

Hydrophobic modification of PVDF hollow fiber membranes using polydimethylsiloxane for VMD process

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Abstract. Fabricating hydrophobic porous membrane is important for exploring the applications of membrane distillation (MD). In the present paper, poly(vinylidene fluoride) (PVDF) hollow fiber membrane was modified by coating polydimethylsiloxane (PDMS) on its surface. The effects of PDMS concentration, cross-linking temperature and cross-linking time on the performance of the composite membranes in a vacuum membrane distillation (VMD) process were investigated. It was found that the hydrophobicity and the VMD performance of the PVDF hollow fiber membrane were obviously improved by coating PDMS. The optimal PDMS concentration, cross-linking temperature and cross-linking time were 0.5 wt%, 80°C, and 9 hr, respectively.

Keywords: poly(vinylidene fluoride) membrane; polydimethylsiloxane; hydrophobic modification; vacuum membrane distillation

1. Introduction

Membrane distillation (MD) is one type of membrane contactors using a vapor pressure difference across a hydrophobic porous membrane as driving force for mass transfer. Thanks to its merits such as low operation temperature, low energy consumption, high separation efficiency, it has found various applications in ultrapure water production, seawater/brackish water desalination, wastewater treatment, medical, food industry, etc. (Khayet 2011, Drioli *et al.* 2015, Duong *et al.* 2015, Guan *et al.* 2015, Meng *et al.* 2015, Jang *et al.* 2015, Li *et al.* 2015, Li *et al.* 2013, Koo *et al.* 2013, Xu *et al.* 2015, Zhao *et al.* 2013, Zhao *et al.* 2011).

Microporous polymeric membranes such as polypropylene (PP), polyvinylidene fluoride (PVDF), and polytetrafluoroethylene (PTFE) membranes are available candidates used in MD process, although they were initially manufactured for microfiltration (MF) or ultrafiltration (UF) (Khayet *et al.* 2005, El-Bourawi *et al.* 2006). Recently attention has been paid to manufacturing specific membranes for MD applications (Khayet *et al.* 2005), for which, membranes should be hydrophobic, and have narrow pore size distribution. The well controlled pore size is reasonably large for achieving higher flux but sufficiently small for satisfactorily large liquid entrance pressure (LEP_w) to keep liquid water from permeating through membrane pores (Li *et al.* 2015, Koo *et al.* 2013, Alkudhri

et al. 2012).

It has been demonstrated that PVDF, which are usually produced by phase inversion process with low cost and high quality, is an ideal membrane material for UF and MF (Cui *et al.* 2013, Cui *et al.* 2014, Hassankiadeh *et al.* 2014). Its pore size can be controlled through the adjustment of the formulation of polymer solution and process parameters. Even though PVDF membranes show good hydrophobicity, the pore wetting still cannot be avoided in the long-term VMD operation for the treatment of high-salinity solution (Li *et al.* 2013, El-bourawi *et al.* 2006, Gugliuzza *et al.* 2006, Huo *et al.* 2009, Gryta 2008, Yun *et al.* 2006). Thus, PVDF membranes need hydrophobic modification before employed in MD applications.

Surface coating is a simple way to modify PVDF membrane endowing it specific characteristics. It is a practical way to modify PVDF membrane by coating a highly hydrophobic material on its surface. Finding a proper hydrophobic polymer is very important to realize this method (Zhang *et al.* 2016). Polydimethylsiloxane (PDMS) is a hydrophobic membrane material which has been widely adopted in pervaporation (Xiangli *et al.* 2007, Xiangli *et al.* 2008, Izak 2008, Chen *et al.* 2008) and nanofiltration (Gevers *et al.* 2006, Gevers *et al.* 2005). Superhydrophobic flat sheet membranes for DCMD were fabricated *via* spraying a mixture of PDMS and hydrophobic SiO₂ nanoparticles on PVDF flat sheet membranes (Zhang *et al.* 2013). By mixing PDMS and PVDF, PDMS-PVDF hydrophobic microporous membranes were prepared through NIPS process for VMD (Sun *et al.* 2015). As the results of the above papers, the water contact angle and the LEP_w of the flat sheet membranes were significantly improved.

For the membrane industrialization, due to its high packing density, hollow fiber is a much attractive

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configuration (Zhang *et al.* 2017). So it is practical to research on the preparation of hydrophobic hollow fiber membrane (Yao *et al.* 2013). In this study, PDMS was employed to fabricate composite hollow fiber membrane by coating it on the surface of PVDF hollow fiber membrane. The morphology, properties and VMD performance of the composite hollow fiber membrane were investigated. We choose the VMD configuration, because of the high flux and thermal energy efficiency it can achieve (Eykens *et al.* 2016).

2. Experimental

2.1 Materials

PVDF hollow fiber membranes used as the support membrane in this study were kindly supplied by Jiushi Hi-Tech Co., Ltd. (Nanjing, China), which were manufactured by the dry jet-wet spinning phase inversion method. Sylgard® 184 (PDMS) is a silicone elastomer consisting of Sylgard® 184A and Sylgard® 184B. They were purchased from Dow Corning Corporation. Sylgard® 184A is a viscous liquid of vinyl-terminated linear oligomeric dimethylsiloxane, containing 30–60 wt% dimethylvinylated and trimethylated silica fillers. Sylgard® 184B contains methyl hydrosiloxane as a crosslinking agent, a platinum complex as a catalyst for the hydrosilation reaction, and 10–30 wt% dimethylvinylated and trimethylated silica fillers (Efimenko *et al.* 2002).

DI water was produced by a home-made RO system. Ethanol, sodium chloride (NaCl) and sodium dodecyl benzene sulfonate (SDBS) were obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). Sodium hypochlorite (NaClO) was purchased from Jiangsu Yangnong Chemical Group Co., Ltd (Yangzhou, China). *n*-hexane was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2 Preparation of PDMS/PVDF composite hollow fiber membranes

PDMS solution was prepared by mixing PDMS Sylgard® 184A and Sylgard® 184B with weight ratio of 10:1, and was diluted with a volatile solvent (*n*-hexane). Commercially available PVDF hollow fiber membranes were pre-treated by sodium hypochlorite (NaClO) with concentration of 8000 mg×L⁻¹ to remove the entrapped PVP at 45°C. The pre-treated PVDF hollow fiber membranes were named as original PVDF hollow fiber membrane, and were cut to length of 15–20 cm. The original PVDF membranes were dipped into the PDMS solutions with different concentrations. After certain periods, the prepared membranes were dried and heat treated at different temperatures within different intervals.

2.3 Membrane characterization

2.3.1 The contact angle

The contact angle was measured by the same method as described in our previous paper (Tong *et al.* 2016), using

KSV Sigma70 Tensiometer (KSV Instruments Ltd., Finland) at 25°C. A vertically suspended hollow fiber membrane touched a liquid surface with a force (*F*) acted on the sample. The force was correlated with the surface tension or interfacial tension σ and with the contact angle θ according to the following equation (Eq. (1)):

$$\sigma = \left(\frac{F}{L \cdot \cos \theta} \right) \quad (1)$$

L presents the wetted length of the sample that is equal to its perimeter. The sample was attached to a force sensor of a tensiometer for measuring the force.

To measure the contact angle, the hollow fiber membrane was immersed in DI water. The contact angle was calculated from the measured force by transposing the Wilhelmy equation (Eq. (2)):

$$\theta = \arccos \left(\frac{F}{L \cdot \sigma} \right) \quad (2)$$

2.3.2 LEP_w

MD membrane must be prepared with at least one hydrophobic material to avoid membrane pore wetting. However there is a minimum required pressure, which is named LEP_w. When the applied transmembrane hydrostatic pressure exceeds LEP_w, pore wetting may occur and the aqueous solution may go into dry membrane pores. The quality of the produced water may be deteriorated. For determining LEP_w, the hollow fiber membranes were mounted in a tubular stainless steel module. The shell side was filled with DI water, and a slight pressure of about 0.1 bar was applied for 10 min; then the pressure was increased stepwise with a increment of 0.05 bar, and the membrane LEP_w was record as applied pressure at which a first water drop appeared on the lumen side. To ensure a proper operation under fluctuating pressures and temperatures in the operation plant, a minimum LEP_w of 2.5 bar was recommended for aqueous solutions (Eykens *et al.* 2016).

2.3.3 SEM

A field emission scanning electronic microscopy (FESEM, Hitachi S4800, Japan) was employed to observe the morphology of the hollow fiber membranes. Prior to SEM tests, the dry hollow fiber samples were immersed in liquid nitrogen and fractured, and then sputtered with gold/palladium alloy. The surface of the hollow fiber membrane was observed to check the structure changes with the PDMS coating.

2.3.4 The tensile strength

The mechanical properties of the hollow fiber membranes were characterized by measuring the tensile stress and the elongation at break. Universal testing machine (AGS-J500N, Shimadzu, Tokyo, Japan) was used at room temperature according to ASTM D638-10.

2.3.5 Porosity

Porosity was determined by gravimetric analysis method. Hollow fiber membranes were immersed in

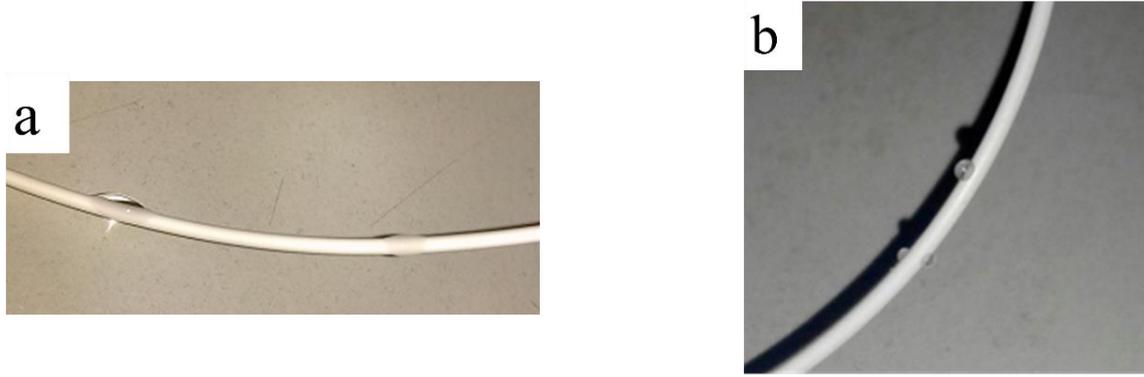


Fig. 1 Photos of a. original PVDF hollow fiber membrane and b. PDMS/PVDF composite hollow fiber membrane

kerosene for wetting the pores, after measuring the dry weight. The weight of the wetted hollow fiber membranes was then measured, and the porosity of the hollow fiber membranes was calculated according to following equation:

$$\varepsilon = \frac{(m_w - m_d) / \rho_w}{(m_w - m_d) / \rho_w + m_d / \rho_p} \times 100\% \quad (3)$$

where m_w and m_d are the weights of the wet and dry membranes, respectively. ρ_w and ρ_p are the densities of kerosene and polymer (approximately 1.78 g/cm³), respectively. At least five hollow fiber membranes were measured, and finally the average values were reported.

2.4 VMD process

A module with seven pieces of dry hollow fiber membranes was prepared. The schematic diagram of VMD experimental system was described in our previous work (Tong *et al.* 2016). Salt solution as feed was prepared with NaCl concentration of 35 g×L⁻¹ for testing the VMD performance. The feed solution was pumped through the shell side, and in the lumen side, a vacuum of 0.09 MPa was applied. The feed temperature and its flow rate were 70°C and 120 L×h⁻¹, respectively.

The permeate flux (J) was calculated by the following equation:

$$J = \frac{m}{A \times t} \quad (4)$$

where m is the weight of permeate during the experimental time interval (t), and A presents the effective surface area of the hollow fiber membranes. The salt rejection (R) was measured by comparing the electrical conductivity of permeate and feed using Eq. (5):

$$R = \left(1 - \frac{\mu_p}{\mu_f} \right) \times 100\% \quad (5)$$

where μ_p and μ_f are the conductivities of the permeate water and the feed, respectively. The conductivity of the permeate was monitored by a conductivity monitor (DDSJ-308A, Shanghai Ray Magnetic Instrument Plant, China).

Table 1 Properties of the original PVDF membrane and the composite PDMS/PVDF composite membranes.

Membrane type	contact angle (°)	LEP _w (MPa)	Porosity (%)	Tensile stress (MPa)	Elongation at break (%)
Original membrane	94.47±2.2	0.26±0.02	75.86±3.10	0.99±0.08	108±3.9
PDMS/PVDF composite membrane	111.38±2.5	0.41±0.04	72.35±2.51	1.48±0.11	167±5.2

3. Result and discussion

3.1 Membrane properties

Table 1 lists some properties of the original membrane and the PDMS/PVDF composite hollow fiber membrane, which was prepared with PDMS concentrations, coating time, cross-linking time and cross-linking temperature of 0.5 wt%, 5 min, 9 hr, and 80°C, respectively. It can be seen that, in comparison to the original membrane, the contact angle of PDMS coated membrane increased obviously because of the deposition of PDMS on the membrane surface. Consequently, as shown in Table 1, the LEP_w significantly increased because of the increase of the contact angle. Meanwhile, the porosity of the PDMS/PVDF composite membranes just decreased slightly compared with the original PVDF membranes. This data, in combining with the SEM images, indicates that the PDMS coating only affected the hollow fiber surface. Fig. 1 shows visually that water droplets were formed on the PDMS/PVDF composite hollow fiber membrane surface, but the original membrane was wetted quickly, indicating that PDMS/PVDF composite hollow fiber membrane had a higher hydrophobic nature than the original one. Additionally, it can be seen from Table 1 that the tensile stress and the elongation at break were significantly enhanced by approximately 50%. This is because the cross-linked PDMS provided additional mechanical strength, even at the low PDMS concentration.

3.2 Morphology

PDMS concentration, cross-linking temperature and cross-linking time are important factors influencing the

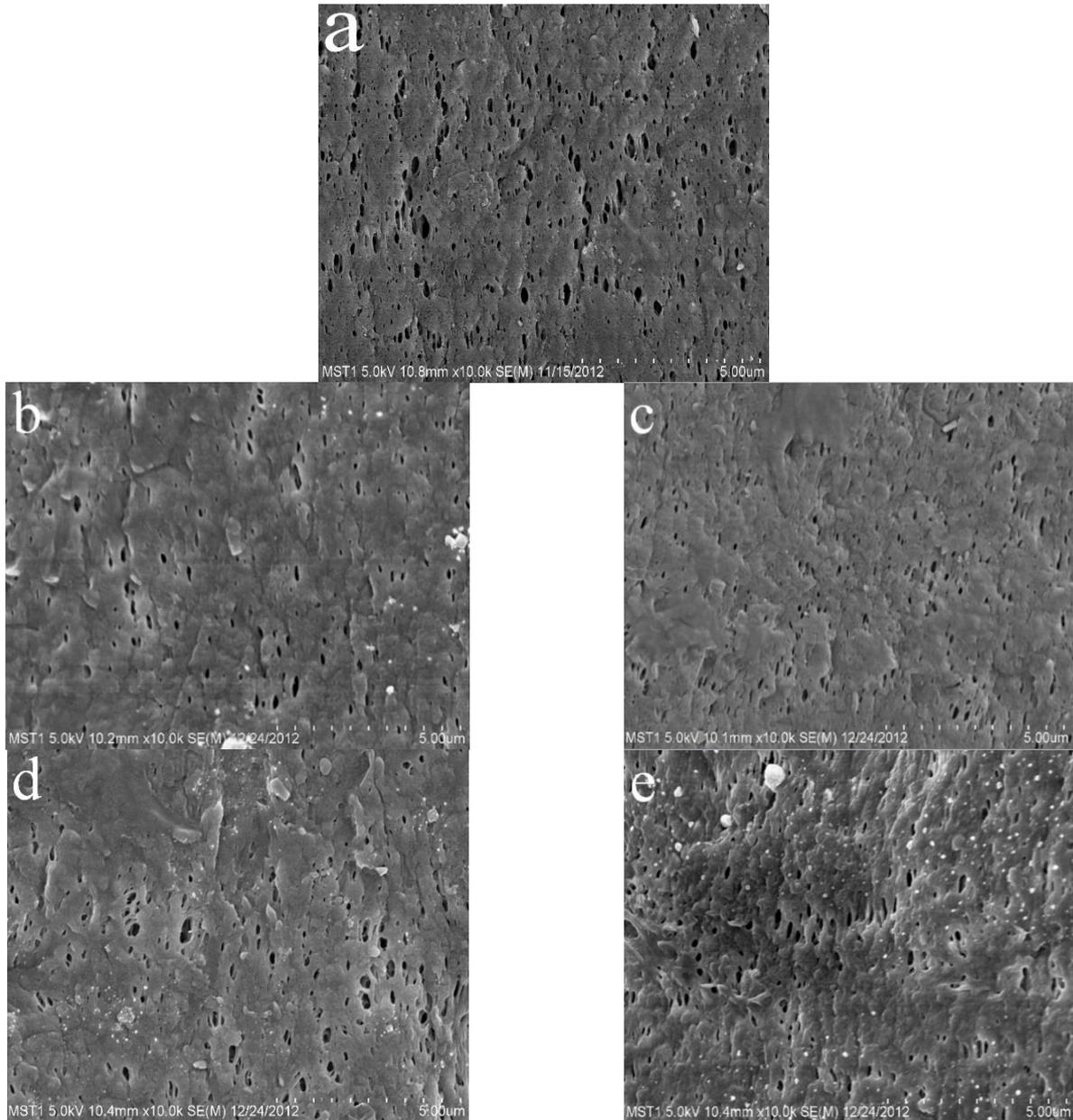


Fig. 2 SEM images of a. original PVDF membrane and composited membranes coated by PDMS concentrations of b. 0.1 wt%, c. 0.3 wt%, d. 0.5 wt% and e. 1.0 wt%. The coating time, cross-linking time and cross-linking temperature were 5 min, 9 hr, and 80 °C, respectively.

final performance of the PDMS/PVDF composite membranes. The effects of those parameters on the morphology and VMD performance of the hollow fiber membranes have been investigated. To investigate the effect of the PDMS concentration, composite membranes were prepared by immersing the original membranes in PDMS solution for 5 min and subsequently post-treated for 5 hr at 80°C. The outer surface SEM images of the hollow fiber membrane are shown in Fig. 2, from which it can be seen that with the increase of the PDMS concentration, the membrane pore size and pore density decreased. This is reasonable to explain by more PDMS depositing on the membrane surface. More Sylgard® 184A and Sylgard® 184B cross-linking on the membrane surface resulted in the increase of PDMS deposition and reduced the pore size and

pore density.

3.3 Effect of the PDMS concentration on the VMD performance

The water vapor flux and the salt rejection in VMD process are shown in Fig. 3. The flux increased with PDMS concentration and presented a peak at the PDMS concentration of 0.5 wt%, after which the flux decreased with the PDMS concentration. When the PDMS concentration was lower than 0.5 wt%, the increase of the PDMS concentration endowed the composite hollow fiber membranes higher hydrophobicity, which is beneficial to the VMD performance. The coating of PDMS on the membrane surface increased the hydrophobicity, and

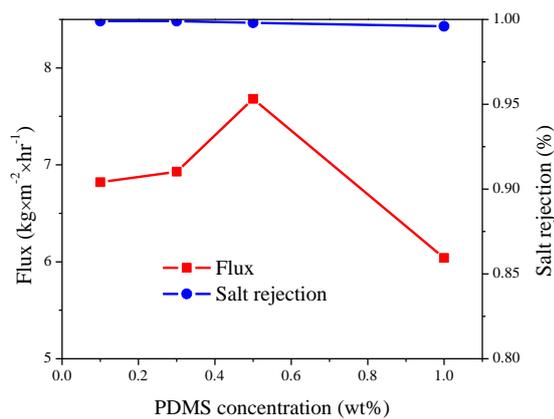


Fig. 3 Effect of PDMS concentration on the VMD performance of the composite hollow fiber membranes. The coating time, cross-linking time and cross-linking temperature were 5 min, 9 hr, and 80°C, respectively

reduced the interaction between water and membrane surface, consequently the concentration/temperature polarization decreased, led to the increase of flux. The declined flux (when the PDMS concentration was higher than 0.5 wt%) was induced by the decrease of pore size and pore density caused by the PDMS accumulation, as discussed above. The decrease of pore size and pore density led to high mass transfer resistance, and finally reduced the VMD permeability. The salt rejection of the membranes, which was above 99.9% constantly, was not significantly influenced by the PDMS concentration, indicating a high selectivity of the PDMS/PVDF composite hollow fiber membranes.

3.4 Effect of cross-linking time on the VMD performance

After dip-coating step, hollow fiber membranes were put into an oven for heat post-treatment, during which time cross-linking was expected to take place at high temperature. Solvent volatilized from the surface and pores of the hollow fiber membrane, and finally PDMS deposited and tightly attached to the membrane surface and pores. Meanwhile, at high temperature, PVDF molecular chain might move in a certain extent, and the PVDF hollow fiber support might shrink, inducing the pore structure change. To investigate the effects of the cross-linking time on VMD performance, PDMS/PVDF composite hollow fiber membranes were prepared by immersing the original hollow fiber in a 0.5% PDMS solution for 10 min and subsequently cross-linked at 80°C for different intervals.

The VMD result in Fig. 4 shows that VMD performance of PDMS/PVDF composite hollow fiber membrane was sensitive to the cross-linking duration. The flux increased with the cross-linking time and went up to the highest value when the cross-linking time increased to 9 hr. Then the flux decreased with the increase of the cross-linking time. Sylgard 184 PDMS can be cured over a range of times and temperatures, spanning 48 hours at room temperature to 10

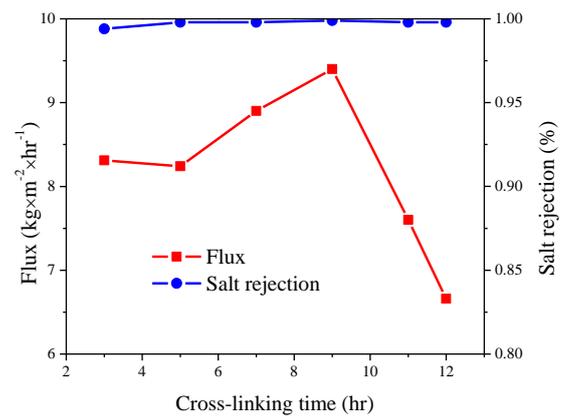


Fig. 4 Effect of cross-linking time on VMD performance of the PDMS/PVDF composite hollow fiber membranes. The PDMS concentration, coating time and cross-linking temperature were 0.5 wt%, 5 min, and 80°C, respectively

minutes at 150°C. Thus, the cross-linking reaction should last a specific time for achieving reliable physical and mechanical properties. Thus, the VMD performance was improved by the increase of the cross-linking time. However, over heating in a comparable long time might result in the severe shrinkage on the pore size of PVDF hollow fiber membranes. The transport resistance increased and VMD flux was lowered. The salt rejection increased to 99.8% when the cross-linking time increased to 5 hr, and was kept in a high level with the increase of the cross-linking time. When time was short, the cross-linking had not finished, and the uncross-linked PDMS might be washed away from the membrane surface and pores, resulting in low salt rejection. Nevertheless, salt rejection kept above 99.8% if cross-linking time was adequate. These experimental results confirmed that hydrophobicity affects the stability of VMD system, and the flux was significantly influenced by coating PDMS on PVDF hollow fiber membranes.

3.5 Effect of cross-linking temperature on the VMD performance

The cross-linking temperature would affect the VMD performance of the composite membrane in two aspects. First, high temperature increases the shrinkage of the PVDF hollow fiber support membrane, and second the adhesion between the coating layer and PVDF support becomes stronger. For coating modification by PDMS, the high temperature is in favor of accelerating the cross-linking reaction. When the cross-linking temperature was low, some PDMS solution penetrated into the membrane pores and blocked or reduced the pores. Therefore, due to an enhancement in the polymer stability on the membrane surface, the flux was expected to increase with the cross-linking temperature going up. However, there is a temperature limitation, above which the PVDF support will be deteriorated even destroyed. To investigate the effect of the cross-linking temperature on the VMD performance, PDMS/PVDF composite membranes were prepared by

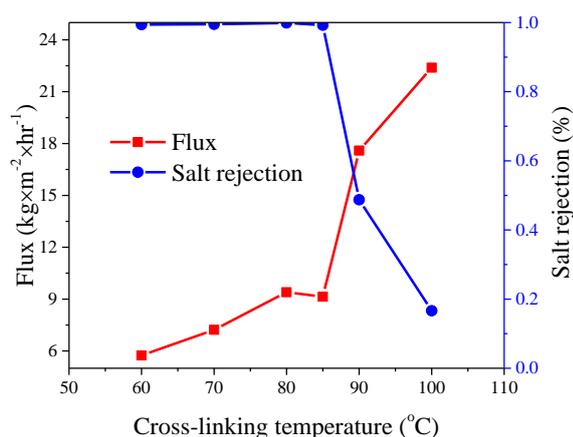


Fig. 5 Effect of cross-linking temperature on VMD performance. The PDMS concentration, coating time and cross-linking time were 0.5 wt%, 5 min, and 9 hr, respectively

immersing the original PVDF hollow fiber membrane in a 0.5% PDMS solution for 10 min and subsequently heat post-treated for 9 hr. It is clear from Fig. 5 that when the cross-linking temperature was lower than 90°C, the permeability increased and the salt rejection kept stable with the increase of the cross-linking temperature because of the more effective cross-linking reaction. However, when the cross-linking temperature exceeded 90°C, the flux for PDMS/PVDF composite hollow fiber membrane increased dramatically, while at the same time, the salt rejection decreased sharply, which indicates a deterioration of the PVDF support membrane because of the high temperature. 80°C was an optimized cross-linking temperature for the preparation of PDMS/PVDF composite hollow fiber membranes. Under this condition, the highest flux of 9.4 kg·m⁻²·hr⁻¹ was obtained.

3.6 Comparison of PVDF hollow fiber membrane on the VMD performance

Compared with the flux of the PVDF hollow fiber membrane from our previous work (8.6 (Zhang *et al.* 2017) and 7.9 (Tong *et al.* 2016)), the data of the membrane we produced is relatively high, at around 9.4, indicating the membrane we produced is of good property.

4. Conclusion

PDMS/PVDF composite hollow fiber membrane was prepared by coating PDMS on the surface of PVDF hollow fiber. The increase of contact angle and LEP_w indicated that the surface of the modified membrane was more hydrophobic than the original membrane. The composite hollow fiber membrane was improved as a promising candidate for VMD process. The flux of the PDMS/PVDF composite hollow fiber membrane reached 9.4 kg·m⁻²·hr⁻¹ at the PDMS concentration, coating time, cross-linking time and cross-linking temperature of 0.5 wt%, 10 min, 9 hr and

80°C, respectively, while, the salt rejection was higher than 99.9% for a NaCl feed solution with concentration of 35 g·L⁻¹.

Compared with the PVDF hollow fiber membranes in literature, the flux of our composite membrane was relatively higher, indicating that the PDMS/PVDF composite membrane is a good candidate for VMD process.

Acknowledgments

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