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Effect of wetting case and softness on adhesion of bioinspired micropatterned surfaces

Meng Li[a], Jun Xie[a], Qingwen Dai[a,b], Wei Huang[a,b], Xiaolei Wang[a,b,*]

[a] College of Mechanical & Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, China
[b] Jiangsu Key Laboratory of Precision and Micro-Manufacturing Technology, Nanjing 210016, China

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ABSTRACT

Inspired by the adhesive ability of amphibian toe-pads, polydimethylsiloxane (PDMS) hexagonal pillar arrayed surfaces with varying softness are fabricated, and their adhesion behaviors in the non-wetting, mostly wetting and totally wetting cases are throughly investigated. Experimental results demonstrate that under a totally wetting case, i.e. the biological toe-pad-like case, besides the long-range capillary force, a short-range interaction caused by close contact plays a significant role for adhesion. Compared with unpatterned surface, hexagonal pillar patterns can lead to a remarkable improvement in both short- and long-range contribution for wet adhesion. Meanwhile, the surface softness performs a beneficial character in the short-range contribution for the adhesion of micropillars. Considering the fact that the soft microstructure and the almost totally wetting case (low surface tension of secretion and high surface energy of epidermis) on the pads of nature species, it is reasonable to suggest that these evolutions are in favor for wet attachments.

1. Introduction

The amphibians such as tree frogs, torrent frogs and newts are remarkable in their ability of attaching and climbing in wet environments without falling (Barnes, 1999; Barnes et al., 2002; Drotlef et al., 2014; Endlein et al., 2013; Huang and Wang, 2013; Wang et al., 2016). This extraordinary ability is widely believed to be a result of the specific topography on their toe-pads, and massive scientific interest has be aroused over the past decade (Barnes et al., 2006; Barnes, 1999; Federle et al., 2006; Hanna and Barnes, 1991). Unlike the hairy tissue of geckos, the toe-pads of above amphibians are usually featured by a polygonal micro-structure of epidermal cells separated by mucus-filled channels (Barnes et al., 2013, 2002; Federle et al., 2006; Green, 1979; Green and Simon, 1986). Though the mechanism underlying natural wet attachments is still not fully clear, acquired experimental evidence suggests that these tailor-made polygonal patterns can allow the toe-pads to expel fluid out of the contact area between the pad epidermis and the substrate to achieve the "close contact" situation, and a boundary friction happens when a shear load is applied (Federle et al., 2006; Lorenz and Persson, 2011; Persson, 2007). These characteristics can significantly enhance the attachment forces of toe-pads on wet surfaces.

Abundant researches have demonstrated and characterized the high friction properties of bioinspired polygonal micropillars in wet sliding (Drotlef et al., 2013; Fischer et al., 2016; Huang and Wang, 2013; Iturri et al., 2015; Li et al., 2015; Roshan et al., 2011; Varenberg and Gorb, 2009). However, considering the various attaching modes of amphibians in nature, the adhesion force is also an important role for wet attachments. For example, tree-frogs can not only climb or attach slippery slopes but also hang upside down on wet leaves without falling. Barnes *et al.* early measured this considerable adhesive interaction on tree-frog toe-pads (about 1.2 mN mm^{-2}), and attributed it to capillary and viscous forces (Stefan adhesion) (Barnes, 1999, 2007; Hanna and Barnes, 1991). Federle et al. (2006) pointed out that the film between the pad and the substrate was extremely thin (mostly less than 35 nm), and this "close contact" played a positive role for wet attachments. Recently, Drotlef et al. (2013) carried out a pioneering adhesive study on tree-frog like micro-patterned PDMS surfaces with Young's modulus about 2 MPa. They found that the not viscous forces but capillary forces (a long-range attractive interaction) make main contribution for wet adhesion in a hydrophilic case (contact angle (CA) = 10°). However, considering biological adhesive toe-pads, there are another two facts that might be ignored in previous studies. First, the secreted mucus can widely spread on toe-pads due to its low surface tension, nearly presenting a totally wetting case (CA = 0°) (Drotlef et al., 2013; Federle et al., 2006; Persson, 2007). And next, as reported by Barnes (2007), Barnes et al. (2011) and (Scholz et al., 2009) the surface of biological toe-pads is extremely soft and malleable with a low Young modulus of approximately 4–40 kPa. Therefore, does the wetting

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* Corresponding author at: College of Mechanical & Electrical Engineering, Nanjing University of Aeronautics & Astronautics, Nanjing 210016, China.
E-mail address: wxl@nuaa.edu.cn (X. Wang).

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case or surface softness have an influence on the wet adhesion of toe-pads? If so, how do the soft micropillars behave for adhesion in different wetting case, and what is the role of softness on micropillars for wet adhesion? To date, little research has been conducted to comprehend the wet adhesion on these aspects.

In this study, very soft hexagonal micropillar patterned surfaces were fabricated with a modified PDMS. Water, sodium dodecyl sulfate solution and dimethyl silicon oil were employed to achieve three different wetting cases (non-wetting case, mostly wetting case, totally wetting case) on PDMS surfaces. Then adhesion properties of micropatterned surfaces to a silica glass probe were studied in different wetting cases. Moreover, the effects of softness on micropatterns on wet adhesion forces were assessed and analyzed.

2. Materials and methods

2.1. Mold preparation

Silica glasses were ultrasonically cleaned by acetone, ethyl alcohol and deionized water. Before lithographic processing, the wafers were rinsed with acetone and blown dry with nitrogen. An AZ P4620 photoresist is spun on these wafers at 2500 rpm for 8.5 µm film, followed by 2 min of soft baking at 100 °C. An optical lithography writer (Durham, Britain) were used to expose with 10 × 10 mm^2 fields and then the film was developed in AZ 400 K of 1:4 for molds.

2.2. Patterned surface preparation

PDMS (Sylgard 184, Dow Corning) was mixed with a prepolymer to cross-linker ratio of 10:1. The soft patterned surfaces were fabricated by filling a low viscosity dimethyl silicon oil (PMX-200, viscosity 10cs, Dow Corning) into the PDMS. The filled silicon oil molecules will stretch the crosslinked network of PDMS to lower the hardness and elasticity modulus of material (Fig. 1a). In this paper, the filling ratios (r) of dimethyl silicon oil were 0.5:1, 1:1 and 1.5:1 to the prepolymer of PDMS. All mixed liquids were degassed in a desiccator until no bubbles and cured in an oven for 12 h at 70 °C. After demoulding, samples were characterized using white-light interferometry (Bruker, USA) and digital microscope (Keyence, Japan). The side length of hexagonal pillars was 15 µm, the side distance was 7 µm and the height was 8.5 µm, as shown Fig. 1b.

2.3. Elastic modulus and hardness measurements

The elastic modulus of flat surfaces was measured using a custom-built equipment consisting of a tungsten steel pin with a flat tip (1 mm diameter, Young's modulus of 7.2 × 10^{11} Pa) mounted at the end of a cantilever (Supplementary material, Fig. S1) (Li et al., 2017). The operational process was similar to a typical elastic modulus test on nanoindentor. The preload of initial indentation on the surface was 30mN, and the unload process was operated by a pizeo at a speed of 0.5 µm/s. The force-distance of elastic recovery of PDMS was used to calculate the elastic modulus by related formulates of contact mechanics (Supplementary material, Eq. S1-4 and Fig. S2). The hardness of flat PDMS was measured using shore A durometer (LX-A, Shanghai Zijiu measuring tool) following “DUROMETER-A Measure of Hardness-Shore A or 00 Scale” CTM0099 (Dow Corning Corp, USA). Fig. 1c show the Shore hardness and Young modulus of PDMS with different filling ratio r.

2.4. Characterizations of wetting case on samples

Water (surface tension 71.97 mN/m), 1% sodium dodecyl sulfate solution (w/w in distilled water, surface tension 32.69 ± 0.47 mN/m, SDSS) and dimethyl silicone oil (viscosity 10 cs, surface tension 19.41 ± 0.15 mN/m) were employed here to achieve there wetting cases (non-wetting, mostly wetting and totally wetting case) (Supplementary material, Fig. S3 for liquid surface tension tests). The details characterized by the static contact angles (CAs) and spreading pictures of liquids. For CA measurements, a drops with the volume of 2 µl liquid was placed onto the sample and its image was caught by a CCD-camera. At least five measurements were performed on each sample. For the glass probe, the contact angles of water, SDSS, and silicone oil were 47.7 ± 0.5°, 10.4 ± 1.2°, ≈ 0° respectively (details are presented in Supplementary material, Fig. S5). For liquid spreading pictures, a 0.5 µl drop was placed onto the sample surface, then a digital microscope (Keyence, Japan) was used to monitor the liquid spreading.

From Fig. 2, it can be seen that the water on flat PDMS clearly exhibits non-wetting case with a static CA of about 100° and the existence of patterns produce a significant decrement in wettability, showing a hydrophobicity. For the SDSS on PDMS surfaces, it is configured as the mostly wetting case with the $0° < CA < 90°$. Because of the lowest surface tension, the silicone oil on flat surface presents a nearly zero CA (Fig. 2a and S4), which means that the liquid drop can totally wet the solid showing a totally wetting case, similar to the mucus secreted by tree-frog toe-pads. Although the CA of silicone oil on hexagonal pillars is also zero, the large drop spreading map on the microscopic picture indicates that this pattern is beneficial for liquid wetting and spreading, showing an excellent drainage effect (Fig. 2b). In fact, the non-wetting and mostly wetting cases can be configured as the spreading parameter $S < 0$ ($S = [E_{subatrate}]_{dry}$- $[E_{subatrate}]_{wet}$) and the totally wetting case shows $S > 0$ (Gennes et al., 2004).

2.5. Adhesion measurements

Wet adhesion measurements were performed using the custom-made setup, as shown in Fig. 3a, which is also detailly described in ref. (Li et al., 2017) The probe used here is a plano-convex lens with a curve radius of 18.5 mm (Purshee, China), Young's modulus of 7.2 × 10^{11} Pa, and Poisson's ratio of 0.2. Owing to the great difference in surface tension, water, SDSS and dimethyl silicone oil were selected to achieve three different wetting cases (non-wetting case, mostly wetting case,

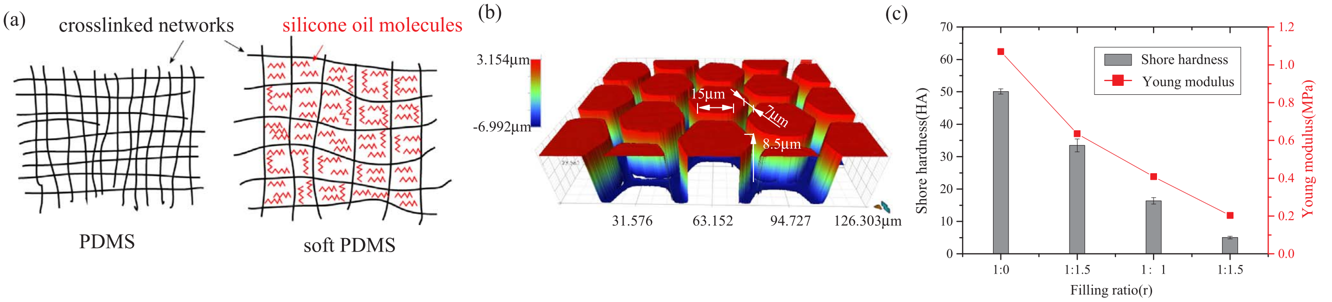

Fig. 1. (a) Schematic illustration of filling silicon oil for soft PDMS, (b) 3D profiles of the hexagonal pillars with the filling ratio r = 1.5:1, (c)shore hardness and Young modulus of flat PDMS with the silicone oil at different filling ratios to prepolymer.