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# Factors affecting pattern fidelity and performance of a patterned membrane

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ABSTRACT

Membranes with a patterned surface have become attractive for the mitigation of biofouling in membrane processes for water and wastewater treatment. However, previous studies have paid little attention to factors affecting pattern fidelity in the preparation of patterned membranes. Here, we examined several parameters such as the molecular weight and concentration of the polymer in the dope solution which might affect the pattern fidelity of prism-patterned membranes. Greater pattern fidelity was achieved as the molecular weight of the polymer decreased and its concentration increased. Pattern fidelity was also dependent on the work of adhesion of the replica mold and the polymer solution. In the crossflow filtration test, deposition of the GFP tagged *P. aeruginosa* PAO1 was decreased on the patterned membranes with a higher pattern height. The mechanisms involved in the preparation of patterned membranes with different fidelities were also investigated.



## 1. Introduction

Membranes have been widely employed in municipal and industrial water and wastewater treatments over the past few decades due to their advantages such as the production of high quality effluents, smaller footprint, etc. However, membrane fouling, due to its complex nature, still remains a critical limiting factor preventing widespread utilization of this technology [1–3].

Recently, novel approaches to membrane preparation have been attempted to mitigate membrane fouling from the viewpoint of converging science [4–6]. Among them, the concept of patterned membranes was introduced in a way to mitigate the membrane fouling [7]. In detail, it was experimentally observed that patterns on the membrane surface could mitigate the deposition of foulants and thus enhance membrane permeability. Won et al. [8] prepared diverse patterned membranes, such as pyramid-, prism-, and embossed-patterned membranes and compared them with a flat membrane in terms of morphology, permeability, and biofouling. Culfaz et al. [9–12] prepared a hollow fiber membrane with an embedded pattern at the membrane surface using a patterned nozzle and found that it showed higher water flux than a conventional hollow fiber membrane. Moreover, Peters prepared a micro-structured membrane which had line and space pattern at the membrane surface [13]. It showed higher gas flux than a conventional flat sheet membrane, indicating that the patterned skin layer on the membrane surface increased its effective surface area and thereby increased the gas flux.

However, previous studies on patterned membranes have paid little attention to (i) the strategy of pattern formation on the membrane surface, and (ii) the relationship between pattern size and membrane performance. One leading study explaining the factors affecting the pattern replication during the preparation of patterned membrane was done by Bikel et al. [14]. They identified the basic mechanisms of replication precision. However, several parameters still remained as unknown. Additionally, to the best of our knowledge, the correlation between pattern size and membrane performance has not been studied until now. Thus the aim of this study was (i) to determine the parameters affecting pattern fidelity, and (ii) to investigate relationship between pattern height and membrane performance.

## 2. Materials and methods

### 2.1. Materials

Polyvinylidene fluoride (PVDF), dimethyl-formamide (DMF), methyl-ethyl-ketone (MEK), Polystyrene (PS) and acetone were

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purchased from Sigma Aldrich Korea. The replica mold was prepared using polydimethylsiloxane (PDMS, Sylgard 184 kit, Dow Corning, USA) and poly(urethaneacrylate) (PUA, MINs, Minuta Tech, Korea). All chemicals were used without further purification.

### 2.2. Preparation of replica mold

The master mold, made from photo-resistant (PR) polymer, was fabricated by a photo lithography process. In this experiment, we used a PDMS replica mold instead of the master mold. Since the photo-resistant polymer was easily dissolved by an organic solvent such as DMF, the pattern of the master mold could be destroyed during the phase inversion process. Thus, we prepared a PDMS replica mold as a substrate. The PDMS replica mold was prepared as following:

1) The polydimethylsiloxane (PDMS) prepolymer was mixed with a curing agent (Sylgard 184 kit) at a ratio of 10:1.
2) The mixed PDMS solution was cast onto the master mold.
3) The PDMS and master mold was baked in the oven at 60 °C for two hours.
4) After the curing, the PDMS was peeled off from the master mold.

### 2.3. Calculation of pattern fidelity

The shape and dimensions of the prism pattern are illustrated in Fig. 1. The width and height of the prism-patterned master mold were 48–50 μm and 18–21 μm, respectively. Bessonov et al. defined pattern fidelity by the ratio of the pattern length (width) in the master mold to that of the replica mold [15]. This definition may be applicable to a one dimensional pattern consisting of lines and spaces, because only the pattern lengths of the master mold and replica mold are compared. However, this does not seem to be suitable to the prism pattern in this study because the width and height of prism should be considered simultaneously. Thus, we introduced “Area Fidelity”, which represents the pattern fidelity based on pattern area instead of pattern length. In order to describe the fidelity of the prism pattern in more detail, however, we also used “Width Fidelity” and “Height Fidelity” in addition to “Area Fidelity”:

$$\text{“Area Fidelity”} = \frac{(\text{Area of pattern in } a \text{ patterned membrane})}{(\text{Area of pattern in a replicated module})}$$

$$\text{“Width Fidelity”} = \frac{(\text{Width of pattern in } a \text{ patterned membrane})}{(\text{Width of pattern in a replicated module})}$$

$$\text{“Height Fidelity”} = \frac{(\text{Height of pattern in a patterned membrane})}{(\text{Height of pattern in a replicated module})}$$

### 2.4. Preparation of patterned membranes

The patterned membranes were prepared as following [8]: PVDF pellets were dissolved in DMF at 60 °C for 6 h and then acetone was added at room temperature. The mixed solution of PVDF and DMF was stirred overnight for complete mixing. Then, the casting solution was poured onto the patterned PDMS replica mold and uniformly cast with the casting knife to make a nascent membrane. The nascent membrane, together with the PDMS replica, was dipped into the precipitation bath and coagulated for 6–10 h. Then, the patterned membrane was released from the PDMS replica mold and stored in a bath filled with de-ionized water.

### 2.5. SEM

The morphology of the dried membranes was observed using scanning electron microscopy (SEM, JSM-6701F, JEOL KOREA LTD., Korea). A piece of the patterned membrane was immersed in liquid nitrogen and carefully fractured. The fractured membrane was attached to the metal mount using conductive copper tape and dried under vacuum. Then, the membrane was coated with platinum (Cressington 108 auto, Cressington, UK). Finally, the platinum-coated sample was placed in the SEM chamber and observed.

### 2.6. Flux and biofouling test

The extent of biofouling of patterned and flat membranes was tested and compared in a crossflow microfiltration (MF) system depicted in Fig. 2. The test cell had dimensions of 64 mm in length, 15 mm in width and 1.8 mm in depth. The effective surface area of the test membrane was 14.1 $cm^2$. At a constant transmembrane pressure (TMP) of 20 kPa, ultrapure water was used as the feed and the retentate was recirculated at a crossflow velocity of 0.3 m/s (Reynolds number; ~1000), while the permeate was collected on a balance to calculate water flux by weighing and recording the mass of the permeate every 10 s.

The anti-fouling characteristic of the patterned membrane was examined with same cross-flow system. *Pseudomonas aeruginosa* PAO1 tagged with green fluorescent protein (GFP) was used as a model strain [16]. PAO1 tagged with GFP was pre-cultured in LB broth agar supplemented with 200 μg/mL of carbenicillin (Gold biotechnology, U.S.) for 24 h at 35 °C in a stirring incubator. A fresh single colony from an agar plate was inoculated in 5 g/L of LB broth and cultured for 24 h at 200 rpm at 35 °C. The LB broth and PAO1 tagged with GFP were diluted (5 g/L) and circulated with two pumps for 2 h of operation under constant pressure (20–22 kPa). The permeate was collected in a bath to calculate the water flux. The schematic diagrams of fluid channel were illustrated in Fig. 3. The height of channel was 2000 μm and the prism pattern and

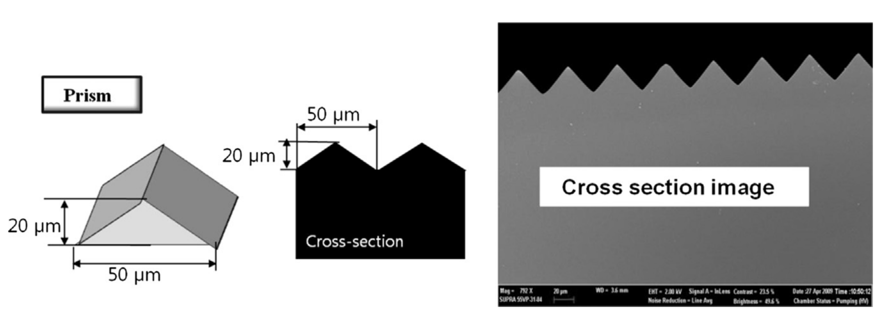


**Fig. 1.** Shape and dimensions of the prism-patterned master mold.