FLEXIBLE AND FREE-STANDING POLYMERIC MEMBRANES WITH MULTI-DIMENSIONAL PORES FOR A MICROFLUIDIC APPLICATION

Hyesung Cho[1], Hyeoncheol Park[1], Jun Soo Kim[1], Hosup Jung[1], and Kahp-Yang Suh[1]
[1]Seoul National University, Korea

ABSTRACT

We present a simple yet robust method for fabrication of polymeric multiscale stencils having multi-dimensional pores. The key idea of our approach is to use a hierarchical structure as a stamp for the fabrication of multi-dimensional pores in flexible and free-standing polymeric membranes. The polymeric membranes presented here are highly flexible yet sufficiently robust so that they can be firmly free-standing and bend well without structural collapse. As a unique application of the polymeric multiscale stencils, we demonstrate a uniform synthesis of lipid vesicle in various sizes by simply integrating the polymeric membrane in a microfluidic channel.

KEYWORDS

Multi-dimensional pores, Polymeric membranes, Lipid vesicle

INTRODUCTION

Free-standing nanomembranes have been fabricated from various materials, such as Si-based inorganics [1] and thin metal foils [2] for use in a wide range of applications, such as the shadow masking technique, plasmonics, and bio-inspired microfluidic devices [3]. To fabricate free-standing nanostencils (nanomembranes with ordered nanopores), a series of standard semiconductor processes and/or specific materials having relatively stiff mechanical rigidity are required to maintain the nanostencils' shape firmly without mechanical fracture or tear against external forces that arise during the handling process. In contrast, elastomeric polydimethylsiloxane (PDMS) membranes with micropores ($> 5\ \mu m$**)** have been made by spin-coating and replica molding PDMS onto the micropillar arrays. With the increasing demand for miniaturized devices, approaches have been developed to reduce the aperture size in polymeric membranes. However, polymeric nanostencils have rarely been reported because they are required to be "free standing" and "residual-layer-free" which are difficult to achieve with existing polymers. Specifically, the low elastic modulus of the polymers causes tears and defects in the nanopore arrays during the manufacturing or handling process. It is also not easy to remove the residual layer to produce clear through-holes; thus, additional etching or specific skills are required. To address some of these challenges, we present here a new type of free-standing polymeric membrane with multi-dimensional pores by simple dewetting assisted molding process with hierarchical stamps. In particular, detailed chemical and mechanical analyses were performed to verify the spontaneous dewetting behavior of the UV-curable resin that occurred during the fabrication of the multi-dimensional pores. Furthermore, we propose a new fabrication method for uniform synthesis of lipid vesicles by simply integrating the polymeric membrane in a microfluidic channel.

EXPERIMENT

The multiscale structure has two distinct functions that allow it to be used as a mold for the fabrication of multi-dimensional pores in a flexible and free-standing polymeric membrane: i) the mold is capable of forming uniform contact with the blanket, which is analogous to the geometric effect of a hierarchically organized gecko foot hairy structure; and ii) the hierarchical mold allows for the direct integration of a seemingly fragile nanopores on a microscale backbone without a residual layer in a single molding step.

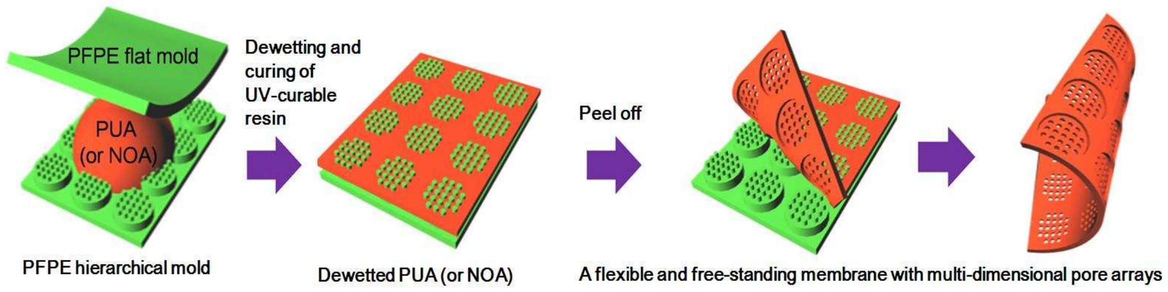

Figure 1. Dewetting-assisted fabrication of multi-dimensional pores on a polymeric hierarchical mold

As described in Fig. 1, a relatively hydrophilic polyurethane acrylate (PUA) or Norland Optical Adhesive (NOA) resin was drop-dispensed and back-filled into the hydrophobic perfluoropolyether (PFPE) hierarchical mold, and the spontaneous dewetting of the PUA resin occurred within the sandwich-like assembly between a flat PFPE blanket and the PFPE mold. Here, a fully dewetted surface of the PUA with through-holes and exposed PFPE pillar arrays was generated after photo-polymerization under a slight pressure. The two materials could be swapped to obtain a similar dewetted PFPE surface within a PUA sandwich assembly without noticeable structural differences.

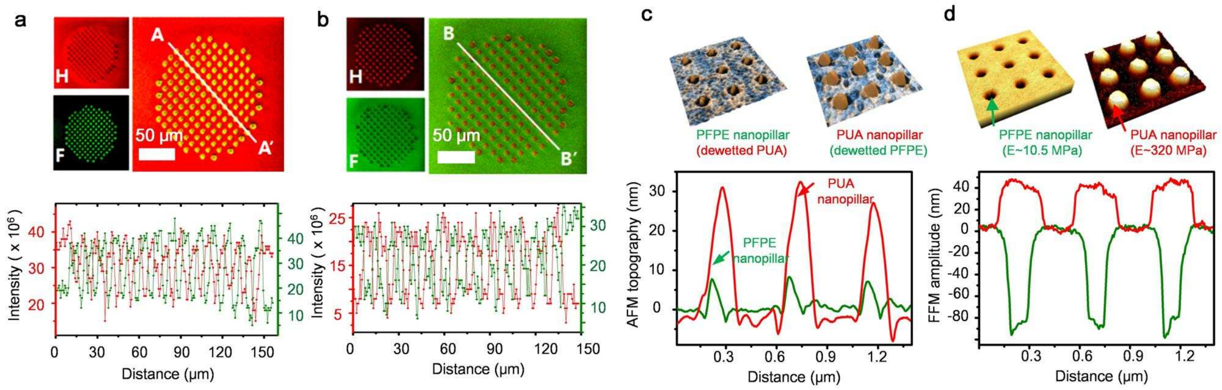

Figure 2. Chemical and mechanical mapping images of dewetting surfaces on hierarchical molds

To further probe the dewetting interface of the two polymers (PUA and PFPE), detailed chemical and mechanical mappings were performed using time-of-flight secondary ion mass spectrometry (TOF-SIMS) and the force modulation microscopy (FMM) mode in atomic force microscopy (AFM). The former provides a spatial distribution of each material at the microscale, while the latter shows the rigidity distribution at the nanoscale. When the Bi$^+$ ion beam was irradiated on the dewetting surface, singly charged secondary ions were easily detected and counted in the TOF-SIMS analysis. The two polymers released specific singly charged ions as material indicators for the chemical mapping of the dewetting surfaces, such as H$^-$ ions from the PUA surface and F$^-$ ions from the PFPE surface. After scanning 50 times and counting the number of ions, two kinds of dewetting surfaces (PUA/PFPE, PFPE/PUA) were imaged successfully in red (H$^-$) and green (F$^-$) (Fig. 2a-b). Because the two chemical maps are complementary, the line scan profiles along with the white lines (AA’ and BB’) show the measured sinusoidal curves, providing the spatial distributions of the two materials at the microscale (pillar diameter: ~ 5 µm). In parallel, the nanoscale distribution obtained from a hierarchical mold (diameter: 150 nm, height: 200 nm) can be measured by AFM topography and the FMM amplitude modes (Fig. 2c-d). The heights of the PFPE and PUA nanopillar array exposed on the dewetting surface were ~ 8 nm on the PUA and ~ 30 nm on the PFPE, respectively. Mechanical mapping using FMM is reliable because the exposed PUA or PFPE pillars affect the bending amplitude of the AFM tips in the FMM mode, depending on the difference in the Young’s modulus of each polymer (PUA: 320 MPa, PFPE: 10.5 MPa). As shown in Fig. 2d, the differences in the FMM amplitude on the dewetting surface were ~ -80 nm and ~ +50 nm from top to valley, respectively. The most significant finding obtained from the FMM analysis was the relatively high exposed height of the PUA nanopillar in the topography (30 nm, Fig. 2c), which was caused by the difference in the dewetting and shrinkage of the UV-curable resin. Consequently, the final thickness of the nanomembranes in the PFPE membrane after peel-off process was approximately 170 nm, despite the 200-nm height of the nanopattern on the original PUA hierarchical mold.

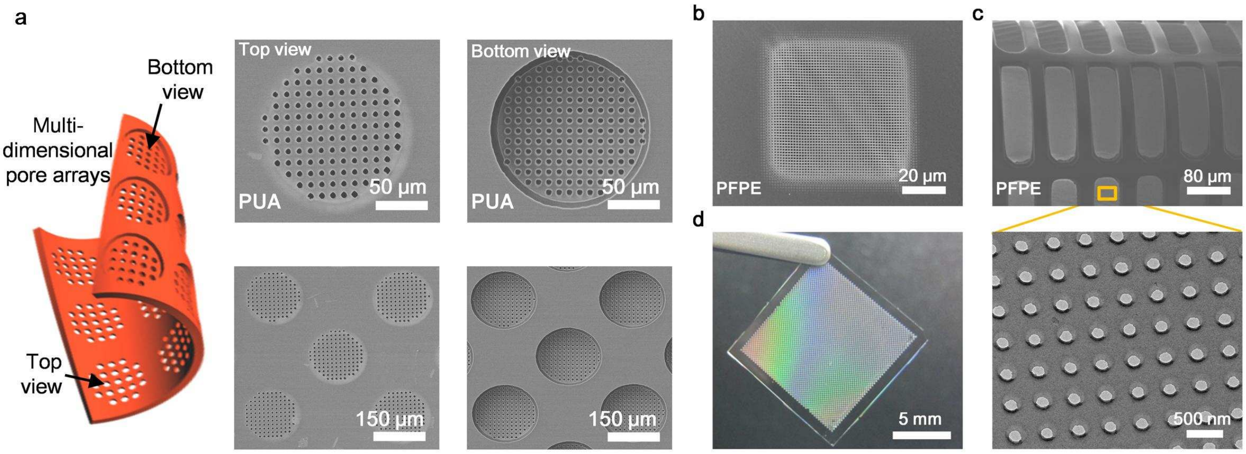

Figure 3. SEM and digital images of polymeric membranes with various sizes of multi-dimensional pores

By peeling the dewetted polymer layer from the hierarchical mold, we obtained multi-dimensional pores in flexible and free-standing polymeric (PUA or PFPE) membranes (Fig. 3a). To visualize the formation of the clear through-holes, the sample was seen from the top and bottom views: an array of 5-µm pores was directly observed from the top, while the same array was also observed through the supportive backbone, which featured 150-µm pores from the bottom. The micro mesh-like backbone plays a role in both increasing the total thickness of the polymeric stencil and decreasing the overall area of the nanostencil, which leads to the increase in effective modulus.

The polymeric membranes presented here are highly flexible yet sufficiently robust such that they can be firmly free-standing and bend well without structural collapse. As shown in Fig. 3d, a PFPE membrane with a pore diameter of 800 nm was formed on a microstencil support of 150 μm pores. The number of defects formed in the nanostencils (< 1 μm) during the peeling-off process was minimal because the hydrophobic, flexible PFPE resin allowed for the successful demolding of the dewetted membranes after photo-polymerization from the PUA hierarchical mold without mechanical fractures, even with the extremely small nanopores (450 in Fig. 3b and 150 nm in Fig. 3c). In addition to the circular arrays, other supporting backbones with different shapes such as square and rectangular patterns were also possible to fabricate (Fig. 3a-c). The through-holes (150 nm diameter) on a rectangular pattern of PFPE membrane (60 × 250 μm^2) were clearly detected via transmission electron microscopy (TEM) image as shown in Fig.3c.

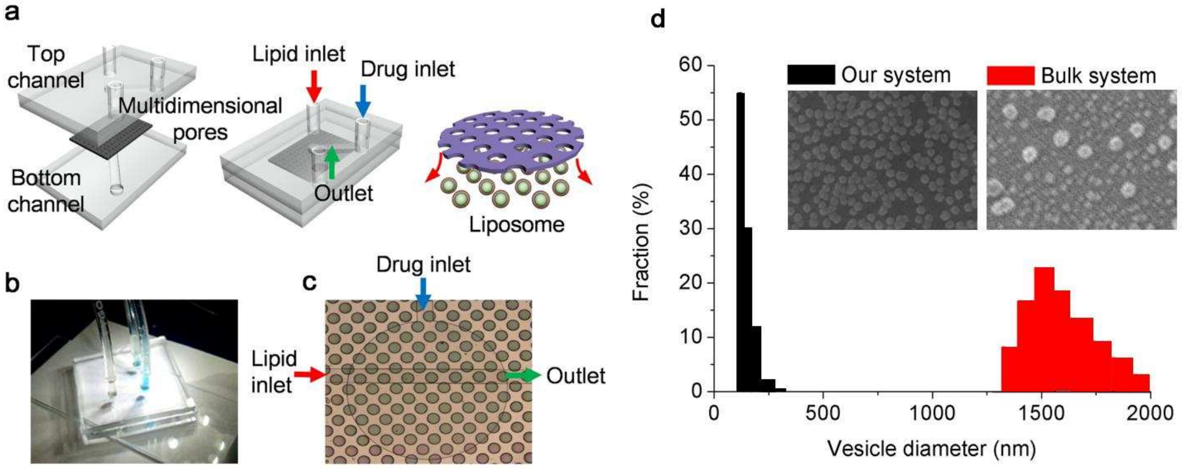

Figure 4. Schematic illustration of the synthesis of lipid vesicle in a microfluidic system with polymeric stencils

As a unique application of the polymeric membranes with ordered pores, we demonstrate uniform synthesis of the lipid vesicle by simply utilizing the hydrophilic polymeric stencil in a microfluidic channel to control nanoscale diffusion of molecules (Fig. 4a). In this experiment, specific iso-propyl alcohol (IPA) solution with 1 mM of lipid molecules (10, 12-Pentacosadiynoic Acid, PCDA) was introduced continuously to the inlet, while amount of phosphate buffered saline (PBS) was introduced via the polymeric stencil having 5-μm pores by two individual syringe pumps. Due to rapid change of the concentration in the IPA solution near the pores, lipid vesicles are uniformly synthesized in the microfluidic channel simply. Our result shows that the distribution of the diameter via pore-based system is more skewed and uniform (mean diameter: ~ 150 nm) compare to the conventional method by rapid mixing. The membrane is highly robust so as to endure the pressure of fluid in microfluidic channel, thus enabling hydrodynamic multi-focusing of the introduced PBS at each pore successfully without any tear or failure of the membrane. The stencil-based system could open up a wide range of microfluidic applications with further modification.

REFERENCES

[1]Rogers, J. A., Lagally, M. G. & Nuzzo, R. G., "Synthesis, assembly and applications of semiconductor nanomembranes". *Nature*, **477**, 45-53 (2011)

[2]Henzie, J., Lee, M. H. & Odom, T. W., "Multiscale patterning of plasmonic metamaterials". *Nature Nanotechnology* **2**, 549-554 (2007)

[3]Huh D., Matthews B. D., Mammoto A., Montoya-Zavala M., Hsin H. Y. and Ingber D. E.. "Reconstituting Organ-Level Lung Functions on a Chip". *Science* **328**, 1662-1668 (2010)

CONTACT

Kahp-Yang Suh +82-2-884-1597 or sky4u@snu.ac.kr