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Tri-bore PVDF hollow fibers with a super-hydrophobic coating for membrane distillationKang-Jia Lu^a, Jian Zuo^a, Tai-Shung Chung^{a,b,*}

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Abstract

Membranes with good mechanical strength, high vapor flux and outstanding anti-wetting properties are essential for membrane distillation (MD) applications. In this work, porous polyvinylidene fluoride (PVDF) tri-bore hollow fiber membranes with super-hydrophobicity are developed to achieve these desired properties. The tri-bore hollow fiber offers better mechanical strength than the conventional single-bore fiber. To improve its anti-wetting properties, Teflon[®] AF 2400 is coated on the membrane surface. The effects of coating on membrane morphology, performance and anti-wetting properties have been thoroughly investigated. With an optimal coating condition (0.025 wt% of Teflon[®] AF 2400, 30 s), a super-hydrophobic surface with a contact angle of 151° is achieved. The resultant membrane shows an increase of 109% in liquid entry pressure (LEP) with a slight sacrifice of 21% in flux. Long term direct contact MD tests

have confirmed that the Teflon[®] AF 2400 coated membrane has enhanced stability with an average flux of $21 \text{ kg m}^{-2} \text{ h}^{-1}$ and rejection of 99.99% at 60°C for desalination application.

Keywords: Membrane distillation, Coating, Teflon[®] AF 2400, Tribore fiber, Desalination

List of abbreviations and symbols

R_a	Mean roughness
ε	Overall membrane porosity
m_{fiber}	Fiber weight
ρ_p	Density of polymer
V_{fiber}	Fiber volume
$V_{channel}$	Internal channel volume
N_w	Permeation flux
ΔW	Change in the permeate mass
A	Effective membrane area
t	Test duration
β	Rejection
C_p	Permeate concentration
C_f	Feed concentration
C_0	Initial salt concentration of the cold stream

C_1	Final salt concentration of the cold stream
m_0	Initial mass of the cold stream
m_1	Final mass of the cold stream
N_{w0}	Permeation flux for pristine membrane
P	Liquid entry pressure
P_0	Liquid entry pressure of pristine membrane

1. Introduction

Membrane distillation (MD) is a thermally driven separation process which has attracted worldwide attention as an alternative to conventional desalination technologies such as distillation and reverse osmosis (RO). The hydrophobic membrane employed in this process is the heart of MD. Not only does it serve as a physical barrier between the hot seawater feed and permeate, but also provide the interface and surface area for water evaporation. Driven by the temperature-induced vapor pressure difference, the hot seawater feed generates vapor which passes through the membrane and condenses on the permeate side [1-6]. Comparing to RO and other pressure-driven membrane processes, MD possesses many unique advantages: (1) it has no hydraulic pressure involved; (2) it has 100% theoretical rejections to nonvolatile impurities like salts and heavy metals [1, 2]; (3) it is less vulnerable to the concentration polarization due to the different driving forces. Thus it can be integrated with other processes like RO, freeze desalination (FD) and forward osmosis (FO) to achieve a higher total water recovery or to further

concentrate valuable products [7, 8]; (4) it has a low temperature operation range of 40-95 °C. The overall energy cost for MD can be reduced by utilizing waste heat or solar energy as heating sources [9-11].

However, even with the aforementioned advantages, MD is still in its infancy. One of the major reasons is that MD membranes require high porosity (over 75%) and large pore size (100-300 nm) in order to achieve competitive performance [8, 12, 13]; however, the high porosity and large pore size reduce the membrane strength and make the membrane vulnerable during real industrial applications. Therefore, many efforts have been made in the past decades to improve the mechanical strength of MD membranes. For example, Teoh et al., Wang et al., and Su et al. have incorporated polytetrafluoroethylene (PTFE) particles, clay and carbon nanotube (CNT) into the polyvinylidene fluoride (PVDF) matrix to form reinforced mixed matrix MD membranes [14-16]. However, further improvements are still required in order to achieve long term stability in aggressive environments. Chemical modifications have been tried to solve the problems. For example, Yang et al. have produced a PVDF membrane which was chemically cross-linked with a perfluoro-compound of perfluoropolyether containing ethoxysilane terminal groups. The resultant membrane shows improved mechanical strength [17].

Since the multi-bore hollow fiber configuration not only provides good mechanical strength but also potentially possesses high porosity. It received our attention for MD applications. Inge GmbH (part of BASF) was the first company commercializing the multi-bore hollow fiber membrane with seven inner bores for ultra-filtration (UF) [18]. This membrane has a round shape with improved operation stability and minimal fiber breakage [19]. The concept of using

multi-bore hollow fiber membranes with different multi-bore geometries have been explored for MD. For example, Teoh et al. and Wang et al. have designed rectangular and lotus-root-like multi-bore hollow fiber membranes with superior mechanical stability for MD, respectively [20-23]. It was found that forming rectangular multi-bore membranes are very challenging because of rapid die swell and chain relaxation [20], while forming lotus-root-like multi-bore hollow fibers are easier but many bore channels may complicate the flow balance, spinneret design and module fabrication. Therefore, we intend to fabricate tri-bore hollow fibers with enhanced hydrophobicity in this work to maximize the potential of multi-bore hollow fiber membranes for MD applications.

To improve the liquid entry pressure (LEP) and anti-wetting properties of the tri-bore MD hollow fiber, amorphous Teflon[®] AF 2400 would be coated on its surface. Since Teflon[®] AF2400 has a perfluorinated structure with low surface energy, the Teflon[®] AF2400 coated tri-bore membrane may exhibit super hydrophobicity [24, 25]. In addition, because it is an amorphous copolymer and can be dissolved in certain perfluorinated solvents, this makes possible to coat it onto various surfaces via simple dip- or spray-coating techniques. Another amorphous perfluoropolymer—Hyflon[®] AD which shows a similar chemical structure and properties has been used to coat PVDF substrates for pervaporation, membrane contactor and other applications. A significant increase in the water contact angle has been reported in each case [26-28]. To our best knowledge, this is the first time that Teflon[®] AF2400 is used to modify membranes for MD applications. This work may provide useful insights to prepare new generation MD membranes with high mechanical strength, good separation performance and long term stability.

2. Experimental

2.1 Materials

The polymer PVDF Kynar HSV900 resin (specific gravity: 1.76-1.79) was acquired from Arkema Inc. N-methyl-2-pyrrolidone (NMP, >99.5%), ethylene glycol (EG, >99.5%), isopropanol (>99.5%) and sodium chloride (NaCl, 99.5%) were purchased from Merck. PTFE particles (<1 μm) and Teflon® AF 2400 were ordered from Sigma–Aldrich. De-ionized (DI) water was produced by a Milli-Q unit (MilliPore) with the resistivity of 18 M Ω cm. HT-70 Galdden heat transfer fluid was bought from APP Systems Services Pte Ltd. All chemicals were used as received.

2.2 Fabrication of hollow fiber membranes

The tri-bore (TB) hollow fiber membranes were fabricated via a dry-jet wet phase inversion spinning process using a specially designed tri-bore spinneret with blossom geometry, as shown in Figure.1 [29]. For comparison, conventional single bore (SB) hollow fiber membranes were also prepared. The details of hollow fiber spinning have been documented elsewhere [29]. Table 1 summarizes the dope formulations and spinning conditions. Each condition was repeated for three times to ensure the repeatability.

The as-spun fibers were placed in water for 3 days to remove the residual solvents. Subsequently, the fibers were frozen in a refrigerator for 5 hours followed by being freeze dried for 24 hours in a freeze dryer (S61-Modulyo-D, Thermo Electron Corp.) for later usage. The freeze dried fibers

were then assembled into a plastic module holder. Each module contains one fiber with an effective length of 13 cm.

2.3 Membrane coating

To study the effects of Teflon[®] AF2400 coating, the tri-bore hollow fiber membrane formed by applying 60/40 isopropanol/water coagulant bath (TB-D) was used as a demonstration. The Teflon[®] AF2400 coating solutions were prepared in a HT-70 Galden fluid for 12 hours at seven designated concentrations: 0.01, 0.025, 0.05, 0.1, 0.25, 0.4, and 0.5 wt%. A coating duration of 30 s was used for the coatings.

A dip-coating method was applied when coating the Teflon[®] AF2400 solutions onto the outer surface of the hollow fibers. As shown in Figure 2 (A), one end of the fiber was sealed by epoxy (KS Bond EP231, Bondtec) to prevent the solution from entering the lumen side. After coating, the fiber was dried under the ambient condition before being tested. For comparison, an inner surface coating was also performed. In this case, the fiber was firstly potted in a module and then fixed vertically as shown in Figure 2 (B). Subsequently, the Teflon[®] AF 2400 solution was circulated through the lumen side of the hollow fiber by a rotary pump at 1 L/min for 30 s.

2.4 Membrane Characterizations

Membrane morphology was observed by a field-emission scanning electron microscope (FESEM JEOL JSM-6700LV). Before the observation, platinum was sputtered on the samples by a JEOL JEC-1100E ion sputtering device. The surface topology was analyzed using Nanoscope IIIa atomic force microscopy (AFM) (Digital Instruments Inc) with a tapping mode (Acoustic AC).

An area of $5 \times 5 \mu\text{m}$ was scanned at a rate of 1 Hz for each sample. The mean roughness (R_a) was used to quantify the membrane surface roughness.

The concentrations of surface elements were analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra^{DLD} Spectrometer (Kratos Analytical Ltd). The dynamic water contact angle of the fiber was measured using a KSV Sigma 701 tensiometer ($\pm 0.01^\circ$, KSV Instruments Ltd., Finland) through a force tensiometry method at 25°C . Five samples were measured for each condition and the average reading was reported.

Mechanical properties were determined by an Instron tensiometer (Model 5542, Instron Corp.). The elongation rate and starting gauge length were set at 10 mm min^{-1} and 50 mm, respectively. For each condition, ten samples were tested to ensure the result accuracy.

The overall membrane porosity was calculated by equation (1) [21].

$$\varepsilon = \left(1 - \frac{m_{\text{fiber}}/\rho_p}{V_{\text{fiber}} - V_{\text{channel}}} \right) \times 100\% \quad (1)$$

where m_{fiber} is the fiber weight measured by an accurate beam balance (A&D, GR-200); ρ_p is the polymer density which is 1.775 g cm^{-3} for PVDF HSV 900; V_{fiber} is the fiber volume which is a product of the overall cross sectional area and the fiber length; V_{channel} is the volume of the fiber's bore channel. Ten samples were measured for each condition and the average value was reported.

Membrane surface porosity and pore size distribution were analyzed by ImageJ software (NIH) using SEM images as discussed elsewhere [30].

2.5 Direct contact MD (DCMD) tests

DCMD tests were conducted using a laboratory setup depicted in Figure 3. The saline solution comprising 3.5 wt% NaCl was prepared as the feed and heated to 60 ± 0.5 °C using a heating circulator (F12, Julabo). The feed was circulated through the shell side of the membrane with a centrifugal pump at a flow rate of 0.5 L min^{-1} . Simultaneously, the permeate solution (DI water) at 16 ± 0.5 °C by means of a refrigerated circulator (RT7, Thermo Scientific) was circulated to the lumen side of the membrane using a rotary pump at a flow rate of 0.1 L min^{-1} . The feed and the permeate flowed concurrently. The temperatures of both feed and permeate sides were monitored by four Fluke 52 II digital thermocouples with an accuracy of $\pm [0.05\% \text{ of reading} + 0.3 \text{ °C}]$. The system was allowed to run for 30 min until the set temperatures were reached, then the weight change of the permeate solution was recorded. The conductivity of the permeate solution was measured by dipping the probe of an electric conductivity meter (Lab 960, Schott) into the beaker that contains the permeate solution. In order to accurately detect the salt leakage, the volume of the permeate solution inside the beaker was controlled below 300 mL by transferring the excess water back to the feed tank. For performance comparison, DCMD tests were also conducted by facing the feed to the lumen side.

The permeation flux was calculated using equation (2):

$$N_w = \frac{\Delta W}{At} \quad (2)$$

where ΔW (kg) is the increase in permeate mass over a predetermined time duration t (s); A (m^2) is the effective membrane area based on the side facing the feed solution. The rejection was determined using equation (3):

$$\beta = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where C_p and C_f (mol/L) are NaCl concentrations of the permeate and feed streams, respectively.

The permeate concentration was calculated based on the following equation by considering the dilution effect:

$$C_p = \frac{C_1 m_1 - C_0 m_0}{m_1 - m_0} \quad (4)$$

Where m_0 and m_1 are the initial and final masses of the cold stream, C_0 and C_1 are the initial and final salt concentrations of the cold stream which could be determined based on the conductivity.

Continuous DCMD performance tests were also conducted for the pristine and Teflon[®] AF2400 coated membranes where the hot brine was fed via the shell side. The feed and permeate temperatures were set at 60 °C and 16 °C, respectively. The product water was recycled back to the feed tank in order to maintain the feed concentration. The tests were stopped when a significant change in flux was observed or when 250 hours were reached.

2.6 Tests of the liquid entry pressure (LEP)

The LEP value of the MD membrane was measured using a set-up as shown in Figure 4. As the lumen side is more rigid and less susceptible to the deformation, the LEP test was performed from the lumen side. A 250 mL stainless steel cell was used as the reservoir of the 3.5 wt% NaCl solution. The top end of the test cell was connected to a compressed nitrogen cylinder. A manual control valve was used to regulate the gas supply and the pressure inside the test cell was monitored by a pressure gauge (Range: 0-2 Bar, ± 0.001 Bar, Wika). The top end of the test tube was connected to the lumen side of the module, while the other end of the module was sealed by a stainless steel cap. DI water with a volume of 200 mL was circulated through the shell side of

the module at a flow rate of 0.1 L min^{-1} , and its conductivity was monitored via an electric conductivity meter. Then, the pressure inside the test cell was regularly increased with a rate of $0.1 \text{ bar per } 10 \text{ min}$. Once the permeate conductivity started to increase gradually with an increase in pressure, that pressure was recorded as the LEP.

3. Results and Discussion

3.1 Comparison of tri-bore and single-bore hollow fiber membranes

Figure 5 shows SEM pictures of both tri-bore and single-bore hollow fibers. For a fair comparison, both fibers were spun under specific conditions so that they have comparable wall thicknesses and cross-section morphology. Table 2 compares their mechanical strengths. The maximum load, tensile stress and Young's modulus of the tri-bore fiber are higher than those of the single-bore fiber. This is mainly attributed to the additional spokes in the middle of the tri-bore fiber. The spokes not only bridge the cross sectional area and dissipate the axial load, but also restrain the radial deformation induced by the non-uniform axial force and/or radial compression or expansion. As a result, the tri-bore hollow fiber is mechanically stronger than the single-bore fiber. The maximum tensile strain of the tri-bore hollow fiber is slightly lower than that of single bore one because the internal spokes decreases the membrane flexibility by a small extent.

Table 2 also compares the DCMD performance between tri-bore and single-bore fibers. The tri-bore fiber has a slightly lower water flux because the effective membrane area for vapor transport is reduced due to the existing of the internal spokes. On the other hand, since the tri-

bore hollow fiber has superior mechanical strength, it can tolerate with a more porous structure in order to improve its flux. Thus, the tri-bore fiber is used in the following sections.

3.2 Development of highly porous tri-bore hollow fiber membranes

To improve the flux of tri-bore hollow fibers, the membrane porosity is manipulated by changing the phase inversion mechanism from rapid demixing to delayed demixing using different water and isopropanol (water/isopropanol) mixtures in the external coagulation bath [2, 8]. Figure 6 shows the resultant membrane morphology as a function of isopropanol concentration. The outer surface gradually shifts from a dense and smooth structure to a porous and rough morphology. This is because a higher isopropanol concentration results in a weaker coagulation bath that tends to induce delayed demixing and porous surface [31]. Table 3 lists the surface porosity and the maximum surface pore sizes of these hollow fibers. The surface porosity increases from 5.1% to 24.4%, while the maximum surface pore size enlarges from 128.7 to 406.8 nm when isopropanol content changes from 0 to 80%. The elimination of the dense skin and the introduction of surface porosity would greatly reduce the vapor transport resistance and enhances the MD flux. As shown in Figure 7, a flux improvement of nearly 70% is achieved when the isopropanol content increases from 0 to 80%.

Even though increasing isopropanol content could enhance the membrane flux by increasing the surface porosity, this enhancement would eventually reach a limit. As shown in Figure 7, the permeation flux increases with isopropanol concentration in the coagulation bath. However, this improvement becomes unobvious after the isopropanol content increases beyond 60%. This trend might be explained by two competing factors; namely, the increase in surface porosity and the

change of cross-section morphology as shown in Figure 6. The evolution of cross-section morphology from an interconnected cellular structure to a globule structure rises from the fact that the addition of isopropanol into the coagulant delays the liquid-liquid de-mixing while enhances the solid-liquid de-mixing and crystallization. A similar effect has been observed elsewhere [32, 33]. Compared to the cellular structure, the globule structure occupies more cross-section areas and increases the vapor transport resistance. As a result, the flux improvement beyond 60% isopropanol is insignificant. On the other hand, the surface pore size will keep increasing with an increase in isopropanol and eventually compromise the anti-wetting properties. The hollow fiber fabricated from a coagulant bath of 60/40 isopropanol/water with an ID of TB-D is therefore chosen as the substrate for the subsequent study of super-hydrophobic coating.

3.3 Effects of super-hydrophobic coating

As shown in the previous section, a weak coagulant can effectively increase surface porosity and enhance membrane flux; nonetheless, it will also sacrifice the anti-wetting properties as predicted by the Young's Laplace equation [34]. To mitigate this problem, a Teflon[®] AF2400 coating is deposited on top of the membrane surface and its effect is discussed in the following sections.

3.3.1 Effects of Teflon[®] AF2400 coating on membrane morphology and hydrophobicity

Figure 8 shows the outer surface morphology before and after the coating as a function of Teflon[®] AF2400 concentration. The obvious change in surface porosity indicates the successful coating. Visible pores are still noticeable when the Teflon[®] AF2400 concentration is smaller than

0.05 wt%. As the concentration increases further, a less porous coating layer is formed. At the same time, an increase in coating layer thickness can also be observed, as illustrated in Figure 8. Similar effects can be found when the coating is applied to the lumen side of the hollow fiber, as illustrated in Figure 9.

The surface fluorine/carbon (F/C) atomic ratios before and after the Teflon[®] AF2400 coating are analyzed by XPS and the results are tabulated in Table 4. For the pristine PVDF membrane, the F/C ratio is 0.81. The F/C ratio increases by 18% after coating with a 0.01 wt% Teflon[®] AF 2400 solution, but reaches a plateau of about 1.5 once the coating concentration is higher than 0.05 wt%. This plateau indicates a full coverage of Teflon[®] AF 2400 layer on the membrane surface. The increase in F/C ratio can be easily explained by the polymer structures of PVDF and Teflon[®] AF2400, as shown in Figure 10 [35]. Teflon[®] AF2400 contains the trifluoromethyl group and tetrafluoroethylene which have much higher fluorine content than PVDF.

Due to the nonpolar nature of the fluorine, an increase in fluorine content will enhance the surface hydrophobicity. Table 4 tabulates the water contact angle as a function of Teflon[®] AF2400 concentration. A super-hydrophobic surface with a water contact angle of 151.35 ° is achieved when the coating concentration is 0.025 wt%. However, as the coating concentration increases further, the contact angle shows a declining trend. The phenomenon is attributed to the reduction of surface roughness, as illustrated in Table 4. Figure 11 compares the AFM morphology of membrane surfaces coated by different Teflon[®] AF2400 concentrations. The membrane coated by a 0.025 wt% concentration exhibits a hierarchical structure where air can be trapped inside the valley, forms a gas-liquid interface with the feed solution, and results in a

highly hydrophobic surface [36, 37]. In contrast, the hierarchical structure vanishes once a high coating concentration of 0.5 wt% is employed. The surface becomes less porous and smoother with less roughness.

Considering the very short coating duration and low coating concentration, the coating process is very effective. This may be due to three factors. Firstly, the substrate surface is rough and hydrophobic. The former facilitates the deposition and immobilization of the coating agent, while the latter results in a good adhesion with hydrophobic Teflon[®] AF2400 molecules. Secondly, Teflon[®] AF2400 has good film-forming properties. It has been reported to form protection layers via various coating techniques [38-40]. Thirdly, the special solvent, HT-70 Galden fluid, also contributes to the good coating. Since it has a low boiling temperature around 70 °C, a uniform coating thickness along the fiber length can be formed when the fiber is taken out from the coating solution because of fast evaporation.

3.3.2 Effects of Teflon[®] AF 2400 coating on membrane flux

Figure 12 (A) shows the effects of Teflon[®] AF2400 coating on membrane flux for both feed-at-lumen side and feed-at-shell side configurations. The flux decreases with an increase in coating concentration for both configurations. Figure 12 (B) displays their normalized fluxes by dividing their flux values to those of their pristine membranes. The flux reduction shows a two-step trend which can be explained by the pore size and coating thickness. As the Teflon[®] AF 2400 concentration increases from 0 to 0.05 wt%, the membrane flux declines because of the rapid blockage of surface pores, as shown in Figures 8 and 9. A reduction of more than 67.3% in the maximum pore size (Table 4) occurs when a Teflon[®] AF 2400 coating solution of 0.05 wt% is

used. In contrast, the membrane flux experiences a continuous drop but at a slower rate when a higher coating concentration is applied. This is because the membrane surface has already been covered by the coating layer, thus a further increase in coating concentration does not have much effect on surface porosity. Figure 12 (B) shows that the normalized fluxes of both feed-at-lumen and feed-at-shell side configurations nearly coincide with each other. This can be explained by the similar coating extent as shown in Figures 8 and 9.

3.3.3 Effects of Teflon[®] AF2400 coating on anti-wetting properties

The anti-wetting properties of the newly developed tri-bore hollow fiber are characterized by its LEP value and long term performance stability [41]. The LEP tests were conducted using the inner coated membranes since the lumen side is more rigid and less susceptible to deformation under pressures. Figure 13 shows that the LEP value increases rapidly and then reaches a plateau with an increase in Teflon[®] AF2400 concentration. The LEP value is improved by 145% when a 0.05 wt% coating solution is used. A further increase in coating concentration does not affect the LEP value much. The initial improvement in LEP is resulted from the reduction in the maximum pore size and the increase in hydrophobicity. Once a Teflon[®] AF2400 film is formed on the membrane surface, a further increase in coating concentration have negligible effects on surface properties thus the increase in LEP becomes unobvious.

Figure 14 shows the membrane flux and permeate conductivity for over 200 hours at 60 °C. A pristine membrane formed from a coagulant bath of 60/40 isopropanol/water (TB-D) and a TB-D coated by 0.025 wt% Teflon[®] AF 2400 are chosen because the latter exhibits super-hydrophobicity with a good combination of flux and LEP. For the pristine membrane, a dramatic

drop in flux and a sudden increase in permeate conductivity are observed after 210 hours. This indicates that the membrane has been partially wetted. As for the coated membrane, the flux and permeate conductivity remain stable throughout 250 hours with a flux varying from 24 to 18 kg m⁻² h⁻¹ and rejection over 99.99. The superior anti-wetting properties of the coated membrane could be explained from two aspects. Firstly, due to the lower surface tension and smaller maximum pore size of the coated surface, it is more difficult for the liquid to penetrate into the pores [42]. Therefore, the wetting is less likely to happen. Secondly, the super-hydrophobic surface has prominent anti-scaling properties because a low surface energy reduces the possibility of surface nucleation [43]. At the same time, the lotus-leave-like hierarchical super-hydrophobic surface has been extensively reported to exhibit self-cleaning effect [44-46], allowing the deposited crystals to be easily washed off by the feed stream. Figure 15 compares the surface morphology of the membranes after long term tests and confirms that fouling and scaling of the coated membrane are significantly lower than those of the pristine membranes.

4. Conclusions

In this work, super-hydrophobic tri-bore hollow fiber membranes have been fabricated via tri-bore spinning and Teflon[®] AF2400 coating. It is proven that the tri-bore hollow fiber possesses much better mechanical properties than the single-bore one. By using a weak isopropanol/water coagulant, an increase in membrane flux up to 70% was achieved because of the increased surface porosity. To enhance the membrane wetting resistance, a hydrophobic Teflon[®] AF 2400 coating was deposited on top of the membrane surface. Experiment results show that a super-hydrophobic surface with a contact angle of 151.35° could be achieved by coating the tri-bore membrane with a 0.025 wt% Teflon[®] AF 2400 solution for 30 s. The resultant membrane

exhibits an increment of 109% in LEP and a 21% sacrifice in flux. Long term performance tests also confirm that the Teflon[®] AF 2400 coated membrane has enhanced performance stability with an average flux of $21 \text{ kg m}^{-2} \text{ h}^{-1}$ and rejection of 99.99% at 60 ° C.

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Fig 1. Tri-bore spinneret with a blossom geometry [26]

Fig 2. Schematics for (A) outer surface coating; (B) inner surface coating

Fig 3. Laboratory setup for DCMD experiments

Fig 4. Setup for the LEP test

Fig 5. Single-bore (SB) and tri-bore (TB-A) hollow fiber membranes

Fig 6. SEM pictures of the outer surface (top) and cross section (middle), and AFM pictures (bottom) using various isopropanol/Water compositions in the coagulation bath: (A) 0/100; (B) 20/80; (C) 40/60; (D) 60/40; (E) 80/20 (wt%)

Fig 7. Effect of coagulant composition on membrane performance

Fig 8. SEM pictures depicting the change in outer surface morphology with Teflon® AF2400 concentration (A) pristine membrane; (B) 0.01 wt%; (C) 0.025 wt%; (D) 0.05 wt%; (E) 0.1 wt%; (F) 0.25 wt%; (G) 0.4 wt%; (H) 0.5 wt%. (I) to (L) show the corresponding cross sections and coating thicknesses of (E) to (H) respectively

Fig 9. SEM pictures depicting the change in inner surface morphology with Teflon® AF2400 concentration (A) pristine membrane, (B) 0.01 wt%, (C) 0.025 wt%, (D) 0.05 wt%, (E) 0.1 wt%, (F) 0.25 wt%, (G) 0.4%, (H) 0.5%. (I) to (L) show the corresponding cross sections and coating thicknesses of (E) to (H) respectively

Fig 10. Chemical structures of (A) PVDF and (B) Teflon® AF 2400

Fig 11. AFM pictures depicting the change of outer surface morphology as a function of Teflon® AF2400 concentration (A) 0.025 wt% and (B) 0.5 wt%

Fig 12. (A) Membrane flux for both feed at shell and feed at lumen side configurations;
(B) Normalized membrane flux for both configurations

Fig 13. Effect of coating concentration on LEP

Fig 14. Long term performance tests

Fig 15. SEM pictures of membrane surfaces after long term tests (A) TB-D and (B) 0.025 wt%

Teflon[®] AF 2400 coated TB-D

Table 1. Spinning condition for tri-bore hollow fiber membranes

Membrane ID	TB-A	TB-B	TB-C	TB-D	TB-E	SB
Dope composition (wt%)	PVDF/PTFE/EG/NMP=10/3/12/75					
Bore fluid	Water					
Coagulant (IPA/Water wt%)	0/100	20/80	40/60	60/40	80/20	0/100
Air gap (cm)			4			4
Dope flow rate (ml/min)			5			2
Bore fluid flow rate (ml/min)			4			1.5
Take-up speed			Free Fall			

Table 2. Comparison of single bore and tri-bore membranes

Membrane ID	Inner diameter (mm)	Outer diameter (mm)	Max load (N)	Max tensile stress (Mpa)	Max tensile strain (%)	Young's modulus	Flux ($\text{kg m}^{-2} \text{h}^{-1}$)	Rejection (%)
TBA	1.95±0.35	2.19±0.09	3.0±0.2	1.8±0.1	122.4±8.5	30.5±4.9	17.2±0.2	99.99
SB	0.79±0.05	0.94±0.02	0.9±0.1	1.6±0.1	137.6±12.3	27.5±9.1	19.9±0.4	99.99

Table 3. Effects of coagulant concentration on membrane properties

Membrane ID	TB-A	TB-B	TB-C	TB-D	TB-E
External coagulant (IPA/Water)	0/100	20/80	40/60	60/40	80/20
Overall porosity (%)	86.2±2.4	86.6±0.5	86.6±0.2	86.1±0.6	87.7±0.7
Surface porosity (%)	5.1±1.8	10.0±0.5	14.0±0.6	19.0±0.3	24.4±0.7
Max pore size (nm)	129±10	226±21	247±8	327±30	407±6
Surface roughness Ra (nm)	22±5	27±12	33±6	43±3	93±12
Contact angle (°)	75±11	93±3	105±9	105±1	112±5

Table 4. Effects of Teflon[®] AF 2400 concentration on the outer surface properties

Teflon [®] concentration n (%)	0	0.01	0.025	0.05	0.1	0.25	0.4	0.5
Surface porosity (%)	19.0±0.3	10.1±0.2	7.2±0.2	5.7±0.8	5.4±1.4	5.5±0.8	5.9±0.5	5.5±0.4
Max pore size (nm)	327±30	313±2	262±1	107±20	124±11	125±9	119±7	126±11
F/C atom percentage ratio	0.8±0.1	1.0±0.1	1.4±0.1	1.5±0.3	1.6±0.1	1.5±0.3	1.6±0.1	1.5±0.1
Contact angle (°)	105±1	144±1	151±1	149±3	143±1	143±3	141±5	140±1
Surface roughness Ra (nm)	43±3	50±14	54±6	53±9	42±12	26±17	23±7	24±10

Highlights

- Tri-bore hollow fiber to improve mechanical strength
- Teflon[®] AF 2400 coating to form super-hydrophobic surface with a contact angle of 151°

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(A) TB-D and (B) 0.025 wt% Teflon[®] AF 2400 coated TB-D