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Fabrication and characterization of hierarchical nanostructured smart adhesion surfaces

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ABSTRACT

The mechanics of fibrillar adhesive surfaces of biological systems such as a Lotus leaf and a gecko are widely studied due to their unique surface properties. The Lotus leaf is a model for superhydrophobic surfaces, self-cleaning properties, and low adhesion. Gecko feet have high adhesion due to the high micro/nanofibrillar hierarchical structures. A nanostructured surface may exhibit low adhesion or high adhesion depending upon fibrillar density, and it presents the possibility of realizing eco-friendly surface structures with desirable adhesion. The current research, for the first time uses a patterning technique to fabricate smart adhesion surfaces: single- and two-level hierarchical synthetic adhesive structure surfaces with various fibrillar densities and diameters that allows the observation of either the Lotus or gecko adhesion effects. Contact angles of the fabricated structured samples were measured to characterize their wettability, and contamination experiments were performed to study for self-cleaning ability. A conventional and a glass ball attached to an atomic force microscope (AFM) tip were used to obtain the adhesive forces via force-distance curves to study scale effect. A further increase of the adhesive forces on the samples was achieved by applying an adhesive to the surfaces.

1. Introduction

Superhydrophobic surfaces exhibit extreme water repellent properties. Certain plant leaves, notably Lotus leaves, are known to be superhydrophobic and self-cleaning with low adhesion, known as the Lotus effect [1–5]. These properties are achieved by having a hydrophobic surface and a hierarchical structure with both micro- and nanoscale dimensions. These surfaces are of interest in various applications, such as self-cleaning windows and display screens for electronic devices, exterior paints for building, navigation ships, textiles, and solar panels. The leg attachment pads of several creatures, including many insects, spiders, and lizards, are capable of attaching to a variety of surfaces and are used for locomotion, known as the gecko effect [5–9]. Geckos, in particular, have the largest mass and have developed the most complex hairy attachment structures capable of smart adhesion, which is the ability to cling to different smooth and rough surfaces and detach at will. The high-adhesion mechanism of geckos is based on so-called division of contacts [6,10]. Cumulative van der Waals attraction results in strong adhesion. In addition to strong adhesion, because of a three level hierarchical structure, they have the ability to adapt to a variety of surfaces. They exhibit wear resistance and self-cleaning. They can also detach via peeling action to provide reversible adhesion. Attempts are being made to develop climbing robots using gecko inspired structures [11].

Due to the highly optimized and efficient properties of living nature organism surfaces and their potential applications, researchers have studied their mechanisms and exploited them for commercial applications [5,9,12,13]. In order to get the Lotus effect, hierarchical structures using wax structures, nanotubes, and nanoparticles have been fabricated by a large number of investigators; for a review, see Bhushan and Jung [4]. In order to obtain the gecko effect, a high density of nanofibers is required. Hard materials such as carbon nanotubes have been used to fabricate gecko-like structures to get high fiber density [7,14]. The hard materials provide high resistance to wear and surface contamination. To provide higher adhesion and adaptability to mating surfaces, soft materials such as polymers have been used to fabricate a one-level fibril structure [15–19]. The fabrication processes used are complicated and generally provide a low aspect ratio of length (height) to diameter of fibers, and the diameter of the fibers is generally on the microscale. Murphy et al. [20] had suggested a fabrication technique of two-level polymer gecko structures, but the fabricated fibers are on the microscale.

In the present study, two-level polymer fibril structures with high aspect ratio are fabricated using stacked porous membranes as a template with nanoscale pores. For the first time, by changing the densities and diameter of nanofibers, superhydrophobic surfaces with either Lotus effect or gecko effect have been fabricated.

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Contact angle and AFM adhesion measurements have been made. By applying an adhesive to the fiber structure surfaces, an increase of adhesion on the fiber structures was achieved by combining the gecko effect and a classical adhesive approach.

2. Mechanisms of Lotus and gecko

2.1. Contact angle

The primary parameter that characterizes wetting is the static contact angle, which is defined as the angle that a liquid makes with a solid. The contact angle depends on several factors, such as surface energy, surface roughness, and its cleanliness [3,21–24]. Surfaces with contact angles in the $0^\circ \leqslant \theta \leqslant 90^\circ$ and $90^\circ \leqslant \theta \leqslant 180^\circ$ ranges are hydrophilic and hydrophobic, respectively. In particular, surfaces with contact angles between 150° and 180° are called superhydrophobic. Water contact angle hysteresis (CAH) is another property of interest to reduce drag in fluid flow. CAH occurs due to surface roughness and heterogeneity. Contact angle hysteresis is a measure of energy dissipation during the flow of a droplet along a solid surface. A liquid droplet on a solid surface removes contaminant particles by rolling in addition to sliding at low CAH. Surfaces with low CAH (<10°) are generally referred to as self-cleaning [3]. The contact angle can be determined by minimizing the net surface free energy of the system of a liquid droplet on a solid surface. The well-known Young equation for the contact angle provides an expression for the static contact angle for given surface energies. On rough surfaces such as hierarchical structures, the contact angle is dependent upon the heterogeneous (composite) interface present. For the heterogeneous interface, the contact angle is given by the Cassie–Baxter equation:

$$\cos\theta = R_f \cos\theta_0 - f_{LA}(R_f \cos\theta_0 + 1) \qquad (1)$$

where θ is the contact angle on a rough surface, θ_0 is the contact angle on a smooth surface, f_{LA} is the fractional contact area of the liquid–air, and R_f is the surface roughness factor (>1) equal to the ratio of the real interface surface area (A_{SL}) to its geometric interface area (A_F), $R_f = A_{SL}/A_F$.

An expression for CAH as a function of roughness has been developed. The difference of cosines of the advancing (θ_{adv}) and receding (θ_{rec}) angles is related to the difference of those for a nominally smooth surface (θ_{adv0} and θ_{rec0}) and is given as [3]:

$$\cos\theta_{adv} - \cos\theta_{rec} = R_f(1 - f_{LA})\,(\cos\theta_{adv0} - \cos\theta_{rec0}) + H_r \qquad (2)$$

where H_r is the effect of surface roughness, which is equal to the total perimeter of the asperity per unit area. Thus, CAH is proportional to the fraction of the solid–liquid contact area ($f_{SL} = 1 - f_{LA}$).

2.2. Adhesion

The explanation for the adhesion properties of the Lotus surface and gecko feet can be found in the morphology of the Lotus surface structure and the skin on the toes of the gecko. On the Lotus surface, the papillose epidermal cells form asperities and provide microscale roughness. A range of waxes made from a mixture of long chain hydrocarbon compounds which are not easily wetted are usually present on the Lotus surface. A microscale roughness surface is covered by sub-microscale asperities of three-dimensional epicuticular waxes, creating a hierarchical structure. The hierarchical structure of the Lotus surface has low adhesion due to the low density of the sub-microscale asperities. Nanoscale roughness allows water droplets to sit easily on the apex of the nanostructures, because air pockets occur in the valleys of the structure under the droplet, resulting in high contact angle and low CAH. Therefore, the Lotus leaves have low adhesion, superhydrophobicity, and self-cleaning.

The toe skin of the gecko is also comprised of a complex hierarchical structure of lamellae, setae, branches, and spatulae [25]. The division of contacts serves as a means for increasing adhesion [10]. The surface energy approach can be used to calculate adhesion force in a dry environment in order to calculate the effect of division of contacts. The adhesion force of a single contact F_{ad}, based on the so-called Johnson-Kendall-Roberts (JKR) theory, is given by [26]:

$$F_{ad} = \frac{3}{2}\pi W_{ad} R \qquad (3)$$

where R is the radius of a spatula hemisphere tip, and W_{ad} is the work of adhesion (unit of energy per unit area). It shows that the adhesion force of a single contact is proportional to the linear dimension of the contact. For a constant area divided into a large number of contacts or setae n the radius of a divided contact, R_1, is given by [6]:

$$R_1 = \frac{R}{\sqrt{n}} \qquad (4)$$

Therefore, the total adhesion force (F'_{ad}) for multiple contacts can be given by:

$$F'_{ad} = \frac{3}{2}\pi W_{ad}\left(\frac{R}{\sqrt{n}}\right)n = \sqrt{n}F_{ad} \qquad (5)$$

Thus, the total adhesive force increases linearly with the square root of the number of contacts. Based on this analysis, one needs to develop structures with a high density of nanofibers. A hierarchical structure is needed to provide adaptability to a variety of rough surfaces [8].

3. Experimental

3.1. Materials and sample preparation

Polycarbonate, (PC) (MILLIPORE, MA) a porous membrane (30 μm thickness) with various pore sizes (50 nm, 100 nm, 600 nm, and 5 μm diameter) was used to create structures with different diameters and density of fibers. All samples were fabricated using polypropylene (PP) (OC01, Laird Plastics, OH), a thermoplastic polymer. Its molecular chain is $(C_3H_6)_n$ with a melting temperature of 130–171 °C and a Young's modulus of 1.5–2 GPa [27]. PP has low surface energy (about 30 mJ/m^2). Fig. 1 shows the stacks used to fabricate one- or two-layered structures. For the samples with a one-layer structure (Fig. 1a), a 1-mm thick PP film and a PC membrane were sandwiched between two polydimethylsiloxane (PDMS) disks, and the whole stack was again sandwiched with two aluminum sheets to provide support [28]. For fabricating the two-layer structure (Fig. 1b), PP film was placed on top of two PC membranes with different sizes corresponding to two layers. The stacked layers were placed in an oven at 200 °C for 40–50 min with a weight of 1 kg in order to melt the PP and fill the pores in the membrane. For reference, polycarbonate melting temperature is 267 °C. After heating in an oven, the sandwiched samples were dipped into methylene chloride for 1 h to etch the membranes to realize the polypropylene fibers.

To fabricate large diameter fiber structures, a micropatterned silicon mold with 14 μm diameter, 21 μm pitch, and 30 μm height was used. A negative replica was created using dental wax [29]. PP was melted into the negative mold in the oven at 200 °C for 40–50 min. The melted samples were dipped into methylene chloride or a mixture of methyl chloride and chloroform for 1 h as in other cases.

The fiber size and geometry of the fabricated arrays are described in Table 1. Due to the high aspect ratio (length/diame-