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Fabrication and characterization of a surface-patterned thin film composite membrane

Sajjad H. Maruf, Alan R. Greenberg, John Pellegrino, Yifu Ding *

Membrane Science, Engineering and Technology Center, Department of Mechanical Engineering, 427 UCB, University of Colorado Boulder, 1111 Eng. Drive, Boulder, CO 80309-0427, USA

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ABSTRACT

Thin film composite (TFC) membranes are critical components for reverse osmosis (RO) and nanofiltration (NF) processes. Similar to other liquid-based filtration membranes, TFC membranes are susceptible to concentration polarization and fouling/scaling. Recently, surface topography modification has been shown as a potential approach for fouling mitigation. However, for TFC membranes, tailoring the surface topography remains a challenge. Here, we demonstrate for the first time, successful fabrication of a patterned TFC membrane. A two-step fabrication process was carried out by (1) nanoimprinting a polyethersulfone (PES) support, and (2) forming a thin dense film atop the PES support via interfacial polymerization (IP) with trimesoyl chloride and 1,3-phenylenediamine solutions. Chemical, topographic, and permeation characterization was performed on the imprinted IP membranes, and their permselectivity was compared with that of a flat (non-imprinted) TFC membrane prepared using the same IP procedure.

1. Introduction

Thin film composite (TFC) membranes have experienced remarkable development since the concept of interfacial polymerization (IP) was introduced [1]. Cadotte and co-workers developed the first TFC membrane that has since become the most widely used membrane for a multitude of reverse osmosis (RO) and nanofiltration (NF) applications [2]. Among the different types of TFC membranes, the use of a crosslinked aromatic polyamide thin film as a barrier layer is a highly-cited chemistry [3–5]. TFC membranes have become the industry standard over the last several decades because of continuing research and development efforts that improved their selectivity and permeability together with excellent mechanical strength and fouling resistance by modifying both the barrier layer and the porous support [2,6].

A crosslinked aromatic (or semi-aromatic) polyamide barrier layer in TFC membranes is typically formed over the porous supports via in-situ IP of a poly-functional amine and an acid chloride at the organic solvent/aqueous solution interface [7,8]. Often, ultrafiltration (UF) membranes based on polysulfone (PS), polyethersulfone (PES) and polyvinylidene fluoride (PVDF) are used as the porous support [9,10]. Like other liquid-filtration membranes, TFC membranes are subject to concentration polarization and fouling, which reduce membrane performance during filtration [11]. Hence, much research continues to be carried out to address fouling issues, including various chemical treatments, adsorption of surfactants, low-temperature plasma treatments, irradiation methods and addition of hydrophilic particles on the membrane surface [7,12]. By comparison, the use of controlled surface topography to mitigate concentration polarization or fouling in TFC membranes has been scarce mainly due to the lack of methods to create targeted topography on the membrane surface. The nature of the IP process, i.e. fast reaction at the organic/water interface, presents a major obstacle for tailoring the structures and properties of the polyamide barrier layers [13,14].

On the other hand, a patterned surface has been proven effective for controlling cellular responses [15,16], which can be utilized as an effective anti-fouling approach. A polydimethylsiloxane (PDMS) surface containing sharkskin-like micropatterns [17] showed a ~86% reduction in the settling density of spores when compared with an otherwise similar, but smooth, PDMS surface. The extension of surface patterning to membranes has been previously reported in the literature. Micro-molding in combination with phase inversion has been utilized to fabricate surface-patterned flat membranes [18], as well as hollow fiber membranes [19,20]. Using this method, Won et al. created PVDF microfiltration (MF) membranes with ~10 μm-scale features [21], which resulted in reduction of microbial fouling [22]. Recently, we demonstrated the use of nanoimprint lithography (NIL) to impart sub-micron surface patterns directly onto a commercial PES UF

* Corresponding author. Tel.: +1 303 492 2036; fax: +1 303 492 3498.
E-mail address: yifu.ding@colorado.edu (Y. Ding).

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membrane without sacrificing its permselectivity [23,24]. The presence of these patterns significantly reduced deposition of both colloidal particles and protein during filtration.

In this study, we report the first fabrication of a functional TFC membrane with well-controlled surface patterns. The two-step fabrication process consisted of forming a dense polyamide barrier layer via IP atop a nanoimprinted UF support membrane. Systematic characterization of the patterned TFC membrane was carried out, and the results show that this approach can indeed create reliable TFC membranes with separation performance comparable with current commercial TFC RO/NF membranes. The comparison between the patterned and non-patterned TFC membrane indicates that surface patterns can be an effective approach to mitigate concentration polarization and scaling.

2. Experimental

2.1. Fabrication of patterned and non-patterned TFC membranes

Patterned TFC membranes were fabricated via a two-step process that consisted of (1) nanoimprinting a PES support, and (2) forming a thin dense film atop the PES support via IP process. A commercial PES UF membrane (PW, GE Water and Infrastructure) with a nominal 30 kg/mol molecular mass cutoff (MWCO) was used as the substrate on which the polyamide thin film was hand-cast via IP. The nanoimprinting process for the UF membrane was described in detail in our previous work [24]. Briefly, the NIL process was carried out in an Eitrie 3 (Obducat, Inc.) nanoimprinter, using a silicon mold containing parallel line-and-space gratings (a periodicity of 834 nm, groove depth of 200 nm, and a line-to-space ratio of 1:1). The Si mold surface was treated with a Piranha® solution (3:1 concentrated sulfuric acid to 30% hydrogen peroxide solution) prior to the imprinting. The NIL process was carried out at 120 °C with a pressure of 4 MPa for 180 s, and the mold was separated from the membrane samples at 40 °C. The imprinted UF membranes were cleaned with and stored in de-ionized (DI) water in the dark until forming the polyamide layer. Non-patterned TFC membranes that served as a reference were fabricated using the same IP process on the PES UF membranes.

Both patterned and non-patterned UF membranes were taped to a glass plate with the skin layer facing upwards, and placed in an aqueous amine monomer solution (Fig. 1). The aqueous amine solution was prepared by adding 2 g of triethylamine (TEA, 99.5%, Sigma Aldrich), and 4 g of (+)10-camphor sulfonic acid (CSA, 99.0%, Sigma Aldrich), to ~80 mL of DI water under vigorous stirring. CSA improves the absorption of the amine solution in the support membrane, while TEA accelerates the MPD–TMC reaction [25]. After complete dissolution of the TEA–CSA mixture, DI water was added to reach a total solution of 100 mL. Next, 2 g of 1, 3-phenylenediamine (MPD, Sigma Aldrich) was added to the TEA–CSA solution. The entire UF membrane was then immersed in the aqueous MPD–TEA–CSA solution for 8 s, and the excess solution on the membrane surfaces was removed with an air blower. Subsequently, the amine-soaked UF membrane was immersed in a hexane solution (Fisher scientific) containing 0.1% (w/v) trimesoyl chloride (TMC, 99%, Sigma-Aldrich) for 8 s. The resulting membrane was withdrawn from the hexane solution, cured at 70 °C for 10 min, and washed thoroughly with DI water. Here, the protocols for the polyamide thin film formation were based on the formulation used by Ghosh et al. with the exception of a much shorter IP exposure time [9,25]. Finally, the as-prepared TFC membranes,

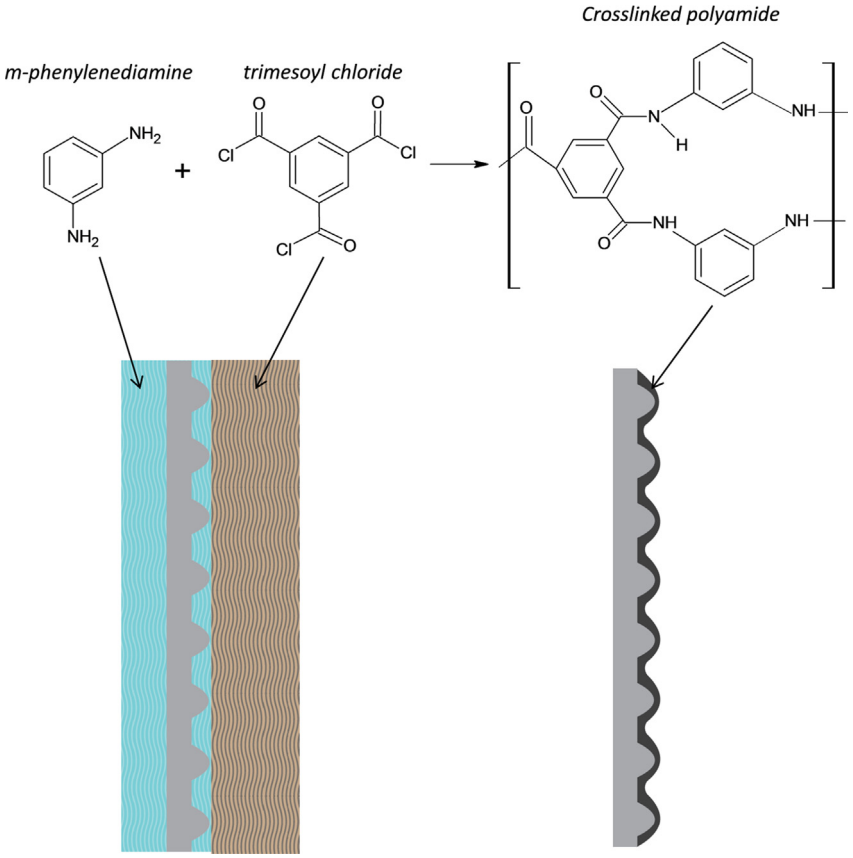

Fig. 1. A schematic representation of the interfacial polymerization process used to fabricate the patterned TFC membranes. The monomers *m*-phenylenediamine and trimesoyl chloride react to form a highly cross-linked polyamide layer atop the patterned polyethersulfone UF membrane used as a support.