Preparation of PVDF/PTFE Hollow Fiber Membranes for Direct Contact Membrane Distillation via Thermally Induced Phase Separation Method

Jie Zhao\textsuperscript{1,2}, Lei Shi\textsuperscript{1}, Chun Heng Loh\textsuperscript{1}, Rong Wang*\textsuperscript{1,2}

1. Singapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1 Cleantech Loop, Singapore 637141, Singapore

2. School of Civil and Environmental Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

*Corresponding author at: School of Civil and Environmental Engineering,
Nanyang Technological University, 639798 Singapore, Singapore. Tel.: +65 6790 5327; fax: +65 6791 0676.

E-mail address: rwang@ntu.edu.sg (R. Wang).
Abstract

Polyvinylidene fluoride (PVDF)/polytetrafluoroethylene (PTFE) hollow fiber membranes were developed via thermally induced phase separation (TIPS) method for direct contact membrane distillation (DCMD). The effects of PTFE addition on the thermal behavior of the dope mixtures and membrane formation were investigated. It was found that the crystallization of PVDF was significantly enhanced with increased nucleation sites provided by PTFE particles, leading to promoted formation of smaller spherulites in a greater density. Furthermore, the improved uniformity and increased amount of cavity between the spherical crystallites coherently facilitated the formation of smaller pores ranging from 0.08 to 0.12 µm. With certain PTFE loading, the membranes exhibited improved porosity, water permeability and hydrophobicity as well as enhanced tensile strength of 9.4 ± 0.3 MPa. To examine the DCMD performance, the membranes were tested under various conditions using 3.5 wt.% NaCl solution. A stable permeation flux of 28.3 kg m⁻² h⁻¹ at the feed temperature of 60 °C with 99.99 % NaCl rejection for over 50 hours of operation was achieved, which is comparable with similar type of PVDF membranes while the newly developed membrane exhibited better mechanical strength. This study suggests that the as-spun PVDF/PTFE hollow fiber membranes have potential for DCMD applications.

Keywords: Hollow fiber membrane; thermally induced phase separation; polyvinylidene fluoride; polytetrafluoroethylene; membrane distillation
1 Introduction

Membrane distillation (MD) is a non-isothermal membrane-based separation process involving vapor transport through non-wetted microporous membranes thermally driven by vapor pressure difference between two sides of the membranes [1]. It provides attractive features such as theoretically 100% rejection of salts and less fouling as compared with pressure driven membrane processes, insensitivity to salt concentration and lower requirements on membrane mechanical properties in comparison with other separation techniques [2]. As a promising alternative to reverse osmosis (RO), MD could be applied in seawater desalination [3], industrial wastewater treatment [4] and many other applications if waste or low-grade heat resources are accessible [5].

To maintain the effectiveness and stability of the MD process over a long-term operation, the membrane should possess reasonably high water vapor transfer with minimized tendency of wetting and fouling [6]. With regard to the materials utilized for MD membrane development, fluoropolymers, such as polyvinylidene fluoride (PVDF), have been well-investigated owing to their notable chemical and thermal stabilities, hydrophobicity and good mechanical properties [7]. Various fabrication methods have been employed in hollow fiber membrane development for MD applications [8], among which, two techniques of phase inversion are commonly applied: nonsolvent induced phase separation (NIPS) and thermally induced phase separation (TIPS) [9]. Compared with the NIPS, the TIPS method offers many advantages for porous membrane preparation: (1) fewer influence parameters; (2) ease of operation and scale-up; (3) narrow pore size distribution and large porosity; (3) outstanding mechanical strength [10, 11]. In addition, the TIPS method has been demonstrated to have a high commercial maturity for PVDF membrane development in the industry [12-14].
In a typical TIPS process, a homogeneous solution is formed by dissolving a polymer in a low-molecular-weight diluent with a high boiling point at high temperature. The diluent could be a single solvent or a combination of different solvents and non-solvents [12]. By cooling down or quenching (cooling down at a rapid rate) the homogeneous solution, the phase inversion occurs. After the nucleation and solidification of the polymer-rich phase, a membrane with porous structure can be obtained by extracting the solvent [13]. To achieve an optimum structure, numerous attempts on membrane surface modification or blending have been made to enhance the properties of PVDF membranes [8]. Compared with surface modification, blending of polymers or inorganic particles is more practical in industrial manufacturing as the membranes can be fabricated in a single step.

Due to its semi-crystalline property, the nucleation and crystallization of PVDF could play a significant role in the formation of membrane microstructures during thermal processes such as the TIPS. Therefore, in recent studies of the TIPS method, a number of additives have been used in PVDF/diluent systems to adjust these two processes during membrane formation, as summarized in Table 1. Based on the effects of the additives on membrane formation, they can be generally classified into two major types: nucleating agents and crystallization inhibitors. In the first category, the nucleating agents represent those additives that can enhance the nucleation and growth (NG) of the polymer-rich phase, as they are able to act as crystal nuclei during the nucleation process. The additives with such functions include CaCO₃ [14, 15], TiO₂ [16], montmorillonite (MMT) [17], polytetrafluoroethylene (PTFE) [17], oxidized multi-wall carbon nanotubes (O-MWCNTs) [18], etc. The additives in the second category normally act as crystallization inhibitors due to their ability on suppressing the crystallization process of PVDF crystalline phase. Examples from previous study include blending PVDF with poly(vinylpyrrolidone) PVP [19, 20], poly(methyl methacrylate) PMMA [19, 21], SiO₂ [22], glycerol [11, 23], etc.
## Table 1. Effects of additives on PVDF membranes through TIPS method

<table>
<thead>
<tr>
<th>Type of additive</th>
<th>Additive</th>
<th>Solvent</th>
<th>Structure</th>
<th>Spherulite formation</th>
<th>Polymorphism</th>
<th>Tensile strength</th>
<th>Hydrophilicity</th>
<th>Porosity</th>
<th>Water permeability</th>
<th>Geometry</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleating agent</td>
<td>CaCO₃</td>
<td>DBP, GBL/DOP</td>
<td>Cellular</td>
<td>Decrease size, improve uniformity</td>
<td>\</td>
<td>Increase</td>
<td>Decrease</td>
<td>Increase</td>
<td>Increase</td>
<td>HF/FS</td>
<td>[14, 15]</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>DMP</td>
<td>Spherulitic</td>
<td>Decrease size, increase amount</td>
<td>α</td>
<td>Increase</td>
<td>Decrease</td>
<td>Increase</td>
<td>Increase</td>
<td>FS</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>MMT</td>
<td>DPK</td>
<td>Spherulitic</td>
<td>Decrease size, increase amount</td>
<td>α, β</td>
<td>Increase</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>FS</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>PTFE</td>
<td>DPK</td>
<td>Spherulitic</td>
<td>Decrease size, increase amount</td>
<td>α</td>
<td>Increase</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>FS</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>O-MWCNTs</td>
<td>DBP</td>
<td>Cellular</td>
<td>Decrease size, improve uniformity</td>
<td>\</td>
<td>Increase</td>
<td>Increase</td>
<td>Decrease</td>
<td>Decrease</td>
<td>FS</td>
<td>[18]</td>
</tr>
<tr>
<td>Crystallization inhibitor</td>
<td>PVP</td>
<td>GBL, DEP</td>
<td>Spherulitic</td>
<td>Decrease size, improve uniformity</td>
<td>α, β to γ</td>
<td>Increase</td>
<td>\</td>
<td>Decrease</td>
<td>Decrease</td>
<td>HF</td>
<td>[19, 20]</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>Sulfolane, DEP</td>
<td>Cellular (Sulfolane), spherulitic (DEP)</td>
<td>Decrease size, improve uniformity</td>
<td>\</td>
<td>Decrease</td>
<td>Increase</td>
<td>\</td>
<td>Decrease</td>
<td>HF/FS</td>
<td>[19, 21]</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>DBP</td>
<td>Spherulitic</td>
<td>Decrease size, improve uniformity</td>
<td>\</td>
<td>Increase</td>
<td>Increase</td>
<td>Increase</td>
<td>Increase</td>
<td>FS</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td>Glycerol</td>
<td>Triacetin</td>
<td>Spherulitic</td>
<td>Improve connectivity</td>
<td>\</td>
<td>Decrease</td>
<td>\</td>
<td>Increase</td>
<td>Increase</td>
<td>HF</td>
<td>[11, 23]</td>
</tr>
</tbody>
</table>

*Note: this summary is based on the effects of additives before the occurrence of aggregation above the optimum loading. Abbreviations: HF, hollow fiber; FS, flat sheet; DBP, dibutyl phthalate; DEP, diethyl phthalate; DMP, dimethyl phthalate; DOP, dioctyl phthalate; DPK, diphenyl ketone; GBL, γ-butyrolactone; MMT, montmorillonite; O-MWCNTs, oxidized multi-wall carbon nanotubes; PMMA, poly(methyl methacrylate); PTFE, polytetrafluoroethylene; PVP, polyvinylpyrrolidone.
Among those additives, PTFE was found to be an effective enhancer for the heterogeneous nucleation of PVDF [17, 24]. In the study reported by Schneider et al., it was observed that the PVDF matrix could epitaxially crystallized on PTFE chains, resulting in increased nucleation density [24]. This phenomenon also suggested good compatibility between PVDF and PTFE. Ma et al. examined the effect of PTFE on the crystallization and melting characteristics of PVDF/diphenyl ketone (DPK) flat sheet membranes [17, 25]. The results showed that the addition of PTFE could enhance the nucleation of PVDF during TIPS process. On the other hand, PTFE was demonstrated to be an effective additive to enhance the anti-wetting property of membranes for MD applications given its outstanding hydrophobicity [26]. By using the conventional NIPS method, Teoh et al. obtained single-layer and dual-layer PVDF/PTFE hollow fiber membranes with increased hydrophobicity and improved long-term MD performance [27]. Despite these reports involving PVDF and PTFE blending, there are few studies on how the nucleation enhancing capability of PTFE particles in TIPS affects the properties of PVDF membranes such as pore structure, mechanical strength and water permeability.

In this work, PVDF/PTFE hollow fiber membranes were fabricated via the TIPS method with various PTFE loadings to thoroughly investigate the impact of PTFE addition on membrane properties and possible mechanisms behind. The addition of PTFE is expected to exert dual effects on PVDF membranes including controlling the microstructures during the TIPS process and enhancing the wetting resistance in MD applications. The characteristics of prepared membranes were examined and the pure water permeability and performance of direct contact membrane distillation (DCMD) were also evaluated. To our best knowledge, there is no report on the development of PVDF/PTFE hollow fiber membranes via TIPS method for MD application. It is anticipated that this work is able to provide a better
understanding on the PVDF membrane formation mechanism involving PTFE particles in the TIPS process, and to demonstrate the potential of PVDF/PTFE hollow fiber membranes in MD applications.

2 Experimental

2.1 Materials

Polyvinylidene fluoride (PVDF Solef® 6020, $M_w = 670$-700 kDa, Solvay) were used to make porous hollow fiber membranes. Polytetrafluoroethylene (PTFE microparticles, Microdispers-200, MW ~ 80,000, Size ~ 200 - 300 nm, Polysciences) were used as additives for PVDF membrane fabrication. Dimethyl phthalate (DMP, Merck KGaA, Germany) was used as diluent and bore fluid. Ethanol (Merck KGaA, Germany) and n-hexane (Merck KGaA, Germany) were used to conduct the post-treatment for the porous hollow fiber membranes. For pure water permeability (PWP) experiments, deionized (DI) water by a Milli-Q system (18MΩcm) was used. All the reagents were used as received.

2.2 Preparation of hollow fiber membranes

Hollow fiber membranes were fabricated by a set of spinning apparatus shown in Fig.1 [19]. To achieve a homogeneous solution, certain amounts of PVDF, PTFE and diluents with predetermined compositions as described in Table 2 were fed to the dope tank, heated up to 220 °C which was higher than the cloud point, and then mixed in a dry nitrogen (with purity of 99.9995%) atmosphere for 2 h. The gas bubbles in the dope solution were eliminated during a 1-h standstill. Meanwhile, the spinneret was heated up to 200 °C. During the spinning process, the dope was dispensed into the spinneret using a gear pump under a
positive pressure of less than 1 bar using nitrogen gas. The bore fluid with desired compositions was used as inner coagulant and pumped into the spinneret at room temperature using a syringe pump (Teledyne ISCO Inc., Model 1000D) at various flow rates. Tap water was used as the outer coagulant. Together with the bore fluid, the hot polymer solution was extruded from spinneret and travelled a short air gap before entering the coagulation bath. Phase separation started at both lumen and the outer side, leading to membrane formation. The spinning parameters are listed in Table 2. The samples with PTFE loadings from 0 to 5 wt.% were designated as PE-0 to PE-5, accordingly. To achieve sufficient solidification, the nascent hollow fiber membranes were immersed into DI water for 24 h. The post-treatment was then performed by soaking the membranes in ethanol for 24 h to extract the residual diluent and subsequently immersing into n-hexane for 3 h. The hollow fiber membranes were air-dried at room temperature (24 - 26 °C) prior to characterization [28].

Fig. 1. Schematic diagram of spinning line for hollow fiber membrane preparation
### Table 2. Spinning parameters for hollow fiber membranes

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>PE-0</th>
<th>PE-1</th>
<th>PE-2</th>
<th>PE-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope composition (PVDF/PTFE/DMP (wt.%%))</td>
<td>35/0/65</td>
<td>34/1/65</td>
<td>33/2/65</td>
<td>30/5/65</td>
</tr>
<tr>
<td>Extrusion rate (g min⁻¹)</td>
<td></td>
<td></td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Extrusion temperature (°C)</td>
<td></td>
<td></td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Bore fluid composition (wt.%%)</td>
<td>DMP (100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bore fluid flow rate (mL min⁻¹)</td>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Quenching temperature (°C)</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Spinneret dimension (mm)</td>
<td>OD/ID = 1.84/0.92</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 2.3 Phase diagram determination

The samples of PVDF/DMP and PVDF/PTFE/DMP dope solution were prepared separately using a StarFish Workstation (Heidolph Instruments, Germany) at 220 °C. The cloud point ($T_{\text{cloud}}$) measurement of the polymer-diluent system was conducted following the method used in a previous study [29]. The cooled dope mixture was sliced into small pieces of samples (diameter around 0.5 cm) and carefully sandwiched between two transparent cover slips. The prepared sample was mounted on a hot stage (Linkam THMS600, UK) and heated up to 220 °C and then cooled down to 40 °C. The cooling rate was controlled at 10 °C min⁻¹. Through the observation under an optical microscope (Nikon Eclipse 50i, Japan), the $T_{\text{cloud}}$ can be determined visually at the point of the first appearance of liquid droplets.

Thermal behavior analysis of PVDF/DMP and PVDF/PTFE/DMP dope mixtures was performed by using a differential scanning calorimeter (DSC, Q20, TA Instruments, USA) in a dry nitrogen atmosphere. For each measurement, about 5 mg of dope mixture was tightly
encapsulated into an aluminum pan (Tzero pan and Tzero hermetic lid, TA Instruments, USA). The thermal history of the sample was removed by a rapid ramp to 200 °C at a controlled rate of 40 °C min\(^{-1}\) prior to the melting tests. The dynamic crystallization temperature \(T_c\) (the point at which the system begins to crystallize) was determined as the onset temperature of the exothermic peak during the cooling process [30]. The crystallization curve was subsequently obtained by cooling to 40 °C at a rate of 10 °C min\(^{-1}\) after equilibrating at 200 °C for 2 min. [17, 19, 31]. The phase diagrams of both PVDF/DMP and PVDF/PTFE/DMP systems were obtained by depicting the cloud points (if any) along with the crystallization curve. Following the cooling process, the melting behavior of PVDF/PTFE/DMP samples was also analyzed at a heating rate of 10 °C min\(^{-1}\).

### 2.4 Characterization of hollow fiber membranes

A digital microscope (VHX-500F, Keyence, USA) was used to measure the dimension of resultant hollow fiber membranes. For each sample, at least two different fibers were measured and an average value was calculated. The morphology of hollow fiber membranes was examined by scanning electron microscope (SEM, Zeiss EVO 50, Carl Zeiss AG, Germany). The cross-sections of membrane were obtained by snapping the hollow fiber samples frozen in the liquid nitrogen. Prior to the observation, the samples were coated with a conductive gold layer by using a gold sputter coater (Emitech SC7620, Quorum Technologies, UK) [28].

The degree of crystallinity of the resultant membranes was measured by a DSC. 4 - 5 mg of dried hollow fibers were sealed in an aluminum pan and then tested using the same cool-heat procedure as described in Section 2.3. The degree of crystallinity of membranes was calculated according to the following equation [32]:

\[
\text{Degree of Crystallinity} = \frac{\text{Heat of Fusion}}{\text{Heat of Fusion of 100\% Crystalline PVDF}} \times 100\% \]

\[
\text{Heat of Fusion} = \int_{T_m}^{T_c} \text{Heating Rate} \times \text{Heat Capacity} \, dT
\]

\[
\text{Heat of Fusion of 100\% Crystalline PVDF} = 93 \text{ J g}^{-1}
\]
\[ \chi_c = \frac{\Delta H}{\Delta H_m} \times 100\% \]  

where \( \chi_c \) is the degree of crystallinity (\%); \( \Delta H \) and \( \Delta H_m \) represent the fusion enthalpy (melting enthalpy) of the membrane and PVDF with 100\% crystallinity, respectively. The value of \( \Delta H_m \) is 104.5 J g\(^{-1}\) [33].

Wide angle X-ray diffraction (WAXD) was conducted to analyze the PVDF crystal structure of the prepared membranes in a Bruker D8-Advance diffractometer (Cu Ka radiation, 40 kV and 40 mA). The scanning angle ranged from 5 to 50 with a scanning velocity of 4° min\(^{-1}\). The crystal size of PVDF was estimated by Scherrer’s equation as follows [34, 35]:

\[ D = \frac{R \lambda}{\beta \cos \theta} \]  

where \( D \) is the estimated diameter of the crystals (nm); \( R \) is the Scherrer’s constant (\( R=0.89 \)); \( \lambda \) is the wavelength of the incident x-rays (nm), which is 0.154 in this study; \( \beta \) is the peak width at half height (rad); \( \theta \) is the diffraction angle (rad).

The hydrophobicity of the resultant membranes was determined through the measurement of the dynamic contact angle using a tensiometer (DCAT11 Dataphysics, Germany) based on the Wihelmy method [36]. A dried sample fiber with a length of 1 – 1.5 cm was attached on the suspended mobile arm of an electronic balance. The sample then underwent a cycle of immersion into DI water followed by emersion at an advancing/receding speed of 0.2 mm min\(^{-1}\) with an immersion depth of 5 - 10 mm. The electronic balance continuously recorded the change in weight. Three cycles of advancing-receding were measured for each specimen. At the first cycle of measurement, the membrane surface was dry prior to the immersion into the DI water. The contact angles obtained at the second cycle were lower since some of the surface pores might have been filled with water. This is believed to better represent the real
situation in MD applications, and therefore the contact angle of the second advancing was presented in this study to reflect the membrane hydrophobicity [36]. To ensure the reproducibility, each run was repeated 3 - 5 times for all samples.

The surface topography and roughness of membranes were measured using atomic force microscopy (AFM, NX-10, Park Systems). The images were obtained over both the inner and outer surfaces of each sample using a non-contact mode (NCM) with a consistent scan area of 5 × 5 μm. The mean roughness parameter, $R_a$, was obtained after each test. The procedure for the analysis of AFM images can be found elsewhere [37, 38].

The pore size distribution of membranes was measured using a capillary flow porometer (CFP 1500A, Porous Material. Inc., USA). The pores of hollow fiber membranes were fully wetted by immersing the fibers overnight in a wetting liquid (Galwick, with a low surface tension of 15.9 dynes cm$^{-1}$). The compressed dry nitrogen gas was then used to displace the wetting liquid saturated in the wetted pores. The pore size distribution, bubble point pore size and mean pore size were subsequently calculated by the software provided along with the porometer [39].

The overall porosity of membrane was measured according to the density [33]. A mean value of 3 times of measurement was recorded to reduce the uncertainty which might result from the inner diameter/outer diameter (ID/OD) deviation along the length of fibers. The specific density of PVDF was 1.75 - 1.80 g cm$^{-3}$ according to the Solvay product information [40]. The surface porosity of the membranes was analyzed based on the SEM images using ImageJ software. The detailed procedures can be found elsewhere [41]. The measurement of liquid entry pressure of water (LEPw) was performed using hollow fiber modules with an effective
membrane area of 17.9 – 19.2 cm² in a dead-end configuration. The detailed methodology was well-documented [42, 43].

Membrane modules with cross-flow configuration were made for performance tests. Four hollow fibers were carefully inserted into a polypropylene tube. The tube was then sealed using an epoxy adhesive to prepare a testing module with an effective length of 16.3 cm. The description of set-up for PWP experiments can be found elsewhere [44]. Prior to the test, the compaction of membranes was conducted by circulating the Milli-Q ultra-pure water through the shell side of hollow fiber membranes for 30 min under a pressure of 1 bar. The pure water permeability (PWP, L m⁻²h⁻¹bar⁻¹) was calculated by [44]:

\[
PWP = \frac{V}{tA\Delta\rho} = \frac{V}{tn\pi Dl\Delta\rho}
\]

where \( V \) is the permeate volume (L) measured per determined time, \( t \) (h); \( A \) is the filtration area of the membrane (m²); \( n \) is the number of fibers; \( D \) is the OD of hollow fiber (m); \( l \) is the effective length of fibers in the module (m); \( \Delta\rho \) is the pressure difference between the feed and the permeate sides of the membrane (bar).

The mechanical properties of the resultant membranes were measured by a tensile meter (Zwick/Roell Z 0.5 kN Universal Testing Machine, Germany). The hollow fiber specimen was clamped onto the testing holder and was then pulled longitudinally at an elongation rate of 50 mm min⁻¹ at room temperature. The related mechanical properties which includes the tensile modulus, tensile strength and elongation were determined with the aid of built-in software [45].

2.5 Direct contact MD test of hollow fiber membranes
A direct contact MD experimental setup was used to test the performance of developed membranes [46]. Both the feed (synthetic seawater: 3.5 wt.% sodium chloride (NaCl) with conductivity around 60 ms cm\(^{-1}\)) and permeate (Milli-Q ultra-pure water, with conductivity below 1.0 \(\mu\)s cm\(^{-1}\)) solutions were circulated through the hollow fiber module in a counter-current mode. The feed solution on the shell side was heated up to the determined operating temperature and circulated using a customized electrical water heater together with a peristaltic pump (0 - 12 L min\(^{-1}\)). The permeate solution on the lumen side was cooled down to 20 °C using a water bath and circulated by another peristaltic pump (0 - 4 L min\(^{-1}\)). The distillate that overflowed from the permeate water bath was weighed by a balance (± 0.1 g).

To ensure comparable hydrodynamic conditions for different samples, the flow rates were adjusted to achieve the same Reynolds numbers (Re) for feed (Re = 2553) and permeate (Re = 310) streams, respectively. The permeate flux of membrane distillation was calculated using the following equation [46, 47]:

\[
F = \frac{\Delta W}{A \Delta t} \tag{4}
\]

where \(F\) is the permeate flux (kg m\(^{-2}\) h\(^{-1}\)); \(\Delta W\) is the weight of distillate (kg); \(A\) is the outer surface area of the hollow fiber membranes (m\(^2\)); \(\Delta t\) is the testing time (h).

3 **Results and discussion**

3.1 **Phase diagrams for PVDF binary and ternary systems**

The phase diagrams for the PVDF/DMP binary system and PVDF/PTFE/DMP ternary system are shown in Fig.2. As depicted in Fig.2 (A), the monotectic point of the binary system without the addition of PTFE particles is around 28 wt.%. Governed by NG or spinodal decomposition (SD) mechanisms, the phase separation occurs following different
routes: liquid-liquid (L-L) separation (route A), solid-liquid (S-L) separation (route B) or their combination (route through the monotectic point). The concentrations of PVDF used in this study were greater than 30 wt.%, suggesting the occurrence of S-L phase separation [16]. Since DMP could not dissolve PTFE particles and the melting point of PTFE particles (326.8 °C) was much higher than the processing temperature (220 °C), the PTFE particles was more considered as an additive in the system that would not play a major role in the phase separation process [25]. However, the impact of PTFE cannot be simply ignored as it might affect the crystallization of PVDF during the phase separation. Therefore, both PVDF/DMP and PVDF/PTFE/DMP systems should be examined by cross-over analysis of their phase diagrams.

In this study, the concentration of the diluent was kept constant, while the concentrations of PVDF and PTFE were kept as a whole. Based on previous findings [48], $T_c$ would decrease with increasing PVDF concentration if the effect of additive (in this case, PTFE) was negligible. However, it can be seen from Fig.2 (B) that $T_c$ gradually increased even with the decrease of PVDF concentration (increase of PTFE loadings), which means PTFE particles played a significant role in the heterogeneous NG. PTFE particles might act as crystal nuclei whereby PVDF crystals could grow and develop due to its good compatibility with PTFE [24]. Hence, the crystallization process could be accelerated by the addition of PTFE particles. Similar results were found by Ma et al. in a comparative study on MMT and PTFE [17].
Fig. 2. Phase diagrams for (A) PVDF/DMP binary system and (B) PVDF/PTFE/DMP system, where an increase in PTFE weight fraction was compensated by a decrease in PVDF weight fraction.
3.2 Morphology of the prepared membranes

Fig. 3 shows the cross-sectional images of the membranes obtained from PVDF/DMP system with various loadings of PTFE. Typical spherulitic structures can be found in all SEM images, indicating that the system might have undergone the S-L phase separation as discussed in Section 3.1. The spherulites are known as a typical type of monocystal aggregates in terms of their spherical crystallographic orientation resulted from isotropic and static temperature distribution during the growth of crystals [49]. Theoretically, the lamellae are shaped first by the orderly alignment of polymer chains during the crystallization process. The lamellae can grow further in all directions into spherulites in the absence of thermal gradient [50]. The amount and size of spherulites can be affected by the nucleation which is the inception of the whole crystallization process [49, 50].

It can be seen in Fig. 3 that the virgin PVDF membrane (PE-0) possessed spherulites with large sizes since the homogeneous nucleation was dominant without PTFE addition. As shown in Fig. 2 (B), PE-0 had the lowest $T_c$, suggesting that it required the longest time to reach the crystallization point, i.e., the highest activation energy for forming crystal nuclei. Due to the smaller number of nuclei formed, the crystals were able to grow into large diameters before impinging with each other. In contrast, when PTFE particles were incorporated into the blend, a heterogeneous nucleation occurred as the PTFE particles were likely to act as nucleating agents [16]. As such, the crystallization process was probably facilitated with a larger number of nucleation sites supplied, which is consistent with the results of increased $T_c$ at higher PTFE loadings. The larger number of available nuclei might eventually inhibit each spherulites to grow into a larger size, generating spherulites with smaller size and more uniform shape, as shown in Fig. 3. However, when the loading of PTFE exceeded 1 wt.%, interconnected fibril structures can be found in the enlarged images,
suggesting the planar growth of crystalline lamellae under anisotropic temperature distribution. Therefore, the over-supply of PTFE particles in some regions might affect the temperature gradient.

Fig.3. Cross-section morphology of hollow fiber membranes spun from the PVDF/DMP dopes with different PTFE loadings
3.3 Crystalline properties of the prepared membranes

DSC and WAXD analysis was conducted to study the thermal behaviors of PVDF/PTFE/DMP blends and the crystalline characteristics of resultant membranes. The corresponding results for crystallization and subsequent melting are presented in Table 3 and Table 4, respectively.

Table 3. Crystallization behaviors of polymer dope mixtures with different PTFE loadings

<table>
<thead>
<tr>
<th>Code</th>
<th>$T_{c}^{on}$ (°C)</th>
<th>$T_{c}^{P}$ (°C)</th>
<th>$T_{c}^{f}$ (°C)</th>
<th>$\Delta T_{c}$ (°C)</th>
<th>$\Delta H_{c}$ (J g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-0</td>
<td>104.3 ± 2.1</td>
<td>93.2 ± 0.8</td>
<td>86.5 ± 0.6</td>
<td>11.1 ± 0.2</td>
<td>34.2 ± 1.2</td>
</tr>
<tr>
<td>PE-1</td>
<td>99.5 ± 1.2</td>
<td>94.1 ± 1.1</td>
<td>85.7 ± 0.8</td>
<td>5.4 ± 0.3</td>
<td>35.1 ± 2.1</td>
</tr>
<tr>
<td>PE-2</td>
<td>100.2 ± 2.2</td>
<td>95.2 ± 1.0</td>
<td>86.3 ± 1.1</td>
<td>5.0 ± 0.1</td>
<td>35.4 ± 0.6</td>
</tr>
<tr>
<td>PE-5</td>
<td>110.3 ± 1.6</td>
<td>105.2 ± 2.1</td>
<td>96.9 ± 1.2</td>
<td>5.1 ± 0.1</td>
<td>30.6 ± 1.1</td>
</tr>
</tbody>
</table>

Notes: $T_{c}^{on}$, onset crystallization temperature of PVDF; $T_{c}^{P}$, peak crystallization temperature of PVDF; $T_{c}^{f}$, final crystallization temperature of PVDF; $\Delta T_{c} = T_{c}^{on} - T_{c}^{P}$.

Table 4. Melting behaviors of polymer dope mixtures and crystalline properties of membranes with different PTFE loadings

<table>
<thead>
<tr>
<th>Code</th>
<th>$T_{m}^{on}$ (°C)</th>
<th>$T_{m}^{P}$ (°C)</th>
<th>$T_{m}^{f}$ (°C)</th>
<th>$\Delta T_{m}$ (°C)</th>
<th>$\Delta H_{m}$ (J g$^{-1}$)</th>
<th>$\chi$ (%)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-0</td>
<td>123.1 ± 2.5</td>
<td>144.7 ± 3.2</td>
<td>148.8 ± 2.1</td>
<td>25.7 ± 0.3</td>
<td>45.6 ± 2.1</td>
<td>43.6 ± 2.1</td>
<td>6.42 ± 0.32</td>
</tr>
<tr>
<td>PE-1</td>
<td>111.3 ± 2.1</td>
<td>126.5 ± 3.0</td>
<td>136.4 ± 2.2</td>
<td>25.1 ± 0.2</td>
<td>51.9 ± 3.1</td>
<td>49.7 ± 1.9</td>
<td>6.10 ± 0.29</td>
</tr>
<tr>
<td>PE-2</td>
<td>112.9 ± 1.5</td>
<td>128.2 ± 2.6</td>
<td>137.7 ± 1.2</td>
<td>24.8 ± 0.1</td>
<td>51.0 ± 2.2</td>
<td>48.8 ± 1.5</td>
<td>5.53 ± 0.15</td>
</tr>
<tr>
<td>PE-5</td>
<td>122.1 ± 2.1</td>
<td>137.0 ± 2.2</td>
<td>145.6 ± 3.2</td>
<td>23.5 ± 0.1</td>
<td>49.2 ± 1.6</td>
<td>47.1 ± 2.0</td>
<td>4.52 ± 0.06</td>
</tr>
</tbody>
</table>
Notes: \( T_{on}^m \): onset melting temperature of PVDF; \( T_{mp}^P \): peak melting temperature of PVDF; \( T_m^f \): final melting temperature of PVDF; \( \Delta T_m = T_m^f - T_{on}^m \), \( \Delta H_m \): melting enthalpy; \( \chi_c \): crystallinity of PVDF, \( D \): crystal size.

As shown in Table 3, the peak crystallization temperatures, \( T_{cp}^P \), gradually increased as PTFE particles were added into the dope mixtures. The observation indicates that PTFE particles could bring down the threshold of activation energy for crystallization of nuclei [17]. In addition, the difference between the onset and peak temperature of crystallization, \( \Delta T_c \), was calculated to further investigate the kinetic characteristics of the crystallization process. It can be seen that the \( \Delta T_c \) of the dope mixtures decreased with the addition of PTFE particles. This indicates that the crystallization half-time \( (t_{1/2}) \) for PVDF with PTFE addition was much shorter than that without PTFE addition when the same cooling rate was applied. Hence, the crystallization of PVDF in the mixture was probably promoted due to the accelerated nucleation in the presence of PTFE particles.

From the results of melting scans shown in Table 4, the peak melting temperature, \( T_{mp}^P \), decreased sharply with 1 wt.% PTFE loading, but then gradually bounced back as the PTFE loading was increased to 5 wt.%. The \( T_{mp}^P \) describes the point at which the heat absorption is happening at the utmost rate [50, 51]. It indicates the degree of the long-range order in the crystalline structure, which is commonly reflected by the size of spherulites. However, the size of crystal decreased with increasing amount of PTFE loadings as shown in Table 4, suggesting a decreasing trend of \( T_{mp}^P \) which does not match the experimental observation. This reveals that other factors should also be taken into account. As discussed in Section 3.2, the planar growth of lamellae probably occurred due to over-supply of PTFE particles. Hence, the increase in \( T_{mp}^P \) with increasing PTFE loadings from 1 to 5 wt.% may be attributed to the enhanced degree of the long-range order contributed by the lamellae structure. On the
other hand, the difference between the final and onset temperatures of melting, \( \Delta T_m \), decreased with increasing PTFE loading. This suggests that more uniform spherulites could be obtained with PTFE addition [17], which agrees with the trend observed from the cross-section analysis presented in Fig.3. Moreover, the crystallinity (\( \chi_c \)) of the mixture increased first with PTFE addition at 1 wt.% and then slightly decreased with further loading, which could be due to the relatively increased fraction of amorphous region between the lamellae structure. This trend also implies that the addition of an appropriate amount of PTFE particles into the PVDF/DMP mixture could facilitate the crystallization of PVDF.

To further interpret the impact of PTFE particles on the crystallization process of PVDF, X-ray diffraction measurement was conducted as depicted in Fig.4. The peaks at \( 2\theta = 17.66^\circ \), \( 18.30^\circ \) and \( 19.90^\circ \) in the patterns for both virgin and PTFE-incorporated membranes correspond to the diffractions in planes (100), (020), and (110), respectively, suggesting the presence of only the \( \alpha \)-phase crystal of PVDF. However, it should be pointed out that the peak of plane (100) and (020) gradually merged together and finally manifested as a single strong peak of plane (100) with increasing PTFE loading from 0 to 5 wt.%. The observation suggests that although the crystal types remained to be the \( \alpha \)-phase, the crystallographic orientation of crystal growth was actually changed. This supports the speculation stated in Section 3.2 that the lamellae developed sideward without growing into radial-structured spherulites in certain regions with the addition of PTFE particles.
3.4 Pore size distribution and water permeability of prepared membranes

In the S-L phase separation, the pore structure of a membrane forms along with the NG of crystals [10]. Thus, the crystallization process could strongly affect the pore structure. The effect of PTFE loading on the mean pore size and pore size distribution of resultant membranes is shown in Fig.5. The related characteristics of prepared membranes are listed in Table 5. It can be seen that both mean and maximum pore sizes of membranes decreased first (0 to 2 wt.%) and then slightly increased (2 to 5 wt.%) with the addition of PTFE particles. As explained earlier, the heterogeneous nucleation promoted by PTFE particles could facilitate the formation of more crystals. Given a faster rate of NG, more spherulites could be shaped with higher uniformity and smaller cavity in between. Therefore, smaller pore diameters and a narrower pore size distribution should be expected. However, the effects of changes in PVDF fraction in the dope system should also be taken into account since the
skeleton of membrane is mainly structured by PVDF. In this study, a fixed portion of PVDF/PTFE in the dope mixture was applied so that the PVDF fraction decreased as the PTFE loading went higher. Hence, considering the tradeoff between the promoted density of spherulites and the lowered PVDF fraction, the slight increase in the pore sizes as the PTFE loading was changed from 2 to 5 wt.% could be attributed to stronger impact from the decreased PVDF fraction. On the other hand, compared with virgin PVDF membranes, smaller pore sizes and much narrower pore size distributions can be obtained from the membranes with the addition of PTFE particles.

Fig. 5. Pore size distribution of membranes obtained with different PTFE loadings

Table 5. Characteristics of membranes with different PTFE loadings

<table>
<thead>
<tr>
<th>Membranes</th>
<th>OD (µm)</th>
<th>ID (µm)</th>
<th>Thickness (µm)</th>
<th>Mean pore size (nm)</th>
<th>Maximum pore size (µm)</th>
<th>LEPw (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-0</td>
<td>1032 ± 2</td>
<td>610 ± 4</td>
<td>211 ± 7</td>
<td>0.18 ± 0.02</td>
<td>0.35 ± 0.03</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>PE-1</td>
<td>1015 ± 5</td>
<td>547 ± 8</td>
<td>234 ± 9</td>
<td>0.10 ± 0.01</td>
<td>0.28 ± 0.02</td>
<td>1.42 ± 0.05</td>
</tr>
<tr>
<td>PE-2</td>
<td>1022 ± 11</td>
<td>574 ± 4</td>
<td>224 ± 6</td>
<td>0.08 ± 0.01</td>
<td>0.12 ± 0.01</td>
<td>2.32 ± 0.10</td>
</tr>
<tr>
<td>PE-5</td>
<td>1098 ± 12</td>
<td>651 ± 9</td>
<td>224 ± 8</td>
<td>0.12 ± 0.01</td>
<td>0.25 ± 0.03</td>
<td>1.60 ± 0.06</td>
</tr>
<tr>
<td>Commerciala</td>
<td>1549 ± 10</td>
<td>855 ± 5</td>
<td>347 ± 6</td>
<td>0.02 ± 0.01</td>
<td>0.18 ± 0.02</td>
<td>1.70 ± 0.05</td>
</tr>
</tbody>
</table>

Notes: aThe commercial membrane was selected for DCMD test as benchmark in Section 3.7.
The impact of PTFE addition can also be reflected in the porosity and water permeability of the resultant membranes, which are commonly used to indicate the interconnectivity of the pore structure. Generally, the interconnectivity of spherulitic structure is mainly determined by the tradeoff between the size and amount of cavities among the spherulites [49, 50]. Fig.6 shows that, the porosity of the prepared membranes initially reached the highest value at the loading of 1 wt.% and then decreased with PTFE addition. As discussed in Section 3.2 and 3.3, the presence of an appropriate amount of PTFE could enhance the nucleation process, resulting in spherulites with smaller size but larger number. The size and density of spherulites normally have a positive relationship with those of cavities [52]. Therefore, when the PTFE loading exceeded 1 wt.%, the impact from decreased cavity sizes might surpass that from increased cavity numbers, leading to the reduction in the porosity. This trend is in accordance with the results of water permeability presented in Fig.6. Pure water permeability was observed to be directly related to both pore size distribution and porosity, and the membrane with 1 wt.% of PTFE loading possessed the highest water permeability due to its relatively high overall and surface porosities.
Fig. 6. Porosity and pure water permeability of membranes obtained with different PTFE loadings

3.5 Hydrophobicity of the prepared membranes

Water contact angle is an important indication to the surface hydrophobicity of hollow fiber membranes. The enhancement of hydrophobicity is a major concern on wetting control as this study aims at developing membranes suitable for MD process [37]. The addition of PTFE particles is expected to serve dual functions: (1) to adjust the membrane pore structure, which has been verified in the prior sections; and (2) to improve the hydrophobicity of the PVDF membranes. The variations of dynamic contact angle of prepared membranes are shown in Fig. 7. Compared with the virgin PVDF membrane with a contact angle of 95 ± 1°, all prepared membranes with PTFE addition exhibited a higher water contact angle of more than
105°, suggesting that the incorporation of PTFE particles is an effective way to enhance the surface hydrophobicity of membranes. In addition to the intrinsic hydrophobic nature of PTFE particles, the enhanced hydrophobicity could also be attributed to the surface topography of the membranes, which contains information of the surface roughness. As presented in Fig. 8, the outer surface of the membranes becomes more rugged with increasing loading of PTFE particles. Furthermore, it can be seen from Table 6 that the roughness of both the internal and external surfaces of the PTFE-incorporated membranes are noticeably higher than those of virgin membranes. The mean roughness increased slightly as PTFE loading was further increased from 2 to 5 wt.%. This result may be attributed to the intensified impingement among spherulites resulted from the addition of PTFE particles. Such spherulite-led rugged structures could be essential to improve the hydrophobicity of membranes.

LEPw is one of the critical characteristics commonly used to select the suitable membranes for MD application as it indicates the anti-wetting properties of the membranes [37, 38]. It can be found from Table 5 and Fig.7 that the LEPw values of the PTFE-incorporated membranes are much higher than that of virgin membranes. This is possibly due to the reduced maximum pore size as well as the increased hydrophobicity. PE-2 exhibits the largest LEPw of 2.32 ± 0.10 bar given its smallest maximum pore size among all the in-house fabricated membranes.
Fig. 7. Dynamic contact angle and LEPw of membranes obtained with different PTFE loadings

Fig. 8. AFM images (3D) of the outer surface of membranes obtained with different PTFE loadings
Table 6. Surface properties of membranes with different PTFE loadings

<table>
<thead>
<tr>
<th>Membranes</th>
<th>( R_a ) of inner surface (nm)</th>
<th>( R_a ) of outer surface (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE-0</td>
<td>69.2 ± 1.2</td>
<td>45.7 ± 0.6</td>
</tr>
<tr>
<td>PE-1</td>
<td>73.0 ± 1.3</td>
<td>55.8 ± 0.9</td>
</tr>
<tr>
<td>PE-2</td>
<td>74.2 ± 1.2</td>
<td>56.7 ± 1.3</td>
</tr>
<tr>
<td>PE-5</td>
<td>78.5 ± 1.5</td>
<td>58.9 ± 1.5</td>
</tr>
</tbody>
</table>

3.6 Mechanical properties of the prepared membranes

Instinctively, the mechanical strength of TIPS membranes can be improved by increasing the polymer concentration. However, as discussed in Section 3.1, a high polymer concentration could make it possible for the occurrence of phase separation at the region beyond the monotectic point, which results in the formation of spherulitic structure. This structure is considered relatively weaker than the bicontinous structure owing to the low interconnectivity between the spherulites [52]. Nevertheless, the formation of bicontinuous structure often requires a low polymer concentration in most dope systems, resulting in membranes with a low mechanical strength. Therefore, improving the mechanical strength by adjusting the polymer concentration remains a dilemma. The effect of PTFE addition on the tensile strength and elongation at break is depicted in Fig.9. The tensile strength and elongation could reach the maximum values of 9.4 ± 0.3 MPa and 235 ± 36 %, respectively, showing outstanding durability and ductility. It can be seen clearly that the tensile strength, representing the toughness, was improved as the loading of PTFE particles varied from 0 to 5 wt.%. However, the elongation, which indicates the elasticity, experienced ups and downs along with the addition of PTFE particles. This may be due to two factors: (1) the nucleation
effect of PTFE; and (2) the formation of lamellae structure which contained more amorphous regions with higher loadings PTFE. Generally, the spherulites in the PVDF-based membranes contain semi-crystalline structure where lamellae crystallites with orderly polymer alignment are embedded between amorphous regions [50]. It is widely accepted that the toughness is mainly contributed by the intermolecular interactions within the crystallites, while the elasticity is dependent more on the amorphous regions between the lamellae [49, 50, 53]. As PTFE loading increased, the nucleation of PVDF was probably promoted as discussed before, suggesting stronger intermolecular interactions within spherulites and tighter impingement between spherulites. This could be responsible for the increase in the tensile strength. On the other hand, it was also found that the planar formation of lamellae structure might be enhanced as discussed previously in Section 3.2 and 3.3. In addition, the crystallinity of membranes was also decreased with higher loadings of PTFE, indicating the increase in the amorphous region as shown in Table 4. The elasticity was therefore improved noticeably as the loading of PTFE was increased from 2 to 5 wt.%. It should be pointed out that the toughness was supposed to be slightly compromised with increased amorphous regions. However, it was not obviously reflected in the trend of tensile strength probably due to a stronger impact from increased interconnectivity between spherulites.
3.7 Direct contact MD test of hollow fiber membranes

DCMD tests were conducted to evaluate the MD performance of the PVDF hollow fiber membranes with and without PTFE addition. The permeation flux of each test was recorded after a 3-h stabilization. The effect of feed temperature on the permeation flux for the membranes with different PTFE loadings is plotted in Fig.10. It can be observed that all membranes with PTFE incorporation exhibited enhanced flux over the virgin membrane (PE-0). The membrane with 1 wt.% PTFE addition (PE-1) achieved the best performance, which possessed a flux of 28.3 kg m\(^{-2}\) h\(^{-1}\) at a feed temperature of 60 ºC. Such results agree well with the tendency of pore size, porosity and water permeability presented in Table 5 and Fig.6, which show that the PE-1 membrane possessed the largest porosity and water permeability. As discussed previously, an appropriate PTFE addition improved the
interconnectivity and uniformity of the pore structure, so that it could greatly reduce the resistance for water vapor transport [15, 46-48]. To better assess the long-term performance, a continuous study was performed at a feed temperature of 60 °C. One commercial hollow fiber membrane was selected for comparison with PE-0 and PE-1 membranes. The characteristics of the selected commercial membrane are summarized in Table 5.

Fig.11 shows that the PVDF/PTFE hollow fiber membranes achieved a relatively stable permeation flux throughout the entire testing period of 50 h, which was much better than the performance of the selected commercial membrane. In contrast, the virgin PVDF (PE-0) membranes was easily wetted within only 5 h, possibly due to its relatively low anti-wetting property which is closely linked with the LEPw of membrane [37]. When PTFE particles were introduced, the reduced pore sizes and improved hydrophobicity resulted in a higher LEPw as presented in Section 3.4 and 3.5, and hence a better wetting resistance. A further benchmark comparison of the selected PE-1 membrane and other membranes reported in the literature is shown in Table 7. The PVDF/PTFE membrane showed comparable performance with others, while it exhibited better mechanical strength, indicating its good potential in MD application.
Fig. 10. DCMD permeation flux of membranes with different PTFE loadings.

Fig. 11. Effect of PTFE addition on PVDF membranes for DCMD application (3.5 wt% NaCl as feed, $T_f = 60 \, ^\circ C$, $T_p = 20 \, ^\circ C$)
Table 7. Performance and properties of different PVDF hollow fiber membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Method</th>
<th>Mean pore size (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Feed solution</th>
<th>Permeate solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NaCl concentration (wt.%)</td>
<td>Flow velocity (°C)</td>
<td>Flow velocity (°C)</td>
<td>Permeate flux (kg m⁻² h⁻¹)</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>NIPS</td>
<td>0.25</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/CaCO(_3) hollow fiber</td>
<td>NIPS</td>
<td>0.25</td>
<td>5.7</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>NIPS</td>
<td>0.16</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/PTFE hollow fiber</td>
<td>NIPS</td>
<td>0.25</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF dual-layer hollow fiber</td>
<td>NIPS</td>
<td>0.41</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF dual-layer hollow fiber</td>
<td>NIPS</td>
<td>0.41</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/clay hollow fiber</td>
<td>NIPS</td>
<td>(\bigtriangledown)</td>
<td>1.0</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/PTFE dual-layer hollow fiber</td>
<td>NIPS</td>
<td>(\bigtriangledown)</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>TIPS</td>
<td>0.28</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>TIPS</td>
<td>0.31</td>
<td>6.8</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/CaCO(_3) hollow fiber</td>
<td>TIPS</td>
<td>0.28</td>
<td>(\bigtriangledown)</td>
<td>3.5</td>
<td>60.0</td>
</tr>
<tr>
<td>PVDF/PTFE hollow fiber (PE-1)</td>
<td>TIPS</td>
<td>0.10</td>
<td>7.4</td>
<td>3.5</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Notes: \(^a\)The data were collected from figures in the literature by using the Digitizer function in *Origin* 9.1. \(^b\)The data were not shown in the paper.
4 Conclusions

In this study, PVDF/PTFE hollow fiber membranes with various PTFE loadings have been developed via the TIPS method for DCMD. PTFE particles were found to play an important role in the crystallization of PVDF polymer matrix during the S-L phase separation. Acting as the nucleating agent, PTFE particles could significantly enhance the NG of PVDF. In this way, more uniform and smaller spherulites in a greater number were generated, which further resulted in smaller cavities in between. As a result, narrower pore size distributions of the resultant membranes can be achieved with smaller mean pore sizes varying from 0.08 to 0.12 µm. The porosity and water permeability initially increased with PTFE content and then declined with the addition of PTFE particles above 1 wt.%. Moreover, the tensile strength and elongation were noticeably improved to as high as 9.4 ± 0.3 MPa and 235 ± 36 %, respectively. On the other hand, owing to PTFE’s good intrinsic hydrophobicity, the water contact angle of resultant membranes increased from 94 ± 1 to 106 ± 3º. With all these enhanced properties, the prepared PVDF/PTFE membranes achieved good performance in the MD process. The membranes with the optimum PTFE loading of 1 wt.% exhibited a flux of 28.3 kg m⁻² h⁻¹ at the feed temperature of 60 ºC with 99.99 % NaCl rejection over a 50-h continuous test. Above all, the DCMD performance demonstrated that the newly developed PVDF/PTFE membranes had improved anti-wetting and mechanical properties over the virgin PVDF membranes, suggesting its good potential in DCMD applications.
Acknowledgments

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References


