Sulfonated Polysulfone Supported High Performance **Thin Film Composite Membranes for Forward Osmosis**

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Abstract

Sulfonated polymers have shown great promise as a material for membranes in water purification. Their hydrophilic nature combined with impressive chemical stability has yielded unique membranes with desalination capacity combined with chlorine tolerance. In this work, we explore the use of these polymers in support materials for thin film composite (TFC) membranes for forward osmosis (FO). Our reasoning behind their use lies in their intrinsic hydrophilicity, which promotes wetting and mass transfer in this support layer. We combine the use of this supporting material with different polyester (PET) nonwoven backings in order to better understand how backing choice and membrane midlayer material choice interrelate. By varying the degree of sulfonation in the support midlayer, along with selecting backing nonwovens with appropriate characteristics, our best membranes exhibited water flux of about $70 \text{ L m}^{-2} \text{ h}^{-1}$ using 1 M sodium chloride draw solution against deionized water in PRO mode. The use of the PET in these membrane imparted impressive mechanical properties while still keeping the structural parameter low (as low as $277 \text{ }\mu\text{m}$). This is the lowest structural parameter of the fabric backed TFC membranes reported in the open literature. These results suggest that the combination of sulfonated polymer midlayers with appropriate PET nonwovens could serve to inform next generation membrane designs for forward and pressure retarded osmosis.

Keywords: sulfonated polymer; forward osmosis; thin film composite.

1. Introduction

Forward osmosis (FO) is an emerging membrane technology that utilizes osmotic pressure difference to drive water across a semipermeable membrane from a diluted feed solution, to a concentrated draw solution while rejecting most solutes [1-3]. FO has been touted as a high water recovery and low cost option for seawater desalination and wastewater concentration [4-6]. However, the large-scale commercialization of FO is in part hindered by the lack of a specifically designed cost-efficient membrane with high performance [6-8].

Thin film composite (TFC) membranes have become a popular platform for membrane design, as an ultra-thin selective layer could be supported on a chemically different porous support layer wherein the benefits of two separate layers can be combined [9, 10]. Unlike integrated asymmetric membranes, the TFC membrane selective layer and porous support layer should be tailored independently towards a good FO performance. The selective layer needs to be extremely thin and have high water permeance and solute selectivity. On the other hand, support layers need to be thin, highly porous, and minimally tortuous (a low structural parameter [11-14]) to minimize the mass transfer resistance, which is known as internal concentration polarization (ICP) [15, 16].

Today's TFC reverse osmosis (RO) membranes meet the selectivity criteria

with their highly selective polyamide layers, but they fall short with regards to their support layers [17, 18]. They typically have high structural parameters and in fact are designed with thicker midlayer and polyester (PET) backing layer to maintain integrity under high pressure conditions [19, 20]. This has caused many researchers and companies to combine the selective polyamide layer with a tailored, low structural parameter support layer for FO [21-23].

Some of these tailored FO membranes strive to maintain robust mechanical properties by inheriting RO-type PET backing layers. However, these layers limit the further reduction of structural parameter [13, 14, 24, 25]. To offset the high structural parameter caused by PET backing fabric, optimization of the support midlayer alongside choice of the PET backing must be considered.

We propose here the consideration of sulfonated polymers as support midlayer materials for FO membranes. Sulfonated polymer is typically obtained by either directly introducing the sulfonic acid group onto the polymer backbone by modification or by polymerizing sulfonated monomers [26-28]. Sulfonated polymers have shown great promise as a material for membranes in water purification [29-31]. Their hydrophilic nature combined with impressive chemical stability has yielded unique membranes with desalination capacity combined with chlorine tolerance [31-35]. Our reasoning behind the use of sulfonated polymers lies in their intrinsic hydrophilicity, which was found to be essential to promote wetting and mass transfer in FO membranes support layer [20].

Previous studies in FO membrane development have shown that by employing sulfonated polymers, the support layer hydrophilicity could be tailored towards improved FO performance [36-39]. However, these membranes exhibited noticeable impaired mechanical strength, which calls into question the viability of these membranes under practical conditions.

In this study, PET nonwoven fabrics were employed to reinforce the sulfonated polymer membrane supports. Sulfonated polysulfone (SPSU) was blended with polysulfone (PSU) and cast on one of two PET nonwoven fabrics. The polymer solution had properties that enhanced the integration of the PET fabric layer with the polysulfone layer, creating what we refer to as a fabric integrated support layer. The polyamide selective layer was formed *in-situ* on the top surface of polysulfone via interfacial polymerization (IP). The resultant TFC membranes exhibited excellent performance while retaining enhanced strength because of the embedded fabric. **This is the first time that sulfonated polymer was integrated with a PET nonwoven for the fabrication of low structural parameter TFC membranes for FO applications.** Such efforts could lead to commercialization of membranes that utilize hydrophilic polymers with integrated nonwovens.

2. Experimental

2.1 Materials

Polysulfone (PSU, Udel P-3500 LCD MB7, $M_w = 77,000\text{-}83,000$ g/mol), sulfonated polysulfone-17 (SPSU-17, $M_w = 56,023$ g/mol, sulfonation degree = 9%) and sulfonated polysulfone-45 (SPSU-45, $M_w = 58,495$ g/mol, sulfonation degree = 16%) were kindly provided by Solvay Advanced Polymers (Alpharetta, GA). The sulfonation of PSU followed protocols in the literature. The reaction product was isolated by precipitation from a non-solvent, followed by drying [40, 41]. The chemical structures of PSU and SPSU are illustrated in Figure 1. *m*-phenylene diamine (MPD, >99.0%), triethylamine (TEA, >99.0%), sodium dodecyl sulfate (SDS, >99.0%) and 1, 3, 5-benzenetricarbonyl trichloride (trimesoyl chloride, TMC, 98.0%) were purchased from Sigma Aldrich (St. Louis, MO). 1-methyl-2-pyrrolidone (NMP, laboratory grade), *n*-hexane (HPLC, >98.5%), 2-propanol (isopropyl alcohol, IPA, >99.5%) and sodium chloride (NaCl, crystalline, >99.0%) were purchased from Fisher Scientific (Pittsburgh, PA). Deionized water (DI) was obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA). Two commercial polyester nonwoven fabrics, Sanko PET 16-1 and Ahlstrom PET 3256, were acquired from the Sanko Junyaku Co., Ltd (Japan) and Ahlstrom Filtration LLC (Finland), respectively. The thick (107 μm) PET fabric Sanko has a relatively

dense structure, while the thin ($45\ \mu\text{m}$) PET fabric Ahlstrom has an open structure. Commercial TFC FO membranes were provided by Hydration Technology Innovations (HTI, Albany, OR) for comparison and these membranes were designated as HTI TFC hereafter.

Figure 1: Chemical structures of: (a) Polysulfone (PSU); (b) Sulfonated polysulfone (SPSU)

Figure 2: Photograph of two PET nonwoven fabrics on a grid background (0.5 inch grid size) to show fiber density. PET Sanko was acquired from Sanko

Junyaku Co., Ltd (Japan). PET Ahlstrom was acquired from Ahlstrom Filtration LLC (Finland).

Figure 3: Cross-sectional and surface FESEM images of PET nonwovens.

Cross-sections of Sanko and Ahlstrom at 500×. Top surfaces of Sanko and Ahlstrom at 100×.

2.2 Fabrication of membrane substrates

The membrane substrates were prepared by non-solvent induced phase separation. 16 wt. % polymer beads were dissolved in NMP with three formulations: pure PSU (SPSU-0), PSU blend with SPSU-17, and SPSU-45 at a ratio of 3:1 (*i.e.* 12 wt. % of PSU and 4 wt. % of SPSU), respectively. The solutions were continuously stirred at room temperature for 24 h and then rested overnight to allow air bubbles to escape. PET Sanko and Ahlstrom nonwovens were taped onto glass plate and uniformly wetted out by spreading 3-4 mL of NMP evenly using a rubber roller [42]. Polymer solution was then cast on PET nonwoven with a 150 μm casting knife. The as-cast membrane substrates were evaporated in a fume hood for 10 sec and then immersed into a DI water bath for 10 min at room temperature. Afterwards, the membrane substrates were rinsed with DI water several times then stored at 5 °C until further use.

2.3 Synthesis of polyamide selective layer

The thin film polyamide layer was synthesized on the membrane substrate surface via *in-situ* interfacial polymerization. First, the top (skin layer) surface of membrane substrate was wetted out with isopropyl alcohol (IPA) for 1 min. After a 30 min DI water rinse, the membrane substrate was immersed in a 2/2/0.1 wt. % MPD/TEA/SDS aqueous solution for 5 min [43]. The excess MPD solution residual was removed by rubber roller and dried in a fume hood

for 2 min. After that, a 0.1 wv. % TMC/hexane solution was brought into contact with the MPD-saturated membrane substrate for 1 min. After the reaction, the membrane top surface was rinsed with hexane to remove unreacted monomers and dried in air at room temperature for 1 min. Afterwards, the membrane was further cured in oven at 70 °C for 1 min. Finally, the membrane was dried in fume hood at room temperature for 3 min and then stored in DI water at 5 °C until further tests.

Two types of membranes with different PET nonwoven fabrics (PET Sanko and PET Ahlstrom) were fabricated. The polysulfone membranes with thick PET Sanko and thin PET Ahlstrom were designated as SPSU-0 Sanko and SPSU-0 Ahlstrom, respectively. For better FO performance, the thick PET Sanko nonwoven was peeled off from TFC membranes in some tests. Those membranes without PET nonwoven were designated as SPSU-0 No-PET. A similar designation is used for the SPSU-17 and SPSU-45 blend membranes. It is worth noting that due to the open structure of PET Ahlstrom, the polymer solution can easily penetrate into the nonwoven fabric. This caused the fabric to be integrated into the membrane and therefore PET removal was impossible. As a result, there are no “No-PET” samples for membranes cast on PET Ahlstrom.

2.4 Characterization of substrates and TFC membranes

2.4.1 Cloud point measurement

The cloud point curves of ternary membrane forming systems were determined by rapid titration method at 21 °C for the three polymer solutions with the same formulation of casting solutions [44-46]. The blend solutions were used to conduct the determinations because the pure sulfonated polymer would form transparent gel during phase separation and was therefore difficult to distinguish at the cloud point. This is due to the presence of hydrophilic sulfonic groups, which are prone to form swollen gel phase rather than white polymer [47]. PSU, PSU and SPSU-17, PSU and SPSU-45 (both at the ratio of 3:1) were dissolved in NMP to obtain homogenous solutions. DI water was slowly added to the solution, while thorough mixing was applied by a magnetic stirrer. The cloud point composition was calculated from the mass balance in the system corresponding to the added volume at which permanent turbidity was detected visually [45].

2.4.2 Scanning electron microscopy

The morphology of the membrane substrates and TFC membranes were imaged with a cold cathode field emission scanning electron microscope JSM-6335F (FESEM, JEOL Ltd., Japan). To view the cross sections of the

membrane substrates, the samples were submerged in liquid nitrogen in order to preserve the pore structure and then cut with a razor blade. Prior to imaging, the samples were sputter coated with gold.

2.4.3 Contact angle

The contact angles of the top surfaces of the membrane substrates were measured using the sessile drop method on a CAM 101 series contact angle goniometer (KSV Company Linthicum Heights, MD). The values were taken as an average of six points with a droplet volume of 10 ± 1 μL . All measurements were taken at room temperature.

2.4.4 Porosity and moisture sorption

The membrane substrate porosity was determined using gravimetric measurements [48, 49]. The hydrated SPSU membrane substrates were cut into sample discs using a punch die. The volume of a membrane disc is determined via measuring its physical dimensions at hydrated state. Its diameter and thickness were measured with a coolant proof digital micrometer (IP65-MX, Mitutoyo, IL). The membrane discs were dried in a vacuum oven for 24 h and were periodically weighed until a constant weight was obtained. Then the discs were immersed in IPA at 25°C. IPA was selected as the wetting reagent because of its sufficient wetting property. The weights of dry and IPA wetted membrane substrates were

measured at room temperature. The residual IPA on the surface of wetted membranes was quickly removed using tissue paper before weighing. The membrane porosity can be determined as the volume of wetting reagent (*i.e.* IPA) divided by the total volume of the membrane, defined as:

$$\varepsilon = \frac{m_{wet} - m_{dry}}{\rho_{IPA} \cdot A \cdot t} \quad (1)$$

where m_{wet} is the weight of wet membrane; m_{dry} is the weight of dry membrane; ρ_{IPA} is the density of IPA (0.786 kg/m³); A is the effective area of membrane sample disc; t is the membrane substrate thickness.

To rule out the possible influence of wetting agent absorption in membrane substrates, a moisture sorption study was conducted [35, 50]. The membrane substrates were vacuum dried for 24 h and then weighed (m_i). The dried membrane were placed in a sealed sorption cell as described in an early study with the exposure of pure IPA vapor at room temperature [50]. IPA vapor was used (rather than liquid IPA) to avoid having IPA fill the pores and bias the results. The membrane substrates were weighed every 12 h on an analytical balance until a constant saturated sorption weight (m_f) was obtained after 96 h of IPA vapor exposure. The moisture sorption degree is defined at as:

$$moisture\ sorption\ degree = \frac{m_f - m_i}{m_i} \times 100\% \quad (2)$$

where m_i and m_f are the initial and final mass of the membrane substrate sample.

2.4.5 Mechanical properties

The mechanical properties of TFC FO membranes were obtained from the tensile tests in air at 25°C using a Dynamic Mechanical Analyzer 2980 (DMA, TA Instruments, New Castle, DE). Membranes were cut into 15 mm × 5 mm samples and stored in DI water before measurement. Tests were run at a preload force of 0.5 N and a ramp rate of 0.5 N/min and conducted on wet TFC membranes. Data acquisition and analysis was completed using Universal Analysis software from TA Instruments. Values presented are the average of four tests.

2.5 Osmotic flux performance of TFC membranes

2.5.1 Osmotic flux tests

Osmotic water flux and reverse salt flux through TFC membranes were characterized using a custom lab-scale cross-flow forward osmosis system. The similar experimental setup was described in earlier investigations [21, 22, 25, 51]. Osmotic flux tests were carried out with the membrane oriented in both FO mode (the membrane selective layer faces the feed solution) and PRO mode (the membrane selective layer faces the draw solution). The TFC membranes were tested under a previously provided standard method in which water and salt fluxes were measured at 20±0.5°C using DI feed and 1 M NaCl draw solution

[52]. The hydraulic pressure and Reynolds number (1125) were equal on both sides of membrane. The osmotic water flux, J_w , was calculated by dividing the volumetric flux by the membrane area. By measuring the conductivity of the feed solutions at certain time points during the tests, the reverse salt flux, J_s , was calculated by dividing the NaCl mass flow rate by the membrane area. The specific salt flux is simply a ratio of salt flux to water flux, J_s/J_w .

2.5.2 Determination of transport and structural parameter

The water permeance (A), salt permeability coefficient (B) and structural parameter (S) of the TFC FO membranes were determined by adopting the Excel-based method developed by Tiraferri et al [53]. The method allows the simultaneous determination of A, B and S parameters of FO membranes by dividing the FO experiment into discrete number of stages. In this work, the experiments were carried out in four stages using different draw solution concentrations (0.5 M, 1 M, 1.5 M and 2 M).

3. Results and discussion

3.1 Phase separation properties

The ternary phase diagram with the binodal curves of the three polymer blends (pure PSU, PSU/SPSU-17=3/1, PSU/SPSU-45=3/1) is shown in Figure 4. It can be observed that in the sulfonated polymer blend systems, the area of the

one-phase region would be bigger than that in the PSU system, which means the path taken by the polymer solution of fixed starting composition to reach the phase border line (binodal curve) will be longer for a more sulfonated polymer [47]. In other words, this suggests that the dope solution with a higher sulfonation degree would result in a slower phase separation rate. This is mainly due to the presence of hydrophilic sulfonic groups, which are prone to bond with water. The much greater affinity of the sulfonated materials to water (non-solvent) leads to a longer time for the solvent and non-solvent exchange [47].

Figure 4: Ternary phase diagram showing binodal curves of three blend polymers (SPSU-0: pure PSU; SPSU-17: PSU/SPSU-17=3/1; SPSU-45: PSU/SPSU-45=3/1).

3.2 Morphology of membranes

3.2.1 Morphology of membrane substrates

For the ease of sample fracture, No-PET membrane films (*i.e.* Sanko PET nonwoven removed from membrane substrates) were used in FESEM imaging. Figure 5 shows the top surfaces, cross sections, and bottom surfaces of three No-PET membranes. Due to the same polymer concentration in dope solution and same casting protocol, all the three membranes showed fixed thicknesses of about 60 μm . The top surfaces of the three membranes showed less difference because of the instantaneous demixing on the top skin layers.

Figure 5: FESEM images of No-PET membranes films. Top surfaces of membrane films at 40,000 $\times$. Cross-sections of membrane films at 500 $\times$. Bottom surfaces of membrane films at 100 $\times$.

The influence of the SPSU polymer is noticeable from the cross section morphology changes with the increased sulfonation degree. For the SPSU-0, numerous small macrovoids were separated by a loose sponge-like porous

medium in between. However, for the SPSU-17 and SPSU-45, as the sulfonation degree increased, the membranes showed fewer larger, finger-like pores separated by denser sponge-like porous medium in between. As shown in the ternary phase diagram, the more sulfonated SPSU blend has a slower phase separation rate. Therefore, a longer time was required for solvent and non-solvent exchange in SPSU blended dope solution when immersed in water. A more developed process of polymer-lean phase growth and coalescence resulted in larger finger-like pores [47, 54]. Similarly, denser spongy-like structures were formed between finger-like structures in the SPSU blend membranes because the growth of the large finger-like structure extracted more solvent from the polymer dope surrounding the growing macrovoids. This was due to the longer phase separation time [47]. For the SPSU-0 membrane, the macrovoids were formed at a rapid phase separation rate while the sponge-like pores were formed at the same time by binodal phase separation.

The bottom surfaces of all three membranes exhibited an open and porous morphology with very large surface pores. Some polymer was inevitably removed during the removal of the Sanko PET nonwoven from the membrane, as the imprints of nonwoven fiber can still be seen on the bottom surface. Compared to other membranes cast on glass plates[13, 39, 55], our membranes have a more open and porous morphology on the bottom surfaces. We attribute this to the delayed phase separation on the bottom surface. Such a structure is favorable for FO membranes due to the facilitation of water and solute transport.

The morphology of three integrated membrane substrates cast on Ahlstrom PET nonwoven are shown in Figure 6. The membrane substrate thickness was about 95 μm and included the thickness from the embedded PET nonwoven. Similarly to the No-PET membrane samples, all three membranes showed dense and uniform top surfaces and finger-like cross-sectional structures. With higher sulfonation degree, the SPSU-45 sample showed wider macrovoids separated by sponge-like pores.

Figure 6: FESEM images of Ahlstrom membrane substrates. Top surfaces of membrane substrates at 40,000 $\times$. Cross-sections of membrane substrates at 500 $\times$. Bottom surfaces of membrane substrates at 100 $\times$.

3.2.2 Morphology of TFC membranes

Figure 7 and Figure 8 show the TFC membrane selective layer surface morphology of the Sanko and Ahlstrom PET supported membranes, respectively. Uniform and defect-free thin polyamide selective layers were successfully formed onto each of the membrane samples. The polyamide surface showed characteristic ridge-and-valley morphology for the PSU samples and more leaf-like morphology for the SPSU samples. This may be due to the enhanced surface saturation of MPD molecules in the more hydrophilic surfaces of SPSU blend membranes [56, 57].

Figure 7: Top surface FESEM images of Sanko TFC membranes at 10,000 $\times$.

Figure 8: Top surface FESEM images of Ahlstrom TFC membranes at 10,000 $\times$.

3.3 Characterization of membranes

3.3.1 Contact angle

The contact angle data of the top and bottom surfaces of membrane substrates based on Sanko and Ahlstrom PET were tabulated in Table 1. Generally the SPSU membranes have slightly lower contact angles. This hydrophilicity is important when trying to promote wetting and mitigate ICP [36, 39, 58]. For the bottom surfaces, the three Sanko membranes showed similar results because they used the same PET backing. The Ahlstrom membranes showed a clear trend of increasing hydrophilicity with increasing sulfonation on the bottom surface due to the penetration of polymer solution through the more open PET fabric.

Membranes	Sanko		Ahlstrom	
	Top	Bottom	Top	Bottom
SPSU-0	82.7 ± 2.2	72.5 ± 3.0	74.3 ± 3.6	102.7 ± 4.5
SPSU-17	79.0 ± 2.7	71.4 ± 2.5	71.3 ± 0.9	80.4 ± 5.7
SPSU-45	77.1 ± 1.7	70.9 ± 1.6	65.7 ± 4.4	79.5 ± 3.4

Table 1: Contact angles of top and bottom surfaces of Sanko and Ahlstrom membrane substrates from polymer blends SPSU-0, SPSU-17 and SPSU-45, respectively. Results are an average of 6 samples and the range is the standard deviation.

3.3.2 Porosity and moisture sorption degree

To rule out the possible influence of swelling issues on the SPSU, a moisture sorption study was conducted on the No-PET membrane films of SPSU-0, SPSU-17, and SPSU-45 polymer blends. The results showed that the weight fraction of IPA vapor absorbed in the membrane films for the three polymer blend films were comparable as 5.3%, 6.3%, and 5.8%, respectively. While these results suggest that the uptake of the wetting reagent was generally low, the difference between the non-sulfonated and sulfonated polymers was

negligible [35]. Therefore, the porosity measurement was minimally impacted by the different chemistries of the samples and can be compared side by side.

The porosity data of Sanko, Ahlstrom and No-PET membrane substrates cast from SPSU-0, SPSU-17, and SPSU-45 blend solutions are shown in Figure 9. The Sanko membranes generally exhibited a much lower porosity than the polymer film because of the dense, low-porosity PET backing. The fabric integrated membranes (PET Ahlstrom) exhibited comparable porosity with the polymer film because of its open structure, which facilitates the integration with polymer solution. SPSU-17 and SPSU-45 showed slightly higher porosity compared to the SPSU-0. This is probably due to the larger macrovoids caused by the slower phase separation rate.

Figure 9: Porosity of Sanko, Ahlstrom and No-PET membrane substrates

from SPSU-0, SPSU-17, and SPSU-45 polymer blends.

3.3.3 Mechanical properties

The mechanical properties of the No-PET and Ahlstrom TFC membranes from three polymer blends were measured at room temperature and presented in Figure 10. The mechanical properties of Sanko membranes are not presented since the results mainly showed the features of the Sanko PET nonwoven itself and were so high when compared with the membrane films that the results were not very meaningful.

As expected, the No-PET membrane samples showed low Young's modulus and tensile strength compared to the fabric integrated ones. These membranes exhibited similar mechanical properties to other unsupported cast membranes from the literature [23, 39, 55]. While the thinner structure is preferred for FO applications, their relative weakness compared to fabric supported membranes made them difficult to handle.

The Ahlstrom PET fabric integrated membranes showed significant enhancement in both rigidity and strength compared to No-PET samples. The Ahlstrom membrane samples generally exhibited 3-8 fold higher Young's modulus and 3-6 fold higher tensile strength than those with no embedded PET. Membranes that based on sulfonated polymers were widely considered as lack of mechanical properties. Previously reported sulfonated polymer based FO

membranes generally exhibited moderate Young's modulus about 50-80 MPa and tensile strength around 3-4 MPa [36, 37, 39]. In this study, the fabric integrated sulfonated polymer based FO membranes exhibited remarkably high Young's modulus of 350-400 MPa as well as tensile strength of 10-12 MPa. This is about 5-7 times more rigid and 3-4 times stronger than their predecessors. These improved mechanical properties made the fabric integrated membrane a much better platform overall. It also allows one to use functional or modified polymers with interesting properties but insufficient mechanical strength.

Figure 10: Young's modulus and tensile strength of Ahlstrom and No-PET

TFC membranes from SPSU-0, SPSU-17, and SPSU-45 polymer blends.

3.3 Performance of TFC membranes

3.3.1 Osmotic flux performance of TFC membranes

The TFC membranes were evaluated under FO and PRO modes using DI water as the feed and 1 M NaCl as the draw solution. The osmotic water fluxes, reverse salt fluxes and specific salt fluxes (J_w , J_s , and J_s/J_w) are presented in Figure 11. The TFC membranes supported by PET nonwovens showed substantial differences in performance to unsupported membranes. The No-PET membranes exhibited 4-9 fold higher J_w compare to a membrane supported by the Sanko PET. This is a result of a reduced ICP due to a reduced thickness. The No-PET membranes did, however, exhibit a much higher J_s due to what we believe to be membrane weakness caused by the relatively thin support layer (60 μm). The weakness of the membrane may result in damage to the selective layer during handling and operation. The Ahlstrom PET supported membranes showed the best performance with a high J_w with reasonably low J_s . The better overall performance can be attributed to the thin ($\sim 95 \mu\text{m}$) and open support layer structure due to the fabric integration with the PET while still garnering strength from the PET.

Figure 11: Water flux, reverse salt flux and specific salt flux (J_w , J_s and specific J_s) of FO and PRO tests for TFC membranes from SPSU-0, SPSU-17, and SPSU-45 polymer blends and benchmark HTI TFC [25]. Results are an average of three experiments with different coupons. Error bars indicate standard deviation. Operating conditions: 1 M NaCl draw solution, DI water

feed, 20 °C feed and draw solution temperature, 0.25 m/s feed and draw solution cross flow velocity, no transmembrane hydraulic pressure.

The membranes fabricated from sulfonated polymer blends generally showed higher J_w and similar J_s when compared with the SPSU-0 membranes. Since the same selective layer formation protocol was used for all membranes, the difference in osmotic flux can be largely attributed to the difference in the support layer, including both the structural and chemical effects of SPSU. The more open and less tortuous finger-like structure in the SPSU membrane supports facilitated the water transport and resulted in a higher water flux. The increase of SPSU support layer hydrophilicity also promoted water transport during osmotic processes [20].

The commercial HTI TFC membranes were compared to the Ahlstrom membranes since both of them were fabricated on thin PET fabrics ($\sim 50 \mu\text{m}$) and have comparable membrane thickness ($115 \mu\text{m}$ and $95 \mu\text{m}$) [25]. It is worth noting that the PET fabric used for the HTI TFC membranes was woven mesh, which is more costly than the PET nonwoven fabric used for our membranes. Our SPSU-0 Ahlstrom membranes exhibited slightly higher J_w and noticeably lower J_s than HTI TFC membranes in both FO and PRO modes. For SPSU-17 and SPSU-45, the Ahlstrom TFC membranes generally exhibited two times higher J_w and comparably low J_s when compared to HTI TFC membranes. SPSU-45 is better performing with a remarkably high J_w of $66.9 \text{ L m}^{-2} \text{ h}^{-1}$

and low J_s of $6.9 \text{ g m}^{-2} \text{ h}^{-1}$ in PRO mode. Again, the excellent performance of SPSU blend membranes is due to the more appropriate pore structure (non-tortuous and dendritic) and increased hydrophilicity of the support layer.

Specific salt flux J_s/J_w is a metric that is used to determine the amount of draw solute loss per unit of water passed. It has been used to compare membrane performance when different membranes and/or draw solutes are used [59]. Lower J_s/J_w is desirable to prevent the loss of draw solutes in FO and help to minimize ICP in PRO. As shown in Figure 11, the membranes generally exhibited higher J_s/J_w in FO mode which indicated more severe ICP (and hence lower water flux) than that in PRO mode. The high J_s/J_w of the No-PET membranes suggests that even though water flux was higher than the PET supported membranes, the salt flux was even higher by comparison. This was attributed to a lower selectivity of the membrane caused by the lack of mechanical support. The SPSU-45 Ahlstrom membranes, with the specific salt flux of 0.10 g/L in both FO and PRO modes, which is just one third of that of HTI TFC membrane, represent our best performing TFC membrane based on this metric of performance.

3.3.2 Structural parameters

The structural parameters were calculated by Tiraferri's method and presented in Figure 12 [53]. The structural parameter gives insight to the extent of ICP,

where a low S value correlates with less ICP. The high S values observed in Sanko TFC membranes are due to the thick and dense PET nonwoven backing layer, which exacerbated ICP during FO operation. The SPSU-45 membranes were observed to have the smallest S values among the three types of membranes due to the less tortuous finger-like morphology. This indicated that using a sulfonated polymer in the casting solution results in a membrane structure that helps alleviate ICP.

Figure 12: Structural parameters of TFC membranes from SPSU-0, SPSU-17, and SPSU-45 polymer blends. Structural parameters were calculated by the Excel-based algorithm developed by Tiraferri [53].

As a membrane with a three-tiered structure (selective PA layer, porous

polymeric layer, and PET woven/nonwoven support), our SPSU-45 Ahlstrom membrane represented the lowest S value (277 μm) among all three-layer TFC FO membranes in the open literatures [13, 14, 24]. In addition, this membrane exhibited the S value about half of the commercial HTI TFC membrane (533 μm) with excellent mechanical strength.

3.3.3 Performance comparison with existing TFC FO membranes reported in literatures

Since the membranes fabricated in this study have two major benefits – adopting novel SPSU material and using an inexpensive nonwoven support – our membranes were compared with existing flat sheet FO membranes with similar features.

Table 2 summarizes the osmotic flux performance of sulfonated materials based TFC FO membranes in this study and open literatures [36-39, 58, 60]. The No PET membranes have similar configuration with the glass plate cast TFC FO membranes in literatures and were therefore taken into comparison. All of the TFC FO membranes were tested under a 1 M NaCl draw solution and DI water feed condition. The water flux of our membranes surpassed almost all the other membranes in both FO and PRO modes. **Since all of these membranes showed improved hydrophilicity due to the use of sulfonated polymer, we attribute the high performance of the No-PET membranes to the support structure differences.**

The No-PET membrane support layer exhibited substantial thinness, a porous bottom surface as well as open and straight finger-like morphology. All these contribute to a reduced mass transfer resistance in the support layer (i.e. ICP) and result in lower structure parameters compared to other sulfonated polymeric membranes in previous work. The low structural parameters of the No-PET membranes also resulted in higher reverse salt flux in this work. This is because the draw solutes can diffuse through the thin support structure rapidly and cause relatively higher reverse salt flux.

Membranes	Feed	Draw	Water flux ($L\ m^{-2}h^{-1}$)		Salt flux ($g\ m^{-2}h^{-1}$)		Specific salt flux (g/L)		Structural parameter (μm)	Reference
			FO mode	PRO mode	FO mode	PRO mode	FO mode	PRO mode		
SPSU-17 No PET	DI	1 M NaCl	34.92	60.02	19.93	27.12	0.57	0.45	201	This work
SPSU-45 No PET	DI	1 M NaCl	39.00	69.44	18.90	15.19	0.48	0.22	114	This work
50 wt. % sulfonated polymer	DI	1 M NaCl	20.00	27.47	4.04	3.60	0.20	0.13	324	[36]
50 wt. % SPEK	DI	1 M NaCl	22.65	32.24	4.73	6.10	0.21	0.19	107	[37]
PES/SPSf	DI	1 M NaCl	17.81	32.25	5.44	7.59	0.31	0.24	238	[38]
sPPSU-2.5	DI	1 M NaCl	41.50	44.86	7.21	6.85	0.17	0.15	652	[39]
SPPO/PSf (50:50)-45	DI	1 M NaCl	26.67	38.30	5.18	5.34	0.19	0.14	293	[60]

1.5 mol. % sPPSU HFM	DI	1 M NaCl	28.15	69.63	6.30	12.37	0.22	0.18	163	[58]
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Table 2: Comparison with sulfonated material based TFC FO membranes reported in literatures.

Along with the comparison to other sulfonated polymer based membranes, our fabric integrated Ahlstrom membranes were also compared with three layer TFC FO membranes in the literatures (*i.e.* TFC FO membrane with PET fabric in the structure) [13, 14, 24, 25, 61, 62]. The comparison is summarized in Table 3. Even for the non-sulfonated polymer based membrane, our SPSU-0 membrane exhibited reasonably high water flux yet low reverse salt flux when compared to other literatures. Although it showed slightly lower PRO and FO water fluxes when compared to TFC/PSF9 and 9 wt. % PSf in 100 wt. % DMF, respectively. It is worth noting that these two membranes were fabricated with 9 wt. % casting solution, which was much lower than that of 16 wt. % in this study. This low concentration allowed for a looser pore structure to form and was expected to result in higher porosity as well as FO performance [13, 24, 63]. The SPSU-45 membrane surpassed all the other three layer TFC membranes in the open literature.

Membranes	Feed	Draw	Water flux ($L\ m^{-2}h^{-1}$)	Salt flux ($g\ m^{-2}h^{-1}$)	Specific salt flux (g/L)	Structural parameter	Reference
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			FO mode	PRO mode	FO mode	PRO mode	FO mode	PRO mode		
Integrated SPSU-0	DI	1 M NaCl	18.40	35.91	2.86	6.51	0.15	0.17	580	This work
Integrated SPSU-17	DI	1 M NaCl	24.17	55.05	5.64	9.01	0.23	0.17	401	This work
Integrated SPSU-45	DI	1 M NaCl	29.95	66.89	3.11	6.87	0.10	0.10	277	This work
HTI CTA nonwoven	DI	0.6 M NaCl	7.1	N/A	N/A	N/A	N/A	N/A	N/A	[61]
HTI CTA mesh	DI	1 M NaCl	7.89	17.50	1.05	7.71	0.13	0.44	465	[25]
HTI TFC	DI	1 M NaCl	15.10	30.50	4.37	9.62	0.30	0.32	533	[25]
9 wt. % PSf in 100 wt. % DMF	DI	1 M NaCl	25.00	N/A	N/A	N/A	N/A	N/A	312	[13]
TFC/PSF9	DI	1 M NaCl	17.10	49.4	6.00	7.10	0.35	0.14	314	[24]
TFC-FO	DI	1.5 M NaCl	18.16	N/A	N/A	N/A	N/A	N/A	492	[14]
PAI 2#	DI	0.5 M MgCl ₂	19.20	23.90	9.41	36.33	0.49	1.52	N/A	[62]

Table 3: Comparison with PET fabric integrated TFC FO membranes reported in literature.

4. Conclusions

Hydrophilic sulfonated polymers and appropriate PET nonwovens were combined towards an optimized design of high performance thin film composite membrane for forward osmosis. The PET nonwoven fabrics enable the use of delicate sulfonated polymers by reinforcing the mechanical properties for industrial conditions. Meanwhile, the sulfonated polymers enable the use of hydrophobic PET fabric by integrating it into the support without enhancing mass transfer resistance. These results show the promise of combining sulfonated polymers with appropriate PET nonwoven fabrics for future membrane design for forward and pressure retarded osmosis.

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Graphical Abstract

FESEM images of polyester fabric integrated thin film composite membranes of three sulfonated polysulfone blends (SPSU-0, SPSU-17, and SPSU-45). Top surfaces of membranes at 40,000 $\times$. Cross-sections of membranes at 500 $\times$. Bottom surfaces of membranes at 100 $\times$.