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Enhancing wetting resistance of poly(vinylidene fluoride) membranes for vacuum membrane distillation

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ABSTRACT

Composite membranes were fabricated by coating three types of highly hydrophobic perfluorinated copolymers (commercial name: Hyflon AD) on poly(vinylidene fluoride) hollow fibers. The membrane properties, including morphologies, pore sizes, porosities, liquid entry pressures (LEPs), mechanical strength, and separation performance (flux, rejection and wettability) in vacuum membrane distillation (VMD) were systematically characterized and investigated. The properties of the fabricated membranes, including pore sizes, pore size distributions, porosities, and LEPs were significantly affected by the viscosity of the coating polymer solution. Coating solutions with lower viscosities caused smaller pore sizes, narrower pore size distributions, lower porosities, higher LEPs and less flux decline in VMD. Particularly, LEP of the membrane coated with a lower viscosity solution (0.46 MPa) was two times higher than that of the uncoated membrane (0.23 MPa). As a result, the anti-wetting property of the composite membrane after coating was significantly enhanced compared with that of the original membrane. The coated composite hollow fiber membranes also showed improved hydrophobicity, mechanical strength and separation performance (water flux and salt rejection). The water contact angle of the membrane increased from 94 to 145° after coating with a lower viscosity solution.

1. Introduction

Fresh water shortages have become increasingly salient all over the world in the last two decades [1]. In recent years, desalination technologies such as reverse osmosis, evaporation and distillation of brackish water and seawater, have been widely used to produce fresh water. However, these technologies are generally energy intensive [2]. As an emerging desalination technology, membrane distillation (MD) has drawn growing interest due to its feasibility to use low-grade heat, such as industrial waste heat and solar energy, which may reduce the desalination costs [1–5].

Configurations of MD are typically classified into direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD), and air gap membrane distillation (AGMD) [6–12]. In VMD, heat loss by conduction and molecular diffusion resistance on the permeate side are almost negligible compared with other MD configurations [13–15]. In addition, due to the existence of a certain degree of vacuum on the permeate side, the transmembrane pressure difference is larger than that in other configurations and thus may achieve higher permeate flux [14]. However, the transmembrane pressure in VMD also leads to the risk of membrane wetting.

Several polymer materials such as polypropylene (PP) [16], poly (vinylidene fluoride) (PVDF) [17–19] and polytetrafluoroethylene (PTFE) [20–22] have been employed to prepare porous MD membranes. Poly(vinylidene fluoride) is one of the most popular MD membrane material mainly due to its low costs [18,23–26]. However, the hydrophobicity of commercial PVDF membranes is not satisfactory in long-term VMD operation. Therefore, membrane hydrophobic modification has been adopted to improve VMD performance [27–29].

A number of modification methods such as radiation grafting, plasma polymerization, surface coating and blending have been used to optimize MD membrane properties [30–35]. Zheng et al. [30] prepared super-hydrophobic PVDF membranes by chemical vapor deposition from the methyltrichlorosilane solution. Yang et al. [35] utilized plasma and chemical modification to prepare composite hollow

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fiber membranes and compared membrane properties and performance in DCMD. The modified hollow fiber membranes showed higher hydrophobicity and narrower pore size distributions, leading to more sustainable fluxes and higher water quality.

Surface coating is a simple way to modify MD membranes because it is easy to scale up. Various hydrophobic materials have been applied to modify MD membranes [36–39]. Li and Sirkar [39,40] coated PP hollow fibers with fluorosiloxane and achieved high water vapor flux in DCMD and VMD. A commercial copolymer Hyflon AD, derived from tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), has attracted significant interest due to its excellent hydrophobicity, thermal and chemical stabilities [41–44]. Additionally, it can form uniform and thin films by casting or coating techniques [45]. Jalal et al. [46] prepared hydrophobic HyflonAD/PVDF membranes for butanol dehydration via pervaporation. Gugliuzza et al. [47] selected PVDF and Hyflon AD60 as raw polymers to prepare Hyflon/PVDF composite membranes. The combination of these two fluorinated polymers dramatically improved the membrane hydrophobicity and mechanical strength.

Since composite membranes can combine the advantages of different materials (e.g., well-controlled structures and desirable surface properties), it is interesting to prepare Hyflon AD/PVDF composite membranes for VMD. In our previous work [48], Hyflon AD60 was used to prepare Hyflon AD60/PVDF composite hollow fiber membranes. The hydrophobicity, mechanical strength and separation performance of the composite membranes were significantly improved in VMD. There are three types of Hyflon AD copolymers based on the difference in the contents of TFE and TTD. They possess different chemical compositions and properties, and can form composite MD membranes with various properties. Therefore, it is necessary to select the suitable Hyflon AD to prepare high performance composite membranes for VMD, particularly to enhance the membrane stability.

Wetting is one of the major problems in VMD due to the presence of extra vacuum pressure. However, few anti-wetting studies in VMD membrane development have been done. In this study, we employed three types of Hyflon AD copolymers (i.e. Hyflon AD40L, Hyflon AD40H and Hyflon AD60) to improve the wetting resistance of the membrane for VMD. The properties (e.g. morphologies, pore sizes, porosities, liquid entry pressures and mechanical strength) of the original and modified membranes were systematically investigated. Separation performance in terms of water vapor flux, salt rejection and anti-wetting properties of the membranes were also studied with salt solutions.

2. Experimental

2.1. Materials

Hyflon AD amorphous perfluoropolymers (Hyflon AD40L, HyflonAD40H and Hyflon AD60) were kindly supplied by Solvay Specialty Polymer (Bollate Italy). Their chemical structures and physical properties are shown in Fig. 1 and Table 1, respectively. Hyflon AD40H has the highest molecular weight among them. Hyflon AD60 contains 60 mol% TTD, and Hyflon AD40 has 40 mol% TTD. Commercial PVDF hollow fiber membranes were kindly supplied by Jiusi Hi-Tech Co., Ltd. (Nanjing, China). Novec HFE-7100 Engineered Fluid (3M Inc.) was used as the solvent of Hyflon AD copolymers. Sodium chloride (NaCl, purity > 99.5%) was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Ethanol (> 99.7%) was purchased from Wuxi Yasheng Chemical Co., Ltd. Sodium hypochlorite (NaClO) solution was purchased from Jiangsu Yangnong Chemical Group Co., Ltd. DI water was produced by a home-made RO system. Wetting liquid (GQ-16) was purchased from Jiangsu Gaoqian Function Material Co., Ltd.

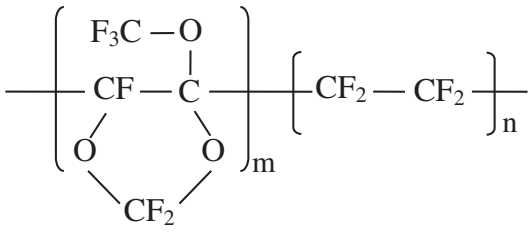

Fig. 1. Chemical structures of Hyflon AD. Hyflon AD40: m = 0.4, n = 0.6; Hyflon AD60: m = 0.6, n = 0.4.

Table 1
Physical properties of Hyflon AD [49].

Parameters	Hyflon AD40L	Hyflon AD40H	Hyflon AD60
Density (g/cm^3)	1.98	1.98	1.93
Intrinsic viscosity (dl/g @ 30 °C)	0.4	1.3	0.5
Glass transition temperature (°C)	90–95	90–95	125
Refractive index	1.331	1.331	1.327

2.2. Preparation of Hyflon AD/PVDF composite hollow fiber membranes

The commercial PVDF hollow fiber membranes were prepared by the phase inversion method and post-treated by glycerol solution to maintain the membrane pore structure. Thus, before coating Hyflon AD solution on PVDF membrane surfaces, the commercial membranes were immersed into ethanol and consequently sodium hypochlorite solution to remove the glycerol and polyvinyl pyrrolidone (PVP). After these treatments, the membranes were named as original hollow fiber membranes (M-0). The membranes coated with Hyflon AD were named as Hyflon AD/PVDF composite hollow fiber membranes. The coating procedure and conditions can be found in our previous study [48].

Different Hyflon AD solutions were prepared by dissolving Hyflon AD powders (Hyflon AD40L, Hyflon AD40H or Hyflon AD60) into the solvent (Novec HFE-7100). PVDF hollow fiber membranes were blocked at both ends and dipped into the Hyflon AD solutions. After 20 min, the hollow fiber membranes were taken out and heated at 45 °C for 9 h. The prepared composite hollow fiber membranes were named as M-40L, M-40H and M-60, indicating the membranes coated by Hyflon AD4 0L, Hyflon AD40H and Hylfon AD60, respectively.

2.3. Viscosity measurement of Hyflon AD coating solution

Viscosity of the Hyflon AD coating solution is expected to significantly affect coating of the PVDF hollow fiber membrane. It was measured by an Ubbelohde viscometer at 25 °C, with the viscosity of DI water as the reference. Viscosity of each coating solution was tested for five times to obtain the average value.

2.4. Membrane characterization

2.4.1. Scanning electron microscopy (SEM) and atomic force microscopy (AFM)

The cross-section and surface morphologies of the hollow fiber membranes were examined by field emission scanning electron microscopy (FESEM, Hitachi S4800, Japan). Before taking SEM images, the original membranes and composite membrane samples were frozen in liquid nitrogen and fractured, then positioned on a holder and sputtered with gold/palladium alloy under vacuum using an E-1010 Ion Sputtering device (HITACHI, Japan).

Membrane surface roughness was characterized by atomic force microscopy (AFM) (XE 100, Park, Korea). All the membrane samples were imaged in a scan size of 10 μm × 10 μm. The roughness parameters of the mean roughness (R_a) and the root mean squared rough-