Preparation and properties of PVDF composite hollow fiber membranes for desalination through direct contact membrane distillation

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ABSTRACT

The polyvinylidene fluoride (PVDF) composite hydrophobic hollow fiber membranes were fabricated for membrane distillation through non-solvent induced phase inversion by dispersing hydrophobic modified calcium carbonate nano-particles in the PVDF casting solution and using the mixture of LiCl and polyethylene glycol (PEG) as non-solvent additive. The influence of nano-particles on the spun hollow fiber membrane characteristics was investigated. The addition of hydrophobic nano-particles could optimize the sandwich-like morphology, narrow the pore size distribution, improve the membrane porosity and increase the membrane surface roughness and contact angle to some extent. The nano-particles also enhanced the crystallinity degree and thermal stability of the hollow fiber. In addition, the composite membranes presented stronger mechanical properties compared to the fiber without particles. During the desalination process of 3.5 wt% sodium chloride solution, the maximum transmembrane permeate flux about 46.3 kg/m² h with a lower thermal loss was obtained from the composite fiber when the hot feed inlet temperature and the cold distillate inlet temperature were at 80.5 °C and 20.0 °C respectively. Furthermore, the composite membrane exhibited satisfying performance stability compared with the pure PVDF membrane in the 30 days continuous desalination experiments, indicating that the as-spun composite fiber may be of great potential to be utilized in MD process for desalination.

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1. Introduction

Membrane distillation (MD) is a new membrane separation technology using the temperature gradient created on membrane surfaces as a driving force and usually applied in which water is the major component present in the feed solution to be treated [1]. In MD process, a porous non-selective hydrophobic membrane acts as a physical support separating a warm solution from a cooler chamber containing either a liquid or gas [2]. Compared with conventional separation processes such as evaporation, distillation and reverse osmosis, MD can be operated under relatively low temperature or low pressure with low energy consumption and high productivity [3–5]. There have been extensive researches on MD for the past three decades [2] and various configurations have been developed including direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) [6]. Up to the present, MD has been applied to water desalination, wastewater reuse, juice concentration and other industrial areas [7–11].

Although the porous membrane only acts as a physical barrier, it plays a crucial role during MD process. The membrane designed for MD process should be hydrophobic to prevent the aqueous solution from entering into its dry pores until the operating pressure exceeds the liquid entry pressure of water (LEPw) [12]. Besides, other membrane characteristics, such as thickness, porosity, pore size and pore size distribution can also influence membrane performance [13–15]. Because the hot feed to be treated must be in direct contact with one side of membrane, a desirable thermal stability and chemical resistance to feed solution are necessary for the membrane used in MD [16].

Currently, the membranes used in MD process are mainly made of hydrophobic materials such as polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [17]. The membrane from PP can be prepared by thermally induced phase separation (TIPS) process or melt-spinning and cold-stretching (MSCS) method [18]. PTFE membrane is formed by stretching and heating process [19]. Among these three materials, only PVDF can be fabricated by non-solvent induced phase separation (NIPS) method and form asymmetric membranes morphology, which is important for achieving a high permeability of the MD membranes [14,20]. In recent years, more attention has gone into preparing hydrophobic membranes, particularly the PVDF membrane specifically for MD process.
Tomaszewsk [21] studied the preparation of flat-sheet PVDF membranes suitable for MD and a permeate flux about 9.7 kg/m² h was achieved at the temperature of the feed and permeate of 60 °C and 20 °C, respectively. Khayet and Matsura [22] fabricated supported and unsupported PVDF flat-sheet membranes using pure water as pore-forming additive, while Huo et al. [17] prepared flat-sheet PVDF-fabric composite membrane by introducing polyester (PET) filament woven fabric as the support. Peng et al. [23] prepared a flat-sheet composite membrane for MD with a PVA/PEG hydrophilic layer on PVDF hydrophobic substrate, and found that the permeate flux did not deteriorate by adopting the additional hydrophilic layer. Feng et al. [19,24] fabricated flat-sheet membranes with poly(vinylidene fluoride-co-tetrafluoroethylene) (PVDF-co-TFE) and poly(vinylidene fluoride-co-hexafluoropropylen) (PVDF-co-HFP), the flux of the obtained membrane was higher than that of PVDF membrane. Recently, Khayet et al. [25] prepared flat-sheet PVDF–HFP membranes based on fractional factorial design and optimized membrane preparation conditions using a minimum number of experiments and applying Lagrange multipliers optimization method.

Hollow fiber membranes are considered more desirable for industrial applications due to their higher membrane area per unit volume [26]. Wang et al. [27] prepared PVDF asymmetric hollow fiber membranes by introducing small molecular additives such as water, ethanol and 1-propanol, and found that the spun PVDF membranes exhibited good mechanical strength and excellent hydrophobicity. Yeow et al. [28] and Wang et al. [1] fabricated PVDF hollow fiber membranes via phase inversion method using lithium perchlorate (LiClO4) and ethylene glycol (EG) as an additive, respectively. Simone et al. [29] prepared microporous hydrophobic PVDF hollow fibers for VMD by using water and poly(vinyl pyrrolidone) (PVP) as pore forming additives, the flux reaching as high as 18 kg/m² h at 50 °C and 20 mbar vacuum pressure. Teoh and Chung [30] fabricated PVDF–PTFE hollow fiber membranes showing improved hydrophobicity and macrovoid free structure. Bonyadi and Chung [31] used the co-extrusion method to fabricate PVDF–polyacrylonitrile (PAN) dual layer hydrophilic–hydrophobic hollow fiber membranes for the first time, and a permeate flux about 55 kg/m² h at 90 °C was achieved using DCMD configuration.

Although many researchers have been working on the preparation of suitable membranes for MD, most works focus on the enhancement of permeate flux and surface hydrophobicity. It seems that the porous fibers with a thinner thickness would obtain a higher permeate flux due to low resistance for mass transfer [32]. However, the porous hollow fiber membranes fabricated by NIPS method with such thin wall is too vulnerable to withstand the hydraulic pressure from either lumen or shell side and the membrane mechanical properties are practically unsatisfactory from an industrial application perspective [19]. As far as we know, studies related to the fabrication of hydrophobic PVDF hollow fibers with good mechanical properties are rather limited. It has been demonstrated that the composite membrane modified by addition of nano-particles can effectively overcome material deficiencies, enhance membrane mechanical properties, permeate flux and surface hydrophobicity [3,30–33].

The objective of the present research is to fabricate PVDF/nano-particles composite hollow fiber membranes with good mechanical properties, high permeate flux and excellent surface hydrophobicity. The hydrophobic modified CaCO3 nano-particles were chosen as the inorganic phase of the composite membranes because hydrophobic CaCO3 nano-particles had well dispersity in organic solvent and high interface adhesive force with polymer matrix [34]. In this work, the effect of nano-particles percentage in the polymeric dope on fibers characteristics and performance was investigated comprehensively. The fabricated composite membranes were also tested via DCMD process using 3.5 wt% sodium chloride solution as feed.

2. Materials and methods

2.1. Materials

PVDF (FR-904) was obtained from Shanghai 3F new materials Co., Ltd. (China). The molecular weight (MW) of PVDF is about 1.02 × 10⁶ g/mol, measured by GPC (waters, 515). N,N-dimethylacetamide (DMAc, >99%) was employed as the solvent, purchased from Shanghai Jingwei Chemical Co., Ltd. (China). Hydrophobic CaCO3 nano-particles (>98.7%) modified with octadecyl dihydrogen phosphate were supplied by Nanomaterials Technology Co., Ltd. (China) and the contact angel of the modified nano-particles is about 120°. The mean particle size and specific surface area are about 36 nm and 45 m²/g, respectively. A mixture of LiCl and polyethylene glycol (PEG) used as non-solvent additive in the polymer solution, LiCl (95.0%) and PEG (Mw = 1500, >99.5%) were supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering (China). Ethanol (GR grade, 99.9%) and NaCl (99.5%) were from Beijing Chemical works (China). Ultapure water and tap water were used as the internal and external coagulant respectively.

2.2. Hollow fiber fabrication

The PVDF powder was dried at 100 °C under vacuum for 24 h to remove its moisture content before it was used for dope preparation. A desired amount of dried PVDF powder was weighed and poured into a tank containing DMAc solvent and non-solvent additive, then the polymer dope mixture was subjected to continuous stirring at 50 °C until it was homogeneous. In another tank, the emulsion of CaCO3/DMAc was made without heating, only with agitation. After complete dissolution of PVDF polymer, the CaCO3 emulsion was added, the temperature and agitation were kept until the new polymer dope mixture became homogeneous again. Afterwards, the stirring was stopped and release the gas bubbles in the dope at 50 °C for about 72 h.

In this work, the mixture of LiCl and PEG was chosen as non-solvent additive and DMAc was used as solvent. The dope solutions contained 12 wt% PVDF, 5 wt% LiCl and 3 wt% PEG, the mixing ration for CaCO3/PVDF was in the range of 0/100–50/100 in weight. The dope solutions compositions used in membrane fabrication are listed in Table 1.

The homogenous dope solution was fed into the spinneret after passing through a metal filter (15 µm) under the nitrogen pressure of 0.2 MPa, and the dope flow rate was adjusted by a gear pump with a speed controller. Ultapure water was used as bore liquid and fed into the spinneret through a flow meter under the same nitrogen pressure to make a lumen of the hollow fiber. More details about phase inversion method and the spinning set-up were reported in related research [35], and the spinning conditions for all experiments are listed in Table 2.

The hollow fiber was extruded from the spinneret and wound onto a take-up winder after entering into a water bath kept at 20 °C to induce the complete phase separation and solidify the membrane. Then the fibers were soaked in ethanol bath for 3 days to remove the residual solvent and non-solvent additive. At last, the wet fibers were dried in air at room temperature until to receive hydrophobic porous membranes.

2.3. Membrane morphology study

The morphology of membrane was investigated with a HITACHI S-3000N scanning electron microscope (SEM) (Hitachi Ltd., Japan).
Membrane samples were frozen in liquid nitrogen, fractured to obtain fragments, and sputtered with platinum using a HITACHI E-1010 Ion Sputtering device for SEM observation.

2.4. Membrane surface analysis

The contact angle (CA) of the PVDF hollow fiber was measured by a tensiometer (DCAT11, DataPhysics Instruments Ltd., Germany). A sample fiber was held on the arm of an electrobalance, and then immersed 5 mm long into Milli-Q water and successively emerged out at an interfacial moving rate of 0.2 mm/min to complete a cycle. In the loop, the weight difference was continuously recorded by the electrobalance and contact angle was calculated based on the Wilhelmy method. Three immersion-emersion cycles were carried out for each specimen, and each run was repeated three times for all the hollow fiber samples.

It has been demonstrated that the hydrophilic/hydrophobic property of hollow fiber is related to surface roughness [36]. An atomic force microscope (AFM) (NanoScope Illa, Digital Instruments, USA) was employed to analyze the surface states of the prepared membranes. All the membrane samples were measured by using a same tip and the surface roughness was obtained by tapping mode.

2.5. Porosity, pore size and pore size distribution

The overall porosity was usually determined by gravimetric method, determining the weight of liquid contained in the membrane pores. The porosity $\varepsilon$ of the PVDF hollow fiber was calculated by the following equation [37]:

$$\varepsilon = \frac{m_1 - m_2}{\rho_l \cdot \pi (R^2 - r^2) \cdot l}$$  \hspace{1cm} (1)

where $m_1$ is the weight of the wet membrane, $m_2$ is the weight of the dry membrane, $\rho_l$ is the liquid density, $l$ is the fiber length, $R$ and $r$ are the outer radius and the inner radius of the hollow fiber, respectively. The liquid used for porosity measurement named Porefil was supported by IB-FT GmbH (Germany) and its surface tension and density were 16 dyn/cm and 1.87 g/ml, respectively.

The bubble point and pore size distribution of the prepared membrane were investigated by using a Capillary Flow Porometer (Porolux 1000, IB-FT GmbH, Germany). The fibers were fully wetted with the Porefil, and then the measurements were carried out following the procedure described in literature [1]. The bubble point and pore size distribution were determined with the aid of the computer software coupled to CFP.

2.6. Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the thermal properties of the composite membranes with a differential scanning calorimeter (Q100, Thermal Analysis, USA) and a thermogravimetric analyzer (Q50, Thermal Analysis, USA), respectively. DSC data were obtained in the temperature range of 30–250 °C. Firstly, the sample was heated from 30 to 250 °C. After thermal stabilization, the sample underwent DSC measurement while being cooled to 30 °C at a cooling rate of 10 °C/min with the help of liquid nitrogen and then being heated to 250 °C at a heating rate of 10 °C/min. The TGA measurements were conducted under nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 800 °C.

2.7. Mechanical properties test

Mechanical properties of the fabricated membranes were investigated by measurements with an Instron tensiometer (Instron 5565-5kN, Instron Corporation, USA) at room temperature. The sample was clamped at both ends and pulled in tension at a constant elongation rate of 10 mm/min with an initial length of 20 cm, five specimens were tested for each hollow fiber sample.

2.8. DCMD test

The dry membranes in the number of 50 pieces were assembled into a polyester tube (diameter (mm) $d_{out}/d_{in} = 15/20$) with two UPVC T-tubes and two ends of the bundle of fibers were sealed with solidified epoxy resin to form a membrane module, the effective membrane length was about 100 mm.

The permeability of prepared membranes was tested through DCMD experiment with 3.5 wt% sodium chloride solution as feed. The simplified scheme of DCMD set-up is shown in Fig. 1. The hot salt solution as feed flowed through the lumen side of the fibers, whereas the cold water flowed through the shell side. Both solutions were circulated in the membrane module with the help of two magnetic pumps (MP-15RN, Shanghai Seisun Pumps, China). The feed and the cold water flowed co-currently through the module, and the circulation feed rate was 0.50 m/s, while the cold side being 0.15 m/s. The feed temperature was controlled by a Pt-100 sensor and a heater connected to an external thermostat (XMTD-2202, Yongshang Instruments, China) and the temperature of cold distillate water was controlled by pumping through a spiral glass heat exchanger located in the constant temperature trough of the cooler (SDC-6, Nanjing Xinchen Biotechnology, China). The temperature of both fluids was monitored at the inlet and outlet of the membrane module using four Pt-100 thermoresistances connected to a digital

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### Table 1 Compositions of dope solutions for hollow fiber membranes preparation.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>CaCO$_3$/PVDF</th>
<th>CaCO$_3$ (wt%)</th>
<th>PVDF (wt%)</th>
<th>LiCl (wt%)</th>
<th>PEG (wt%)</th>
<th>DMAc (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>0/100</td>
<td>0.0</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>80.0</td>
</tr>
<tr>
<td>M-2</td>
<td>10/100</td>
<td>1.2</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>78.8</td>
</tr>
<tr>
<td>M-3</td>
<td>20/100</td>
<td>2.4</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>77.6</td>
</tr>
<tr>
<td>M-4</td>
<td>30/100</td>
<td>3.6</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>76.4</td>
</tr>
<tr>
<td>M-5</td>
<td>40/100</td>
<td>4.8</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>75.2</td>
</tr>
<tr>
<td>M-6</td>
<td>50/100</td>
<td>6.0</td>
<td>12.0</td>
<td>5.0</td>
<td>3.0</td>
<td>74.0</td>
</tr>
</tbody>
</table>

---

### Table 2 Hollow fiber spinning conditions.

<table>
<thead>
<tr>
<th>Spinning conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing temperature (°C)</td>
<td>50</td>
</tr>
<tr>
<td>Spineret temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Dope extrusion rate (ml/min)</td>
<td>20</td>
</tr>
<tr>
<td>Spineret OD/DD (mm/mm)</td>
<td>1.4/0.7</td>
</tr>
<tr>
<td>Bore liquid</td>
<td>Ultrapure water</td>
</tr>
<tr>
<td>Bore liquid flow rate (ml/min)</td>
<td>10–20</td>
</tr>
<tr>
<td>External coagulant</td>
<td>Tap water</td>
</tr>
<tr>
<td>Air-gap distance (cm)</td>
<td>8–10</td>
</tr>
<tr>
<td>Bore liquid temperature (°C)</td>
<td>20</td>
</tr>
<tr>
<td>External coagulant temperaure (°C)</td>
<td>20</td>
</tr>
<tr>
<td>Take-up speed (m/s)</td>
<td>0.35</td>
</tr>
<tr>
<td>Room relative humidity (%)</td>
<td>60–75</td>
</tr>
</tbody>
</table>

* Outer diameter/inner diameter.
meter (Digit RTD, model XMT-808, Yuyao Changjiang Temperature Meter Instruments, China) with an accuracy of ±0.1 °C. An electric conductivity monitor (CM-230A, Shijiazhuang Create Instrumentation Technologies, China) was used to monitor the distillate cold water quality. The permeate flux was calculated by the following equation:

\[ J = \frac{\Delta W}{A \cdot \Delta t} \]  

where \( J \) is the permeate flux (kg/m² h), \( \Delta W \) is the mass of the permeate (kg), \( A \) is the inner surface area of the hollow fiber membranes (m²) and \( \Delta t \) is the time interval (h).

3. Results and discussion

3.1. Membrane morphology examination by SEM

The SEM images of pure PVDF membrane and PVDF/CaCO₃ composite membranes are presented in Fig. 2. It can be seen that the spun fibers show a sandwich-like structure between the ultra thin skin layers and this structure consists of three layers, where a sponge-like porous layer located between two layers full of finger-like macrovoids. With the addition of hydrophobic modified CaCO₃ nano-particles, the finger-like macrovoids became long and narrow, the number of the macrovoids increased. It can also be observed that the sponge-like porous layers got looser and the size of micropores in the middle structure increased obviously, and this kind of microstructure would enhance the porosity of the spun membranes. It should be noticed that when the mixing ration for CaCO₃/PVDF exceeded 20/100, the membrane porosity began to decrease, and this can be explained by the dispersity of the nano-particles in the spun membranes. With the increase of the particles addition, part of nano-particles would agglomerate in the prepared dope. As a result, the inhomogeneity of the particles distribution in the spun membranes had negative effects on membrane porosity, which can be observed clearly in the membrane middle structure in Fig. 2(M-6c, M-5c and M-6c).

The change of membrane morphology can be associated with the nano-particles addition. When appropriate amount of CaCO₃ nano-particles were added, they dispersed homogeneously in the dope. During the phase inversion membrane formation process, the nano-particles acted as nucleation agent and elevated the polymer crystallization rate, which meant a rapid phase separation and would result in macrovoids and ultra thin skin formation. The nano-particles were embedded in the PVDF polymer matrix and would decrease the mean pore diameter of the spun membranes. With the increase of CaCO₃ particles in the CaCO₃/PVDF mixture, the pore diameter became smaller and smaller, and the dense membrane structure formed at last. The dense membrane structure was harmful for the double diffusion rate between solvent and non-solvent, the phase separation rate declined and the membrane porosity began to decrease. In this case, the CaCO₃ nano-particles acted as anti-nucleating agent, and the excessive addition of it would lead the membrane permeability to deteriorate.

3.2. Porosity, LEPw, pore size and pore size distribution

The pore size distribution of the spun membrane is presented in Fig. 3. For all the PVDF/CaCO₃ composite membranes, the pore size distribution became narrower around the mean pore diameters compared with the pure PVDF hollow fiber. The maximum pore size and the mean pore diameter are listed in Table 3. It can be found that the pore size of the spun membranes decreased with increase of the nano-particles addition, which was in agreement with the analysis of membrane morphology. The LEPw values can be obtained using the method described by Smolders and Franken [38], From Table 3, it can be demonstrated that the reduction of the maximum pore size would improve the LEPw value, which was helpful to prevent liquid from passing through the membrane pores.

Although the porosity of the M-2, M-3 and M-4 hollow fibers were 81.5%, 85.3% and 82.6%, respectively, higher than the porosity of the pure PVDF membrane, the porosity of M-5 and M-6 membranes became lower than 79.8%, which indicated that the influence of nano-particles addition on membrane porosity was not always positive. The wall thickness of the composite membranes was higher than that of the pure PVDF hollow fiber. This is because the nano-particles were embedded in the PVDF polymer matrix and decreased the degree of the nascent fibers deformation in membrane preparation process compared with the pure PVDF membrane.

3.3. Membrane surface analysis

The surface topography and three-dimensional surface images of the pure PVDF membrane and PVDF/CaCO₃ composite membranes can be observed in Figs. 4 and 5. Roughness parameters were obtained with the AFM analysis software, the average roughness (\( R_a \)) for the image is defined as the arithmetical average of the absolute values of the surface height deviations measured from the center plane, the root mean square roughness (\( R_q \)) represents the standard deviation from the mean surface plane and the maximum roughness (\( R_{max} \)) is the vertical distance between the highest peaks and the lowest valleys in the image. All roughness parameters are given in Table 4. \( R_a \) and \( R_q \) seem to be the most helpful and consistent to characterize surface topography of the spun membranes. \( R_{max} \) can be affected by local imperfections or sample contamination leading to higher values than expected and so material characterization based on this parameter could be unreliable [39].
Fig. 2. SEM images of the hollow fiber membranes spun from different dope solutions.

Table 3
Measured data of the spun hollow fiber membranes characteristics.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Porosity (%)</th>
<th>Outer diameter (mm)</th>
<th>Inner diameter (mm)</th>
<th>Wall thickness (mm)</th>
<th>Mean pore diameter (µm)</th>
<th>Maximum pore size (µm)</th>
<th>LEPw (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>79.8</td>
<td>1.20</td>
<td>0.94</td>
<td>0.13</td>
<td>0.32</td>
<td>0.75</td>
<td>3.07</td>
</tr>
<tr>
<td>M-2</td>
<td>81.5</td>
<td>1.36</td>
<td>1.06</td>
<td>0.15</td>
<td>0.29</td>
<td>0.62</td>
<td>3.56</td>
</tr>
<tr>
<td>M-3</td>
<td>85.3</td>
<td>1.45</td>
<td>1.15</td>
<td>0.15</td>
<td>0.25</td>
<td>0.56</td>
<td>4.03</td>
</tr>
<tr>
<td>M-4</td>
<td>82.6</td>
<td>1.31</td>
<td>1.01</td>
<td>0.15</td>
<td>0.18</td>
<td>0.43</td>
<td>5.16</td>
</tr>
<tr>
<td>M-5</td>
<td>78.7</td>
<td>1.43</td>
<td>1.11</td>
<td>0.15</td>
<td>0.095</td>
<td>0.18</td>
<td>11.8</td>
</tr>
<tr>
<td>M-6</td>
<td>73.3</td>
<td>1.40</td>
<td>1.10</td>
<td>0.15</td>
<td>0.036</td>
<td>0.11</td>
<td>19.2</td>
</tr>
</tbody>
</table>
Table 4
Roughness parameters and contact angle values of the hollow fiber membranes spun from different dope solutions.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>Inner surface</th>
<th>Outer surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_a$ (nm)</td>
<td>$R_m$ (nm)</td>
</tr>
<tr>
<td>M-1</td>
<td>10.73</td>
<td>13.45</td>
</tr>
<tr>
<td>M-2</td>
<td>10.70</td>
<td>14.15</td>
</tr>
<tr>
<td>M-3</td>
<td>11.26</td>
<td>14.20</td>
</tr>
<tr>
<td>M-4</td>
<td>15.26</td>
<td>19.13</td>
</tr>
<tr>
<td>M-5</td>
<td>15.64</td>
<td>19.70</td>
</tr>
<tr>
<td>M-6</td>
<td>20.10</td>
<td>27.39</td>
</tr>
</tbody>
</table>
The pure PVDF membrane presented the smoothest and its surface was covered with a multitude of small peak ($R_a = 10.73$ nm and $R_q = 13.45$ nm for inner surface, $R_a = 16.66$ nm and $R_q = 21.06$ nm for outer surface). The M-6 composite membrane exhibited the roughest surface ($R_a = 20.10$ nm and $R_q = 27.39$ nm for inner surface, $R_a = 28.06$ nm and $R_q = 35.35$ nm for outer surface). As shown in Table 4, the membrane roughness and contact angle increased with the CaCO$_3$ nano-particles addition, and it indicated that the addition of nano-particles can be a useful way to improve membrane hydrophobicity. For all the spun membranes, the roughness and contact angle of the outer surface were higher than those of the inner surface, which may be attributed to the process of membrane formation. The dope solution directly contacted with the bore liquid to make a lumen for the inner surface and it facilitated an immediate phase separation, for the outer surface, the dope solution firstly contacted with air and it induced a delayed phase separation [1]. For the above reasons, the pore diameter and porosity of the inner surface would be higher than those of the outer surface.
The contact angle can be influenced by the membrane surface composition, porosity and pore diameter except for the roughness [40]. The water drop could gradually penetrate into the porous surface due to the capillary force and the larger pores meant lower resistance for water entering according to the Laplace–Young equation [3]. Thus, the contact angle of the inner surface became lower than that of the corresponding outer surface.

### 3.4. Thermal properties analysis

DSC analysis of pure PVDF membrane and PVDF composite membranes was conducted to examine the effect of CaCO₃ nanoparticles on the crystallinity degree \(X_c\) of the spun membranes. The DSC heating and cooling curves are presented in Figs. 6 and 7, respectively, and the test results are listed in Table 5. The crystallinity degree of the spun membranes, based on either the melting \(X_c^m\) or crystallization \(X_c^c\) DSC scans, can be obtained from the following equation [41]:

\[
X_c = \frac{\Delta H_f}{\Delta H_f^c} \times 100\%
\]

where \(\Delta H_f\) is the experimental heat of fusion \(\Delta H_f^c\) or the experimental heat of crystallization \(\Delta H_c\), \(W\) is the weight fraction of polymer in the PVDF/CaCO₃ mixture and \(\Delta H_f^c\) is the heat of fusion of the 100% crystalline PVDF, which is reported to be about 105 J/g [42].

It is observed that all the spun membranes show an endothermic melting peak around 170 °C and an exothermic crystallization peak around 150 °C in Figs. 6 and 7, respectively, which verifies that the nano-particles have no significant influence on the thermal properties of PVDF. From Table 5, it can be found that the crystallinity degree \(X_c\) tended to increase while CaCO₃ was incorporated in PVDF matrix, however, the \(X_c\) began to decrease from the M-4 composite membrane. The \(X_c\) increases up to the M-3 composite membrane can be explained by the fact that the CaCO₃ nano-particles promote nucleation of PVDF crystalline phase and the nano-particles act as anti-nucleating agent when the mixing ration for CaCO₃/PVDF exceeds 20/100. The similar experimental results are in agreement with the related literature [43].

TGA results of the spun membranes are displayed in Fig. 8. The temperature at which the weight loss was 3% from its original weight was defined as the decomposition temperature \(T_d\) to
Fig. 4. AFM images of the inner surfaces of the hollow fiber membranes spun from different dope solutions.
evaluate the thermal stability and the $T_d$ was in the range of 430–448 °C for the pure PVDF membrane and composite membranes. Form Fig. 8, it is found that the $T_d$ of the M-2 and M-3 composite membrane was higher than that of the pure PVDF membrane, but the $T_d$ of the M-5 and M-6 composite membrane was lower. The $T_d$ decrease was related to an increase in the amorphous fraction of the composite membranes due to agglomeration of the nano-particles. With regard to the residual portion, for temperature between 500 and 800 °C, a higher fraction of residue can be clearly observed with increased nano-particles concentration.

3.5. Mechanical properties test

In order to investigate mechanical performance of the spun fibers, the pure PVDF membrane and PVDF/CaCO₃ composite membranes were both stretched. The stress–strain curves of the hollow fibers are shown in Fig. 9 and the relevant experimental data were listed in Table 6.

It can be seen that stretching strength of composite membranes is stronger than that of pure PVDF membrane. For example, the stretching strain of the M-3 membrane was about 140% and much higher than that of the pure PVDF membrane. The improvement of membrane mechanical properties is further proved by breaking energy and load at break, which are 252.97 MJ and 3.75 N for the M-3 composite fiber, respectively, and the corresponding values only 143.19 MJ and 2.97 N for the pure PVDF membrane. The nanoparticles were mixed into the dope solution as nucleation agent and accelerated the phase separation during the membrane fabrication process, which not only optimized the membrane structure, but also acted as the bridging point to enhance the membrane mechanical strength. However, excessive particles addition would cause the nano-particles agglomerate and the fiber structure was no longer uniform, where the particles agglomerate became the weak point of membrane mechanical properties. Although membrane distillation process is usually operated in normal atmospheric pressure or below it and the requirement of hydrophobic membrane mechanical properties is lower than that of the membrane used for pressure-driven membrane process such as microfiltration and ultrafiltration, superior mechanical properties offers hydrophobic membrane great potential to be applied in MD industrialization process considering the hydraulic impact and flow disturbance.

**Table 5**

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X^a$ (%)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$X^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-1</td>
<td>166.87</td>
<td>38.90</td>
<td>37.05</td>
<td>145.61</td>
<td>37.62</td>
<td>35.83</td>
</tr>
<tr>
<td>M-2</td>
<td>166.74</td>
<td>42.84</td>
<td>44.88</td>
<td>145.90</td>
<td>40.40</td>
<td>42.32</td>
</tr>
<tr>
<td>M-3</td>
<td>166.81</td>
<td>35.47</td>
<td>45.11</td>
<td>145.53</td>
<td>38.29</td>
<td>43.76</td>
</tr>
<tr>
<td>M-4</td>
<td>166.73</td>
<td>36.15</td>
<td>44.76</td>
<td>145.68</td>
<td>35.16</td>
<td>43.53</td>
</tr>
<tr>
<td>M-5</td>
<td>166.56</td>
<td>33.76</td>
<td>45.01</td>
<td>146.12</td>
<td>32.70</td>
<td>43.60</td>
</tr>
<tr>
<td>M-6</td>
<td>166.55</td>
<td>30.55</td>
<td>43.64</td>
<td>146.62</td>
<td>29.81</td>
<td>42.59</td>
</tr>
</tbody>
</table>

$T_m$ = melting temperature, $T_c$ = crystallization temperature.
Fig. 5. AFM images of the outer surfaces of the hollow fiber membranes spun from different dope solutions.
Fig. 5. (Continued)

Table 6
Mechanical properties of the hollow fiber membranes spun from different dope solutions.

<table>
<thead>
<tr>
<th>Membrane code</th>
<th>M-1</th>
<th>M-2</th>
<th>M-3</th>
<th>M-4</th>
<th>M-5</th>
<th>M-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching strain at break (%)</td>
<td>101.12</td>
<td>134.76</td>
<td>140.67</td>
<td>133.65</td>
<td>126.78</td>
<td>112.80</td>
</tr>
<tr>
<td>Stress at break (MPa)</td>
<td>4.66</td>
<td>6.13</td>
<td>5.68</td>
<td>5.31</td>
<td>5.78</td>
<td>5.06</td>
</tr>
<tr>
<td>Load at break (N)</td>
<td>2.97</td>
<td>3.41</td>
<td>3.75</td>
<td>3.43</td>
<td>3.21</td>
<td>3.19</td>
</tr>
<tr>
<td>Elastic modulus (MPa)</td>
<td>160.87</td>
<td>173.77</td>
<td>192.44</td>
<td>155.80</td>
<td>185.19</td>
<td>200.41</td>
</tr>
<tr>
<td>Breaking energy (MJ)</td>
<td>143.19</td>
<td>221.34</td>
<td>252.97</td>
<td>250.46</td>
<td>193.42</td>
<td>173.21</td>
</tr>
</tbody>
</table>

3.6. Membrane performance

The fabricated fibers were tested for the DCMD process. During the experiment, the membrane module was vertically mounted on the MD installation to diminish the effects of free convection and remove air bubbles. The hot feed temperature at the inlet of membrane module, $T_{f\text{-inlet}}$, is adjusted from 30 to 80 ºC, and the inlet temperature of the cold distillate, $T_{p\text{-inlet}}$, is kept at constant 20 ºC. The permeate flux based on the fibers inner surface area is shown in Fig. 10.

It can be observed that the membrane permeate flux increased with the nano-particles addition, with a peak value when the proportion of CaCO$_3$ in the CaCO$_3$/PVDF mixture at 20/100, and the maximum permeate flux about 46.3 kg/m$^2$ h was achieved for the M-3 membrane. However, more nano-particles addition led to the permeate flux decrease. The membrane porosity increase and thin skin layer formation enhanced the membrane permeability, but more CaCO$_3$ addition caused the skin layers become thicker and also reduced membrane pore size greatly, thereby exerted a negative impact on membrane permeability. During the membrane permeability test process, the conductivity of the distillate from the composite membranes were all less than 10.0 µS/cm, and the conductivity of the distillate produced from the pure PVDF membrane.

Fig. 6. DSC endotherms of the hollow fiber membranes spun from different dope solutions.
was no more than 15.0 µS/cm, the test results indicated that the salt rejection achieved 99.99% for all the spun fibers.

To achieve a high-performance hydrophobic membrane, it is important to sustain the permeate flux and solute rejection during the practical application. To investigate the retaining performance stability of the spun membranes, the M-1 and M-3 membranes were selected to be applied in 30 days continuous desalination process of sodium chloride solution. The results of desalination performance are presented in Figs. 11 and 12. It can be seen that

**Fig. 7.** DSC exotherms of the hollow fiber membranes spun from different dope solutions.

**Fig. 8.** TGA thermograms of the hollow fiber membranes spun from different dope solutions.

**Fig. 9.** Stress–strain curves of the hollow fiber membranes spun from different dope solutions.

**Fig. 10.** Permeate flux of the hollow fiber membranes spun from different dope solutions.

**Fig. 11.** Variation of membrane permeability along with operating time (the M-1 membrane).

**Fig. 12.** Variation of membrane permeability along with operating time (the M-3 membrane).
although the permeate flux maintained 11.0–11.6 kg/m² h during experiment, the permeate conductivity varied 10.0–20.0 μS/cm and showed a slight increase for the pure PVDF membrane. The result indicated that there were small amount of large pores existed on the membrane surface, which could induce membrane partial wetting and salt rejection decline. From Fig. 12, it can be found that the permeate conductivity stabilized at about 6.0–9.0 μS/cm and the permeate flux maintained about 11.8–12.5 kg/m² h during all the experiment process for the M-3 membrane. This result showed that the M-3 composite fiber exhibited satisfying performance stability compared with the pure PVDF membrane, which can be attributed to the narrower pore size distribution of the M-3 membrane as presented in Fig. 3. All the continuous desalination results suggested that the nano-particles addition was not only beneficial for permeate flux enhancement but also good for keeping performance stability of the spun membranes, and the M-3 composite membrane may be of great potential to be utilized in the MD process.

### 3.7. Thermal efficiency analysis

During DCMD process, heat transport can be divided into the latent heat due to the water vaporization and the heat conduction across the membrane. The heat transfer from the hot feed to the cold stream induced temperature decrease from the inlet of the lumen side to the outlet and vice versa for the shell side. Thermal efficiency (evaporation efficiency, EE) was defined as the ratio between the heat which contributed to evaporation and the total heat exchanged between two streams.

The hot feed flowed through the lumen side, so there was no other heat loss except for heat transfer to the shell side. The total heat exchange can be calculated from the enthalpy difference between the inlet and outlet of the hot feed. EE can be calculated by the following equation [38]:

\[
EE = \frac{Q_{\text{eff}}}{Q_{\text{in}}} = \frac{Q_{\text{eff}}}{Q_{\text{eff}} + Q_{\text{cond}}} = \frac{J \cdot A \cdot H_v}{V_f \cdot \bar{C}_f (T_{f,\text{inlet}} - T_{f,\text{outlet}})}
\]

where \(J\) is the permeate flux, \(A\) is the inner surface area of the hollow fibers, \(V_f\) is the hot feed flow rate (in L/h), \(T_{f,\text{inlet}}\) is the hot feed temperature at the inlet of membrane module, \(\bar{C}_f\) is the average specific heat of feed. Because temperature hardly affects \(\bar{C}_f\), it can be considered as a constant value 4200 J/(kg K). \(H_v\) is the latent heat of vaporization, in the range of temperature 273–373 K, \(H_v\) can be expressed as [44]:

\[
H_v = 2024.3 + 1.7535 \cdot T
\]

where \(T\) is the average temperature, and \(T = (T_{f,\text{inlet}} + T_{f,\text{outlet}})/2\), in K.

As shown in Fig. 13, the calculated thermal efficiency varied from 28.2% to 76.5% and increased along with the increase in the feed temperature. For all the spun membranes, the high temperature induced higher permeate flux and the latent heat of water vaporization became the main contribution to total heat transfer. At lower temperature, the heat loss due to heat conduction across the membrane was the major contribution to total heat transfer and the EE was less than 50% when the feed temperature was below 60°C for most fibers except for the M-2 and M-3 membranes. It can be found that the EE for the M-5 and M-6 membranes was obviously lower than that for the M-3 membrane, which can be attributed to two factors: the permeate flux decrease and the thermal conductivity increase with the nano-particles excess addition. Therefore, the higher feed temperature together with lower

---

**Table 7**

Comparison of the maximum flux obtained in this study with the literature for DCMD processes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Reference</th>
<th>Permeate flux (kg/m² h)</th>
<th>Feed solution</th>
<th>Permeate solution</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP hollow fiber</td>
<td>[45]</td>
<td>28</td>
<td>1.0 wt%</td>
<td>0.11</td>
<td>Concurrent</td>
</tr>
<tr>
<td>PP hollow fiber</td>
<td>[46]</td>
<td>13.5</td>
<td>3.5 wt%</td>
<td>0.37</td>
<td>Concurrent</td>
</tr>
<tr>
<td>PP hollow fiber</td>
<td>[47]</td>
<td>38.8</td>
<td>3.0 wt%</td>
<td>0.04</td>
<td>Cross-flow</td>
</tr>
<tr>
<td>PVDF flat sheet membrane</td>
<td>[44]</td>
<td>32.4</td>
<td>Distilled water</td>
<td>2.59</td>
<td>Cross-flow</td>
</tr>
<tr>
<td>PVDF/PDVF single-layer composite hollow fiber</td>
<td>[30]</td>
<td>40.4</td>
<td>3.5 wt%</td>
<td>1.94</td>
<td>Concurrent</td>
</tr>
<tr>
<td>PVDF hollow fiber</td>
<td>[11]</td>
<td>41.5</td>
<td>3.5 wt%</td>
<td>1.60</td>
<td>Concurrent</td>
</tr>
<tr>
<td>PVDF/PDVF dual-layer composite hollow fiber</td>
<td>[48]</td>
<td>52.5</td>
<td>3.5 wt%</td>
<td>1.90</td>
<td>90.0</td>
</tr>
<tr>
<td>PVDF/PAN dual-layer hollow fiber</td>
<td>[31]</td>
<td>55.2</td>
<td>3.5 wt%</td>
<td>1.60</td>
<td>16.5</td>
</tr>
<tr>
<td>PVDF/CaCO3 composite hollow fiber</td>
<td>This study</td>
<td>46.3</td>
<td>3.5 wt%</td>
<td>0.50</td>
<td>Concurrent</td>
</tr>
</tbody>
</table>

\(^{a}\) The membrane used in DCMD was commercial membrane,
\(^{b}\) The permeate flow rate in m/s was not provided in Ref. [46].

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Fig. 13. Thermal efficiency of the DCMD process for the hollow fiber membranes spun from different dope solutions.
thermal conductivity membrane material meant higher thermal efficiency for DCMD process.

3.8. Comparison with other MD membranes

Table 7 lists a performance comparison between the current work and the previous investigations. It can be observed that the obtained data in this study is comparable or even better than most of the previous reports. The permeate flux of the PVDF/PTE dual-layer composite hollow fiber and the PVDF/PAN dual-layer hollow fiber fabricated by Chung are higher than that of the PVDF/CaCO₃ hollow fiber. But it must be noted that the hot feed and the cold distillate temperatures in Ref. [31] were 90.3 °C and 16.5 °C, respectively, which meant the driving force for the vapor transport in DCMD process was enhanced. The flow rates of feed and permeate in Ref. [48] were 1.90 m/s and 0.90 m/s, respectively, which were much higher than that of the present. It has been demonstrated that the permeate flux increased by improving flow rate because the high flow rate can diminish the polarization effect [49]. It is believed that if the membrane fabrication optimizations which were attempted in this work are accompanied with higher flow rate, higher feed temperature, lower cold distillate temperature and more efficient module designs to improve the flow pattern and diminish the polarization effect, even higher flux is achievable in the DCMD process.

4. Conclusions

In the present work, the PVDF composite hydrophobic hollow fibers were prepared for MD through the non-solvent induced phase inversion by dispersing hydrophobic modified CaCO₃ nanoparticles in the PVDF casting solution and using the mixture of LiCl and PEG as non-solvent additive. The effects of nano-particles/PVDF mixing ratio on the morphology, porosity, pore size and pore size distribution, hydrophilicity, thermal properties, mechanical properties, permeability and thermal efficiency of the resultant hollow fibers were evaluated.

Although the addition of hydrophobic nano-particles reduced the pore diameter, the nano-particles could optimize the sandwich-like morphology, narrow the pore size distribution, and improve the membrane porosity to some extent. AFM studies revealed that the membrane surface roughness and contact angle increased with the CaCO₃ nano-particles addition. The nano-particles in PVDF matrix could also increase the crystallinity degree and thermal stability of the spun membrane. In addition, compared with the pure PVDF membrane, the composite membranes exhibited stronger mechanical properties, which was important from an industrial application standpoint.

The produced fibers were tested through DCMD process and the maximum permeate flux about 46.3 kg/m²h was obtained with the hot feed and cold distillate temperatures at 80.5 °C and 20.0 °C, respectively. The thermal efficiency analysis results revealed that the nano-particles addition could decrease the thermal conduction and enhance evaporation efficiency. The 30 days continuous DCMD experiment results showed that the composite fiber achieved a satisfying performance stability compared with the pure PVDF membrane. All of the results demonstrated that the addition of hydrophobic nano-particles was not only beneficial for membrane permeate flux enhancement but also good for keeping performance stability. It is believed that the composite membrane may be of great potential to be utilized in the MD process.

Acknowledgments

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References


