Effect of Membrane Thickness on Properties of FO Membranes with Nanofibrous Substrate

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Abstract. One of the most challenges for forward osmosis (FO) application is the internal concentration polarization (ICP), which can severely reduce the water flux. In this study, the effect of membrane thickness on FO membranes with nanofibrous substrate was studied. The results show that reduction of membrane thickness can greatly reduce the ICP and increase the flux of the FO membrane. Due to the reduction of the structural parameters of the substrates layer, the minimum thickness of the FO membrane can achieve a minimum structural parameter and exhibit better performance than commercial FO membrane.

Keywords: Thickness, Structural parameters, Forward osmosis, Water flux.

1. Introduction

Forward osmosis (FO), an osmotically-driven process, uses osmotic pressure difference to drive water molecules from a low osmotic pressure feed flow through a semipermeable membrane to a high osmotic pressure drive solution[1]. Since the operating pressure required for forward osmosis is very low, FO offers many potential advantages such as less energy input, lower tendency to fouling, easier membrane cleaning and higher water recovery[2].

However, the forward osmosis (FO) process is affected by the concentration polarization within the porous membrane substrates, resulting in a severe flux reduction, a phenomenon known as internal concentration polarization (ICP) [3]. Many studies have shown that low tortuosity, large porosity, and low-thickness membrane materials tend to be less ICP [4-7]. Structural parameters (S) can be used to quantify ICP. A higher S means a more serious ICP problem.

In this study, three nanofiber forward osmosis membranes with different thickness were fabricated. The effect of thickness on the FO membrane properties with respect to morphology, porosity, contact angle, tensile strength, and water flux were systematically studied.
2. Experiment

2.1. Material
The substrates were fabricated by polysulfone (PSF, Mw=22000, Sigma-Aldrich). N-Methyl-2-pyrrolidone (NMP) and N-N dimethylformamide(DMF) were used as solvents, and isopropyl alcohol (IPA) was used as a wetting agent. Both were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Trimesoyl chloride (TMC, 98%) supplied by Sigma-Aldrich and m-phenylenediamine (MPD, >99.5%) supplied by Aladdin (US) were used as monomers for interfacial polymerization. ISOPARG (>99.0%) from Mobil Oil was used as the solvent for the TMC monomer. Nonwoven PET (Grade 3252) was purchased from Shanghai Jieyi Biotechnology Co., Ltd. Deionized water was produced by the laboratory and had a resistivity of 18 MΩ cm-1. All materials are used as received.

2.2. Membrane fabrication
The polymer was continuously stirred in a mixed solvent at 60°C. The final solution was sonicated for 1 hour to remove air bubbles. ENMs are fabricated using a custom electrospinning device[8]. The detailed dope composition and electrospun condition are summarized in Table 1. The ENMs were simply hot-pressed [9]: A paper over-press (DELI, No. 3893) was used to stable substrate.

| Substrate dope solution | Electrospinning condition |    |    |
|-------------------------|---------------------------|----|----|
| PSF (w/w%) NMP/DMv/vLiCl| Flow rate (mL/h) | Applied voltage (kV) | Axis line velocity (m/s) | Working distance (cm) | Temperature (°C) | Humidity (%) |
| 26 3/7 trace     | 1                      | 25                     | 1.25                 | 15                  | 25                  | 25           |

An ultra-thin polyamide selective layer was fabricated on the nanofiber substrate by IP between MPD and TMC monomers, as mentioned of the previously work[10]. Finally, three FO membranes with different thicknesses were named as PSF-1, PSF-2, and PSF-3.

2.3. Membrane Characterization
The morphology of the nanofiber substrate and the FO membrane was characterized using a scanning electron microscope (FESEM, S-4800, Japan), and the average diameter and standard deviation of 50 nanofibers were determined using Image J.

The membrane thickness was measured using a thickness gauge (No. 220197, Exploit, China). The porosity (ε) was measured by weighting membrane before and after it was immersed in the wetting solvent (IPA). The contact angle was measured by the static drop method using a contact angle tester (SL200C, Solon Information, China). The tensile strength of the nanofiber substrates was determined at 20°C using a univariate tensile instrument (Paratronics, ETT-A, China). The above characterizations remove the non-woven fabric.

The evaluation was performed using a lab-scale FO membrane assembly[8]. All membranes were tested in FO mode. The FW was the DI water and the DS was 0.25–1 M NaCl solution. After the water flux and temperature have stabilized, the flux is taken as the average reading over 1 hour. The water flux (Jw, Lm-2h-1, in short LMH) is determined by the volume change of the DS.

\[ J_w = \frac{\Delta V}{\Delta t \times A} \] (1)
Where ΔV(L) is the volume of permeate water collected during a period of time Δt(h) during FO process; A is the effective membrane area (m²).

The salt content in the FW was determined from the conductivity measurement based on the standard salt concentration-conductivity curve. The solute flux \( J_s \) (gm⁻²h⁻¹, in short gMH) is determined by the conductivity increase of the FW.

\[
J_s = \frac{V_2 \times C_2 - V_1 \times C_1}{\Delta t \times A}
\]  

(2)

Where \( C_1 \), \( C_2 \), and \( V_1 \), \( V_2 \) are the salt content and FW volume at time \( t_1 \) and \( t_2 \), respectively.

The structural parameter is a measure of the effective diffusion distance of the solute through the FO membrane. Tiraferri et al. [11] developed a method to simultaneously measure A, B and S in FO experiments.

\[
S = \frac{D \times \tau}{\varepsilon}
\]  

(3)

The structural parameter S is proportional to the substrate thickness (D) and curvature (\( \tau \)) and inversely proportional to the porosity (\( \varepsilon \)).

3. Results and discussions

3.1. Characterization of nanofibrous substrates

Fig. 1. (a) the statistical diameter size distribution of nanofibers and FESEM image; (b) pure water permeation flux and mechanical strength at three different thicknesses

The contact angle of the original PSF nanofibers was measured to be approximately 128°, which is consistent with other studies on PSF nanofibers [12, 13]. The porosity of three different thicknesses of membranes are almost unchanged. Pure water permeability maintains the trend as thickness variation: PSF-1>PSF-2>PSF-3. The S values for PSF-1, PSF-2, and PSF-3 were 486, 522, and 716 μm, respectively, showing a high correlation between S value and thickness. However, we must also pay attention to the adverse effects of thickness on mechanical strength.

3.2. Performance of TFC FO membranes

As shown in Fig. 2, the polyamide forms a dense, continuous membrane that is tightly bound to the top PSF nanofiber layer, which is similar to some reports [14]. Higher-resolution FESEM shows the typical
ridge-and-valley morphology of polyamides with "worm-like" characteristics, but not as evident as most TFC membranes [15, 16], which may be related to the hydrophobicity of the substrate. The effective thickness of the PA layer is only ~20 nm, which is consistent with the literature [10], and the thinner active layer is also more conducive to the improvement of water flux.

Fig. 2. FESEM micrographs showing the polyamide active surfaces and cross-sections of the FO membranes (a) top view; (b) cross-section

The A value of the in-hand FO membrane is 2.03-2.27 LMH/bar, which is twice the CTA-W film (1.34 LMH/bar) almost. This is mainly attributed to the large porosity of the in-hand membrane substrates layer, large pore size and thinness. The B value reaches 0.10-0.14 LMH, which is mainly attributed to the strong binding of the PA layer and PSF substrates layer and thin and dense PA layer[14]. Compared with the CTA-W membrane (101 kPa), the internally manufactured TFN membrane has a relatively low B/A ratio (4.54-7.62 kPa), which indicates that the in-hand membrane has excellent selective permeability.

By appropriately reducing the thickness of the substrates layer, the mass transfer resistance of the modified membrane was greatly reduced. The psf-1 exhibited the smallest structural parameter S value of ~486 micrometers, which was 32% lower than that of the thicker psf-3. This indicates the great potential to use the appropriate thickness reduction to improve the structural parameters S of the FO membrane.

Fig. 3. Structural parameters of FO Membranes. The S value is measured by FO experiments. Error rods are calculated according to 2-3 repeated tests.
FO membrane performance was evaluated by FO water flux and specific solute flux. FO water flux of the active layer facing the feed water (AL-FW) at 1 M NaCl. PSF-1 FO membrane showed an improved water flux of 20.61 L/hm than the commercial FO membrane [8]. The increased water flux is consistent with the decrease in the S value and the increase in the A value.

4. Conclusion
In our work, we successfully fabricated three TFC FO membranes with different thicknesses, consisting of a PSF nanofiber substrate and an ultra-thin polyamide layer. The experimental results show that proper reduction of membrane thickness can greatly reduce the mass transfer resistance and increase the water flux of the membrane. Due to the reduction of the structural parameters of the substrates layer, the minimum thickness of the TFC-1 FO membrane can achieve a minimum structural parameter (~486 μm). This study shows that proper reduction of membrane thickness can reduce ICP and significantly improve FO performance.

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