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Optimizing stretching conditions in fabrication of PTFE hollow fiber membrane for performance improvement in membrane distillation

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ABSTRACT

PTFE is one of the most approved hydrophobic materials for MD membranes. However, PTFE membrane was researched and applied on MD insufficiently due to its complex fabrication process. In this work, stretching conditions were comprehensively investigated to form a membrane with high flux and salt rejection. It was found that stretching led to increased cracks at an early stage, and turned to lead to the elongation of fibrils and physical dimension shrinkage of hollow fibers. A porosity prediction model was established to evaluate the improvement of porosity. It was found that a low stretching temperature was helpful for pore size control and hence a relative high stretching ratio can be carried out to achieve a higher porosity. Therefore high flux and rejection was achieved due to the higher porosity and well controlled pore size. Stretching rate of 30%/s gave rise to the most concentrated pore size distribution. NaCl rejection rate was high up to 99.99% for the membrane fabricated at a stretching ratio of 2.4 and a stretching temperature of 40 °C.

1. Introduction

Membrane distillation (MD) is a non-isothermal process in which the mass transfer is driven by a partial vapor pressure difference across a hydrophobic membrane that directly contacts with the high temperature feed liquid solution to be treated [1]. For a nonvolatile solute aqueous solution, water evaporates at the interface of liquid/membrane and only vapors pass across the membrane. To overcome the challenge of fresh water scarcity in a world scale, MD is a promising alternative way to provide fresh water from desalination of sea water and treatment of wastewater [2,3]. Compared with conventional pressure driven membrane processes such as nanofiltration (NF) and reverse osmosis (RO), MD has some obvious advantages. For instance, the rejection rate for nonvolatile solute is 100% (theoretical) and the operation pressure is much lower [4]. Moreover, the feed side needs much lower temperature compared with multiple-stage flash distillation, and it has the potential of using low grade heat resources [5]. MD has received considerable attention in the past decades and been applied in many fields such as juice concentration, chemical production and removal or resource recovery [6–8]. MD is also a good approach to be hybrid with other membrane processes such as ultrafiltration (UF), RO and forward osmosis (FO) [9–11].

Hydrophobic membrane is a critical part in MD process. Polytetrafluoroethylene (PTFE) is one of the most approved hydrophobic membrane materials for MD [12]. An ideal membrane for MD should be with good mechanical strength, high porosity, low thickness, appropriate pore size, narrow pore size distribution, chemical stability and solvent resistance [13]. Among the most widely used membrane materials, PTFE was expected as the most promising polymer due to its chemical stability, solvent resistance and good mechanical strength [14]. However, PTFE can neither be processed by a phase inversion process [15] due to its resistance to most of the solvents [16] nor by melting-stretching method due to its high viscosity (10 GPa s, at 380 °C) at a temperature over its melting point [17]. PTFE membrane can generally be fabricated through a cold processing including extrusion, stretching and sintering.

Optimizing the operation parameters is key to form membranes with high flux and rejection. Kurumada et al. investigated the effect of uniaxial and biaxial stretching on microporous structure and found that uniaxial stretching led to island-like structure and biaxial stretching led

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to lattice-like porous structure [18]. Kitamura et al. found that it was easy for the fibrils to be stretched out from PTFE particles and form a periodic "fibril – node" structure. The periodic structure can be varied and controlled by adjusting stretching conditions including stretching ratio, stretching temperature and stretching rate [19]. Asymmetric heating during stretching increased the membrane porosity and reduced the pore size [20]. Zhu et al. found that the increase of stretching ratio led to higher porosity and bigger pore size, and the fabricated PTFE hollow fiber membrane achieved a salt retention of 99.9% in its application on vacuum membrane distillation [21].

Despite some efforts in changing the pore structure of PTFE membrane by varying stretching conditions, there remains an insufficient understanding of the effect of stretching conditions on membrane pore structure, pore size distribution and porosity, especially their effect on membrane performance on MD process [22].

Therefore, the aims of this paper are: (i) to determine on which stretching condition the pore size can be well controlled and the porosity can be critically improved; (ii) to compose the stretching conditions to develop PTFE hollow fiber membrane with high permeate flux and salt rejection in MD process.

In terms of this, the crack number and fibril length were measured to investigate the effects of stretching on pore size at different stages of stretching. A porosity prediction model was created to evaluate on which condition the porosity was critically improved. The combination of stretching ratio and temperature was determined based on liquid entry pressure of water (LEP_w) and permeate flux. The effect of stretching ratio on pore size distribution was also studied. Membrane fabricated at optimal stretching ratio and temperature was employed on MD process to evaluate its performance.

2. Materials and methods

2.1. Materials

PTFE resin (F106C) was purchased from Daikin Fluorochemicals (China) Co., Ltd. Isoparl G obtained from Shanghai Huishuo Technology Co., Ltd was used as lubricant. NaCl (AR, ≥ 99.5%) was purchased from Sinopharm Chemical Reagent Co.,Ltd.

2.2. PTFE membrane fabrication

Lubricant (25 wt%) was mixed up with PTFE resin and then the mixture was shaken for 2 h. The mixture was then aged in an oven at 36 °C for 8 h to homogeneously distribute the lubricant in the mixture. Then the mixture was compact at a pressure of 1.5 MPa to produce a billet preform free of air voids. Inner and outer diameter of the billet preform was 16 mm and 32 mm, respectively. Height of billet preform was 200 mm. The billet preform was then extruded from a die to form hollow fibers at 35 °C. The die orifice is 2 mm, and the core pin is 1 mm. Then the extrudate was stretched at temperatures ranging from 40 °C to 240 °C. Finally, hollow fibers were sintered at 365 °C for 60 s to fix porous structure and prevent shrinkage. Fig. 1 displays the PTFE membrane preparation process.

Stretching rate is the speed of stretching and described as the deformation per unit time. Stretching ratio is the ratio of the length after stretching to the initial length, and it's calculated using Eq. (1):

$$R_s = \frac{L_f}{L_i} \tag{1}$$

where R_s is the stretching ratio, L_f is the final length of the hollow fiber after stretching and L_i is the initial length of the hollow fiber. In this study, stretching rate varied from 10%/s to 60%/s, and stretching ratio varied from 1.2 to 4.0.

In order to explain how membrane characters were affected by stretching conditions as briefly and clearly, only 40 °C and 240 °C were the temperature conditions that were further discussed. 240 °C was chosen since it is among the temperature ranges in most of the reference and it also competently represents the high temperatures. 40 °C was chosen because it was the optimal temperature in this study.

2.3. Membrane morphology characterization

The morphology of membrane was imaged by using scanning electron microscopy (SEM) (SU-8000, Hitachi, Ltd., Japan). Membrane samples were cut a little bit at one end and then were gently tore into half. The prepared samples were observed on inner surface, outer surface and the longitudinal-section. Longitudinal-section was observed instead of cross-section. One reason is that it was difficult to break the PTFE hollow fiber membrane even in liquid nitrogen while it was easy to tear the fibrils which was parallel to the tearing direction. The other reason is that the longitudinal-section gave better microporous structure than fracture surface. The prepared samples were coated with a thin platinum layer using a sputter coater (HITACHI E-1010 Ion) for SEM observation.

2.4. pore size, pore size distribution and LEP_w

Pore size and pore size distribution were determined using Capillary Flow Porometer Porolux 1000 (Porolux, Belgium) by gas-liquid displacement method [23]. However, some data of pore size is not achieved due to the limitation of this method. It was difficult to measure the pore size for membrane with stretching ratio of 1.2 due to poor gas permeation and stretching ratio of 4.0 due to extreme large gas flow during measurement. *Porefil* with surface tension of 16 N/cm was used as wetting liquid. The gas was provided by nitrogen. Bubble point, mean pore size, biggest pore size and pore size distribution were calculated and reported by the computer connected with the equipment. LEP_w was measured by the same equipment using water rather than *Porefil* filled in the lumen side of membranes.

The contact angle of fabricated membranes varied around 110° and it was not found to be affected by stretching conditions. So it was not discussed in the following sections.

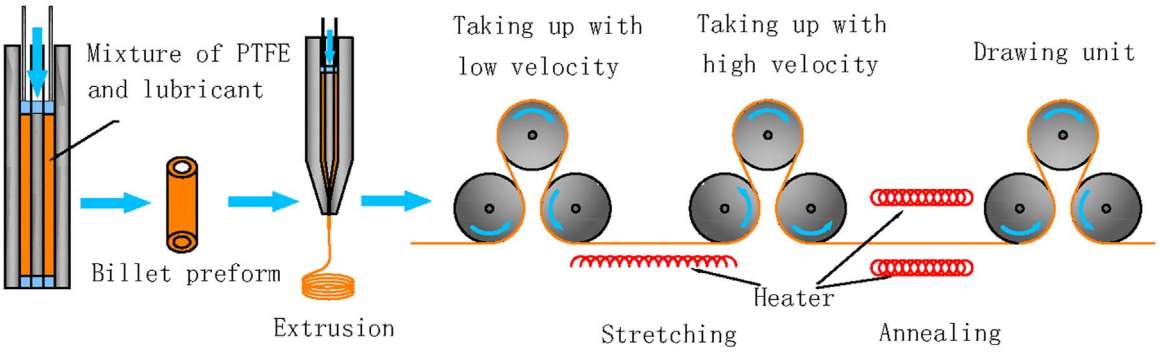

Fig. 1. Schematic of PTFE hollow fiber membrane fabrication process.