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High Performance Thin-film Composite Membranes with Mesh-Reinforced Hydrophilic Sulfonated Polyphenylenesulfone (sPPSU) Substrates for Osmotically Driven Processes

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Abstract

We have for the first time combined the strength of hydrophilic sulfonated material and thin woven open-mesh via a continuous casting process to fabricate mesh-reinforced ultrafiltration (UF) membrane substrates with desirable structure and morphology for the development of high-performance thin-film composite (TFC) osmosis membranes. A new sulfonated polyphenylenesulfone (sPPSU) polymer with super-hydrophilic nature is used as the substrate

material, while a hydrophilic polyester (PET) open-mesh with a small thickness of 45 μm and an open area of 44.5% is employed as the reinforcing fabric during membrane casting. The newly developed sPPSU-TFC membranes not only exhibit a fully sponge-like cross-section morphology, but also possess excellent water permeability ($A = 3.4\text{--}3.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and selectivity toward NaCl ($B = 0.10\text{--}0.23 \text{ L m}^{-2} \text{ h}^{-1}$). Due to the hydrophilic nature and low membrane thickness of 53–67 μm , the PET-woven reinforced sPPSU substrates have remarkably small structural parameters (S) of less than 300 μm . The sPPSU-TFC membranes thereby display impressive water fluxes (J_w) of 69.3–76.5 $\text{L m}^{-2} \text{ h}^{-1}$ and 38.7–47.0 $\text{L m}^{-2} \text{ h}^{-1}$ against a deionized water feed using 2 M NaCl as the draw solution under pressure retarded osmosis (PRO) and forward osmosis (FO) modes, respectively. This performance surpasses the state-of-the-art commercially available FO membranes. The sPPSU-TFC membranes also show exciting performance for synthetic seawater (3.5 wt% NaCl) desalination and water reclamation from real municipal wastewater. The newly developed PET-woven sPPSU-TFC membranes may have great potential to become a new generation membrane for osmotically driven processes.

Keywords: sulphonated polyphenylenesulfone; membrane casting; thin-film composite membranes; osmotically driven membrane processes; wastewater reuse

Introduction

Leveraging on the natural phenomenon of osmosis, osmotically driven membrane processes (ODMPs) such as forward osmosis (FO) and pressure retarded osmosis (PRO) are the emerging technologies for seawater or brackish water desalination, wastewater treatment, food and pharmaceutical processing, and renewable osmotic energy production [1-4]. Fundamentally, ODMPs employ the osmotic pressure difference ($\Delta\pi$) of the solutions across a semipermeable membrane to spontaneously extract water from a feed stream into a more concentrated draw solution, leading to a diluted brackish water and a concentrated feed stream with much reduced volume [3,4]. This unique feature makes ODMPs significantly different from the conventional pressure-driven membrane processes, such as (1) low energy consumption to induce a net flow of water, (2) great rejection toward a wide range of contaminants, (3) efficient water recovery, and (4) less and more reversible membrane fouling [1-4]. When the hydraulic pressure in the draw solution side is smaller than the $\Delta\pi$ across the membrane, one can harvest the osmotic energy via the environment-friendly PRO process [4-7]. The projected global osmotic energy from the mixing of fresh river-water and ocean is approximately 1750–2000 TWh/year [6,7].

However, the lack of adequately designed osmosis membranes hinders the applications of ODMPs beyond conceptualization and lab-scale studies. The bottleneck arises from the internal concentration polarization (ICP) which is resulted from the restricted mass transfer and the accumulation of solutes within the tortuous, hydrophobic and thick substrate layer [8-10]. ICP has been found to dramatically reduce the effective osmotic driving force across the membrane for water transport. The performance of the current osmotic-driven polymeric membranes is still

much limited by ICP, particularly for commercially available thin-film composite (TFC) membranes cast on nonwoven/woven fabrics [7,11-13]. The detrimental effects of ICP can be quantitatively modeled by membrane structural parameter, S , which is partially determined by substrate materials, porosity and structure [8-10]. Generally, an ideal substrate for osmosis membranes should be highly porous and as thin as possible with a low tortuosity [8-13]. Improvements in substrate hydrophilicity could also reduce ICP via enhancing pore wettability [14-16]. Several effective osmosis membranes have been developed in labs by using freestanding polymeric substrates without fabric supports [14-27]. However, the fabric-free osmosis membranes are not practical for large-scale manufacturing and industrial applications. Membranes normally need reasonable mechanical properties for easy shipping and handling. Therefore, there is a need to explore effective materials and fabrication methods for high performance mesh-reinforced osmosis membranes.

Herein, we report for the first time the fabrication of highly permeable mesh-reinforced substrate membranes consisting of a thin cross-section structure, super-hydrophilic nature and good mechanical durability. High-performance TFC osmosis membranes were thereafter constructed by a continuous casting process for easy scale-up and manufacturing. Specifically, the newly developed flat-sheet TFC membranes comprise three layers: (1) an ultrathin polyamide selective skin formed via interfacial polymerization, (2) a hydrophilic sulfonated polyphenylenesulfone (sPPSU) polymeric sublayer, and (3) a thin and hydrophilic open mesh embedded within the sPPSU sublayer for mechanical reinforcement. Comparing to the state-of-the-art commercial TFC-FO membranes, the membranes produced in this study possess high permeability and

selectivity, extremely low structural parameter, remarkable osmotic water flux and low reverse solute flux, excellent hydrophilicity and mechanical strength.

2. Materials and Methods

2.1 Materials

Sulfonated polyphenylenesulfone (sPPSU) was provided by BASF SE Company, Germany, and used as the material for the fabrication of membrane substrates. The sPPSU was synthesized via the directly copolymerized sulfonation method with 2.5 mol% 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone monomer in the copolymerization reaction [15,28]. The 2.5 mol% sPPSU (termed as sPPSU2.5) has an ion exchange capacity (IEC) value of 8.2 meq/100g polymer. Fig. 1 (A) shows the chemical structure of the sPPSU2.5 polymer. A polyester (PET) open mesh with specifications of 45 μm thickness, 64 μm mesh opening, and 44.5% open area was obtained from SEFAR, Switzerland, and employed as the backing fabric during casting. N-methyl-2-pyrrolidone (NMP) and polyethylene glycol with a molecular weight of 400 g/mol (PEG400) from Merck were utilized as the solvent and additive in the dope solutions, respectively. Polyethylene glycol (PEG) and polyethylene oxide (PEO) with different molecular weights were purchased from Sigma-Aldrich. *m*-phenylenediamine (MPD) with >99% purity and trimesoyl chloride (TMC) with 98% purity supplied by Sigma-Aldrich were used as received for the formation of the polyamide selective skin via interfacial polymerization. *n*-hexane (>99.0%) and sodium chloride (NaCl, 99.5%) were ordered from Merck. Sodium dodecyl sulphate (SDS, >97%) was purchased from Fluka and used as the additive. Deionized water was produced by a Milli-Q unit (Millipore) with a resistivity of 15 M Ω cm. To study the relationship among

membrane materials, structures and their osmosis performances, a commercial flat-sheet TFC-FO membrane from Hydration Technology Innovations (HTI, Albany, OR) was included for performance comparison.

2.2 Fabrication of sPPSU flat-sheet membrane substrates

The sPPSU membrane substrates were prepared via the conventional non-solvent induced phase-separation (NIPS) method by using a continuous casting process. Fig. 2 shows the schematic of the industry-scale casting machine used in the current work, and Table 1 summarizes the detailed formulation of dope solutions and the optimized casting parameters. The dope solutions were allowed to degas overnight at room temperature prior to casting onto the mesh fabric. The as-cast membranes were immersed into a water coagulation bath at room temperature to induce phase separation, and then kept at least for 2 days in deionized water to ensure complete precipitation and remove additives.

2.3 Fabrication of polyamide TFC membranes

The polyamide selective skin was formed on the top surfaces of the as-cast sPPSU substrates by interfacial polymerization between MPD and TMC as shown in Fig. 1 (B) [29]. The membrane substrate was firstly immersed in a 2 wt% MPD aqueous solution containing 0.1 wt% SDS for 2 min. After removing the excess water droplets, the top surface of the saturated substrate was subsequently brought into contact with a 0.15 wt% TMC/hexane solution for 1 min. The resultant TFC membrane was then kept in deionized water at room temperature for further characterizations.

2.4 Characterizations

2.4.1 Membrane morphology, thickness, hydrophilicity, mechanical properties and porosity

A field emission scanning electron microscope (FESEM, JEOL JSM-6700LV) was used to observe the membrane morphology. In order to acquire the cross-section morphology, the membrane samples were firstly dried by a freeze dryer (ModulyoD, Thermo Electron Corporation, USA), and then freeze-fractured in liquid nitrogen. Prior to observation, all the samples were coated with platinum by using a sputtering coater (JEOL LFC-1300). The membrane overall thickness was measured by a digital micrometer, while the average water contact angle of the substrate top surface was obtained using a Contact Angle Geniometer at room temperature. Membrane mechanical properties were characterized by using an Instron 5542 tensile testing equipment. The membrane samples were cut into stripes with 5 mm width and clamped at both ends with an initial gauge length of 30 mm and a testing rate of 10 mm/min. At least five stripes were tested for each substrate to obtain the average values of tensile strength, Young's modulus and elongation at break.

To measure the substrate membrane porosity, the wet samples were weighed (m_1 , g), freeze dried overnight, and reweighed (m_2 , g). The absorbed water was therefore calculated as $m_1 - m_2$. Since the densities of both water (ρ_w , 1.00 g/cm³) and sPPSU (ρ_p , 1.35 g/cm³) are known, the overall porosity ε (%) was then obtained as [29]:

$$\varepsilon = \frac{(m_1 - m_2)/\rho_w}{(m_1 - m_2)/\rho_w + m_2/\rho_p} \quad (1)$$

2.4.2 Pure water permeability (PWP) and pore-size distribution of membrane substrates

The pure water permeability (PWP), molecular weight cut-off (MWCO), mean pore size and its distribution of the sPPSU membrane substrates were measured by using an ultrafiltration permeation setup at a trans-membrane pressure of 1 bar. The PWP (in $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$) was firstly tested using deionized water as the feed. Then, the mean effective pore size, pore-size distribution and MWCO of the membrane substrates were characterized by solute rejection experiments [30,31]. The membrane was subjected to neutral solutes PEG and PEO of progressively larger molecular weights at 200 ppm. The solute concentrations in the feed (C_f) and permeate (C_p) were measured via a total organic carbon analyzer (TOC ASI-5000A, Shimadzu, Japan). The effective solute rejection coefficient R (%) was then calculated as:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

The relationship between Stokes radius (r_s , nm) and molecular weight (M_w , g mol^{-1}) of PEG and PEO solutes can be expressed as [30,31]:

$$\text{For PEG: } r_s = 16.73 \times 10^{-12} \times M_w^{0.557} \quad (3)$$

$$\text{For PEO: } r_s = 10.44 \times 10^{-12} \times M_w^{0.587} \quad (4)$$

The mean effective pore size and pore size distribution were then obtained according to the traditional solute transport method by ignoring the influences of the steric and hydrodynamic interaction between solute and membrane pores. When the solute rejection R is plotted versus r_s on a log-normal probability paper, a straight line is obtained. The mean effective pore radius (μ_p) and the geometric standard deviation (σ_p) can be assumed to be the same as μ_s (the geometric

mean radius of the solute at $R=50\%$) and σ_g (the geometric standard deviation defined as the ratio of r_s at $R=84.13\%$ over that at $R=50\%$). Based on μ_p and σ_p , the pore size distribution of a membrane can be expressed as the following probability density function [29-31]:

$$\frac{dR(d_p)}{dd_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (5)$$

2.4.3 Mass transport characteristics of TFC membranes

The water permeability and salt rejection of the TFC membranes were measured by using a bench-scale RO testing unit at a trans-membrane pressure of 1 bar. The water permeability coefficient, A (in $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$), was obtained from the pure water permeation flux by using deionized water as the feed. The salt rejection, R_s (in %), was determined from the conductivity measurements of the permeate and the feed solution that contains 1000 ppm NaCl at 1 bar. The salt permeability coefficient, B (in $\text{L m}^{-2} \text{h}^{-1}$), was then acquired based on the solution-diffusion theory [18,32]:

$$B = A(\Delta P - \Delta \pi) \frac{1 - R_s}{R_s} \quad (6)$$

where ΔP and $\Delta \pi$ are the pressure difference and osmotic pressure gradient across the membrane, respectively.

2.4.4 Osmosis performance tests and structural parameter determination of TFC membranes

The osmotic water flux, J_w , and reverse salt diffusion flux, J_s , of the TFC membranes were characterized using a lab-scale cross-flow FO system [18]. The membrane permeation cell was a plate-and-frame design with a spacer-free rectangular channel at both sides. The fluxes were measured under both the PRO mode (i.e., the active layer facing the draw solution) and FO mode (i.e., the active layer facing the feed solution) at 22 ± 0.5 °C using deionized water as the feed. The draw solutions are NaCl solutions with various molar concentrations. For each test, the NaCl concentration of the draw solution was maintained constant throughout the test. The counter-current flow configuration was operated in all osmosis tests with a cross-flow velocity of 0.2 L/min (0.017 m/s) at both sides of the membrane. Note that there was no hydraulic-pressure difference across the membrane. To apply the TFC membranes for seawater desalination, a synthetic seawater solution (3.5 wt% NaCl) was used as the feed.

The weight change in the feed solution over a selected period was monitored by a balance (EK-4100i, A&D Company Ltd., Japan) that was connected to a computer. The J_w (in $\text{L m}^{-2} \text{h}^{-1}$, abbreviated as LMH) across the membrane was then calculated from the volume change of the feed:

$$J_w = \frac{\Delta V}{A_m \Delta t} \quad (7)$$

where ΔV (L) is the permeation water collected over a predetermined time Δt (h) and A_m is the effective membrane surface area (m^2).

The salt concentration in the feed was determined by measuring the solution conductivity based on a concentration-conductivity calibration curve of NaCl solutions. The J_s (in $\text{g m}^{-2} \text{h}^{-1}$, abbreviated as gMH) is thereafter determined as:

$$J_s = \frac{\Delta(C_f V_f)}{A_m \Delta t} \quad (8)$$

where C_f and V_f are the salt concentration and the feed volume at the end of FO tests, respectively.

The membrane structural parameter, S , was derived from the obtained A , B , and J_w with the following equation [18,33]:

$$S = \frac{D_s}{J_w} \ln \frac{A\pi_{D,b} + B}{A\pi_{F,m} + J_w + B} \quad (9)$$

where D_s is the diffusion coefficient of the draw solute NaCl, J_w is the experimental water flux obtained under the FO mode, $\pi_{D,b}$ is the bulk osmotic pressure of the draw solution, and $\pi_{F,m}$ refers to the osmotic pressure at the membrane surface on the feed side. S is a key intrinsic characteristic of the substrate layer which is indicative of the degree of ICP effects. The relationship among solute diffusion resistivity within the substrate layer (K_m), diffusivity (D_s), substrate tortuosity (τ), thickness (l), porosity (ε), and S can be represented as:

$$K_m = \frac{S}{D_s} = \frac{l\tau}{\varepsilon D_s} \quad (10)$$

2.5 Water reclamation from municipal wastewater via FO

During the FO performance tests of the sPPSU-TFC membranes for water reclamation from impaired waters, a real municipal wastewater collected from NEWater municipal wastewater treatment plants, Singapore, was used as the feed and its key characteristics are summarized in Table 2 [34]. A 1 M NaCl solution was used as the draw solution and the salt concentration was kept constant throughout the tests. The wastewater with an initial volume, $V_{f,i}$, of 0.5 L was used as the feed and was continuously run through the membrane under the FO mode until reaching a recovery rate with a total permeate water of ΔV . The feed recovery percentage, R_f , is defined as the amount of permeate water over the initial feed volume:

$$R_f = \frac{\Delta V}{V_{f,i}} \times 100\% \quad (11)$$

In order to minimize experimental errors, three membrane samples were tested for each data and the average value was reported.

3. Results and Discussion

3.1 Characteristics of PET open mesh and mesh-reinforced sPPSU membrane substrates

In order to minimize the effects of nonwoven or woven fabrics on osmosis performance, a specially chosen polyester (PET) open mesh is employed as the reinforcing fabric during the substrate membrane casting. As shown in Fig. 3 (A), the PET mesh not only possesses a small thickness of only 45 μm , a large mesh opening of 64 μm and a high open area of 45%, but also is robust and hydrophilic (water contact angle is around 50-60 °C). Theoretically, these characteristics would make the PET mesh as an effective supporting fabric for high-performance osmosis membranes [11,12]. Compared to cellulose esters and other conventional materials

[21,32], the sulfonated polyphenylenesulfone (sPPSU) is a preferred substrate material for osmosis membranes because of its super-hydrophilic nature and good mechanical and chemical robustness [15,16,18,35]. The details on the material characterization of the sPPSU polymer can be found in our previous work [15,28,35]. During the casting, it is found that the hydrophilic nature of sPPSU induces a delayed demixing and a slower phase inversion as compared to conventional hydrophobic materials [15]. As a result, it enables an easy casting process and produces membranes with desirable morphology where the thin PET mesh is fully embedded in the sPPSU matrix as the mechanical support.

Inspired from the structure of HTI-CTA membranes [12], embedding the PET mesh into the sPPSU polymer matrix instead of attaching onto the bottom surface is applied to reduce the membrane overall thickness. As displayed in Fig. 3 (B) and (C), sPPSU substrates with smooth top surfaces and small surface pores in nanometer ranges have been successfully prepared. On top surface of the #1 sPPSU substrate, the PET mesh pattern and some large umbilicate parts are visibly observed at a low magnification, indicating its ultra-thin structure. As tabulated in Table 3, the #1 sPPSU has an average thickness of 53 μm , which indicates that the sPPSU thickness is only 8 μm higher than the PET mesh thickness of 45 μm . In addition, its top surface has relatively large pores visible at a high magnification of 30,000. These large pores may humble the selectivity and stability of the polyamide selective skin formed via interfacial polymerization [36,37]. This drawback could be solved by slightly increasing the polymer concentration and membrane thickness. As illustrated in Fig. 3 (C), the #2 sPPSU substrate exhibits a flatted top surface with a larger thickness of 67 μm (Table 3) when the polymer concentration is increased

from 15 wt% (for #1 sPPSU) to 17 wt%. Consequently, the top surface becomes more uniform and denser without many visible pores.

The morphology of the membrane bottom surface is closely related to the polymer concentration. For the #1 sPPSU substrate cast from a low polymer concentration of 15 wt%, numerous large pores are observed on its backside surface. When increasing the polymer concentration to 17 wt%, the PET mesh in the #2 sPPSU substrate moves toward the center of the membrane cross-section and consequently reduces the macroscopic pores on its bottom surface. Since a higher polymer concentration could result in a slower demixing rate during the phase inversion, the polymer solution has more time to penetrate into the mesh and form a more continuous polymer layer underneath the mesh [11]. The commercial HTI-TFC membrane possesses a quite different bottom surface morphology compared to the sPPSU ones. As shown in Fig 5 (A), the fabric of the HTI-TFC is attached onto the bottom surface of the substrate which induces larger backside openings and a thicker cross-section of 85 μm (Table 5).

Table 3 summarizes the PWP, MWCO, porosity, contact angle and pore size characteristics of the newly prepared sPPSU membrane substrates. The two sPPSU membranes display large PWP values with mean pore sizes and MWCO in the UF range. With an increase in polymer concentration in casting solutions, the #2 sPPSU substrate (17 wt%) shows a slight decline in mean pore size, d_p , (23.7 to 22.0 nm) and porosity (87.5 to 84.2%) as compared to those of the #1 sPPSU (15 wt%), but possesses a much narrower pore size distribution, as illustrated in Fig. 4. As a consequence, the MWCO of the former drops from 479.2 of the latter to 212.7 KDa and

PWP from 1353.3 to 1013.4 L m⁻² bar⁻¹ h⁻¹, respectively. These results are well aligned with the observations from the SEM images displayed in Fig. 3. Since the #2 sPPSU substrate has a smaller mean pore size, narrower pore-size distribution, and more uniform surface morphology, it would form a better polyamide selective layer during interfacial polymerization than the #1 sPPSU substrate [36,37]. In addition, Table 4 shows that the newly developed sPPSU membrane substrates possess excellent mechanical robustness mainly due to the incorporation of the PET woven fabric.

3.2 Characteristics of TFC membranes

3.2.1 TFC membrane morphology and transport characteristics

As displayed in Fig. 5, both the newly fabricated #2 sPPSU-TFC and commercial HTI-TFC membranes have the typical “ridge-and-valley” top surface morphology. However, the polyamide surface of the #2 sPPSU-TFC shows a much bigger and rougher tuft structure than the HTI-TFC. This is possibly attributed to the super-hydrophilic nature and the relative large pore size of the sPPSU substrate. Both factors have been found to facilitate the diffusion of MPD molecules to the interface for interfacial polymerization with TMC [18,36,37]. Since rough polyamide topography with a big tuft structure would provide a large surface area for water transport [38-40], the rough polyamide structure observed on the sPPSU-TFC membranes may enable them with a high permeability. A comparison of the cross-section morphology beneath the TFC layers indicates that the #2 sPPSU-TFC has a fully sponge-like structure without macrovoids, while the HTI-TFC membrane possesses a fully finger-like morphology. The

macrovoid-free structure may provide the sPPSU-TFC membranes with stable long-term performance as it would result in better mechanical stability under high pressures [41].

Table 5 summarizes the intrinsic transport properties of the newly developed sPPSU-TFC and commercial HTI-TFC membranes. The water permeability (A) and the salt permeability coefficient (B) describe the mass transport characteristics of the polyamide selective layer. The sPPSU-TFC membranes have comparatively higher A values than that of the HTI-TFC membrane (i.e., 3.4-3.7 L m⁻² h⁻¹ bar⁻¹ vs. 2.3 L m⁻² h⁻¹ bar⁻¹) and other reported TFC membranes [4,7]. We attribute these greater A values to the larger surface areas of the rougher polyamide layers and the hydrophilic nature of the sPPSU substrates. In addition, the sPPSU-TFC membranes exhibit good salt rejections (R_s) of 73.6-84.8% toward NaCl even at a low hydraulic testing pressure of 1 bar, while the HTI-TFC has a relative low R_s of 65.7%. As a result, the #2 sPPSU-TFC possesses the smallest B of 0.103 L m⁻² h⁻¹, while the #1 sPPSU-TFC and the HTI-TFC have larger B of 0.228 L m⁻² h⁻¹ and 0.206 L m⁻² h⁻¹, respectively. Again, this suggests that the newly developed sPPSU substrates possess suitable structures to form highly selective polyamide layers. As osmosis membranes, another advantage of the sPPSU-TFC membranes over the commercial one is the dramatically reduced thickness (i.e., 53-67 vs. 85 μ m), which would be expected to advance the osmotic fluxes of the TFC membranes.

3.2.2 Osmotic fluxes performance of TFC membranes

The trends of osmotic flux performance of the TFC membranes are in good correlation with their intrinsic transporting characteristics. As depicted in Fig. 6, the newly developed sPPSU-TFC

membranes gain much higher water fluxes, J_w , than the HTI-TFC over a wide range of draw solution concentrations under both PRO and FO modes. In specific, the #1 sPPSU-TFC membrane possessing the largest A and B shows the highest J_w of 76.5 LMH with the highest J_s of 28.4 gMH under the PRO mode when using a 2 M NaCl as the draw solution. The #2 sPPSU-TFC exhibits a slightly smaller J_w of 69.3 LMH yet a much lower J_s of 14.5 gMH at the same testing conditions because of its better permselectivity (Table 5). In comparison, the HTI-TFC membrane only shows a J_w of 44.0 LMH with a J_s of 11.0 gMH. Under the FO mode where ICP effects are amplified, the sPPSU-TFC membranes outperform the HTI-TFC more significantly. The acquired J_w can be up to 47.0 LMH and 38.5 LMH for the #1 sPPSU-TFC and #2 sPPSU-TFC membranes, respectively, when using 2 M NaCl as the draw solution. This is approximately 2.1-2.5 times higher than the J_w of HTI-TFC ($J_w = 18.5$ LMH) under the same conditions. Fig. 6 also shows that J_w and J_s under the PRO mode are larger than those under the FO mode, and their values increase with a raise in draw solution concentration. However, it is interesting to note that the difference in J_w between PRO and FO modes for the sPPSU-TFC membranes is smaller than that for the HTI-TFC. This again is an indication of less ICP effects within the sPPSU substrates.

Specific reverse salt flux, J_s/J_w , is another metric that further discloses the membrane selectivity by measuring the amount of draw solute leakage per unit of water permeated across the membrane [42]. As presented in Fig. 6 (c) and (d), the #2 sPPSU-TFC always shows a lowest J_s/J_w than other membranes at all testing conditions. For example, a low J_s/J_w of less than 0.208 g/L and 0.217 g/L is achieved by the #2 sPPSU-TFC membrane under PRO and FO modes, respectively, even when the draw solution concentration goes up to 2 M. Compared to the HTI-

TFC, the #1 sPPSU-TFC membrane exhibits a similar J_s/J_w of 0.362 g/L in FO mode yet a slightly higher J_s/J_w of less than 0.371 g/L in PRO mode. This is attributed in part to the higher B/A ratio of #1 sPPSU-TFC (Table 5).

In order to further access the membrane stability, the long-term FO performance of the newly developed #2 sPPSU-TFC membrane as a function of time is examined using deionized water as the feed and 1 M NaCl as the draw solution. As shown in Fig. 7, the initial J_w varies with operation mode which is 47.7 LMH and 30.5 LMH under PRO and FO modes, respectively. With the increase in testing duration, there is a slight reduction in J_w under both PRO and FO modes even the draw solution concentration is maintained throughout the tests. This is likely because of the J_s which induces ICP and rapidly reduces the effective osmotic pressure gradient. However, the #2 sPPSU-TFC membrane maintains almost unchanged J_s/J_w throughout the tests of up to 4000 min, confirming that the newly developed sPPSU-TFC membranes possess good structure durability and performance stability.

3.2.3 Structural parameters

The structural parameter, S , is another key intrinsic characteristic of osmosis membranes, which quantifies the extent of ICP effects occurring in the substrate layer. In this work, the sPPSU-TFC membranes surpass the HTI-TFC and other commercially available osmosis membranes in terms of S values [7,12,43,44]. As tabulated in Table 5, the HTI-TFC possesses an averaged S of 577 μm , while the S values of #1 sPPSU-TFC and #2 sPPSU-TFC membranes are about 256 μm and 300 μm , respectively. In other words, the S value of HTI-TFC is 2.2 times and 1.9 times larger

than those of #1 sPPSU-TFC and #2 sPPSU-TFC, respectively. To the best of our knowledge, the currently achieved S values are much lower than those flat-sheet membranes with a backing fabric reported in prior studies [4,7,11,12,43]. Clearly, the novel structure and super-hydrophilic nature of the newly developed sPPSU-TFC membranes are highly effective in minimizing ICP and thus enhancing water flux in osmotically driven processes.

3.3 Osmotic seawater desalination

The newly developed sPPSU-TFC membranes are further tested for seawater desalination. As tabulated in Table 6, the J_w declines significantly for all TFC membranes when using a synthetic seawater solution (3.5 wt% NaCl) as the feed owing to the much reduced osmotic pressure gradient. However, the sPPSU-TFC membranes still could achieve great J_w as high as 17.3-19.7 LMH and 10.0-12.0 LMH under the PRO mode when using 2 M NaCl and 1 M NaCl as draw solutions, respectively. These values are approximately 2.2-2.5 and 1.8-2.2 times of the J_w of HTI-TFC membrane (i.e., 8.0 LMH (2 M NaCl) and 5.5 LMH (1 M NaCl)) under the same conditions. The dramatically improved seawater desalination performance of the sPPSU-TFC membranes should be attributed to their high A/B ratios, small S , and improved hydrophilicity.

3.4 Water reclamation from municipal wastewater

Since FO has gained renewed interests to treat wastewater [30,31,45-48], the newly developed #2 sPPSU-TFC membranes are investigated for water reclamation from impaired water resources by using a real municipal wastewater as the feed. In order to accurately assess the membrane fouling behavior, the draw solution concentration was maintained at 1M throughout the tests to

exclude the effects of draw solution dilution. All tests are operated under the FO mode because it shows lower fouling tendency despite of its lower initial J_w when compared to the PRO mode [33]. As shown in Fig. 8, there is a mild decline in J_w from 30.5 LMH to 26.7 LMH when the recovery rate reaches 85% using deionized water as the reference feed. The initial J_w (i.e., the averaged J_w in the first 10 min) drops to 26.5 LMH when the municipal wastewater is used as the feed due to its higher salinity. Compared to deionized water, J_w of the wastewater feed undergoes a faster decline as a function of recovery rate. Obviously, this severe decrease is attributed to the membrane fouling happening on the polyamide surface. Since the initial J_w of the #2 sPPSU-TFC membrane is high and the surface of the polyamide skin is relative rough, the fouling layer is formed fast. As observed in Fig. 8 (a), J_w of the real municipal wastewater feed is reduced to approximately 64.1% of the initial value when the recovery rate reaches 20%. Once the membrane surface is gradually stabilized and saturated, the decay of J_w with the increment in feed recovery becomes mild till the maximum recovery rate. However, the fouling layer is apparently loose, thus J_w of the #2 sPPSU-TFC membrane is always above 10.9 LMH even at a high recovery rate of 85% when using a relatively low salinity draw solution of 1M NaCl. In other words, the water reclamation rate could be maintained at a relatively high flux in the FO process even though fouling is taking place on the polyamide surfaces. Similar fouling behaviors are observed by the HTI-TFC membrane as shown in Fig. 8 (b), while its J_w is much lower than that of the #2 sPPSU-TFC. This, in turn, demonstrates the promising potential of the newly developed sPPSU-TFC membranes for wastewater treatment and reuse via osmotically driven processes.

4. Conclusions

The current study has investigated the fabrication of mesh-reinforced ultrafiltration (UF) membrane substrates with desirable structure and morphology for the development of high-performance thin-film composite (TFC) membranes for osmotically driven processes. For the first time, a robust polyester (PET) open mesh with a relatively high open area and a small thickness is successfully embedded into a super-hydrophilic sulfonated polyphenylenesulfone (sPPSU) polymer matrix via a continuous casting process. The resultant membrane substrates not only have small thicknesses of about 53–67 μm but also possess good mechanical strength for practical applications. The newly developed sPPSU–TFC membranes exhibit a fully sponge-like cross-section morphology, excellent water permeability ($A = 3.4\text{--}3.7 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) and good selectivity ($B = 0.10\text{--}0.23 \text{ L m}^{-2} \text{ h}^{-1}$) with remarkably small structural parameters of less than 300 μm . Dramatically high and stable osmotic water fluxes of 69.3–76.5 LMH and 38.5–47.0 LMH with low reverse salt fluxes of less than 0.22 g/L have been achieved by the sPPSU–TFC membranes using deionized water as the feed and 2 M NaCl as the draw solution under PRO and FO modes, respectively. The sPPSU–TFC membranes also perform very well in synthetic seawater (3.5 wt% NaCl) desalination and water reclamation from real municipal wastewater at high water recovery rates (i.e., 85%). This study not only combines the strengths of sPPSU and hydrophilic PET woven fabric to fabricate effective UF substrate membranes, but also creates a new kind of high-performance TFC membranes for osmotically driven processes.

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List of Figures

Fig. 1 Molecular structures of (A) the sulfonated polyphenylenesulfone (sPPSU) polymer material ($p = 97.5$ mol%; $q = 2.5$ mol%) and (B) the polyamide selective layer derived from *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) via interfacial polymerization.

Fig. 2 A schematic diagram of the industry-scale casting machine used in this study.

Fig. 3 FESEM images of (A) the polyester (PET) open mesh fabric, (B) the mesh-embedded #1 sPPSU membrane substrate, and (C) the #2 sPPSU membrane substrate.

Fig. 4 Probability density function curves of the newly developed sPPSU membrane substrates.

Fig. 5 FESEM images of (A) the HTI-TFC FO membrane and (B) the newly developed #2 sPPSU-TFC flat-sheet membrane.

Fig. 6 Water flux, J_w , (a, b) and specific reverse salt flux, J_s/J_w (c, d) of the newly developed sPPSU-TFC membranes and the HTI-TFC FO membrane as a function of draw solution concentration and operation mode. Feed is deionized water.

Fig. 7 Water flux, J_w , (a), and specific reverse salt flux, J_s/J_w (b) of the newly developed #2 sPPSU-TFC membrane as a function of testing duration. Draw solution is 1 M NaCl with an initial volume of 5 L and the salinity is maintained throughout the test. The feed is deionized water.

Fig. 8 Water flux, J_w , of the newly developed #2 sPPSU-TFC membrane (a), and the HTI-TFC FO membrane (b) as a function of feed recovery rate. Draw solution is 1 M NaCl with an initial volume of 5 L and the salinity is maintained throughout the test. The feed is a real municipal wastewater with an initial volume of 0.5 L.

List of Tables

Table 1. Casting parameters for the mesh-embedded sulfonated polyphenylenesulfone (sPPSU) flat-sheet membrane substrates

Table 2. Key characteristic parameters of the real municipal wastewater [34]

Table 3. The mean effective pore size (d_p) in diameter, PWP, MWCO and thickness of the newly developed sPPSU membrane substrates

Table 4. Mechanical properties of the newly developed sPPSU membrane substrates

Table 5. Transport properties and structural parameters of the newly developed sPPSU-TFC membranes and the HTI-TFC FO membrane

Table 6. FO synthetic seawater desalination performance of the newly developed sPPSU-TFC membranes and the HTI-TFC FO membrane as a function of draw solution concentration and operation mode

Research highlights:

1. High-performance TFC membranes with mesh-reinforced hydrophilic substrates are developed for osmotically driven processes.
2. Novel sulfonated polyphenylenesulfone (sPPSU) polymer with super-hydrophilic nature is used as the substrate material.
3. Hydrophilic open-mesh with small thickness and high open area is used as supporting fabric.
4. sPPSU-TFC membranes possess high A of 3.4–3.7 LMH/bar and low B of 0.10–0.22 LMH.
5. sPPSU-TFC membranes have remarkably low structural parameters (S) of less than 300 μm .

Figure

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Table

Table 1. Casting parameters for the mesh-embedded sulfonated polyphenylenesulfone (sPPSU) flat-sheet membrane substrates

Casting parameters	#1 sPPSU substrate	#2 sPPSU substrate
Polymer dope composition (wt. %)	15/30/50/5 (sPPSU/PEG400/NMP/Water)	17/28/50/5 (sPPSU/PEG400/NMP/Water)
Casting speed (m/min)	7	7
Casting knife gap (μm)	170	170
External coagulant	Water	Water
PET mesh thickness (μm)/Open area (%)	45/44.5	45/44.5

Table 2. Key characteristic parameters of the real municipal wastewater [34]

Characteristics	COD	TOC	TDS	TP	TN	SS	pH	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	PO ₄ ³⁻	NH ₄ ⁴⁺	Unit
Concentration	57.5	472.4	423.5	8.32	51.1	43.5	7.02	78.5	25.8	5.58	17.7	6.99	47.4	mg/L

Table 3. The mean effective pore size (d_p) in diameter, PWP, MWCO and thickness of the newly developed sPPSU membrane substrates

Membrane code	d_p (nm)	σ_p	PWP (L m ⁻² h ⁻¹ bar ⁻¹)	MWCO (KDa)	Porosity (%)	Membrane thickness (μ m)
#1 sPPSU	23.7	1.65	1353.3	479.2	87.5	53.0
#2 sPPSU	22.0	1.15	1013.4	212.7	84.2	67.0

Table 4. Mechanical properties of the newly developed sPPSU membrane substrates

Membrane code	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
#1 sPPSU	272.6±13.7	59.2±3.7	35.7±4.5
#2 sPPSU	379.2±18.6	80.0±5.3	37.8±1.5

Table 5. Transport properties and structural parameters of the newly developed sPPSU-TFC membranes and the HTI-TFC FO membrane

Membrane code	Water permeability, A (L m ⁻² h ⁻¹ bar ⁻¹)	Salt rejection ^a R_s (%)	Salt permeability, B (L m ⁻² h ⁻¹)	K_m ($\times 10^5$ s m ⁻¹)	S^b ($\times 10^{-6}$ m)	Thickness (μ m)
#1 sPPSU-TFC	3.7 $\pm$ 0.38	73.6 $\pm$ 2.6	0.228 $\pm$ 0.012	1.69	256	53
#2 sPPSU-TFC	3.4. $\pm$ 0.26	84.8 $\pm$ 1.5	0.103 $\pm$ 0.008	1.97	300	67
HTI-TFC FO	2.3 $\pm$ 0.52	65.7 $\pm$ 3.1	0.206 $\pm$ 0.036	3.82	577	85

^a Tested at 1 bar using 1000 ppm NaCl as the RO feed solution.

^b Structural parameter, S , was obtained based on A and B , and the water flux tested under the FO mode.

Table 6. FO synthetic seawater desalination performance of the newly developed sPPSU-TFC membranes and the HTI-TFC FO membrane as a function of draw solution concentration and operation mode

Membrane code	Substrate	Draw solution (M)	Water flux, J_w (LMH)	
			PRO mode	FO mode
#1 sPPSU-TFC	#1 sPPSU	1.0	12.0±1.8	9.5±1.5
		2.0	19.7±2.2	17.5±2.0
#2 sPPSU-TFC	#2 sPPSU	1.0	10.0±0.9	7.8±0.7
		2.0	17.3±1.1	13.2±1.0
HTI-TFC-FO	unknown	1.0	5.5±0.2	3.5±0.6
		2.0	8.0±1.3	6.0±1.1

Feed is the synthetic seawater (3.5 wt% NaCl) solution and the testing duration for each flux is 30 min.