

Biomimetically Engineered Polymeric Surfaces for Micro-scale Tribology

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Abstract: In this paper, we report on the replication of surface topography of natural leaf of Lotus onto thin polymeric films using a capillarity-directed soft lithographic technique. PDMS molds were used to replicate the surface. The replication was carried out on poly(methyl methacrylate) (PMMA) film coated on silicon wafer. The patterns so obtained were investigated for their friction properties at micro-scale using a ball-on-flat type micro-tribo tester, under reciprocating motion. Soda lime balls (1 mm diameter) were used as counterface sliders. Friction tests were conducted at a constant applied normal load of 3000 μN and speed of 1mm/s. All experiments were conducted at ambient temperature ($24\pm 1^\circ\text{C}$) and relative humidity ($45\pm 5\%$). Results showed that the patterned samples exhibited superior tribological properties when compared to the silicon wafer and non-patterned sample (PMMA thin film). The reduced real area of contact projected by the surfaces was the main reason for their enhanced friction property.

Keywords: biomimetic, lithography, polymer, micro, friction, tribology

1. Introduction

Nature offers a variety of surfaces, which exhibit evolutionarily optimized functional properties. In recent years, researchers have been exploring the design principles of biological systems for various applications in newly emerging fields such as micro/nano-electronics to structural engineering [1,2]. The study and simulation of biological systems with desired properties is popularly known as "Biomimetics" (meaning to mimic life) [3]. Such an approach involves the transformation of the underlying principles discovered in nature into man made technology [4]. As an example, Lotus leaf has unique ability to avoid getting wet by the surrounding water, which is due to the combination of its surface roughness and the presence of wax. This phenomenon is popularly known as the 'Lotus Effect' [5] and has inspired scientists world wide to modify/fabricate surfaces for creating artificial superhydrophobic surfaces [1,2]. Motivated by the surface topography of Lotus leaf, tribologists have modified/fabricated surfaces by means of laser texturing, ion-beam roughening and fabrication of biomimetic nano-patterns in order to enhance the tribological performance at micro/nano-scale [6-11]. Most of these investigations [6-11] are directed towards enhancing the tribological performance of MEMS (Micro-Electro-Mechanical Systems) elements, which are small in size and operate at nano/micro-scales. At these small scales of operation, the large surface-to-volume ratio results in high surface forces such as adhesion and friction [12], which decrease the performance of MEMS devices [12]. On the contrary, synthetic adhesives have been made from polymeric materials by mimicking the shape

and geometry of gecko setae [13,14]. Thus, it seems that learning from nature's ability to create functional structures would immensely benefit the development of novel functional surfaces/materials.

In this paper, we report on a simple biomimetic approach to obtain enhanced micro-tribological property, which involves the direct replication of Lotus leaf using a capillarity-directed soft lithographic technique. This method provides a fast and efficient route to create artificial functional surfaces using natural templates, which are potentially useful for a range of tribological applications.

2. Experimental

The replication of the surface of Lotus (*Nelumbo nucifera*) leaf in its fresh condition was carried out on poly(methyl methacrylate) (PMMA) film coated on silicon wafer, using a simple capillarity-directed soft lithography technique, which principally utilizes the competition between capillary and hydrodynamic forces in the course of pattern formation [15]. The replicated surfaces so fabricated were investigated for their micro-friction property. Friction tests were performed using Soda lime glass balls of radius 0.5 mm (normal load 3000 μN , sliding speed 1mm/s, scan length 3 mm) in a ball-on-flat type micro-tribotester under reciprocating motion [10]. Fig. 1 shows a close-up view of the reciprocating micro-tribotester that was used to conduct the friction tests. All experiments were conducted at controlled conditions of temperature ($24 \pm 1^\circ\text{C}$) and relative humidity ($45 \pm 5\%$). Tests were repeated more than five times and the average values were plotted.

The details of the replication procedure of the surface of a fresh Lotus leaf are given below. In the first step, a PDMS

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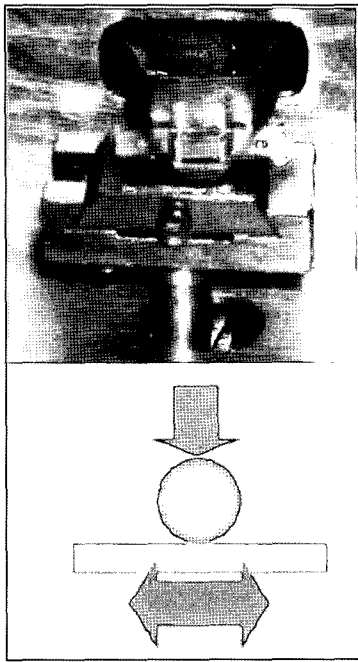


Fig. 1. A close-up view of the ball-on-flat type configuration in the reciprocating micro-tribotester that was used to measure the micro-scale friction of the test samples.

mold was made using a real Lotus (*Nelumbo nucifera*) leaf as the natural template. The PDMS mold was prepared by casting PDMS (10% curing agent) against the surface of a Lotus leaf, which was followed by heating in an oven at 70°C for a duration of ~1 hour. This treatment was done to remove the bubbles present in the PDMS solution. Following this treatment, the mold was peeled off from the leaf surface. Next, PMMA (poly(methylmethacrylate) dissolved in toluene (15 wt%) was spin-coated onto a cleaned silicon wafer. Finally, the PDMS mold was placed on the PMMA surface under a slight pressure of about ~0.2 to 0.3 MPa for conformal contact with the polymer. For a uniform pressure distribution, a thin PDMS block was placed as a buffer on top of the PDMS mold prior to the application of pressure. The sample was thus annealed at 140~150°C, well above the glass transition temperature for 30 minutes on a hot stage, after which the PDMS mold was removed.

3. Results and Discussion

Fig. 2 (A) shows the surface of real Lotus (*Nelumbo nucifera*) leaf. From this figure it could be observed that the surface of the Lotus leaf has randomly distributed protuberances on it [5]. Fig. 2 (B) shows the scanning electron microscope (SEM) image of the surface morphology of replicated Lotus-like surface. It can be seen that the surface of the real leaf has been replicated on a smoother scale. However, the polymeric material (PDMS) seems to have filled the recesses (spaces) between the randomly distributed protuberances, during the process of molding. The replicated surface was characterized for its static contact angle of water using the sessile-drop

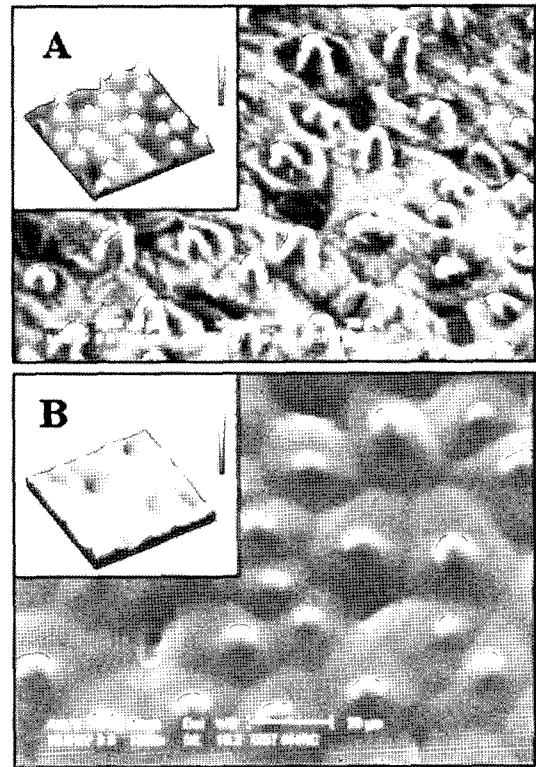


Fig. 2. SEM images showing (A) surface morphology of real Lotus leaf and (B) replicated Lotus-like surface. The insets show their surface images taken using a confocal microscope.

method. Measurements were done more than ten times. It was found that these surfaces were hydrophobic in nature with water contact angle ~91° (Fig. 3). Real Lotus leaf is superhydrophobic in nature and has water contact angle value of about 162°, which is because of the combination of the protuberances and the wax on it [5]. Un-coated silicon wafer is hydrophilic in nature and has a water contact angle of about 22° [16]. The water contact angle of PMMA thin film is 69° (Fig. 3) [10].

The replicated surface was investigated for its micro-friction property and was compared with those of the un-coated silicon wafer and PMMA thin film. In micro/nano-scale devices such as micro/nano-electromechanical systems (MEMS/NEMS), silicon (Si(100)) is a traditionally used material and PMMA is a polymer often found in these devices [17]. Hence, from the tribological point of view, a comparison of the friction behaviour of the replicated surface with silicon wafer and PMMA thin film becomes important.

Fig. 4 shows the values of the coefficient of friction in the case of silicon wafer, PMMA thin film and the replicated surface. From this figure, it could be observed that the replicated surface exhibits superior friction behaviour.

Interestingly, the value of the coefficient of friction of the replicated surface is almost five times lower than that of the PMMA thin film and four times lower than that of the silicon wafer. According to the fundamental law of friction given by Bowden and Tabor, for a single asperity contact, friction force is directly proportional to the real area of contact [18]. Eq. (1)

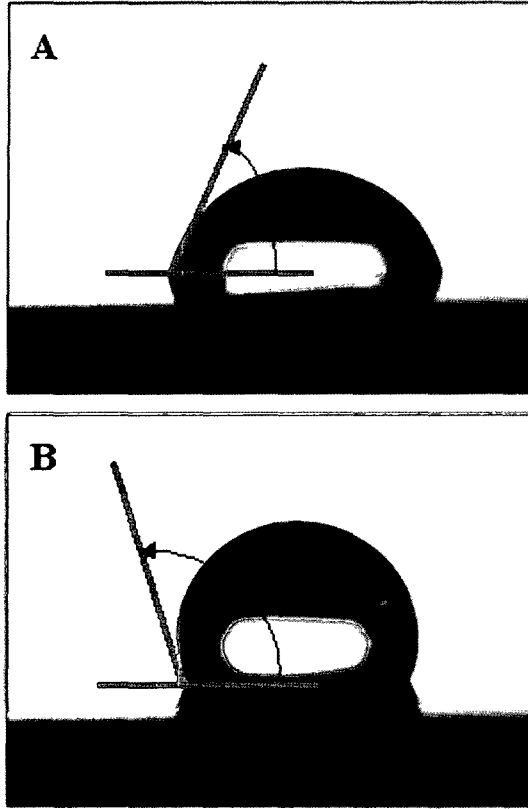


Fig. 3. Optical photos showing water droplet on (A) PMMA thin film and (B) Lotus-like surface. PMMA thin film is hydrophilic (water contact angle $<90^\circ$) and Lotus-like surface is hydrophobic (water contact angle $>90^\circ$) in nature.

gives the expression for the friction force.

$$F_r = \tau A_r \quad (1)$$

where, τ is the shear strength, an interfacial property and A_r , the real area of contact.

In the present case, the lower value of coefficient of friction exhibited by the replicated surface when compared to silicon wafer and PMMA thin film is due to the reduced real area of contact. It is well known that patterning of surfaces causes a reduction in the real area of contact when the size of the asperities (protuberances) is considerably smaller than that of the counterface slider (glass ball in the present case) [8,19]. Further, considering the JKR theory, the contact area not only depends on the applied normal load and the radius of the ball, but also on the interfacial energy [20]. According to this theory, the contact area is related to the applied normal load, the ball size and the interfacial energy of a material as given in equation (2).

$$A_r = \pi \left[\frac{R}{K} (F_n + 6\pi\gamma R + [12\pi\gamma R F_n + (6\pi\gamma R)^2]^{1/2}) \right]^{2/3} \quad (2)$$

where, R is the size of the ball, K the effective elastic modulus, F_n the applied normal load and γ the interfacial energy of the material.

When compared to the silicon wafer and PMMA thin film, the replicated surface has lower surface energy indicated by its higher value of water contact angle (cosine of water contact

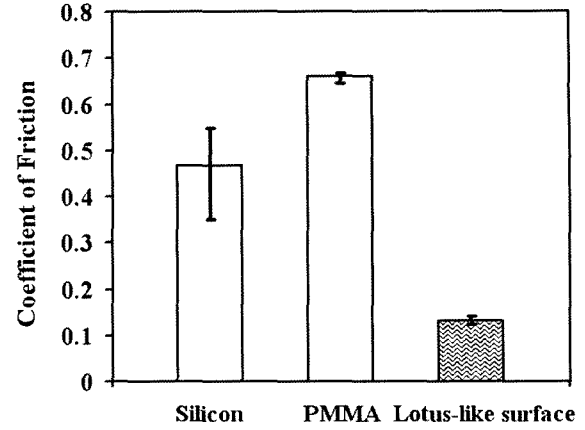


Fig. 4. Coefficient of friction of silicon wafer, PMMA thin film and Lotus-like surface at micro-scale.

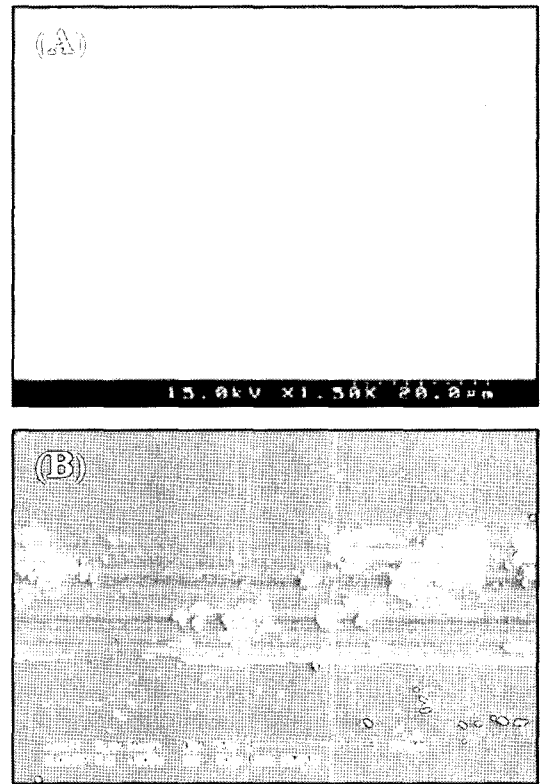


Fig. 5. Worn surfaces of (A) un-coated silicon wafer and (B) PMMA thin film.

angle is a measure of surface energy [21]). Thus, the lower surface energy of the replicated surface further contributes towards reducing the real area of contact thereby lowering its friction value.

Fig. 5 shows the representative surfaces of silicon wafer and PMMA thin film after the friction tests. The silicon wafer and PMMA thin film undergo wear, whereas the patterned surface shows roughening and deformation at the tip of the asperities (protuberances/bumps) (Fig. 6). In our earlier work, we investigated on micro-scale friction property of patterned surfaces with various geometrical parameters (size and shape) fabricated using an artificial template by the same soft

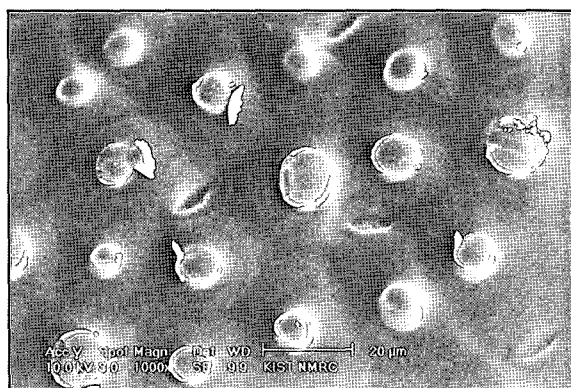


Fig. 6. SEM image of Lotus-like surface taken after friction test.

lithographic method (under the same experimental conditions as those in the present investigation) [10]. Results showed that the lowest possible value of coefficient of friction was about one third of the PMMA thin film [10]. This finding indicates that the natural surface of Lotus leaf appears to be highly optimized in terms of friction despite the fact that one might be able to create low-friction surfaces using artificial templates with carefully designed parameters. As a part of our ongoing research work, we are exploring the replication with different polymeric materials to ensure flexibility of the fabrication method.

4. Conclusions

In conclusion, we have presented a novel method to enhance micro-scale tribological property by the replication of natural surface of Lotus leaf on thin polymeric films, which is simple and cost-effective. Looking at the enhanced tribological properties exhibited by these surfaces, we believe that in the future, these kinds of surfaces would have potential application in small-scale devices.

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