Journal of Membrane Science 428 (2013) 598–607

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

Use of nanoimprinted surface patterns to mitigate colloidal deposition on ultrafiltration membranes

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

Department of Mechanical Engineering, University of Colorado Boulder, Boulder, CO 80309-0427, USA

ARTICLE INFO

Article history:
Received 10 September 2012
Received in revised form
22 October 2012
Accepted 26 October 2012
Available online 16 November 2012

Keywords:
Ultrafiltration
Surface pattern
Surface modification
Nanoimprint lithography
Colloidal fouling

ABSTRACT

Flux decline due to membrane fouling prevails in almost all pressure-driven liquid separations. The factors controlling fouling, ranging from surface chemistry to topographic roughness, have been extensively investigated. However, the role of surface patterns, particularly at a submicron scale, on membrane fouling remains unclear. Herein, we demonstrate that submicron patterns can be successfully imprinted onto a commercial polysulfone ultrafiltration membrane surface using nanoimprint lithography (NIL) without sacrificing its permeability properties. The presence of these patterns led to significantly improved deposition resistance during filtration of colloidal silica particle suspensions, as evidenced by a 19–45% increase in the apparent critical flux, with the magnitude dependent on particle size. Post-filtration visualization reveals an intriguing anisotropy in the particle deposition, whereby the degree of anisotropy depends on the orientation angle between the surface pattern and the flow direction of the feed. These results suggest a chemical-free route to post-formation, membrane surface modification.

1. Introduction

In this study, we provide the first direct experimental evidence of the effectiveness of using nanoimprint lithography (NIL) [1] to create well-defined, submicron surface patterns on a commercial ultrafiltration (UF) membrane that reduces flux decline during membrane filtration of colloidal species. Flux decline, and its major subset "fouling", is a natural result of selective membrane-based separations [2] and it is a hindrance. The deposition of retained particles, macromolecules, inorganic and biological materials, at the membrane surface and/or inside the pores [3,4], often can only be partially removed under harsh chemical treatment [5,6], causing more energy consumption, loss of productivity, and shortened membrane lifetime [3]. Mitigation of membrane fouling still remains a grand challenge for most membrane applications. Controlling interactions between the membrane surface and the feed solution is critical for fouling mitigation [4,7].

Interactions at the membrane surface have been addressed by a multitude of approaches including increasing the "mixing" that occurs at the fluid-membrane interface (by increasing local hydrodynamic shear stress gradients), and/or modifying the membrane's surface properties (surface chemistry and/or structure) to decrease the adsorption (and possibly deposition) of species "rejected" by the membrane. The latter goal has been addressed by myriad researchers using novel synthetic approaches to create targeted surface chemistries [8–13] and topological structures [14–17], while strategies for increasing "mixing" on the feed side, without incurring high parasitic energy losses from simply increasing flow velocities (volumetric pumping rates), include highly complex, kinetic membrane systems (for example, rotating or oscillating membranes) [18,19] and optimizing feed spacers of various types [17,20–25]. And sometimes a combination of operating strategy and surface modification can also be useful [26].

The research on surface modification has often been conducted with a focus on increasing the hydrophilicity of the membrane surface as many foulants are suspected of favoring adsorption on hydrophobic surfaces [4]. Demonstrated surface-modification approaches include adsorption of surfactants, coating and grafting of hydrophilic polymers, plasma treatment and the addition of hydrophilic nanoparticles onto the surface [27–31]. However, wider application of these processes has been limited by uncertainty with respect to long-term stability and scalability [4,32].

Membrane-solute interactions are also affected by surface roughness [33,34], but the relationship between membrane surface roughness and fouling remains unclear [35,36]. There have been a number of advances in applying "patterns" into and onto membranes for a variety of applications and rationales. These include creating "spacerless" structures that can enhance

* Corresponding author. Tel.: +1 303 735 2631.
** Corresponding author. Tel.: +1 303 492 2036.
E-mail addresses: john.pellegrino@colorado.edu (J. Pellegrino), Yifu.Ding@colorado.edu (Y. Ding).

0376-7388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2012.10.059

hydrodynamic mass transfer near the interface by embossing reverse osmosis (RO) membranes [37,38], or coating and peeling spacer features onto electrodialysis (ED) membranes [39]. Also, photolithographic and silicon micromachining methods have been used to create molds upon which membranes are cast [40,41] using classical phase inversion approaches. It should be noted that the latter development enables a number of potential attributes, such as, surface energy modification [14] and creating microsieves for particle fractionation and high frequency backwashing [42,43] beyond simply enhancing interfacial mass transfer.

Surface patterning has proven effective for fouling reduction in non-membrane applications. A polydimethylsiloxane (PDMS) surface consisting of micron-sized arrays of riblets strongly resisted the fouling of barnacles [44]. Surface topography has also been reported to control the attachment and growth of biological cells, which are common foulants in membrane processes [45,46]. Recently, the development of an effective anti-fouling system using patterned PDMS was reported [47]. Use of this so-called Sharklet® pattern, which mimics the topography of shark skin, reduced the settlement density of spores by ~86% as compared with a smooth PDMS surface.

These latter studies suggest the potential for a non-chemical approach to fouling control. However, few studies have been carried out that impart a pattern onto porous polymer membranes. Vogelaar et al. [40] introduced the μ-molding technique, which utilizes the phase inversion process within a mold to fabricate porous films with micron-sized surface patterns. However, no performance data for these membranes were reported, possibly due to the dense skin formed at the surface that may well limit filtration [48]. Recently though, Won et al. [49] described the formation of polyvinylidene fluoride (PVDF) microfiltration (MF) membranes on PDMS patterns with ~10 μm scale features. They tested activated sludge dewatering at Reynolds number (*Re*) ~1100–1200 and found evidence for roughness-induced enhancement of filtration rates and resistance to microbial adhesion. Formation of permeable, structured UF hollow fibers with features on the order of 100s μm have also been reported, by Culfaz, et al. [50,51], along with normal flow (aka dead-end) measurements of filtration (and NMR cake visualization) of model colloidal suspensions. Their studies [51] indicated that the structured fibers influenced the position and reversibility of deposition relative to the round fibers, perhaps by a flux-self-regulation mechanism, but the effects were specific to the size distributions of the particular colloidal suspensions.

Herein, we report results of our initial experiments involving the application of a specific, unoptimized NIL pattern to a commercial UF membrane to create submicron scale features. Studies at low *Re* (~2–3) reveal that the presence of these surface patterns provides significant deposition resistance during filtration of colloidal silica suspensions.

2. Experimental

2.1. Nanoimprinting on UF membrane

A commercial polyethersulfone UF-type membrane (PW, GE Water and Infrastructure) with a nominal 30 kg/mol molecular mass cutoff was used for the experiments described herein. It is cast on a 0.004″ polyester backing. The UF membranes used in this study were supplied as flat sheets and were stored dry under ambient conditions. The membranes were not subjected to pretreatment prior to patterning with an Eitrie 3 (Obducat, Inc.) nanoimprinter. The silicon mold used for the patterning had parallel lines and space gratings with a periodicity of 834 nm, groove depth of 200 nm, and a line-to-space ratio of 1:1. The native silicon oxide mold surface was treated with a Piranha® solution prior to the fabrication. Patterning 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.

2.2. Filtration measurements with the pristine and imprinted membranes

All filtration experiments were conducted in a bench-scale module at 21 °C, as schematically shown in Fig. 1. The module is

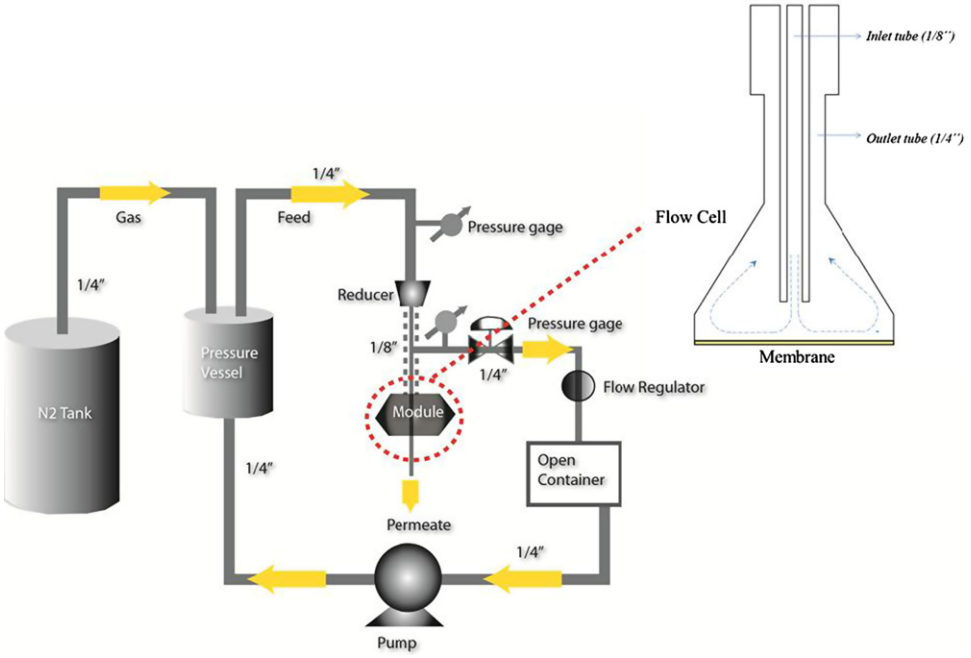

Fig. 1. Schematic illustration of the filtration setup, and the inset shows the details of the membrane cell, with the dashed lines corresponding to the nominal flow streamline.