Desalination 308 (2013) 73–81

Contents lists available at SciVerse ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Nanofibers in thin-film composite membrane support layers: Enabling expanded application of forward and pressure retarded osmosis

Laura A. Hoover [a], Jessica D. Schiffman [b], Menachem Elimelech [a,*]

[a] Department of Chemical and Environmental Engineering, P.O. Box 208286, Yale University, New Haven, CT 06520-8286, USA
[b] Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, Massachusetts 01003-9303, USA

HIGHLIGHTS

- ► Thin-film composite membranes for forward and pressure retarded osmosis were fabricated.
- ► Electrospun mats served as a base onto which a support layer was formed by phase separation.
- ► Thin-film composite membranes had high salt rejection and high water flux in forward osmosis.
- ► Membrane resistance to shear stress and hydraulic pressure was evaluated.
- ► Nanofibers enmeshed with microporous layer to enhance resistance to delamination.

ARTICLE INFO

Article history:
Received 1 April 2012
Received in revised form 16 July 2012
Accepted 20 July 2012
Available online 4 August 2012

Keywords:
Forward osmosis
Pressure retarded osmosis
Electrospinning
Mechanical properties
Thin-film composite membrane

ABSTRACT

Re-engineering the support layers of membranes for forward and pressure retarded osmosis is critical for making these technologies commercially viable. Real-world applications of forward and pressure retarded osmosis, especially those involving natural and waste waters, will require membranes to withstand significant stresses. Therefore, structural changes to the support layer, which are necessary in minimizing internal concentration polarization, must not compromise its critical abilities to resist mechanical stress and provide a suitable surface for the interfacial polymerization of a robust and selective active layer. Electrospinning can provide nanofibers for support layers to potentially overcome the limitations of traditional membrane fabrication techniques in fulfilling these challenging design criteria. In this work, we present the fabrication and evaluation of thin-film composite membranes composed of electrospun polyethylene terephthalate nanofibers, a phase separation formed microporous polysulfone layer, and a polyamide selective layer formed by interfacial polymerization. These membranes have active and support layer transport properties that are suitable for engineered osmosis, with water permeability of 1.13 L m^{-2} h^{-1} bar^{-1} (3.14×10^{-7} m s^{-1} bar^{-1}), salt permeability of 0.23 L m^{-2} h^{-1} (6.4×10^{-8} m s^{-1}), and a structural parameter of 651 μm. Relevant and easily reproducible tests for membrane resistance to mechanical stress were performed. The use of electrospun fibers in the support layer enhanced membrane resistance to delamination at high cross-flow velocities because the 340 nm diameter electrospun fibers enmesh with the microporous polysulfone layer. A broader discussion of the most promising approaches for using electrospun materials to improve membranes for engineered osmosis is provided.

1. Introduction

Engineered osmosis, the membrane-enabled harnessing of chemical potential energy in the form of osmotic pressure differences, has been proposed as a technology that can re-shape the modern water and energy sectors to more sustainably support human life and health [1–5]. Engineered osmosis refers collectively to forward osmosis (FO), a potentially low energy and waste utilizing separation process, and pressure retarded osmosis (PRO), a means of generating electricity from natural or anthropogenic salinity gradients. The use of a semipermeable membrane to reject solutes and maintain a high osmotic pressure difference while permitting high water flux is key to both FO and PRO.

Current membrane design is based on reverse osmosis (RO) thin-film composite (TFC) membranes, which demonstrate the perm-selectivity, chemical resistance, and mechanical properties required of engineered osmosis membranes. However, the mechanical integrity of RO membranes is provided by support layers that limit performance in engineered osmosis through internal concentration polarization [6]. The extent to which a support layer structure will cause internal concentration polarization is quantified by the structural parameter, S, given by $S = t \cdot \tau / \varepsilon$, where t, τ, and ε are respectively the thickness, tortuosity, and porosity of the membrane support layer [7,8]. Studies have shown that RO-type TFC membranes can be re-designed to dramatically reduce the structural

---

* Corresponding author. Tel.: +1 203 432 2789; fax: +1 203 432 4387.
E-mail address: menachem.elimelech@yale.edu (M. Elimelech).

0011-9164/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.desal.2012.07.019

parameter and enhance osmotically driven water flux [8–13]. Both the support structure and the active layer properties that maximize water flux while maintaining sufficient salt rejection have been investigated [14].

Recent efforts to enhance the transport properties of TFC membranes for engineered osmosis have mostly ignored the importance of mechanical integrity. While the high hydraulic pressures employed in RO are not present in engineered osmosis, membranes will experience significant mechanical stress. PRO performs most efficiently at an operating pressure equal to approximately half of the effective difference in osmotic pressure. Both FO and PRO membranes could be damaged by the high cross-flow velocities used to mitigate fouling and external concentration polarization at their surfaces. Furthermore, FO and PRO membranes must withstand these pressures and shear forces with far less external support than that provided in pressure driven membrane processes.

Membrane support layers with mechanical and transport properties customized for engineered osmosis can potentially be produced via electrospinning. This fabrication technique uses electrostatic forces to produce mats of continuous micro- or nanoscale fibers with high strength-to-weight ratios [15,16]. The chemical and mechanical properties of these fiber mats can be optimized via material selection and post-treatments. A wide variety [17,18] of polymers, solvents, and additives, each with their own unique material properties, can be combined in an electrospinning solution to fabricate fibers. Fiber morphology, surface chemistry, and mechanical properties can be further influenced through the adjustment of electrospinning conditions or post-processing of the as-spun fibers. Additionally, the structural properties of an electrospun fiber mat match the ideal values for each term in the structural parameter, $S = t \cdot \tau / \varepsilon$. Fiber mats typically have high porosity, their interconnected void space minimizes tortuosity, and their thickness can be easily customized.

Electrospun nanofiber mats could replace either or both of the materials traditionally found in a TFC membrane: the polyester non-woven fabric base or the phase separation-formed microporous polysulfone or polyethersulfone support layer. Recently, two studies in which the phase separation-formed layer was replaced with an electrospun support have been published [19,20]. Both studies obtained membranes with a low structural parameter. However, these studies provide little or no examination of the mechanical integrity of the fabricated membranes, and one [19] noted difficulty with active layer selectivity and delamination. Given what is known about the importance of the chemistry and structural characteristics of the support layer surface in interfacial polymerization [9,21–25], forming selective layers directly on electrospun supports may be challenging.

This study presents the first TFC membranes fabricated with electrospun and phase separation formed support layers. Scanning electron microscopy revealed a unique support layer structure having electrospun fibers enmeshed with the microporous polysulfone layer. Transport properties of the active and support layers were experimentally quantified. Methods that reflect real-world membrane operation were devised to evaluate membrane resistance to hydraulic pressure and to high cross-flow velocities. The fabricated membranes demonstrated transport properties suitable for engineered osmosis and enhanced mechanical robustness. Membrane performance and structure were considered together to gain insight into the connections between membrane fabrication, form, and function.

2. Materials and methods

2.1. Materials

All materials were used as received. Polyethylene terephthalate (PET), polysulfone (PSf, $M_n = 22{,}000$ Da), trifluoroacetic acid (TFA, 99%), 1-methyl-2-pyrrolidinone, (NMP, anhydrous, 99.5%), m-phenylenediamine, (MPD, >99%), 1,3,5-benzenetricarbonyl trichloride (TMC, 98%), sodium hypochlorite (NaOCl, reagent grade), and sodium bisulphite ($NaHSO_3$, >99%) were purchased from Sigma-Aldrich (St. Louis, MO). Acetone (99.9%) was purchased from J.T. Baker (Phillipsburg, NJ). Isopar-G, a proprietary non-polar organic solvent, was purchased from Univar (Redmond, WA). A commercial wet-laid PET fabric (wlPET, grade 3249, Ahlstrom, Helsinki, Finland) was used in the control membranes. For the solutions used in membrane performance tests, sodium chloride (NaCl, crystals, ACS reagent) from J.T. Baker was dissolved in deionized (DI) water obtained from a Milli-Q ultrapure water purification system (Millipore, Billerica, MA).

2.2. Thin-film composite membrane fabrication

2.2.1. Electrospun PET support layer fabrication

The electrospinning solution and conditions were similar to those used by Veleirinho et al. [26]. PET in TFA (1.5 g in 5 mL corresponding to 30%, w/v) solutions were mixed for at least 3 h using a Tube Rotator (VWR, Bridgeport, NJ). Approximately 4 mL of the solution was loaded in a Luer-Lok Tip syringe (Becton Dickinson & Co., Franklin Lakes, NJ), to which an 18 1/2 gauge Precision Glide needle (Becton Dickinson & Co.) was attached. The loaded syringe was then secured in an advancement pump (KD Scientific, Holliston, MA), which was located at a fixed needle-to-collection plate separation distance of 11 cm. The speed of the advancement pump was set at 0.87 to 0.90 mL/h. The collector plate comprised a 3 mm thick glass plate (160 mm × 240 mm) backed by a conductive copper plate. Alligator clips connected the needle tip to the positive electrode of a voltage supply (Gamma High Voltage Research, Ormond Beach, FL) and the collector to the negative electrode. An applied voltage of 21.0 to 22.5 kV was employed. The entire electrospinning apparatus [27] was housed in a controlled environment chamber (Electro-Tech Systems, Glenside, PA), inside which the temperature was 27 ± 5 °C and the relative humidity 20 ± 5%. Residual TFA vapor was vented to a fume hood.

2.2.2. Polysulfone porous support fabrication

A microporous layer of PSf was cast over the wlPET according to the procedure outlined previously by Tiraferri et al. [9]. A casting solution of 12 wt.% PSf in NMP was stirred for 8 h and then stored in a desiccator for at least 15 h prior to casting. Laboratory adhesive tape was used to fix the wlPET to a glass plate (3 mm × 160 mm × 240 mm). The wlPET was wet with NMP, and the excess NMP was removed using Kimwipes (Kimberly-Clark, Roswell, GA). The casting solution was drawn over the wlPET using a casting knife (Gardco, Pompano Beach, FL) with a gate height of 6 mils (~150 μm). The glass plate, with the layers of wlPET and PSf, was immediately transferred into a precipitation bath of 3 wt.% NMP in DI water at room temperature (22 ± 1 °C), where phase separation occurred. The assembly remained in the precipitation bath for 10 min and was then transferred to a room temperature DI water bath, where it remained until the polyamide active layer was fabricated.

A similar procedure was used to cast a microporous layer of PSf over the electrospun PET (ePET). A layer of ePET (approximately 10 to 65 μm thick) was electrospun onto a glass plate. The edges of the ePET were fixed to the back and sides of the plate using electrical tape and superglue (Loctite Control Gel Super Glue, Henkel Corporation, Düsseldorf, Germany). The ePET was wet with acetone, and the excess acetone was allowed to vaporize. All subsequent PSf and polyamide casting procedures were identical for wlPET and ePET.

2.2.3. Polyamide active layer fabrication

A thin, dense layer of polyamide was cast on the PSf surface of the wlPET–PSf and ePET–PSf membranes using the interfacial polymerization method previously described [8,9]. Briefly, the PSf surface of the PET–PSf support was contacted with an aqueous solution of 3.4% MPD for 120 s. The excess solution was removed, and the PSf surface