matters, proteins and

micro-organisms. Therefore, it is very important to improve the hydrophilicity of PVDF membranes.

To date, a number of attempts have been made to improve the hydrophilicity of PVDF. First, surface modification including coating and grafting has been considered, such as alkaline solution treatment [13], chitosan coating [14] and plasma treatment [15]. Compared with surface modification, blending modification is the most practical method for industrial production, because the membrane preparation process must remain unchanged. Hydrophilic polymers, such as polyethylene glycol (PEG) [16], sulfonated polycarbonate (SPC) [17] and perfluorosulfonic acid (PFSA) [18], were used as hydrophilic additives and pore-openers in membrane fabrication. The addition of these polymers allows adjustment of the thermodynamics and kinetics phenomenon during the induced phase separation method to control morphology, pore size and pore size distribution [16–19] in addition to increasing the hydrophilicity.

Several attempts have focused on preparation of blended PVDF membranes via the nonsolvent-induced phase separation (NIPS) method [20–22]. To the best of our knowledge, the thermally induced phase separation (TIPS) procedure is more reliable and controllable for PVDF membrane preparation, due to the high porosity and excellent mechanical strength of the resultant membranes. There have been few reports on preparation of PVDF blend hollow fiber membranes by the TIPS method. In our previous study, we used this method to prepare PVDF/PMMA blend hollow fiber membranes [23]. The extraction of PMMA from

* Corresponding author. Tel./fax: +81 78 8036180.

E-mail address: matuyama@kobe-u.ac.jp (H. Matsuyama).

the blend membrane was effective in increasing water permeability and membrane elongation.

In this study, we focused on the preparation of PVDF/PVP blend hollow fiber membranes by the TIPS method and compared the effects of PVP and PMMA on the fabrication of PVDF hollow fiber membranes. PMMA has better compatibility with PVDF over the entire concentration range in the blended polymer, while the hydrophilicity of PVP is higher, which may thereby lead to better membrane fouling resistance. The different properties of these two polymers, such as compatibility with PVDF, may lead to different membrane structures and, in turn, different membrane performance. PVP is a well-known blending material for polyethersulfone (PES) membrane preparation by the NIPS method [24]. Poly(ethylene-co-vinyl alcohol) (EVOH)/PVP membranes are already prepared by TIPS method [25]. However, in our opinion, this is the first work on PVDF blend membrane preparation with PVP by the TIPS method. It is believed that this pioneering work will significantly progress the understanding of PVDF hollow fiber membranes and improve industrial PVDF membrane production.

2. Experimental

2.1. Materials

PVDF ($M_w=322,000$) was purchased from Solvay Co. (Solef 6020). PVP ($M_w=55,000$) and PMMA ($M_w=120,000$) were purchased from Aldrich Co. Diethyl phthalate (DEP, Wako Pure Chemical Industries, Japan) was used as a solvent for membrane preparation. Bovine serum albumin (BSA) solution was prepared by dissolving BSA in a buffer solution of sodium dihydrogen phosphate and disodium hydrogen phosphate at pH 7.0. BSA, sodium dihydrogen phosphate and disodium hydrogen phosphate were purchased from Wako Pure Chemical Industries. All chemicals were used without further purification.

2.2. Phase diagram

PVDF/DEP, PVDF/PVP/DEP or PVDF/PMMA/DEP mixtures were heated to a desired temperature in an oil bath to prepare homogeneous solutions and then cooled to room temperature. Each homogeneous sample was then chopped into small pieces and placed between a pair of microscope cover slips. A 100 μm -thick Teflon film with a square opening in the center was set between the two cover slips to prevent solvent evaporation and to keep each sample with approximately the same thickness. The sample was heated on a LK-600 PH hot stage (Linkam, UK) to 190 $^{\circ}\text{C}$, held for 2 min, and cooled down to 25 $^{\circ}\text{C}$ at a controlled rate of 10 $^{\circ}\text{C}/\text{min}$. Crystallization temperature was determined visually by noting the appearance of turbidity under a BX50 optical microscope (Olympus Co., Japan) equipped with a LK-600 PH hot stage. A Perkin-Elmer DSC-7 was used to determine the crystallization temperatures of PVDF/DEP solutions. The solid samples were sealed in an aluminum pan, melted at 150 $^{\circ}\text{C}$ for 5 min and then cooled at 10 $^{\circ}\text{C}/\text{min}$ to 25 $^{\circ}\text{C}$.

2.3. Hollow fiber membrane preparation

Hollow fiber membranes were prepared by a batch type extruder (BA-0, Imoto Co., Japan) according to a previously described method [26]. A schematic of the membrane fabrication apparatus is shown in Fig. 1. In brief, measured amounts of PVDF, PVP or PMMA, and solvent (DEP) were fed to the vessel, heated to 190 $^{\circ}\text{C}$ and then mixed for 1 h at 90 rpm. After holding at this temperature for 2 h to release air bubbles from solution, the homogeneous polymer solution was fed to a spinneret by a gear

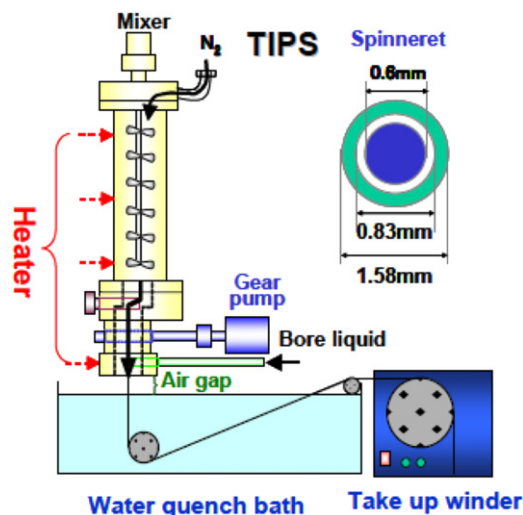


Fig. 1. Schematic of fabrication apparatus.

pump under nitrogen pressure. The spinneret consists of outer and inner tubes with diameters of 1.58 and 0.83 mm, respectively. Solvent was introduced into the inner orifice to make a lumen within the hollow fibers. The hollow fiber was extruded from the spinneret and wound on a take-up winder after entering into a water quench bath to induce phase separation and solidify the membrane.

The velocities of the polymer solution and solvent in the spinneret were fixed at 0.09 and 0.19 m/s, respectively. Take up speed was adjusted to 0.13 m/s and the air gap was fixed at 5 mm. The temperature of water in the quench bath was fixed at 0 $^{\circ}\text{C}$ in this study.

Prepared membranes were immersed into ethanol to extract residual diluent from the membranes and were then washed with deionized water. All membranes were kept in deionized water until use.

2.4. Scanning electron microscopy, energy dispersive X-ray spectrometry and elemental analysis

Hollow fiber membranes were freeze-dried using a freeze dryer (FD-1000, EYELA, Japan). The dry membranes were fractured in liquid nitrogen and treated with Au/Pd sputtering. The surfaces and cross-sections of membranes were observed using a scanning electron microscope (SEM S-800, Hitachi Co., Japan) with an accelerating voltage of 15 kV.

Energy dispersive X-ray spectrometry (EDS) measurement was carried out using FE-SEM (JSM-7500F, JEOL, Japan) equipped with an Energy Dispersive X-ray Spectroscopy (EX-64195JMU, JEOL, Japan).

Elemental analysis was carried out by Sumika Chemical Analysis Service, Ltd. Japan.

2.5. Membrane strength

The tensile strength and elongation of the hollow fiber membranes were measured using a tensile testing instrument (AGS-J, Shimadzu Co. Japan). Membranes were fixed vertically between two pairs of tweezers with the length of 50 mm and then extended at a constant elongation rate of 50 mm/min until failure.

2.6. Water contact angle

Water contact angle of the membranes was measured using a contact angle goniometer (Drop Master 300, Kyowa interface

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