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Mechanism of formation of hollow fiber membranes for membrane distillation: 2. Outer coagulation power effect on morphological characteristics

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ABSTRACT

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) hollow fiber membranes with porous and skinless outer surfaces were prepared for desalination by direct contact membrane distillation (DCMD). *N*,*N*-dimethyl acetamide (DMAC)/distilled water mixtures extruded from the outermost channel of the spinneret were employed as external coagulants along the gap of the spinning process. During membrane formation, various types of interactions studied via Hansen solubility parameters were identified at the outer layer of the nascent fiber. Several characterization techniques and DCMD experiments were carried out in order to analyze the effects of the wet gap on the membrane morphology, properties and desalination performance. The skin-layer was avoided and permeate flux was enhanced when using the DMAC/water mixtures as the external coagulants. Increasing the concentration of DMAC in the nonsolvent mixture weakened the external coagulation power and the outer layer morphology of the fiber became more porous with larger surface pore sizes. Open-porous inner surface, skinless outer layer and spongy cross-section were observed for the hollow fiber membranes prepared with the highest amounts of DMAC in water, 50 and 60 wt%, used simultaneously as internal and external coagulants. The hollow fiber membrane prepared with the coagulant mixture 50 wt% DMAC in water exhibited good mechanical properties and excellent MD membrane characteristics, leading to the highest DCMD permeate flux with a good salt rejection factor.

1. Introduction

Membrane engineering is an important key step for obtaining good morphological characteristics of membrane distillation (MD) membranes. Several studies have demonstrated the membrane structural morphology effects on both the permeate flux and separation factor of this separation process [1–3].

Hydrophobic polymeric hollow fiber membranes are commonly prepared by the dry/wet spinning technique, whose operating parameters affect considerably the final structure of the membrane [4–7]. It was observed that the formation of the fiber´s inner layer structure was mainly determined by the bore liquid composition. By changing the type of the bore liquid it was possible to prepare porous inner surfaces [8–10]. However, the majority of the hollow fibers described in the open literature prepared by the dry/wet technique have a dense skin on the outer layer. Its formation starts with the nascent fiber´s path across de air gap distance (i.e. dry step of the spinning process) due to the forced-convective evaporation of the volatile solvents contained in the dope solution; and then completely formed when finally immersed in the nonsolvent coagulation bath [11]. Solvent evaporation increases the polymer concentration at the outermost layer of the fiber compared to that of the bulk of the spinning solution. Additionally, faster solvent outflow in comparison to the nonsolvent inflow inside the coagulation bath also induced the formation of the skin-layer [11,12].

The denser structure of the outer surface of the hollow fiber membranes induces lower external surface porosity, higher vapor transport resistance and lower MD permeate flux as consequence [13,14]. Therefore, it is necessary to improve the outer surface morphology trying to avoid the outer skin-layer formation. Previous studies have analyzed different options to reduce the thickness of the membrane´s external layer and to obtain more porous surfaces. When the air gap distance was reduced, Clausi and Koros [11] and Tsai et al. [15] were able to reduce the skin-layer thickness of the polyimide and polysulfone (PSf) hollow fiber membranes, respectively. The temperature and composition of the coagulation bath are other fabrication parameters that affect the membrane formation mechanism. Wang

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et al. [16] prepared poly(vinylidene fluoride) (PVDF) membranes by immersing the casting dope solution in de-ionized water coagulation bath at different temperatures (15, 25 and 60 °C). It was observed much shrinkage and denser top surfaces for lower coagulation bath temperatures. By adding solvent into the coagulation bath, the phase inversion rate slows down and porous surfaces could be obtained. Wijmans et al. [17] determined the minimum concentration of solvent in the water coagulation bath required to obtain porous top layers of flat-sheet membranes for various polymer/solvent/nonsolvent systems. Yu et al. [18] used the mixture *N,N*-dimethyl formamide (DMF) and water at different ratios (from 0% to 60% of DMF) in the coagulation bath for the preparation of polyacrylonitrile (PAN) hollow fiber membranes via dry/wet spinning technique. The formation of the outer skin-layer was very slow for 60% of DMF in water leading to observable pores on the external surface of the corresponding hollow fiber membrane. Other researchers [14,19] preferred to use a triple-orifice spinneret to extrude a solvent from the outer channel of the spinneret. He et al. [19] and Bonyadi and Chung [14] employed this technique to prepare PSf and PVDF hollow fiber membranes, respectively. Pure *N*-methylpyrrolidone (NMP) solvent was used in these studies observing porous outer surfaces.

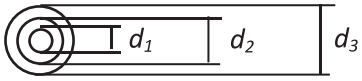
In our previous study [8], hollow fiber membranes were prepared using different nonsolvent mixtures (solvent/water) as internal coagulant. It was observed that these hollow fibers presented a sponge inner layer and skinless and porous inner surface structure, resulting in an improved DCMD performance. This can be enhanced if the formed dense skin-layer at the outer side of the hollow fiber membrane is removed. It is well known that the dry step of the spinning process is the responsible for the formation of the dense outer surface [11,20,21]. The main objective of this study is the change of the outer layer structure from dense skin to open-porous morphology. Two different options have been followed in order to solve the aforementioned drawback: i) eliminating the air gap distance between the spinneret and the liquid coagulation bath and ii) changing the gap type from dry to wet, using different nonsolvent mixtures (solvent/water) as external coagulants through the gap distance. Following these strategies, the solvent evaporation step that occurs through the air gap would be prevented and the polymer concentration on the external interface could be controlled by the solvent outflow and nonsolvent inflow relative ratio [19,22]. In line with previous research studies [8,22,23], the selection of the polymer/solvent/nonsolvent system and the thermodynamic and the kinetics of the phase inversion process play a critical role on the final morphological structure of the membrane. In other words, the solvent-nonsolvent interaction represents the key control factor of the skin-layer thickness. Finally, trying to benefit from the advantages of employing the nonsolvent mixtures as internal and external coagulants, hollow fiber membranes have been prepared using simultaneously the same coagulant solution as both internal and external coagulants.

2. Experimental

2.1. Materials

The spinning solution was composed by the solvents *N,N*-dimethyl acetamide (DMAC) and trimethyl phosphate (TMP), the additive poly(ethylene glycol) (PEG; M_w=6000 g/mol) and the copolymer poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP; M_w=455,000 g/mol). All these reagents were purchased from Sigma-Aldrich. Isopropyl alcohol (IPA, Sigma-Aldrich) was used as the wetting liquid for the void volume fraction or porosity measurements. The sodium chloride (NaCl) was employed as the salt of the aqueous feed solutions of DCMD experiments, and it was purchased from Panreac.

Table 1
Spinning parameters of the PVDF-HFP hollow fiber membranes.

Parameters	Operating conditions
Spinneret: 	d_1=1.0 mm/ d_2=2.4 mm/ d_3=3.4 mm
Extrusion pressure (kPa)	60
Polymeric solution temperature (°C)	42
Internal coagulant	DMAC/distilled water
Internal coagulation temperature (°C)	42
External coagulant	DMAC/distilled water
Internal and external coagulant flow rate (m^3/s) (m^3/s)	2.7×10^{-7}
External coagulation temperature (°C)	Room temperature
Liquid coagulation bath	Tap water
Liquid coagulation bath temperature (°C)	42

2.2. Preparation and characterization of hollow fiber membranes and direct contact membrane distillation experiments

The spinning solution was composed by 19 wt% of the copolymer PVDF-HFP, 5 wt% of the additive PEG and 76 wt% of the solvent mixture combining 40 wt% of DMAC and 60 wt% of TMP. The selection of the dope solution, its preparation procedure and some properties such as viscosity, surface tension and the thermodynamic and kinetics experiments were explained in [8]. More information about the copolymer PVDF-HFP can be found in [8,24]. The hollow fibers were prepared by the dry/wet spinning technique, as described elsewhere [25,26]. The spinning parameters are summarized in Table 1 and the prepared membranes are identified in Table 2 according to the considered fabrication parameters.

The prepared hollow fiber membranes were characterized by means of the following techniques: scanning electron microscope (FESEM, JEOL Model JSM-6335F), optical microscope (OLYMPUS BX60 M), water contact angles, liquid entry pressure, mechanical properties (Instron dynamometer, model 3366), mean pore size (POROLUX™ 100, Porometer), atomic force microscopy (Nanoscope III equipped with 1553D scanner (Digital Instruments Inc., Santa Barbara, Ca)), thermal properties (Differential Scanning Calorimetry (DSC), Mettler-Toledo DSC 1, STAR^e System) and direct contact membrane distillation (DCMD). All the characterization procedures were detailed in the previous study [8]. In this case, the mean pore size of the prepared hollow fiber membranes was obtained by the gas permeation method described elsewhere [27] and using the dry curve obtained from the porometry test.

Table 2
Membranes prepared in this study.

Membrane name	Internal coagulant (wt%)		Gap: type/ distance (m)	External coagulant (EC)	
	DMAC	Water		DMAC	Water
IND0 (GAP 0)[a]	0	100	0	–	
2IND0	0	100	Air/0.275	–	
2OUTD0	0	100	EC/0.275	0	100
2OUTD20	0	100	EC/0.275	20	80
2OUTD40	0	100	EC/0.275	40	60
2OUTD60	0	100	EC/0.275	60	40
2IND50OUTD50	50	50	EC/0.275	50	50
2IND60OUTD60	60	40	EC/0.275	60	40

[a] All the hollow fiber membranes were prepared using the double spinneret described in Table 1 except the membrane called IND0 (GAP 0), which was prepared employing the single spinneret detailed in [8].