Journal of Membrane Science 512 (2016) 50–60

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Influence of substrate processing and interfacial polymerization conditions on the surface topography and permselective properties of surface-patterned thin-film composite membranes

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ARTICLE INFO

Article history:
Received 22 January 2016
Received in revised form
2 March 2016
Accepted 2 April 2016
Available online 5 April 2016

Keywords:
Thin film composite membrane
Interfacial polymerization
Barrier layer
Reverse osmosis
Nanofiltration

ABSTRACT

The influence of substrate topography and interfacial polymerization (IP) conditions were investigated during the fabrication of patterned thin-film composite (TFC) membranes. Aromatic and semi-aromatic polyamide layers were formed atop patterned ultrafiltration (UF) membrane supports by IP using different concentrations of m-phenylenediamine (MPD) or piperazine (PIP) in water of 0.01–2% w/v with a fixed concentration of trimesoyl chloride in hexane of 0.1% w/v. For all the conditions evaluated, TFC membranes with regular surface patterns were achieved by maintaining amine soaking time and IP reaction time within 120 s. Importantly, the surface topography of the patterned TFC membranes was determined to be independent of IP reaction time. Characterization of the morphological details suggests non-conformal growth of the barrier layer on the patterned UF substrates. Results indicate that the extent of such non-conformal growth can be reduced by decreasing the amine concentration as well as by choosing an amine monomer such as PIP that produces a thinner semi-aromatic barrier layer. The overall findings of this study provide a means for achieving desired surface features for specific membrane applications.

1. Introduction

Thin-film composite (TFC) membranes are commonly used in reverse osmosis (RO) and nanofiltration (NF) processes for applications including desalination, wastewater treatment, and organic fractionations [1–3]. Despite the significant progress achieved, these membrane-based processes remain relatively energy intensive [4]. Approaches that can reduce the operational costs are critically needed for these membrane-based processes to be adopted on a much larger scale.

Liquid-based separation processes generally suffer from performance decline associated with the membrane fouling. Reduction of membrane fouling is one of the most challenging tasks affecting the field and one that offers the prospect of improving the energy efficiency of the separation processes in a substantial way [5,6]. The key to fouling mitigation is control of the interactions between the foulants and the membrane surfaces. In this regard methods that can enhance the back-diffusion of the foulants away from the membrane surface during separation are particularly promising for fouling reduction. Recently, studies have demonstrated that the presence of periodic surface patterns can enhance the fluid shear at the membrane surface [7], even though more fouling was observed at the concave sites. This results in overall improved antifouling behavior for ultrafiltration (UF) and microfiltration (MF) membranes against colloidal particles and proteins [8–10]. Given the general nature of the pattern-enhanced shear effect, it is expected that surface patterns, once successfully incorporated onto TFC membranes, will also be effective at reducing concentration polarization and scaling.

In the above-cited studies, the sub-micron surface patterns were directly imparted onto commercial UF membranes with nanoimprint lithography (NIL), a relatively low-cost and potentially scalable fabrication method. The underlying pattern-replication mechanism is the porosity-enhanced plastic deformation of the membranes during the NIL process, and thus is generally applicable to UF and MF membranes. UF or MF membranes based on glassy (e.g. polyethersulfone (PES)) or semi-crystalline (e.g. PVDF) polymers and with porosities ~80% will have yield strengths (σ_y)

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http://dx.doi.org/10.1016/j.memsci.2016.04.003
0376-7388/

of ~ several MPa at room temperature. Under mechanical loading at a stress level above σ_y, such porous membranes will display an extended plastic deformation plateau until a densification stage is reached. Such membrane plasticity allows mechanically patterning (deforming) the membrane surface with NIL, even at temperatures far below the glass transition temperature (T_g) or the melting temperature (T_m) of the polymer. Furthermore, the geometry of the pattern achieved at the membrane surface (corresponding to the degree of local plastic deformation) can be tuned by adjusting the NIL process variables: pressure, temperature, and time [11].

However, the NIL methods developed for surface patterning of UF and MF membranes cannot be directly applied to commercial TFC membranes, which typically have an ultrathin, crosslinked barrier layer (most commonly polyamide) atop a porous support layer (a UF or MF membrane in most cases). It is nearly impossible to plastically deform the membrane surface by employing high pressure without causing fracture in the barrier layer, which will result in membrane failure. To overcome this challenge, we recently demonstrated that surface patterning of TFC membranes can be successfully achieved by subsequently forming the barrier layer on a previously surface-patterned UF membrane support [12]. Specifically, the polyamide barrier layer is conveniently formed via an interfacial polymerization (IP) process that is the standard method for preparing TFC membranes [13,14].

Despite this successful demonstration, the processing-structure-property relationships of this new methodology remain largely unknown. Knowledge of the chemical, physical, [15–17], and topographic properties [18,19] of the barrier layer is crucial for applications of the resulting TFC membranes. Recent work has demonstrated that the magnitude of the antifouling effect directly correlates with the topographic features of the surface-patterned membranes [8,20]. Here we report systematic experimental studies of the morphological properties of the surface-patterned TFC membranes as a function of both the conditions and chemistry of the IP process as well as of the topography of the patterned UF substrates.

2. Materials and methods

2.1. Materials

In this study, PES UF membranes (PW, GE Water and Infrastructure) were used as a substrate for fabricating all the TFC membranes. The as-received UF membrane has a molecular weight cutoff (MWCO) of ~15.4 kg/mol, determined from exclusion measurements using polyethylene glycols (PEG) of different molecular weight [9]. The membranes were not subjected to any pre-treatment prior to either (1) NIL to fabricate patterned UF substrates or (2) IP to fabricate flat TFC membranes as control samples.

Unless otherwise specified, all reagents and chemicals were analytical grade with purity over 99%. 1, 3-phenylenediamine (MPD), piperazine (PIP, 99.5%), trimesoyl chloride (TMC, 99%), triethylamine (TEA, 99.5%), and (+) 10-camphor sulfonic acid (CSA, 99.0%) were purchased from Sigma Aldrich (US), and biograde hexane and sodium chloride were obtained from Fisher Scientific (Santa Clara, CA, US). Deionized (DI) water was supplied in-house from a RiOs-DI water system (EMDMillipore) with a resistivity of 10 MΩ-cm.

2.2. Fabrication of surface-patterned TFC membranes

As shown schematically in Fig. 1, surface-patterned TFC membranes were fabricated via a two-step process: (1) surface patterning of the PES UF membranes via NIL, and (2) forming the thin barrier layer atop the patterned UF membrane supports using IP. Surface-patterning of the UF membranes with NIL has been previously described in detail [11]. Under NIL conditions (Fig. 1), plastic deformation occurs at the membrane-mold contact area, replicating the sub-micron features on the Si mold. In this study, patterning of the UF membranes was carried out in an Eitrie 3 (Obducat, Inc.) nanoimprinter, which provides uniform compression (1% variation over a 3-inch wafer size) [21,22].

A Si mold containing parallel line-and-space grating patterns (a periodicity of 575 nm, line width of 210 nm and groove depth of 180 nm) was used. Prior to the NIL process, the Si mold was treated with a NanoStrip® solution (stabilized 3:1 concentrated sulfuric acid to hydrogen peroxide solution) to remove any organic residue. The UF membranes were imprinted under 4 MPa pressure for 3 min at 80, 120 and 175 °C to impart different pattern heights onto the membranes. For all NIL conditions, the demolding temperature was kept constant at 40 °C. As a control study, a flat Si wafer was used to "imprint" the UF membrane under identical conditions as those for the Si mold to create "flat" UF substrates (Table 1). All the imprinted UF membranes were rinsed with and stored in DI water, and completely sealed under dark conditions prior to IP.

The patterned UF membranes were then used as supports to fabricate the TFC membranes via IP using MPD (or PIP) and TMC, whose chemical structures and the corresponding polyamide

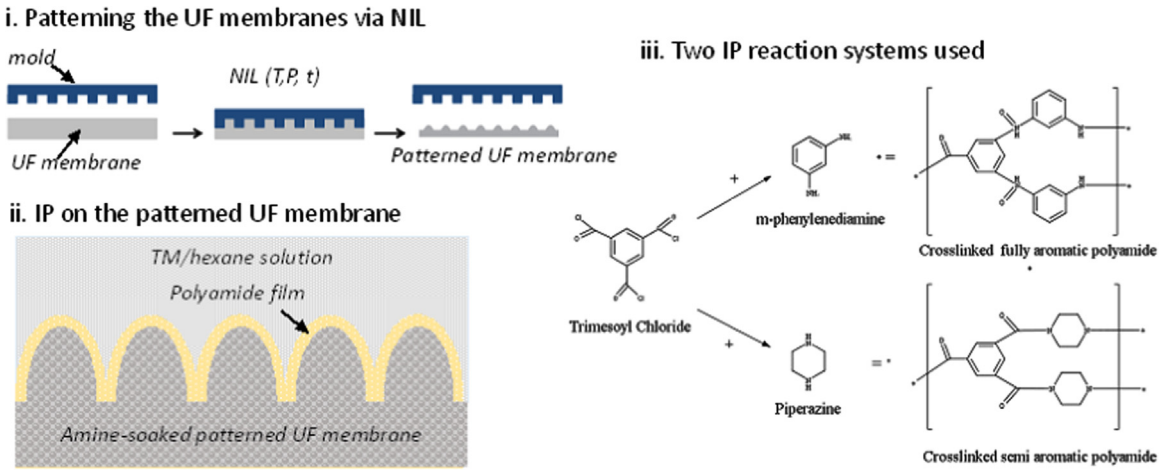

Fig. 1. A schematic illustration of the process used to fabricate the patterned TFC membranes: (i) surface patterning the UF membrane with NIL, and (ii) forming a barrier layer via IP on the patterned UF support. The two IP reaction systems used are shown in (iii).