Surface Modified PVDF Nanofiber Supported Thin

Film Composite Membranes for Forward Osmosis

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Liwei Huang, Jason T. Arena and Jeffrey R. McCutcheon*

University of Connecticut

Department of Chemical and Biomolecular Engineering

191 Auditorium Rd. Unit 3222

Storrs, CT 06269-322

Phone: 860-486-4601

Email: jeff@engr.uconn.edu

***Corresponding author**

Abstract

Hydrophilic electrospun nanofibers supported thin film composite (TFC) membranes have recently been considered for forward osmosis (FO). However, our previous work has shown that the high degree of swelling in hydrophilic nanofibers compromises fiber strength and membrane integrity. To reduce swelling, we propose to modify a non-swelling hydrophobic fiber to make it hydrophilic and fully wettable without negatively impacting the structural properties of the material. The method chosen for this work involves the interfacial polymerization of 1,6-hexane diamine and adipoyl chloride to form nylon 6,6 directly onto electrospun PVDF fibers. The result is a dual benefit of hydrophilization and strengthening of nanofibers to improve their wettability. The modified nanofibers exhibited significantly lower swelling propensity than intrinsically hydrophilic nylon 6,6 nanofibers due to the hydrophobic core fiber, and are thus able to retain strength in an aqueous environment. These modified PVDF supports were used in making TFC membranes that exhibited excellent flux performance and one of the lowest structural parameters reported in open literature.

Keywords: forward osmosis, electrospinning, nanofibers, coating

1 Introduction

Forward Osmosis (FO) is an emerging separation technology that harnesses the natural phenomenon of osmosis to address water and energy scarcity [1-3]. In FO processes, an osmotic pressure difference is generated when a semi-permeable membrane is placed between two solutions of differing concentration, which drives the permeation of water across the membrane from the dilute solution to the concentrated solution known as draw solution. The potential of FO technology has been demonstrated in applications such as seawater desalination [4-6] and waste water treatment [7]. Pressure retarded osmosis (PRO) is another specific application of osmotic potential where the product is electric power instead of clean water [8-10]. Despite immense potential in generating fresh water and electric power, FO processes have not yet become commercialized on a large scale. One major obstacle is the lack of membrane specifically designed for this process [11-14].

One commonly seen membrane platform used in FO is thin film composite (TFC) membrane in both flat-sheet and hollow fiber forms [11-13]. They have begun to replace more conventional asymmetric integral membranes due to their superior permselectivity and design flexibility. However, the conventional TFC-reverse osmosis membrane with hydrophobic phase-inversion polysulfone (PSu) support layer and the thick nonwoven fabric backing layer, while appropriate in reverse osmosis process, have never performed well when tested for FO due to severe mass transfer resistance near the interface of the selective thin film layer. This phenomenon, widely described as internal concentration polarization (ICP), reduces effective osmotic driving force and results in poor water flux performance [5, 15-18]. Therefore, TFC membrane design must be specifically tailored for FO process. Among other characteristics

described in previous work [11, 19, 20], the TFC support layers must be designed to have good strength, high porosity, low tortuosity, and excellent wettability (hydrophilicity).

Electrospun nanofibers are a class of material that exhibits an intrinsically high porosity with an interconnected pore structure. These unique features make nanofiber mats promising candidates for TFC-FO membrane supports. The first generation of nanofiber based TFC-FO membranes has used conventional phase-inversion support materials such as Polysulfone [21] and polyethersulfone [21, 22]. Later, studies have reported membranes made of hydrophilic polymers such as polyacrylonitrile (PAN) [23], PAN/cellulose acetate (CA) blend [24], and PVA [25]. In our previous study, we have demonstrated the fabrication of a TFC membrane based on hydrophilic nylon 6,6 nanofibers [26]. High osmotic flux and low structural parameters were achieved for these membranes as a result of the fully wetted and interconnected porous structure. However, we have also noted that hydrophilic nanofibers undergo dramatic decreases in strength when exposed to water. We attributed this loss to fiber swelling, which weakens individual fibers and the junctions between fibers [26].

To address the swelling issue, we could use hydrophobic fiber with a surface modified to be hydrophilic. We would expect such fiber mats to exhibit good wetting properties but resist swelling because the core polymer would remain hydrophobic. Various surface modification techniques for nanofiber materials have been reported, including wet chemical treatment [27-29], surface graft polymerization [30, 31] and co-polymer electrospinning [32-34]. However, these methods have some inherent limitations and may not be suitable for nanofibers to be applied in liquid flow environments. For instance, wet chemical treatment, such as hydrolysis, involves destructive chemical reactions that may ultimately weaken the fiber mat. Surface graft polymerization usually requires plasma initiation to generate free radicals. Therefore,

modification conditions must be carefully controlled to avoid extensive functionalization that can introduce undesirable effects such as over modification of bulk properties, pore blocking/collapsing, or even fiber degradations [31, 35]. Furthermore, plasma or UV-initiated grafting can only impact the top surface of a fiber mat and will not penetrate beyond the first few fiber layers. Co-polymer electrospinning is limited by material selection (i.e. the compatibility between the hydrophobic polymer and hydrophilic agent in solvent system). Overall, a simple, universal and “non-destructive” modification technique is needed to hydrophilize the surface of hydrophobic nanofibers throughout the mat while not changing the bulk polymer properties.

In this study, a gentle modification approach involving deposition of interfacial polymerized nylon 6,6 onto fiber surface is adopted to impart a hydrophilic character to the hydrophobic PVDF nanofiber support. PVDF is chosen as the bulk material due to its extraordinary properties including easy process-ability, toughness, flexibility, and excellent chemical stability [36]. Nylon 6,6 deposition onto nanofibers was first introduced by Chen [37] as a method to adjust the pore size of nanofibers by controlling the number of reaction cycles. In this study, however, we utilize the hydrophilic nature of nylon 6,6 to modify the fiber surface to make it hydrophilic and to increase mat strength even when wet. We characterized the mechanical and structural properties of these mats and demonstrated their use as supports for TFC membranes for FO.

2 Materials and Methods

2.1 Materials

PVDF (M_w 550 kg/mol) was kindly provided by Solvay Specialty Polymers (Italy). N, N-dimethylformamide (DMF), methanol, toluene, hexane, isopropanol (IPA), sodium dodecyl sulfate (SDS), sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from

Fisher Scientific (Pittsburgh, PA). Tetrahydrofuran (THF), 1,6-hexanediamine, idipoyl chloride and triethylamine were purchased from ACROS organics. M-phenylenediamine (MPD, >99%) and trimesoyl chloride (TMC, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were analytical grade and were used as received without further purifications. Deionized water (DI) was obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA). A commercial polyester nonwoven fabric (PET, grade 3246, Ahlstrom, Helsinki, Finland) was used as a backing layer for spinning PVDF nanofibers. The thickness of the PET nonwoven is approximately 40 μm .

2.2 Preparation of PVDF nanofibers

PVDF powder was mixed in a co-solvent mixture of DMF and THF with 1:1 weight ratio overnight under room temperature to obtain a 13 wt% homogeneous solution. A volume of 3.0 mL of this solution was placed into a syringe pump and electrospun onto the PET backing layer using a laboratory-scale electrospinning system described elsewhere [21, 38]. The polymer solution was delivered to the spinneret at a fixed rate of 1.5 mL/hr. Nanofibers were generated by applying an electric potential of 20 kV at the working distance (i.e. the distance between the spinneret and the grounded collector) of 15 cm. The collector drum rotates at a speed of 70 rpm. The experiments were conducted at room temperature and 10-20% relative humidity. Under the selected spinning conditions, PVDF could be spun easily, producing high-quality fibers with very few defects or beads. The as-spun nanofibers were then heat-treated at 160 °C in a vacuum oven for two hours for further improvement of mechanical strength [39, 40]. Pure nylon 6,6 electrospun nanofibers were also prepared for comparison purposes. The method of spinning nylon 6,6 nanofibers was described in our previous work [26].

2.3 Surface modification with nylon 6,6

The modification method involves interfacial polymerization (IP) of 1,6-hexamethylene diamine and adipoyl chloride to form nylon 6,6. The reaction scheme was described elsewhere [37]. 1,6-hexanediamine was dissolved into methanol to form 10 g/L of diamine solution. The same amount of NaOH was added as an acid acceptor. The solution was stirred over 3 hrs. 5 g/L adipoyl chloride/toluene solution was used as the organic phase monomer solution.

The procedure of IP of nylon 6,6 onto PVDF nanofiber surface is as follows: the PVDF nanofiber mat was dipped into the diamine monomer solution for 120 s, followed by strong air-sweep to evaporate out all the methanol solvent, leaving a solid deposited diamine film on the fiber surface. When the support was dipped into the adipoyl chloride solution for 90 s, the IP reaction takes place at the solid–liquid interface. The formed membrane was then washed by methanol and water subsequently and finally dried at 60 °C for 15 min.

2.4 Polyamide selective layer formation

Aromatic polyamide TFC membranes were made via a polymerization reaction at the aqueous-organic phase interface. The aqueous phase contains 2.0% (wt/v) of MPD as the reagent, 2.0% (wt/v) of TEA as the acid acceptor, and 0.1% of SDS as a surfactant to reduce the surface tension at the interface. The organic phase solution is 0.15% (wt/v) TMC dissolved in hexane.

Due to the fact that the electrospun PVDF nanofibers are very hydrophobic (water contact angle can be as high as 150°), it is difficult to form a uniform liquid layer when they were brought into contact with the aqueous phase. As a result, it is a challenge to obtain a flawless and cohesive barrier layer via IP. Therefore, prior to the IP reaction, the unmodified nanofiber-PET supports were pre-wetted by 70% IPA/water and then rinsed with a large amount of DI to remove the residual IPA. Though the modified nanofibers in fact do not require pre-wetting due

to their improved hydrophilicity, they were still treated the same way in order to rule out the variation that could affect the IP process.

The IP process for making the thin film composite membranes onto both unmodified and modified PVDF nanofibers is as follows. First, the pre-wetted nanofiber mats were taped onto a glass plate with the nanofibers facing up. The nanofiber-PET supports were then immersed into an MPD solution for 120 s. Excess MPD solution was removed from the support membrane surface using a rubber roller. The nanofiber supports were then dipped into TMC solution for 60 s to form an ultrathin polyamide film. The resulting composite membranes were subsequently cured in an oven at 70 °C for 10 min. The TFC polyamide membranes were thoroughly washed with and stored in DI water at 4 °C.

2.5 Membrane characterization

Surface morphology and cross-sectional structure of both the modified and unmodified PVDF nanofibers and corresponding TFC membranes was imaged using a cold cathode field emission scanning electron microscope JSM-6335F (JEOL Company, USA). Cross-sectional samples were prepared for cross-sectional imaging using a freeze fracture technique involving liquid nitrogen. Before imaging, samples were kept overnight in a desiccator and then sputter coated with a thin layer of platinum to obtain better contrast and to avoid charge accumulation. ImageJ software was used to determine the average fiber diameter by measuring 40 different fibers. The thickness of the TFC membranes was measured using both a digital micrometer at 5 different locations for each membrane sample and cross-sectional SEM images.

The surface contact angle of both unmodified and modified PVDF nanofiber support was measured using a CAM 101 series contact angle goniometer (KSV Company, Linthicum

Heights, MD). The values were taken as an average of at least five points with a volume of $10 \pm 1 \mu\text{L}$.

Attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy (FT/IR 670 plus; Jasco, Easton, MD) was used to confirm the successful introduction of a nylon 6,6 coating layer onto PVDF nanofiber support. ATR-FTIR was also conducted on nylon 6,6 nanofibers for comparison purposes. Spectra were taken in with a variable angle attenuated total reflection (ATR) attachment coupled to a germanium crystal operated at 45° in an argon environment.

The water uptake of unmodified and modified PVDF nanofibers along with intrinsic hydrophilic nylon 6,6 nanofibers was examined using gravimetric analysis. Prior to the test, the PET backing layers were removed and nanofibers were dried in a vacuum oven under room temperature overnight. Dry samples were weighed, referring to W_{dry} , and then loaded into a dessicator which was already saturated with water vapor. Water vapor is used (rather than liquid water) to avoid having water fill the pores and bias the results. Samples were exposed to water vapor over 72 hrs to ensure saturated adsorption and then weighed, which were referred to W_{wet} . Water uptake can be determined using the following equation:

$$\text{Water uptake (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

The mechanical properties of the unmodified and modified PVDF nanofibers and their composite membranes were obtained from tensile tests in air at 25°C using a dynamic mechanical analyzer (TA Instruments, USA). For the modified PVDF nanofibers and its corresponding TFC membrane, it is important to understand whether wetting would degrade mechanical properties. Therefore, tests were also conducted on wetted samples by wetting the samples using DI after they were loaded into the instrument, and the result was compared with

nylon 6,6 nanofibers and its TFC membrane [26]. The PET backing layers were removed prior to tests for all samples. A controlled force module was selected and the loading rate was 0.25 N/min. A minimum of three strips of approximate length 40 mm $\times$ 5.5 mm were tested from each type of membrane.

2.6 Osmotic flux tests

Osmotic water flux and reverse salt flux of the unmodified and modified PVDF based TFC membranes were evaluated using a custom lab-scale cross-flow forward osmosis system. The experimental setup was described in detail elsewhere [19, 21, 26]. NaCl at concentrations of 0.5, 1.0, 1.5 and 2.0 M were used as the draw solutions while DI water was used as the feed solution. Osmotic flux tests were conducted with the membrane oriented in both PRO mode (the membrane active layer faces the draw solution) and FO mode (the membrane active layer faces the feed solution). The hydraulic pressures of the feed and draw solutions were the same (1.5 psi) and the cross-flow velocities were kept at 0.18 m/s for both the feed and draw solutions. The temperatures of the feed and draw solutions were maintained at 20 ± 1 °C using a recirculation water bath and a heat exchanger. For unmodified PVDF-TFC, some membranes were also pre-wet prior to test. Membranes were immersed in 50% IPA/water for a short amount of time (30 s) to saturate the entire pore structure without swelling fibers or causing any change of selective layer properties. All Membranes were tested with PET backing layers attached on.

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 a simply a ratio of salt flux to water flux, J_s/J_w .

2.7 Transport properties determination

Standard methodology of characterizing membrane transport properties involves both a RO test to measure pure water permeance, A , and solute permeability coefficient, B , and a FO test to determine the structural parameter S . However, an inherent limitation of this method is that it assumes the membrane properties are the same between two processes. This is usually not the case-. In RO, high hydraulic pressure is applied in order to obtain A and B . This places the membrane and the polyamide layer under stresses that are not present in FO. This method is especially problematic for weak membranes, as the high hydraulic pressure might damage the selective layer, giving an artificially high B value.

Tirafferri developed an alternative methodology for simultaneous determination of A , B and S only by means of a FO experiment run at multiple conditions [41]. This method is reliant on fitting flux data achieved at four stages of FO tests to a model by an error minimization algorithm and is sensitive to high data quality (i.e. consistency in J_s/J_w over four stages). The performance data of our lab-scale fabricated membranes, however, cannot meet these strict requirements.

Therefore, we have proposed a new methodology for measuring the transport properties of intrinsically weak FO membranes with low hydraulic pressure tolerance. In this method, A is measured under low-pressure (25 psi) RO using DI water as the feed. Membranes were tested with cross-flow velocity of 0.25 m/s at 20 ± 1 °C. B and S as the unknowns were determined in FO test mode by simultaneously solving the following equations describing water and reverse salt flux run at each concentration of the draw solutions used in this study.

:

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w S}{D}\right) - \pi_{F,b} \exp\left(\frac{J_w}{k}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w}{k}\right) - \exp\left(-\frac{J_w S}{D}\right) \right]} \right\} \quad (2)$$

$$J_s = A \left\{ \frac{c_{D,b} \exp\left(-\frac{J_w S}{D}\right) - c_{F,b} \exp\left(\frac{J_w}{k}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w}{k}\right) - \exp\left(-\frac{J_w S}{D}\right) \right]} \right\} \quad (3)$$

In these equations, $c_{D,b}$ and $\pi_{D,b}$ are the bulk concentration and osmotic pressure of the draw solution, respectively. $c_{F,b}$ and $\pi_{F,b}$ are the osmotic pressure at the membrane surface on the feed side, respectively (0 for DI feed). D is the diffusion coefficient of the draw solute, k is the external mass transfer coefficient that can be calculated from correlations for the cell geometry, and A is determined from the low-pressure RO test.

3 Results and discussion

3.1 Influence of nylon 6,6 modification on nanofiber properties

The surface morphology and cross-sectional structure of unmodified and modified PVDF nanofibers are shown in Fig. 1. Unlike on the smooth surface of unmodified PVDF, roughness can be observed in the modified PVDF fiber surface, and can be attributed to the formation of nylon 6,6. After modification the average fiber diameter increases slightly, though the increase is not statistically significant. In addition, the formed nylon 6,6 also accumulated on the fiber intersections and filled some voids. The cross-section SEM indicates that that the formed nylon 6,6 existed not only on the surface but throughout the interior fiber network as well, indicating nylon 6,6 modification technique does not limit to fibers on the support surface.

As shown in Table 1, the contact angle of pristine PVDF nanofibers is measured to be approximately 151 °, consistent with other studies on PVDF nanofibers [42]. After nylon 6,6 modification, the contact angle dramatically drops to 48 °, approaching the contact angle of intrinsically hydrophilic nylon 6,6 nanofibers (38 °) [26] due to the same surface chemistry. As discussed above, both the surface and the bulk support exhibit instant wettability, ensuring all the pores available for water and solute transport.

In addition to good wetting properties, osmotic membranes should have sufficient strength for manufacturing, processing, handling, and operation. Nanofibers in general, however, have poor strength, largely a result of low individual fiber strength and poor bonding between the fibers. We must therefore examine whether our modification technique further weakens the nanofibers. The mechanical properties of the pristine and modified PVDF nanofibers are shown in Table 1. Unlike some of the conventional surface modification techniques, nylon 6,6 coating can be considered as an “additive” technique as it simultaneously improves membrane hydrophilicity and mechanical properties. The modified nanofibers exhibit a slight increase in tensile strength, a 6-fold increase in Young’s modulus and a moderate decrease in flexibility (less elongation at break). Overall, these results indicate that the modified fibers are more rigid and slightly stronger. Modified nanofibers showed improved rigidity for two reasons. First, the formed composite structure between nylon 6,6 layer and PVDF bulk might improve the individual fiber strength. Second, when nylon 6,6 forms in the voids between fibers, it solders fibers at their junctions.

Figure 1 – FESEM images of (a) Top view of unmodified PVDF nanofibers. Inserted picture shows the surface contact angle. (b) Top view of nylon 6,6 modified PVDF nanofibers. Inserted picture shows the surface contact angle. (c) Cross-sectional view of unmodified PVDF nanofibers. (d) Cross-sectional view of nylon 6,6 modified PVDF nanofibers. All images were taken at magnification of 5000X.

Table 1 – Summary of properties of unmodified and modified PVDF nanofibers.

Sample	Unmodified	Modified
Average fiber diameter (nm)	860±350	930±280
Contact angle (°)	151±5	48±10
Thickness (No PET) (μm)	13.5±0.5	15.2±1.9
Tensile strength (MPa)	2.88±0.05	3.11±0.01
Young's Modulus (MPa)	4.2±0.3	26.1±2.5
Elongation at break (%)	200.7±19.5	167.8±36.2

3.2 Morphological study of TFC membranes

The cross-section microstructure and surface morphology of TFC membranes supported by both the unmodified and modified nanofibers were shown in Fig. 2. The thickness of both TFC membranes was approximately 15 μm without PET and 50 μm with PET. The top surface SEM indicated that the polyamide formed a continuous film which directly integrates with the top nanofiber layers for both supports. Imprints of nanofibers can be observed on the polyamide films for both membranes. Higher magnification SEMs shows a typical “ridge-and-valley” structure of polyamide with the “worm-like” feature that can be seen on commercial TFC membranes [20]. Generally, no noticeable morphological difference is observed on the selective layers of two TFC membranes, presumably because the same IP protocol was used for making both membranes. While the support layer properties have been shown to impact the polyamide properties in our previous work [43], we see no impact in this work. In our case, the modification does not dramatically change the fiber diameter and hence the pore diameter. The influence of support hydrophilicity on polyamide formation is also minimized by pre-wetting

both supports as well as using a surfactant. The result is a minimal variation of selective layer properties, such as A and B (Table 5), which will be discussed in greater detail in section 3.6.

Figure 2 – FESEM images nanofibers supported TFC membranes. (a) Cross-sectional view of unmodified-TFC without PET backing layer at 2000X. (b) Top view of unmodified-TFC at 2000X. (c) zoom-in of (b) at 10000X. (d) Cross-sectional view of modified-TFC at 2000X. (e) Top view of modified-TFC at 2000X. (f) zoom-in of (e) at 10000X.

3.3 ATR-FTIR spectra

Fig. 3 shows the ATR-FTIR spectra of unmodified and modified PVDF nanofibers and their TFC membranes. Peaks in all supports and composite membranes between 500 and 1400 cm^{-1} are characteristic of the PVDF. Compared to unmodified PVDF, modified PVDF exhibited two new peaks that are specific to C=O stretching of amide at 1661 cm^{-1} , and C-N stretching of amide II at 1544 cm^{-1} . These two characteristic peaks are also seen on nylon 6,6 spectrum. This verifies that nylon 6,6 coating layer has been successfully introduced onto PVDF nanofibers.

Figure 3 – ATR-FTIR spectrum of unmodified and modified PVDF nanofibers. Modified PVDF nanofibers was also compared with nylon 6,6 nanofibers.

3.4 Anti-swelling properties

Our prior study demonstrated that one major challenge of using intrinsic hydrophilic nanofibers in water separation is their high swelling propensity [26]. We therefore compared the swelling behavior of the surface modified PVDF and pure hydrophilic nylon 6,6 nanofibers. As shown in Table 2, pristine PVDF nanofibers have negligible water uptake (swelling) due to a low affinity for water. The modified PVDF nanofibers have water uptake of approximately 6%, which is largely attributed to the nylon 6,6 coating layer. In comparison, the water uptake of intrinsic hydrophilic nylon 6,6 nanofibers is nearly 80%. Results indicate that the modification

effectively imparts a hydrophilic surface to the nanofibers while maintaining a low degree of swelling.

One adverse effect of fiber swelling is the mechanical strength loss when used in water. Fig. 4 represents the mechanical properties change before and after water exposure for both modified PVDF and nylon 6,6 nanofibers along with their TFC membranes. For modified PVDF and its composite membrane, there seems to be no noticeable change of tensile strength after wetting. Nylon 6,6, on the other hand, exhibited approximately 40-50% reduction for both the nanofiber alone and composite membrane. With regard to the Young's Modulus, modified PVDF and its composite membrane only show slight decrease upon wetting, as compared to 4-5X reduction of rigidity for nylon 6,6 nanofibers and its membrane. The wetted nylon 6,6 is more flexible than modified PVDF even though it is a much stronger material when it is dry.

It is worth noting that swelling might not only reduce mat strength, but could also compromise the integrity of its tiered composite structure, especially the interaction between the PET backing layer and nanofiber mid-layer. We have noticed delamination of PET from nanofiber support occurred with some nylon 6,6 samples in the presence of water due to swelling behavior difference between hydrophilic nanofibers and hydrophobic PET. In addition, swelling might also reduce membrane flux performance by shrinking the pore structure. This mechanism will be further discussed in section 3.5. Overall, swelling is one of the major challenges that limit the ultimate utilization of intrinsically hydrophilic nanofibers in water separations, and surface modified hydrophobic nanofibers possess potential benefits as a membrane support with regard to their ability to better maintain membrane integrity and performance.

Table 2 – Water uptake of unmodified and modified PVDF and nylon 6,6 nanofibers. Dry samples were exposed to saturated water vapor at room temperature for over 72 hrs. The mass difference before and after water vapor exposure was used to determine water uptake.

Samples	Water uptake (%)
Unmodified PVDF	0.8 ± 0.7
Modified PVDF	6.3 ± 4.1
Nylon 6,6	78.2 ± 12.3

Figure 4 – Mechanical properties of modified PVDF and nylon 6,6 nanofibers: (a) Tensile strength. (b) Young's Modulus. PET layers were removed in these tests. Some Samples were also pre-wetted by DI water prior to tests.

*Nylon 6,6 and its TFC membrane data is from [26]

3.5 Osmotic Flux Performance of TFC Membranes

The osmotic water fluxes and reverse salt fluxes of the membranes are presented in Fig. 5 and Fig. 6, respectively. Unmodified PVDF membranes were tested in both pre-wet and dry states to illustrate two extremes of real membrane performance. For all membranes, Water flux increased with the increase of the NaCl concentration due to the increase of osmotic driving force. The water flux of each membrane in FO orientation is lower than that in PRO mode due to the more severe ICP induced by the salt accumulation inside the porous support. The pre-wetted unmodified PVDF membrane shows expectedly higher water flux than the dry one in both PRO and FO modes because improved wetting helps to increase effective porosity and reduce solute diffusion distance. However, the difference is more obvious in FO mode where solute must transport through the wetted pores to the interior interface of the polyamide layer. Similar to the pre-wetted PVDF-TFC, the modified PVDF-TFC also showed more improved water flux than the unmodified one in both modes, and its performance is approaching the pre-wetted one. The minor difference can be explained by the fact that nylon 6,6 modification might slightly decrease support porosity by filling the voids.

A similar trend is observed on reverse salt flux data (Fig. 6). Generally, increased water flux performance has been correlated with increased salt flux. For pre-wetted and modified PVDF membranes, the increased wetted porosity promotes salt diffusion through the support layer to enter the feed solution. Therefore, salts are diffusing out of the support layer with greater ease.

The modified PVDF-TFC is also compared with other lab-scale nanofiber based FO membranes [21, 24, 26, 36]. As shown in Table 3, our TFC membrane exhibited comparable water flux and specific salt flux to other nanofiber based TFC membranes, especially in FO

mode. Interestingly enough, the modified PVDF-TFC exhibited even higher water flux than intrinsic hydrophilic nylon 6,6 nanofiber membrane; this is notable given that the two membranes have similar thickness and pore structure and nylon 6,6 is slightly more hydrophilic than the modified PVDF. This in part could be a result of larger fiber size of modified PVDF that gives larger pore size. It has been found that pore size in fact plays an important role in influencing flux performance though it is not a characteristic of structural parameter [43]. Furthermore, it is likely a result of swelling in nylon 6,6 support layer that increases membrane thickness. Swelling may also cause shrinkage of pore structure, increasing the tortuosity and decreasing porosity. Similar effects have been observed on a commercial TFC-FO membrane [44] as well as a hydrophilic nanofiber TFC membrane [25]. The surface modified PVDF nanofibers that resist swelling effectively prevent this negative effect.

Figure 5 – Osmotic water flux performance of unmodified-TFC and modified-TFC membranes as a function of draw solution concentration in (a) PRO mode and (b) FO mode. Unmodified-TFC membranes were tested in both dry and pre-wetted state. *Experimental conditions:* $20 \pm 1^\circ\text{C}$; 0.5, 1.0, 1.5 and 2M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 18 cm/s on both sides of the membrane ($Re \sim 800$).

Figure 6 – Reverse salt flux performance of unmodified-TFC and modified-TFC membranes as a function of draw solution concentration in (a) PRO mode and (b) FO mode. Unmodified-TFC membranes were tested in both dry and pre-wetted state. *Experimental conditions:* $20 \pm 1^\circ\text{C}$; 1.0 M NaCl as the draw solution; DI water as the feed solution; cross-flow velocities of 18 cm/s on both sides of the membrane

Table 3 – Comparison of modified-TFC FO performances to other nanofiber based TFC membranes. All membranes were tested using DI water as the feed.

	Membranes	Draw solution	Water flux	Specific salt flux	reference
PRO mode	modified		31	0.43	This work
	Nylon 6,6	1.0M NaCl	21	0.14	[26]
	PVDF		48	0.45	[36]
	Modified		41	0.47	This work
	PVDF	1.5M NaCl	62	0.63	[36]
	PAN		52	0.06	[24]
	PSu		24	0.36	[21]
	Modified		22	0.17	This work
FO mode	Nylon 6,6	1.0M NaCl	15	0.03	[26]
	PVDF		28	0.46	[36]
	Modified		30	0.30	This work
	PVDF	1.5M NaCl	35	0.48	[36]
	PAN		29	0.29	[24]

3.6 Transport properties determination

The selective layer properties (i.e. A and B) and support structural parameter of unmodified (both pre-wet and dry) and modified PVDF membranes are shown in Table 4. Generally, there is no significant difference of A and B among three membranes within the standard deviation. Again, this is due to the careful control of IP process as well as the addition of pre-wetting step to minimize the effect of hydrophilicity on polyamide formation.

Upon wetting, the structural parameter dramatically decreases from 2410 μm to 160 μm largely a result of increasing porosity available for water and solute transport. The modified nanofiber exhibited slightly higher structural parameter than the pre-wetted one probably due to the slightly reduced porosity. Overall, this result verifies the importance of support wetting, even for a high porosity material like nanofiber. The structural parameter of modified nanofibers is among the lowest ones reported in literature, especially considering these supports also include a PET substrate.

Table 4 – Summary of pure water permeance (A), solute permeability (B) and structural parameter (S) of TFC membranes. A was determined in RO test (*Experimental conditions*: pure water feed solution; cross-flow velocity of 0.25 m/s; 25 psi applied pressure; and temperature of 20°C). B and S were determined in FO tests (*Experimental conditions*: pure water feed solution; 0.5, 1, 1.5 and 2M NaCl draw solutions; cross-flow velocity of 0.18 m/s; and temperature of 20°C) by fitting A into Eqn. (2) and (3) and simultaneously solve these two equations. B and S were averaged from numbers determined at each concentration of draw solution.

Membranes	A (LMH/Bar)	B (LMH)	S (μm)
Unmodified-TFC	1.42 $\pm$ 0.16	0.11 $\pm$ 0.02	2410 $\pm$ 930
Unmodified-TFC pre-wet	1.51 $\pm$ 0.13	0.25 $\pm$ 0.10	163 $\pm$ 15
Modified-TFC	1.28 $\pm$ 0.36	0.25 $\pm$ 0.11	193 $\pm$ 22

4 Conclusions

This study investigates the feasibility of using surface modified hydrophobic PVDF nanofibers as the support to make TFC-FO membrane. Using the nylon 6,6 modification approach, we were able to improve surface hydrophilicity and mechanical properties of nanofibers without greatly changing the nanofiber mat morphology and pore structure. The modified PVDF nanofibers exhibit instant wettability, but substantially lower swelling tendency and less weakening than hydrophilic nylon 6,6 nanofibers when used in water. The resulting TFC membrane showed one of the lowest structural parameters reported in the literature. The concept of using a hydrophobic support that has been surface modified to impart hydrophilicity has application in other substrate types as well.

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