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Repeatable replication method with liquid infiltration to fabricate robust, flexible, and transparent, anti-reflective superhydrophobic polymer films on a large scale

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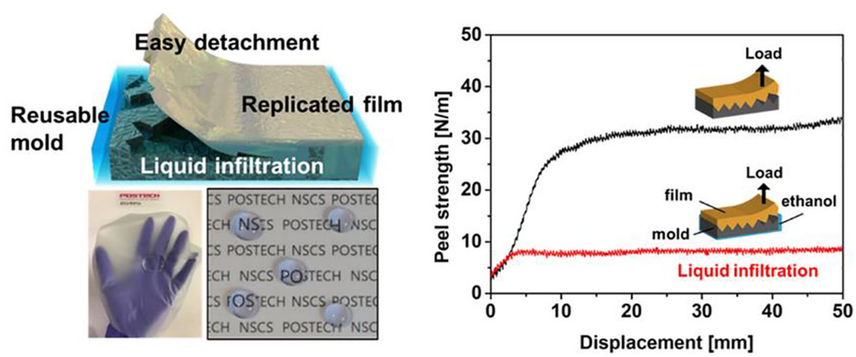
HIGHLIGHTS

- Robust and flexible superhydrophobic polydimethylsiloxane films are formed.
- The films are replicated from a superhydrophobic nano/micro-structured Al mold.
- A single Al mold can be used repeatedly to produce films of the same quality.
- The fabricated films are water-repellent, transparent, and anti-reflective.
- The films maintain their wetting properties under various harsh conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Flexible superhydrophobic films that can be adapted to any target object for practical applications have drawn much attention in recent years. In this paper, we propose a simple method to fabricating highly flexible superhydrophobic polydimethylsiloxane (PDMS) films, via a repeatable replication and nondestructive detachment from a superhydrophobic aluminum mold. Due to the hierarchical surface structures and intrinsic hydrophobicity of PDMS, the fabricated films exhibited superior water repellency without any further modifications using low surface energy materials. Moreover, these water repellent films exhibited excellent mechanical durability and flexibility without losing the anti-wetting property under harsh conditions. The use of a robust superhydrophobic mold and the easy detachment of the film using a solution with a low surface tension allow for the clean release of large-area replicas without any damages to the mold. This enables the repeated fabrication of superhydrophobic PDMS films without the deterioration of their wettability using a single mold. Furthermore, the superhydrophobic PDMS film exhibited an efficient anti-reflection property and high transparency, which allows an enhanced light collection and efficiency when applied to solar cells. Consequently, this simple and inexpensive method is appropriate for diverse applications that require films with superior mechanical and optical properties, and a special wetting behavior.

Abbreviations: Al, aluminum; PDMS, polydimethylsiloxane; SAM, self-assembled monolayer; SEM, scanning electron microscopy; CA, contact angle; SA, sliding angle

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1. Introduction

Surfaces with special wetting behaviors, especially superhydrophobic surfaces which have a high water contact angle (CA) greater than 150° and low sliding angle (SA) lower than 10° [1], have attracted attention because they can be utilized in various applications that require special surface characteristics such as anti-corrosion [2], self-cleaning [3], and drag reduction [4]. Superhydrophobic surfaces can be realized by roughening the surface by several methods such as chemical etching and anodization [5], and by chemically modifying the roughened surface with low surface energy materials [6]. However, these surfaces are still far from meeting the demands of many practical applications owing to their poor mechanical properties, lack of adaptability to target objects, and lack of optical properties such as transparency and anti-reflectance. In this respect, the development of a highly flexible superhydrophobic surface with the ability to withstand large deformations and integrate easily with objects of complex geometries can be a good alternative solution. In addition, the development of a transparent and anti-reflective superhydrophobic surface can be useful in optical applications.

Over the past decade, there have been several attempts to fabricate flexible, transparent or anti-reflective superhydrophobic surfaces. One approach is to introduce nanostructured materials such as ZnO [7], CuO [8], and Al_2O_3 [9] on flexible polymer substrates so that the robust Cassie-Baxter state can be retained under mechanical deformation. Additional approaches to the formation of flexible or anti-reflective superhydrophobic surfaces involve the replication of a patterned surface by a femtosecond laser or lithography [10,11], the replication of bio or porous templates fabricated by anodization or etching [12–16], and the fabrication of morphological features on a polymer film via laser ablation or plasma etching [17–19]. In addition, techniques to fabricating transparent superhydrophobic surfaces on the versatile substrates also include; coating [20,21] or spraying [22] with hydrophobic materials.

Such valuable surfaces can be applied to various fields, for example anti-reflective films for solar panels [23,24], transparent self-cleaning surfaces for building windows [25,26], and surface decoration with structural color [27]. However, despite the outstanding mechanical and optical properties and versatile utilization of superhydrophobic surfaces, several challenges still remain to be overcome: (1) delamination of textured surfaces from the underlying substrates under dynamic deformation or physical stimulation; (2) complicated fabrication processes and high production costs; (3) difficulties in fabricating uniformly superhydrophobic surfaces over a large area; (4) serious damages of the replicated surfaces related to the template-removal issues and the use of strong acids; (5) chemical degradation of the superhydrophobic layer under harsh environments. Because of these limitations, it is difficult to practically use these surfaces in outdoor environments. Therefore, it is necessary to develop a simple and cost effective method, which does not cause any damage to the surface, for the formation of robust and flexible superhydrophobic surface that is transparent and anti-reflective over a large area.

Herein, we propose a method to fabricate a flexible superhydrophobic polymer film by simply replicating a repeatedly usable aluminum mold followed by easy detachment of the replicated film from the mold using a liquid with low surface-energy as a separator. Monolithic hierarchical structures were successfully obtained on a large area of polydimethylsiloxane (PDMS) film, and the resulting film surface exhibited excellent water repellency without further chemical modifications with low-surface-tension materials like fluorine-containing compounds, which could adversely affect the environment. Moreover, the fabricated films exhibited excellent mechanical durability and flexibility, with no deterioration in the wettability or formation of structural defects taking place under harsh conditions. Furthermore, no significant damage to the mold and changes in the wettability of the film were observed even after repeated use of the same mold for 50 times. In addition, the superhydrophobic film has anti-reflective property while being transparent, thereby leading to a higher power conversion efficiency when applied to a solar cell. These features are promising for developing multi-functional superhydrophobic films for practical use in outdoor environments where dynamic deformation/loading is applied regardless of the limitation of the surface shape and motion of the target objects.

2. Experimental work

2.1. Materials

Industrial aluminum (Al) plates (0.5 mm thickness, 99.5%) were purchased from Novelis Korea Co. Sodium hydroxide (NaOH), hydrochloric acid (HCl), ammonium bifluoride ($NH_4F{\cdot}HF$), nitric acid (HNO_3), toluene, ethyl alcohol (CH_3CH_2OH), and *n*-hexane (C_6H_{14}) were purchased from Samchun Chemical, Korea. Heptacedafluoro-1,1,2,2-tetra-hydrodecyl-trichlorosilane (HDFS) was purchased from Alfa Aesar. PDMS (Sylgard 184) was obtained from Dow Corning.

2.2. Replicated PDMS film on the aluminum mold

An ultrasonically cleaned Al plate was immersed in a 0.5 M NaOH solution at room temperature for 1 min. Then, Al was etched in a 2.5 M HCl for 15 min at room temperature. Desmut solution was prepared by dissolving 6 g of ammonium bifluoride in 100 ml of 35 wt% nitric acid solution [28]. The etched Al plate was immersed in the desmut solution for 45 s at room temperature. Then, the Al plate was immersed in a 0.5 M NaOH solution at room temperature for 5 s followed by immersion in deionized water at 95 °C for 5 min. In order to enable the release of polymer replicas from the Al mold, the Al plate was treated with a 0.1% (V/V) hexane solution of HDFS for 10 min at room temperature to render the Al plate surface superhydrophobic. Then, the Al mold was rinsed with hexane and dried in an oven at 110 °C for 10 min.

A PDMS prepolymer was prepared by mixing PDMS base and curing agent at a weight ratio of 10:1, and the mixed polymer was further diluted by adding 20 wt% toluene for more easily penetrating the Al mold. After degassing under vacuum for 30 min at room temperature, the pre-cured PDMS mixture was poured into the superhydrophobic Al mold and held for 1 h under vacuum at room temperature in order to eliminate trapped air at the interface between PDMS and mold surface. Afterwards, PDMS was cured at 70 °C for 5 h and carefully detached from the Al mold under ethyl alcohol. To control the thickness and ensure evenness of the film, PDMS was poured onto the Al mold, which was placed on a horizontal outer case, and PDMS was flattened using a blade (Fig. S1).

2.3. Characterization

The surface morphologies were investigated using field-emission scanning electron microscopy (FE-SEM; SU6600, Hitachi, Japan). The peel strength was measured by a load when a specimen with a 35 mm width was pulled at a speed of 50 mm/min using a test machine (Exceed E42, MTS). The average peel strength was obtained from the average value of the peel strength during the displacement between 20 and 50 mm. The CAs and SAs of the droplets of deionized water were measured using a contact angle analysis device (SmartDrop, Femtofab co., Ltd, Korea). The droplet volumes for the CAs were 5 µl and those for the SAs were 5–70 µl. All CAs and SAs that have been reported are the average of five values measured at different points on each specimen. To evaluate the mechanical properties of the films, abrasion, pushing, bending, and straining tests were conducted. For a sand abrasion test, 20 g of sand (40–100 mesh, Acros Organics) was dropped from 10 or 20 cm height to the film, which was inclined at 45°. Pushing and bending tests were carried out on JIPT-100, JIFT-500, JUNIL TECH Co., Ltd, Korea and stretching tests were carried out on Exceed E42, MTS.