Hydrophilic nylon 6,6 nanofibers supported thin film composite membranes for engineered osmosis

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ABSTRACT

Previous studies have concluded that an ideal thin film composite (TFC) membrane specially designed for Engineered Osmosis (EO) should have an ultra-thin selective layer with excellent permselectivity supported by a hydrophilic, highly porous, non-tortuous and thin support structure. In this study, an emerging TFC supporting material, electrospun nanofibers, were used to fabricate a TFC-EO membrane where the support structure and the selective layer properties were individually optimized. Specifically, nylon 6,6 nanofibers fabricated via electrospinning were used for the first time to form the support structure due to its intrinsic hydrophilicity and superior strength compared to other nanofiber materials. The resulting membrane exhibited half of the structural parameter of a regularly used commercial FO membrane. Furthermore, the selective layer permselectivity could be adjusted using a co-solvent during the interfacial polymerization processes. Adding acetone to the organic phase (hexane) was found to increase permeance and decrease selectivity and hence affect the osmotic flux performance of our membranes. Our best membrane outperformed the standard commercial FO membrane by exhibiting a 1.5 to 2 fold enhanced water flux and an equal or lower specific salt flux.

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1. Introduction

Engineered Osmosis (EO) is an emerging platform technology that harnesses the natural phenomenon of osmosis to address water and energy scarcity [1–3]. In this process, an osmotic pressure difference is generated when two solutions of differing concentration are placed on two sides of a semi-permeable membrane. This difference drives the permeation of water across the membrane from the dilute solution to the concentrated solution. The potential of this technology has been demonstrated in a variety of applications, such as forward osmosis (FO) for seawater desalination [4–7], pressure retarded osmosis (PRO) for electric power generation [8–11], and direct osmotic concentration (DOC) for recovering high-value solutes [12–14]. However, EO processes have not yet become commercialized on a large scale. One major obstacle is the lack of a membrane specifically designed for any of these processes [15–18].

Recently, aromatic polyamide thin film composite (TFC) membranes have become more common as a platform EO membranes. They have begun to replace more conventional asymmetric integral membranes in both flat-sheet [15,17–20] and hollow fiber forms [16,21,22] due to their superior permselectivity.

Furthermore, TFC membranes are more flexible in their design as both the selective and support layers can be independently tailored. While this flexibility accelerated the widespread adoption of reverse osmosis (RO) [23]. Membranes designed for EO must have specific, these membranes performed poorly during early work on the development of osmotic processes [5,24,25]. The hydrophobic cast polysulfone (PSu) support layer and the thick nonwoven fabric baking layer of a conventional TFC membrane [26–28] cause 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 [5,25,29–31].

Membranes tailored for EO must be designed based on specific criteria related to their structure and chemistry. The selective layer must have excellent permeance and selectivity. The support layer must be thin and have a highly porous and interconnected (low tortuosity) structure. The support layer must also be hydrophilic, allowing for complete saturation (i.e. wetting) throughout the structure [32]. Lastly, the membrane as a whole must exhibit excellent chemical and thermal stability while retaining reasonable mechanical strength.

In our previous study, we demonstrated the fabrication of a novel TFC membrane based on a commercially-available hydrophilic nylon 6,6 microfiltration membrane [33]. This TFC membrane exhibits

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higher flux and selectivity compared to a commercially available FO membrane despite the fact that it has a structural parameter 3 times higher than that membrane (about 2000 μm). The improved performance can be attributed to the relatively good permselectivity of the polyamide film coupled with hydrophilicity of the support. We hypothesized that the performance could be further improved by reducing the structural parameter. This can be achieved by replacing this cast support with a thinner, more porous, and less tortuous nylon 6,6 structure.

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-EO membrane supports. Recently, a few studies have been reported on designing TFC-EO membranes based on PSu [20], polyethersulfone (PES) [20,34], polyacrylonitrile (PAN) [35], Polyvinylidene fluoride (PVDF) [36] and PAN/cellulose acetate (CA) blends as an electrospun nanofiber support [37]. High osmotic flux and low structural parameters were achieved for these membranes as a result of the intrinsically high porosity and low tortuosity of the nanofiber mats. Despite the promising flux performance of this new class of TFC-EO membrane, the potential of nanofiber based TFC membranes has not been fully developed considering the large number of materials that are spinnable and post-modifications that can further improve the properties of the nanofibers.

This study introduces a novel type of flat-sheet polyamide TFC membrane supported by a nonwoven web of nylon 6,6 nanofibers spun onto a commercial nonwoven fabric. Nylon 6,6 polymer is a suitable material as a nanofiber support considering its intrinsic hydrophilicity, good mechanical properties, and excellent compatibility with a polyamide selective film [33]. The polyamide selective layer was polymerized in situ onto the nanofiber support using interfacial polymerization (IP). This method is commonly applied in fabricating RO membranes, We have modified the method using the approach reported by Kong et al. [38] referred to as co-solvent assisted interfacial polymerization (CAIP) where a co-solvent (acetone) (Ac) was added to a nonpolar organic (hexane) phase to form a miscibility zone in the hexane/water/acetone system. When a co-solvent is added the reaction zone is changed because of the change in miscibility of the two solutions at the interface. By changing the amount of acetone, we can adjust the permselectivity of the polyamide layer over a wide range. This CAIP approach would help us to understand the support-selective layer interactions as well as structure–performance relationships for this new nanofiber support based TFC-EO membranes. Knowledge of these relationships will provide valuable insight into designing future TFC membranes with low structural parameter supports.

2. Experimental

2.1. Materials

Nylon 6,6 (M_W 262.35), Dichloromethane (DCM, anhydrous, >99.8%), m-phenylenediamine (MPD, >99%) and trimesoyl chloride (TMC, 98%) were purchased from Sigma-Aldrich (St. Louis, MO). Formic acid (FA, 88%, Laboratory), hexane (HPLC, >98.5%), Acetone (Ac, certified ACS) and sodium chloride (NaCl, crystalline, certified ACS) were purchased from Fisher Scientific (Pittsburgh, PA). Deionized water (DI) was obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA). Commercial asymmetric cellulose triacetate (HTI-CTA) FO membrane (Hydration Technology Innovations Inc., Albany, OR) were acquired for comparison and these membranes were designated as HTI hereafter. Polyester nonwoven fabric sheet (PET, Novatexx 2442)

was supplied by Freudenberg (Weinheim, Germany). The thickness of the PET nonwoven is approximately 60 μm.

2.2. Electrospinning nylon 6,6

FA is a commonly used solvent for preparing nylon 6,6 electrospinning solution [39–41]. However, our preliminary work shows that nylon 6,6 dissolved in FA is relatively difficult to spin probably due to the fact that FA has a relatively low vapor pressure. In this study, DCM, a low-boiling point and inexpensive solvent was blended with FA to increase the solvent evaporation rate [42]. The best ratio of FA and DCM solvents was found to be 8:2 in order to facilitate fiber spinning while still maintaining reasonable adhesion between the electrospun nonwoven mid-layer and the PET backing layer [43–46]. Higher ratio of DCM might result in nanofibers drying before depositing onto the PET, preventing good adhesion to other deposited fibers or to the PET substrate. Higher ratio of FA, on the other hand, might not yield high quality fibers or might results in fibers dissolving after deposition.

The nylon 6,6 electrospinning parameters are summarized in Table 1. Nylon 6,6 pellets were mixed in a co-solvent mixture of FA and DCM overnight under room temperature to obtain 10 wt% homogeneous solution. A volume of 2.5 mL of this solution was electrospun onto the PET backing layer under a potential field of 25 kV to form a nanofibrous mat. The experiments were conducted at ambient temperature and humidity using a system described in our previous study [20,45]. Under the selected spinning conditions, nylon 6,6 could be spun easily, producing high-quality fibers with very few defects and beads.

2.3. Polyamide formation

Both conventional IP and CAIP were employed to form polyamide selective layers onto the nylon 6,6 to fabricate the TFC membranes. The conventional IP process is as follows. First, the nylon 6,6 nonwoven mats spun onto a PET were taped onto a glass plate with the nanofibers facing up. The nanofiber-PET support was immersed into a 1.0% (wt/v) aqueous MPD solution for 120 s. Excess MPD solution was removed from the support membrane surface using an air knife. The nanofiber supports were then dipped into a solution of 0.15% (wt/v) TMC in hexane for 60 s to form an ultrathin polyamide film. The resulting composite membranes were subsequently cured in an air-circulation oven at 70 °C for 10 min to attain the desired stability of the formed structure. The TFC polyamide membranes were thoroughly washed and stored in DI water at 4 °C.

The CAIP membranes were prepared using the same process with Ac co-solvent added into the TMC/hexane organic phase.

Table 1
Summary of electrospinning conditions for nylon 6,6 nanofibers support.

Conditions	
Polymer	Nylon 6,6
Solvent	80% FA/20% DCM
Concentration	10 wt%
Voltage	28 kV
Flow rate	0.8 ml/hr
Tip-to-target distance	8 cm
Drum rotating speed	30 rpm
Total volume of solution	2.5 ml
Area of the collector surface	90 cm^2