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# Influence of chemical coating combined with nanopatterning on alginate fouling during nanofiltration

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## ABSTRACT

This contribution describes a method to increase the fouling resistance of nanofiltration membranes by applying both a chemical coating and a nanoscale pattern to the membrane surfaces. A line and groove nano-pattern was applied by thermal embossing directly onto a commercial polyamide thin-film composite nanofiltration membrane. Poly(ethylene glycol) diglycidyl ether (PEGDE) was reacted onto the patterned membrane surfaces by an epoxide ring opening reaction with unreacted carboxyl groups on the polyamide selective layer. Membrane performance was evaluated by measuring flux and salt rejection using a magnesium sulfate solution and by measuring flux reduction using an alginate solution. Surface characterization showed successful patterning and chemical modification of the membrane surface. Flux and salt rejection properties were unaffected by patterning the polyamide membrane surface directly. The fouling results show that combining line and groove nano-patterning with PEGDE chemical modification yields a membrane that is more resistant to fouling than either method alone.

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## 1. Introduction

Membrane biofouling refers to the attachment or adsorption of biopolymers or organisms onto the membrane surface or within the membrane pores. It is a major hindrance to membrane usage [1,2], causing a transient flux decline or pressure increase and a decrease in salt rejection. Fouled membranes require chemical cleaning, which shortens the membrane life and greatly increases membrane operating cost [3]. Biofouling is one of multiple steps in the process that leads to biofilm formation [4]. In this process, a conditioning film is adsorbed to the surface, typically comprising macromolecules from the solution or macromolecules secreted from bacteria. This conditioning of the surface provides favorable conditions for bacteria to adsorb or attach onto the surface, where they grow and form colonies, eventually leading to a biofilm.

Biofouling reduction/elimination has been a common topic in the literature. Specifically, surface modification of membranes is a common strategy [5], with numerous studies describing the use of chemical treatments and coatings. Anti-fouling coatings are designed to make the membrane surface less favorable for bacterial attachment; e.g., by making the surface more hydrophilic, by including hydrogen-bond acceptors, by excluding hydrogen-bond donors, and by having an overall neutral electrical charge [6,7]. Examples of widely studied antifouling coatings include poly

(ethylene glycol) (PEG) due to its high degree of hydration [8,9], and zwitterions, which are net charge neutral molecules that have positive and negative charge groups that can form a strong hydration layer that excludes biopolymers and bacteria [10]. Three zwitterions of interest are carboxybetaine [11], sulfobetaine [12], and phosphobetaine [13], with sulfobetaine being the most commonly used in the literature.

Another common strategy involves coating membranes with anti-microbial agents that are able to kill bacteria. Coatings with quaternary amine groups are common and are thought to disrupt the cell membrane allowing release of intracellular contents causing cell death [14,15]. Graphene oxide and carbon nanotubes have shown promise by deactivating bacteria upon contact with these surfaces [16,17]. Also, silver nanoparticles have been incorporated into membranes, making anti-microbial membranes that severely damage the bacteria cell membrane [18,19].

A more recent area of interest has been physical modification of surfaces with a specific, ordered pattern to disrupt the hydrodynamic boundary layer at the surface, making foulants less likely to adhere. One of the first designs, coined Sharklet™ [20–22], used micron-scale patterns that mimic shark skin. Other groups have placed micro-patterned posts [23] and an imprinted spacer design [24] on membrane surfaces in an attempt to reduce biofouling. Micro-patterned hollow fibers also have been of interest with patterning on the outer skin of the hollow fiber to reduce fouling [25–27]. Other micro-patterns applied onto membranes to reduce fouling include line and groove patterns [28], pyramids [29], and prisms [30]. Nano-scale line and groove patterns have been

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applied onto membranes to reduce protein fouling [31], colloidal particle fouling [32,33], and gypsum scaling [34].

This paper contributes a method for applying both a chemical coating and a nano-pattern to a membrane surface. First, a nano-scale line and groove pattern was applied to a polyamide thin-film composite membrane by thermal embossing. Next, poly(ethylene glycol) diglycidyl ether (PEGDE) was reacted onto the membrane as a PEG-based chemical coating. The membranes were tested for flux and salt rejection pre- and post-modification in a cross-flow system. Alginate was used as a model biopolymer foulant material [35]. To the authors' knowledge, this paper is the first to report combined chemical and physical modification of a membrane surface to study biofouling resistance, but not the first time these two methods have been combined on a surface [36]. It also is the first to demonstrate the successful, direct thermal embossing of a nano-pattern onto a polyamide thin-film composite membrane.

## 2. Materials and methods

### 2.1. Materials

PEGDE ( $M_n=500$  Da), sodium chloride (NaCl,  $\geq 99\%$ ), magnesium sulfate ( $MgSO_4$ ,  $\geq 99.5\%$ ), and sodium alginate (from brown algae) were used as received from Sigma Aldrich. Calcium chloride dihydrate ( $CaCl_2 \cdot 2H_2O$ ) was used as received from Fisher Scientific. Aqueous solutions were made with deionized water from a Milli-Q water purification system (EMD Millipore).

Polyamide thin-film composite nanofiltration (NF) membranes (GE HL series) were purchased from Sterlitech Corporation. This membrane consists of a polyester fabric backing, a polysulfone support layer, and a semi-aromatic polyamide selective layer [37].

### 2.2. Membrane surface modification

#### 2.2.1. Patterning the membrane

Fig. 1 illustrates the two step process of patterning the membrane and applying a chemical coating to the membrane surface. The silicon line and groove stamps used to pattern the membranes were purchased from LightSmyth Technologies, Inc. The stamps were specified to have a 606 nm period between peaks, a 190 nm groove depth, and a 303 nm line width. A 29 mm  $\times$  12 mm stamp was used to prepare membranes for physicochemical characterization and salt rejection experiments. A 29 mm  $\times$  24 mm stamp was used to prepare membranes for the alginate fouling experiments. A Carver press (AutoFour/1512H model) was used to emboss the membranes with the stamp/wafer. First, the press plates were heated to 45 °C. A small aluminum plate was placed on the bottom press plate, the membrane was placed on top of the aluminum plate with polyamide surface facing up, and then the silicon stamp was placed on top of the polyamide surface with the stamp features facing the polyamide surface. A 30 cm  $\times$  30 cm Kimwipe was folded into 1/16th its original size and placed on top

of the stamp to act as a “cushion” to help prevent the stamp from breaking. Another small aluminum plate was placed on top of the Kimwipe. The press plates were closed at 25% pump speed until the force was 6670 N. A force was maintained at  $6670 \pm 1330$  N, which was found to be sufficient for patterning without damaging the silicon stamps. After 20 min, the press was released and the stamp was removed from the membrane, leaving a patterned membrane surface.

Control experiments were done to study the effect of the thermal compression alone. For the control process, a 29 mm  $\times$  10 mm flat silicon wafer from Nova Electronic Materials was used to prepare membranes for physicochemical characterization and salt rejection experiments. A 29 mm  $\times$  24 mm flat wafer was used to prepare membranes for the alginate fouling experiments.

#### 2.2.2. Chemically coating the membrane

PEGDE was used to modify the membrane surface chemically. Aqueous solutions of 5 wt% and 15 wt% PEGDE were used. A control experiment was done using DI water. The reaction process followed that given by Van Wagner et al. [9] with minor modifications. Aluminum foil tape was placed on the membrane edges to create a solution boundary. Next, the reaction solution was heated to  $42 \pm 2$  °C by a hot plate and approximately 0.2 g/cm<sup>2</sup> membrane of solution was pipetted onto the membrane such that the whole membrane surface area was contacted by the solution. The solution was allowed to react on the membrane for 10 min, and then the membrane was rinsed in DI water. The membranes used for the cross-flow filtration experiments were stored in DI water until use. The membranes used for physicochemical characterization were patted dry and then dried fully under vacuum at 20–25 °C and 0.78–0.95 barg. In all cases, the entirety of the membrane testable area was modified with the desired reaction solution.

### 2.3. Membrane characterization techniques

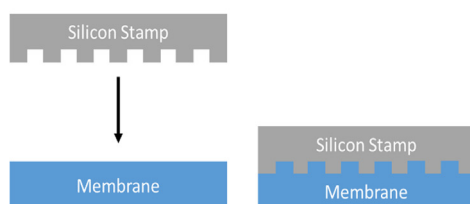
#### 2.3.1. Atomic force microscopy

Atomic force microscopy (AFM) was used to observe the surface morphology of the stamps and the membranes. Images were obtained using a Bioscope AFM (Bruker, Inc.) with NanoScope IIIa controller equipped with Nanoscope version 5.32R1 software. Silicon cantilevers (MikroMasch, Inc., HQ:NSC16/AL BS) were used as probes for the non-contact tapping mode measurements. AFM images were taken with a 256  $\times$  256 pixel resolution over 20  $\mu$ m  $\times$  20  $\mu$ m or 5  $\mu$ m  $\times$  5  $\mu$ m areas at a scan rate of 0.5 Hz. The section analysis feature of the software was used to determine peak heights and peak periods (peak-to-peak distances).

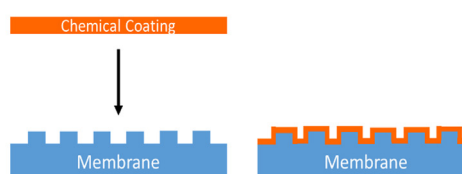
#### 2.3.2. Laser measuring microscopy

An Olympus LEXT OLS4000 3D laser measuring microscope (software version 2.2.3) was used to take images of the stamps and the patterned membrane surfaces on a larger scale than the AFM.

Step 1. Pattern membrane with silicon stamp



Step 2. Apply chemical coating



**Fig. 1.** Methodology of combining chemical coating and physical patterning on a membrane surface by deformation (i.e., embossing) of the membrane substrate. The chemical coating is a poly(ethylene glycol) diglycidyl ether aqueous solution.

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