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SiO_2-PDMS-PVDF hollow fiber membrane with high flux for vacuum membrane distillation

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ABSTRACT

In this study, hydrophobic asymmetric SiO_2-PDMS-PVDF hollow fiber membranes were prepared for the vacuum membrane distillation (VMD). To make PVDF dope solution, hydrophobic nano-fumed silica (SiO_2) and polydimethylsiloxane (PDMS) were used. The effects of SiO_2 concentration on membrane parameters such as membrane morphology, hydrophobicity, porosity, thickness, pore size, liquid entry pressure, burst pressure, Fourier transformed infrared spectroscopy, thermal property, mechanical property and permeability were investigated. With the increasing of nano-particle concentration, membrane hydrophobicity, mechanical property and thermal stability improved. Furthermore, membrane VMD properties under various operation conditions were studied, the membranes showed a stable substantial flux of 44.27 LMH and a stable high salt rejection of over 99.9% under the optimum operation conditions of 75 °C, 35 g/L, 87 kPa, and 50 L/h. The results of our research demonstrated that the prepared hydrophobic asymmetric SiO_2-PDMS-PVDF hollow fiber membranes not only had high permeability and good anti-wetting property but also exhibited a satisfying stability for the vacuum membrane distillation of desalination.

1. Introduction

As water resources are rapidly exhausted, water shortage will be a global concern [1]. Alternatives such as desalinating seawater became an option for the providing of freshwater supplies. Today, reverse osmosis (RO) and electrodialysis are two of the most effective membrane operation methods of desalinating seawater [2]. It is widely recognized that membrane distillation (MD) as a thermal membrane operation technology could be a compelling option for providing freshwater. The basis of MD separation is the saturated pressure difference of volatile substances. The vapor pressure difference between the upstream side and the downstream side of the membrane is the driving force of the MD process [3]. MD process is attractive because of the increased efficiency and the possibility of integrating with alternative energy sources such as industrial low-grade waste heat, solar energy and renewable energy [4]. MD process can also be coupled with other techniques [5–7], many researches also confirmed that it could even recover fresh water from highly concentrated salty solutions [8]. In general, MD has many advantages such as high rejection rate, low feed temperature requirement, lower operating pressure and less affected by concentration polarization [9].

The vaporization of the volatile components at membrane surface consumes a large quantity of heat during MD process. Water vapor is drawn by vacuum pressure, as a result, vapor transportation is intensified for vacuum membrane distillation (VMD) [10] and resulted in a better performance. Membrane is the key factor for a successful MD process. A suitable VMD membrane should have the features of reduced thermal conductivity, low vapor transport resistance, optimal thickness, high porosity, high hydrophobicity, anti-fouling characteristic, reasonable mechanical strength, good chemical resistance and higher wetting resistance. Among these features, high hydrophobicity is crucial for VMD process [11]. Currently, the commonly used methods for the generation of the hydrophobic membrane surfaces include the modification with low surface energy material and the preparation of the micro/nano-scale surface topography [12]. To improve the anti-wetting property of the MD membranes, many polymers with low surface energy were used as the hydrophobic modifier, such as Hyflon AD60 [13], Teflon® AF 2400 [11], PDMS [14], PTFE [15], FEP [16] and SiO2 [17]. Another way to improve membrane anti-wetting property is to build the parahydrophobic membrane surface of micro/nano-scale topography such as the papillae [18], rose petals and gecko feet [12] structures.

Poly(vinylidene fluoride) (PVDF) as a kind of hydrophobic polymer material is commonly used for the fabrication of hollow fiber and flat sheet membranes. To improve the hydrophobicity of the PVDF membranes, a lot of effort has been made by researchers, such as surface

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coating [3], surface grafting [17], blending [19,20] and pore filling [13]. Among these methods, blending is one of the most commonly used ways of making hydrophobic structures. Figoli et al. used different grades PVDF in blend to produce hollow fibers for the application of MD seawater desalination [19]. Rajabzadeh et al. explored the influence of various polymer additives on the fabrication of PVDF hollow fiber membranes [20].

However, a major limitation for the modification of PVDF with hydrophobic polymers is the immiscibility between two different materials which would result in phase separation [14,21,22]. Once the interfacial swelling degree exceeds a certain value, the polymers may come apart and the neighboring polymer structures may be crazed [23,24]. It is recognized that nanoparticles could act as surfactant and compatibilizer for the preparing of immiscible polymer blends [25–27]. Silica is a kind of commonly used nanoparticles [28–30], Dong et al. prepared the superhydrophobic modification PVDF-SiO_2 electrospun nanofiber membranes by the surface fluorosilanization with fluoroalkylsilane (FAS) [17]; superhydrophobic organic/inorganic composite nanofibrous membranes for the direct contact membrane distillation (DCMD) were fabricated via cooperating the hydrophobic silica nanoparticles on PVDF flat sheet membranes [31]. Efome et al. made an innovative modification to PVDF membranes, in their study, electrospun PVDF nano-fibers were coated on the surfaces of VMD and DCMD membranes [32].

In literatures [14,33–34], PDMS is a kind of rubber polymer, which is widely applied as a kind of membrane materials for the reason that it has the advantages of prominent hydrophobicity, superior physical and chemical stabilities and high compressibility. Zhang et al. fabricated the superhydrophobic PVDF membrane with a mixture of hydrophobic SiO_2 nanoparticles and PDMS by spray-deposition process [34]. According to a previous research [14], the adding of PDMS in the PVDF/PDMS blending membrane could decrease the crystallinity, increase the breaking elongation, enhance the hydrophobicity and improve the permeation performances of the blended membranes.

In our previous work [14], the PDMS-PVDF flat-sheet membranes were successfully prepared. In contrast to the flat-sheet membrane, the hollow fiber membrane module was more attractive due to its low boundary layer resistance, high membrane packing density and large specific surface area. In this work, we focused on the fabrication of the PDMS-PVDF hollow fiber membranes by non-solvent induced phase separation (NIPS) method. The major difference between current work and our previous studies was that we introduced different concentration silica into the dope to eliminate the immiscibility. Besides, the cross linking reaction between PDMS and tetraethylorthosilicate (TEOS) happened in this work. Membrane characteristics were tested in many ways, for example, Water contact angle (WCA, °) for membrane hydrophobic property, Attenuated total reflection Fourier transform infrared spectroscopy (ATR–FTIR) for polymer structure, Field emission scanning electron microscopy (FESEM) for membrane structure, TGA analysis (membrane weight, %) for membrane thermal stability, Liquid entry pressure (*LEP*, bar) and mean pore size (r_m, nm). The effects of silica concentration on the production of SiO_2-PVDF-PDMS hollow fiber membranes were investigated and the performances of the resulting membranes for vacuum membrane distillation were explored.

2. Experimental

2.1. Materials

Polydimethylsiloxane (PDMS) (Silicone Rubber 107, 20000 cp) and PVDF (SOLEF® 6020/1001) were obtained from Shanghai resin Company (China) and Solvay Solexis, Inc. (France), respectively. *N,N*-dimethylacetamide (DMAC, > 99.5%), Triethyl phosphate (TEP) and tetrahydrofuran (THF) were used as solvent and were purchased from Tianjin Tiantai Fine Chemical Co., Ltd. (China). Polyvinylpyrrolidone K30 (PVP, Mw30000) as additive was purchased from Tianjin Tiantai Fine Chemical Co., Ltd. (China). Additive hydrophobic nano-fumed silica (Hydrophobic-100, diameter = 7–40 nm, BET surface area = 100 m^2/g) was supplied by Aladdin Chemistry Co. Ltd. (Shanghai, China). Ethyl orthosilicate four (TEOS) as the crosslinking agent and Dibutyltin dilaurate (DBTDL) as the catalyst were supplied by Tianjin Fuchen Chemical Reagent Factory (China). NaCl (GR grade, 99.5%) and ethanol (GR grade, 99.9%) were provided by Beijing Chemical works (China). Deionized water (DI water) was used as the bore fluid and tap water was used as external coagulant. DI water was homemade.

2.2. Polymer dope preparation

To make the dope solution, a mixture of DMAC and TEP was used as the solvent. Firstly, a certain amount of hydrophobic nano-fumed silica, PVP and PVDF were added into the solvent under mechanical stirring for 8 h in a water bath of 60 °C. Afterwards, the SiO_2-PVDF solution was kept in an Electro-Thermostatic Blast Oven at 60 °C for about 24 h. SiO_2-PVDF solution was taken out after 24 h and cooled to ambient temperature. At the same time, PDMS and TEOS were dissolved in THF to make PDMS solution at room temperature. Then the above two solutions were mixed and stirred at 80 rpm until a uniform SiO_2-PDMS-PVDF solution was obtained at room temperature. Finally, catalyst DBTDL was put into the above mixed solution and was stirred for 0.5 h. After 12 h degassing under atmospheric pressure at room temperature, the homogeneous dope solution was obtained and its composition was listed in Table 1. The cross-linking structure of the resulting membrane was shown in Fig. 1 which also showed that the physical cross linking happened among the silica particles and the polymeric chains.

2.3. Measurement of dope solution

2.3.1. Polymeric dope viscosity measurement

Dope viscosity could severely impact membrane precipitation kinetics, so by adjusting dope viscosity, membrane morphology can be controlled. Dope viscosity was measured with rotary viscometer (NDJ-1, Shanghai An De Equipment Co., Ltd., China) at ambient temperature.

2.3.2. Light transmittance

The device for light transmittance measurement was schematically described elsewhere as shown in Fig. 2 [35,36]. During the phase inversion process, deionized water was used as the coagulation bath at 50 °C. The light transmittance curves of the SiO_2-PDMS-PVDF dope solutions were reorganized as time functions.

2.4. Preparation of hollow fiber membranes

The schematic of the hollow fiber spinning equipment was shown in Fig. 3. Dope solution was transferred into a tank and was squeezed out from the spinneret by nitrogen at 0.12 MPa. Simultaneously, bore fluid passed through the inner tube via a constant flow pump with a flow rate of 3 mL/min. After extruding out from the spinneret, the fiber falls along the air and then immersed into the coagulation bath. During the

Table 1
Parameters of SiO_2-PDMS-PVDF dope solutions.

Membrane	PVDF/PVP/SiO_2	DMAc/TEP	PDMS/PVDF	PDMS/THF	PDMS/TEOS/DBTDL
	(Mass ratio)	(Mass ratio)	(Mass ratio)	(Mass ratio)	(Mass ratio)
MS1	18/3/0	2:3	1:10	1:10	10:1:0.5
MS2	18/3/0.5				
MS3	18/3/1.0				
MS4	18/3/1.5				