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Research paper

Effect of hair morphology and elastic stiffness on the wetting properties of hairy surfaces

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ABSTRACT

Biomimetic surfaces with special wetting properties are attracting a lot of attention because of their fundamental and industrial applications. By tuning surface micro-nano structures and composition, it is possible to fabricate superhydrophobic surfaces exhibiting extreme water repellence and self-cleaning properties like the famous Lotus leaves or strong water adhesion as found on rose petals. Here we report results of a comprehensive study of the static and dynamic wetting properties of hairy surfaces produced by polymer replica molding of porous alumina matrices which are able to pin large water drops. The hairs, which have a characteristic diameter of 80 nm and height between 200 and 600 nm, are fabricated by imprinting an alumina (AAO) stamp into hard poly(dimethylsiloxane) (h-PDMS) and polypropylene (PP) samples. These polymers have similar contact angles for water drops on flat surfaces, but have an elastic modulus that differs by a factor of approximately 100. Hairy surfaces significantly increase drop stickiness with respect to the flat ones for either polymer, with the h-PDMS samples capable of holding water drops about 20% larger than those of the more rigid PP. We also imprinted micropatterned stamps covered by the porous alumina layer to produce multi-scale polymer surfaces consisting of a nanometric hairy layer superposed onto micrometric grooves. Water drops are suspended by the micrometric pillars and the resulting adhesion is intermediate between that on flat and on hairy surfaces. Finally, for nanoimprint with extremely deep AAO pores we saw a complete inversion of drop stickiness to the PP surface: long, collapsed hairs assembled a secondary micrometer scale network exhibiting non-stick hydrophobic wetting properties superior even to the hairy micro-patterned surface. This results in a robust technique to tailor the wetting behavior of polymeric surfaces.

1. Introduction

Bio-inspired superhydrophobic surfaces are attracting attention because of their potential applications as smart coatings [1–5]. Superhydrophobicity means that the apparent (static) contact angle θ that a water drop forms with the surface is $>150°$. In nature, the surfaces of many plants exhibit a high θ, the most famous examples being lotus leaves and rose petals. However, the dynamic behavior can vary significantly [6]. On a lotus leaf, water drops roll off very easily even at inclinations below 10°, removing dust particles present on the leaf surface (lotus effect). In contrast, large water drops stick to rose petals even though they are tilted upside down (petal effect). In both cases, an appropriate roughness at the micro/nanometer scale of the surface is required to achieve the specific superhydrophobic behavior because for all known flat surfaces the maximum θ is always below 120° [7,8].

Various methods have been devised for the realization of rough surfaces at the micro/nanoscale to produce low-adhesion superhydrophobic surfaces [9–18]. Attention has also been devoted to the fabrication of smart coatings which can change their wettability when subject to specific external stimuli, like light [19–21], temperature [22,23], and pH [24,25]. More recently, sticky surfaces [26–29] and surfaces with switchable adhesion [30–38] have also been obtained.

One simple and reproducible method of fabricating sticky hairy surfaces relies on replica molding of suitable templates by polymers. The rose-petal surface structure was replicated by employing a UV molding process using polyurethane acrylate (PUA) for the first replica and perfluoropolyether (PFPE) for the second replica [39]. As a result, PFPE micro-nanostructures, which were identical to the rose-petal hierarchical structure, were formed on a glass substrate. A water contact angle of 144° and contact-angle hysteresis of 83° were found. Adhesive superhydrophobic surfaces were obtained by casting poly(dimethylsiloxane) (PDMS) on silicon carbide paper characterized by a rough texture at the micron scale [40]. Two-level polymer fibril structures with high aspect ratio were fabricated using stacked porous polycarbonate membranes as a template with nanoscale pores [41]. Structures

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in polypropylene were created with different diameters and density of fibers. By changing the densities and diameter of nanofibers, superhydrophobic surfaces with either Lotus effect or gecko effect were obtained. Self-ordered nanoporous alumina membranes (AAO) constitute a particularly attractive template characterized by regularly arranged, parallel nanopores with narrow diameter distribution and uniform depth [42,43]. Sticky hairy surfaces were obtained by casting i) hard PDMS in these alumina membranes and peeling off the molded PDMS from the alumina template [44] and ii) polystyrene (PS) followed by dissolution of the template in an etching solution [26]. Water contact angles as high as 150° (162°) were observed on the hairy PDMS (PS) surface, and the maximum water volume they could hold while kept in a vertical position was of 12 μL (6 μL). Polymeric nanopillars of controlled length were fabricated using a two-step wetting method [45]. Firstly, by filling uncured PDMS into the nanopores of an alumina template and then dissolving partially the uncured PDMS, the depth of the nanopores is adjusted and increases with the dissolving time. Subsequently, the second wetting step by polymeric liquid with the PDMS filled alumina template yields length-controlled nanopillars. Polystyrene nanopillars of average height varying between 200 and 1200 nm were obtained and the water contact angle was found to increase from 90° to 150° on the longest hairs.

Controllable adhesive superhydrophobic PDMS surfaces presenting arrays of regular micrometric pillars made by standard photo and soft-lithography [46] have been recently investigated. Square pillars with sides of a few micrometers and height up to 20 μm were prepared with two different mixing ratios (MR) of base to curing agent which alter the pillar stiffness. When the pillar height was larger than 3.3 μm, the patterned PDMS surfaces made with the standard MR = 10:1 exhibited slippery superhydrophobic behavior while those of MR = 20:1 were sticky. This different response was explained by the collapse of the softer PDMS (e.g., MR = 20:1) pillars due to the deposition of water drops.

We have thus decided to explore in more detail the effect of the substrate elasticity by fabricating hairy surfaces having the same morphologies but using two polymers of extremely different elastic modulus. By also choosing systems with nominally equivalent wetting behavior when flat, we tried to distinguish the elasticity contribution to adhesion from the morphology one. Our hairy patterns were produced by casting polymers in porous alumina templates that have pores of characteristic size ~80 nm. In addition, we fabricated stamps with micrometer scale line patterns covered by the porous alumina layer to obtain surfaces that present a micrometric structure superimposed to the nanometric hairy carpet. This results in a robust technique to tailor the wetting behavior of polymeric surfaces. The paper is organized as follows. First, we describe in some detail the experimental methodology used to fabricate the hairy surfaces. We then present the wettability and adhesion data, before summarizing the main results in the conclusions.

2. Materials and methods

2.1. Fabrication of silicon molds

Silicon molds were fabricated using standard photolithography and reactive ion etching. Silicon samples (6″ p type −100 oriented silicon wafers diced in 3 × 3 cm^2 pieces) were first prebaked at 150 °C for 5 min to remove moisture. After that they were spin coated using a positive photoresist (S1813 PR, Shipley). The spinning speed was 5000 round per minute (rpm) for 45 s. Then, a 115 °C soft bake for 90 s was done to remove the remaining solvent in the resist, followed by the exposure using a chromium glass mask with OAI Mask Aligner (Model MBA800). The exposure time was 2.5 s. After the exposure, a development of the resist was done with a developer MF 319 for 45 s. Using the patterned resist as an etch mask, the silicon was etched by reactive ion etching (Oxford ICP etcher). An inductively coupled plasma (ICP) etch was used to etch the Si stamps, using CHF_3 (flowrate = 80 sccm) and SF_6 (flowrate = 15 sccm) with a process pressure of 16 mTorr, RIE power 30 W, ICP power 1200 W, pedestal temperature 20 °C and backside pressure 10 Torr. The etching time was 8 min. The remaining photoresist after etching was removed using acetone in ultra-sound bath for 30 min. The field patterned consisted of 1.5 × 1.5 cm^2 area of silicon mold, containing line grating with 4 μm pitch (2 μm lines and grooves) with ~2 μm groove depth (see Fig. 1.a–c). The molds were finally silanized with Octadecyltrichlorosilane (OTS) solution to obtain a low energy surface.

2.2. Pore generation on Al films

Flat and micropatterned Si substrates were coated with Al using a metal evaporator system. The Al films deposited were of various thicknesses: 200 nm, 300 nm, 400 nm and 600 nm to produce polymer hairs of varying heights. An electro-chemical anodization process with different anodization voltages and different electrolyte solutions were used to produce pores of tunable dimensions [43,47]. For this work, pores of 80 ± 40 nm diameter and 150 ± 50 nm pitch were formed (see Fig. 1.d–e). These molds were finally silanized with an OTS solution to obtain a low energy surface. Silanization provides good anti-sticking surface properties to the molds that allow easy and smooth detachment of the patterned replica from the stamp surface. This helps preventing damage of both the molds and the patterned replica as well.

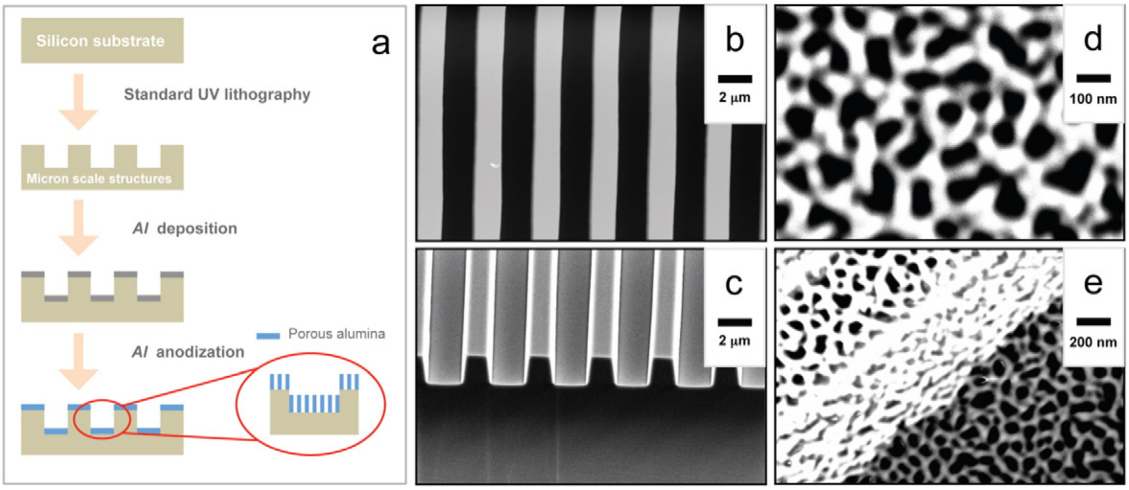

Fig. 1. (a) Novel nanoimprint stamp production via combined optical lithography and self-assembly process. (b + c) A conventional photolithography process provides microscale features. An electro-chemical anodization procedure provides nanoscale pore production of tunable dimension on flat (d) and micropatterned (e) Si surfaces.