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Preparation and characterization of PVDF–HFP copolymer hollow fiber membranes for membrane distillation

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Abstract

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF–HFP) hollow fiber membranes were prepared by the dry/wet spinning technique at different copolymer concentrations from 17 to 24 wt%. All the spinning parameters were kept constant except the copolymer concentration. The temperature of both the internal and external coagulants was maintained at 40ºC. The effects of the copolymer concentration on the morphological properties of the hollow fibers were studied in terms of external and internal diameter and scanning electron microscopy (SEM). It was found that the thickness of all tested hollow fibers did not change significantly. An evolution of the cross-section structure with the increase of the copolymer concentration was detected. The cross-section of the hollow fiber prepared with the lowest copolymer concentration exhibited a *finger-like* structure in both the external and internal layers disappearing in the internal layer as the copolymer concentration increases. Finally, a *sponge-like* structure is formed through all cross-section of the hollow fiber prepared with the highest concentration. This may be explained based on the decrease of the coagulation rate with the increase of the copolymer concentration in the dope solution.

Keywords: Poly(vinylidene fluoride-*co*-hexafluoropropylene); Hollow fiber; Scanning electron microscopy; Membrane distillation

1. Introduction

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF–HFP) is a copolymer which has recently attracted attention as a potential membrane material. PVDF–HFP presents lower crystallinity and higher free volume compared to poly(vinylidene fluoride) (PVDF) homopolymer, due to the incorporation of an amorphous phase of HFP into the main constituent VDF blocks. The fluorine content also increases due to the addition of HFP group, which makes PVDF–HFP more hydrophobic than PVDF [1]. Therefore, PVDF–HFP is a potential candidate for some applications where the hydrophobicity of the

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membrane material is required like in membrane distillation [2,3].

Nowadays hollow fiber configuration is one of the most interesting membrane geometry in most separation applications because of its high surface area per unit volume, flexibility in operation, mechanically self-supporting, etc. [4]. Most of the PVDF–HFP membrane preparation studies reported in the literature were conducted for flat-sheet membranes. Recently, Shi et al. [5,6] studied the effects of the additives poly(vinylpyrrolidone) (PVP), lithium chloride (LiCl) and glycerol on the asymmetric structures of microporous hollow fiber PVDF–HFP hollow fiber membranes.

In the present study, PVDF–HFP hollow fibers have been prepared using the dry/wet spinning technique with different copolymer concentrations. The effects of the copolymer concentration on the cross-section structure of the hollow fibers were studied using scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

PVDF–HFP was purchased from Sigma–Aldrich Chemical Co. Reagent grade *N*,*N*-dimethyl acetamide (DMAC) was used as a solvent and poly(ethylene glycol) (PEG, M_w = 6000) was employed as a non-solvent additive (NSA). All chemicals were also obtained from Sigma–Aldrich Chemical Co. and used without further purification.

2.2. Preparation of hollow fibers and characterization

The solvent DMAC was first mixed with the non-solvent additive PEG at 3 wt.%. PVDF–HFP was added to the mixture and the polymer solution was agitated at 42ºC for about 24 h until the copolymer was totally dissolved. Prior to spinning, the copolymer solution was degassed in an ultrasonic bath for 15 min. A series of PVDF–HFP/DMAC/PEG dope solutions with the copolymer concentration ranging from 17 to 24 wt.% (17, 19, 20, 22 and 24 wt.%) were prepared.

The dry/wet spinning technique was employed for preparation of the hollow fibers as described elsewhere [4]. The spinneret used has 0.7 mm inner diameter and 1 mm outer diameter. In this study, tap water was used as external coagulant while distilled water was used as internal coagulant (bore liquid). Both the bore liquid and the external coagulant were maintained at 40ºC by using a thermostat (Techne, TU-16D). A peristaltic pump was employed for the circulation of the bore liquid at a flow rate of 19 ml/min. The polymer solution was loaded into the spinning dope tank and forced to the spinneret using pressurized nitrogen. The extrusion pressure of the copolymer solution was maintained at 50 kPa. The ratio of dope flow rate to bore fluid rate was constant for all spinning process. The gas gap distance was 27.5 cm and the take-up speed was 18 rpm (i.e. 9.18 m/min). After spinning, the fabricated hollow fibers were stored in a water bath at room temperature for at least 24 h to remove the residual solvent DMAC. Subsequently, the hollow fibers were dried in air at room temperature before characterization tests.

The inner and outer diameters of the fibers were measured by means of an optical microscope (OLYMPUS BX60M) with a precision of ±1 μm. More than six hollow fiber samples and at least 20 measurements were conducted for each sample.

The cross-section of the PVDF–HFP hollow fibers was examined by a field emission scanning electron microscope (FESEM, JEOL Model JSM-6330F). PVDF–HFP hollow fiber samples were fractured in liquid nitrogen and then sputter-coated with a thin layer of gold. The SEM pictures were taken over different regions of the cross-section of each hollow fiber sample.

3. Results and discussion

The inner and outer diameters of all prepared PVDF–HFP hollow fibers were determined. An increase of about 30 % of both diameters was