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Study on the effects and properties of hydrophobic poly(tetrafluoroethylene) membrane

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ABSTRACT

Hydrophobic poly(tetrafluoroethylene) (PTFE) flat-sheet membranes were fabricated from a mixture of PTFE emulsion and polyvinyl alcohol (PVA) aqueous solution. Effects of blend ratio of PTFE to PVA on the morphology and properties of the membrane were investigated. Morphologies of obtained membranes were observed by field emission scanning electron microscopy (FESEM). Unique PTFE 'worm-like' crystals were observed in the PTFE membranes after sintering. As the PTFE/PVA mass ratio increased, the growth of the 'worm-like' crystals improved the hydrophobicity and mechanical strength of PTFE membrane. Moreover, membranes were tested in vacuum membrane distillation (VMD) configuration, using distilled water as feed. The VMD flux increased at first and then decreased with the PTFE/PVA mass ratio rising from 1:1 to 4:1 owing to the change of membrane porosity.

1. Introduction

Nowadays, it is widely realized that water shortage is becoming a very serious problem [1]. In this respect, the importance of desalination technology is more and more evident [2]. However, the conventional desalination technologies such as multi-stage flash vaporization (MSFV) and reverse osmosis (RO) are too expensive to be applied especially for poor countries [3]. Membrane distillation (MD) is a membrane-based water treatment process where the driving force for MD is a vapour pressure difference across the membrane [4]. In comparison with other membrane separation technologies, MD has several advantages including very high rates of rejection for non-volatile components, much larger membrane pore size than that of reverse osmosis (RO), lower operating pressure than driven membrane process, less sensitivity to foul than RO and feed salinity, reduced vapour space compared to conventional distillation, and low feed temperature requirements (40–80 °C). Thus, the possibility of using alternative energy sources such as geothermal and solar energy and exploited low grade or waste energy has been highlighted [5–10].

In an MD process, a porous hydrophobic membrane is used to perform the separation among water and dissolved minerals. Furthermore, the membrane must be resistant to the feed solutions. One of the major requirements of MD process relies on the use of hydrophobic membranes to maintain dry the membrane pores. During this process, a liquid feed is heated up to about 50–90 °C and then brought into contact with one side of the membrane while a condensing and permeating phase is on the other side [11]. Most of the membranes applied for the MD process so far have not been specifically made for this process. The three most common hydrophobic materials are listed as follows, polypropylene (PP), poly (tetrafluoroethylene) (PTFE) and poly (vinylidenefluoride) (PVDF) [12,13].

Currently, the commercial hydrophobic PP porous membrane is produced by melting–stretching method because there is no appropriate solvent to dissolve it [14]. PVDF membrane can be manufactured by the L–B method and thermally induced phase separation (TIPS) to get homogeneous micropores and size-controllable structure [15–17]. Comparing with PP and PVDF, PTFE has the lowest surface energy which induces the highest hydrophobicity [18,19]. In addition, the exceptional combination of properties such as outstanding thermal resistance, good chemical stability, and low surface friction makes PTFE the prime material for MD [20,21].

However, the main disadvantage of PTFE is that its poor processing property can prohibit common phase inversion or melt spinning method from manufacturing porous membrane [22,23]. Therefore, PTFE membrane cannot be produced by such methods used for PP and PVDF [24]. Presently, many patents [25–27] disclosed some methods in which a non-sintered PTFE resin blend containing a liquid lubricant was extruded at a high temperature. The extruded material was drawn by uniaxial or biaxial stretching and heated to about 327 °C or above to form the PTFE resin porous membrane. These methods, however, suffered from inferior performance of the product due to the pore controllability of the porous structure or inferior membrane-formability which results in an impractically large thickness of the product membrane.

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Table 1
Characteristics of PTFE emulsion.

Solid content (wt.%)	Nonionic surfactant content (wt.%)	Average particle size (μm)	Viscosity (Pa s)	Density (g cm^{-3})	pH
60	5	0.19	25×10^{-3}	2.20	9

However, few reports can be found for PTFE membrane preparation with PTFE emulsion, and researches on the effects of the properties of PTFE membrane are even more less. Takashi Kawai [28] in Japan provided a method in which PTFE emulsion was blended with sodium alginate aqueous solution to form a spinning dope. Then the dope was spun into hollow fiber by conventional dry-wet spinning method. Subsequently, the PTFE hollow fiber membrane was finally obtained after removing the sodium alginate by sintering. Xiong [29] in China prepared spinning solution by blending Poly(vinyl alcohol) (PVA) and PTFE emulsion with different mass concentrations. Then the spinning solution was electrospun into composite nanofibers, whereby the PTFE porous membrane was obtained after sintering.

The objective of this article was exploring the effects of PTFE/PVA mass ratios on PTFE membrane's structure and properties. Moreover, the PTFE membranes obtained were also tested in VMD configuration to confirm the permeability of membrane.

2. Experimental

2.1. Materials

The PTFE emulsion is a commercial product (3F new materials co., LTD. Shanghai) designed as FR301B, with characteristics shown in Table 1. Polyvinyl alcohol (PVA) is purchased from Sanwei Group co,. LTD. Shanxi. Type: 2488 (polymerization degree: 2400; alcoholysis: 88%).

2.2. Membrane preparation

The PVA solution was prepared by dissolving PVA powder in distilled water at 90 °C under constant stirring for at least 6 h. When the solution cooled down to room temperature, the PTFE emulsion was added to PVA solution with constant stirring for 3 h to form a homogenous dope of different PTFE/PVA mass ratio. After degassing for 8 h with a vacuum pump, the dope was, then, cast into films on a clean and smooth stainless steel plate. The PTFE/PVA composite films were obtained after the films were immersed in pure ethanol. Composite membranes were then sintered in a muffle furnace at 360 °C for 3 min to obtain the PTFE membranes.

2.3. Method and measurements

2.3.1. Porosity

The porosity which determined the weight of liquid contained in the membrane pores was assessed by gravimetric method [30]. Since the hydrophobicity of PTFE, isopentane was used as the wetting liquid. Eq. (1) was used to calculate ε of the membrane,

$$\varepsilon = \frac{(w_1 - w_2)/D_1}{(w_1 - w_2)/D_1 + w_2/D_p}, \tag{1}$$

where w_1 is the weight of the wet membrane, w_2 is the weight of the dry membrane, D_1 is the isopentane density ($D_1 = 0.62$ g/cm^3), and D_p is the polymer density ($D_{PTFE} = 2.20$ g/cm^3).

2.3.2. Morphologies observation

The morphology of the resulting membranes was examined using field emission scanning electron microscopy (FESEM, X4800, HITACHI Japan). Samples were prepared by platinum coating using a JEPL JFC-1100E ion sputtering device.

2.3.3. Mechanical strength

The mechanical strength was accessed using an YG-061-1500 tensile tester at ambient temperature. The specimens were cut into 5 mm (width) × 50 mm (length) test strips.

2.3.4. Contact angle

The hydrophobicity of the produced membranes was assessed by measurements of the contact angle to water. The contact angles of all the samples were measured by an optical contact angle meter (Jinshengxin Inspection instrument Co., Ltd., model JYSP-180). The measurements were carried out at 25 °C with 40–50% relative humidity. A water droplet was dropped on the sample surface from a distance of 5 cm by vibrating the tip of a micro-syringe. Lasting for 10 s after the droplet was dropped on the sample surface. A lens and a source light were used to create the drop image on a screen. The contact angle was determined with the projected drop image. Five different spots for each sample were measured. The average value of the five spots as the contact angle of the membrane sample was chosen.

2.3.5. VMD tests

The membrane permeability was tested by vacuum membrane distillation (VMD). The VMD set-up used in this study was already described elsewhere [31]. Fig. 1 showed a simplified scheme of the VMD set-up. VMD tests were performed using double distilled water as feed. The feed temperature was 70 °C, the feed flow rate was 32 l/h, and the vacuum pressure was 20 mbar.

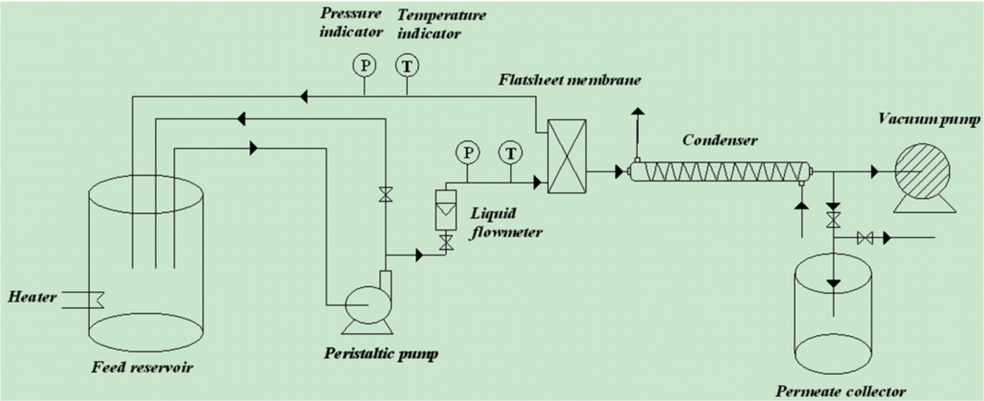

Fig. 1. Simplified scheme of the VMD set-up.