

## Silicone brushes: Omniphobic Surfaces with Low Sliding Angle

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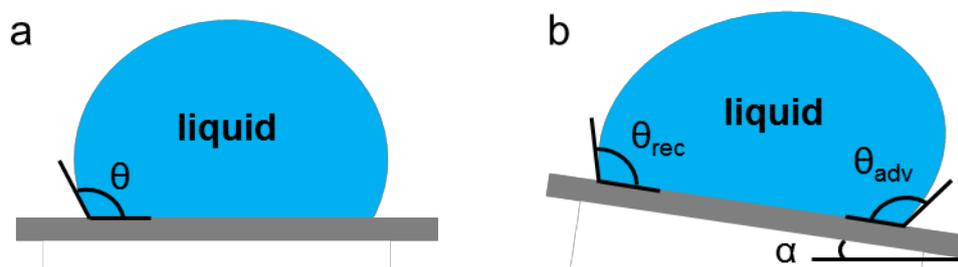
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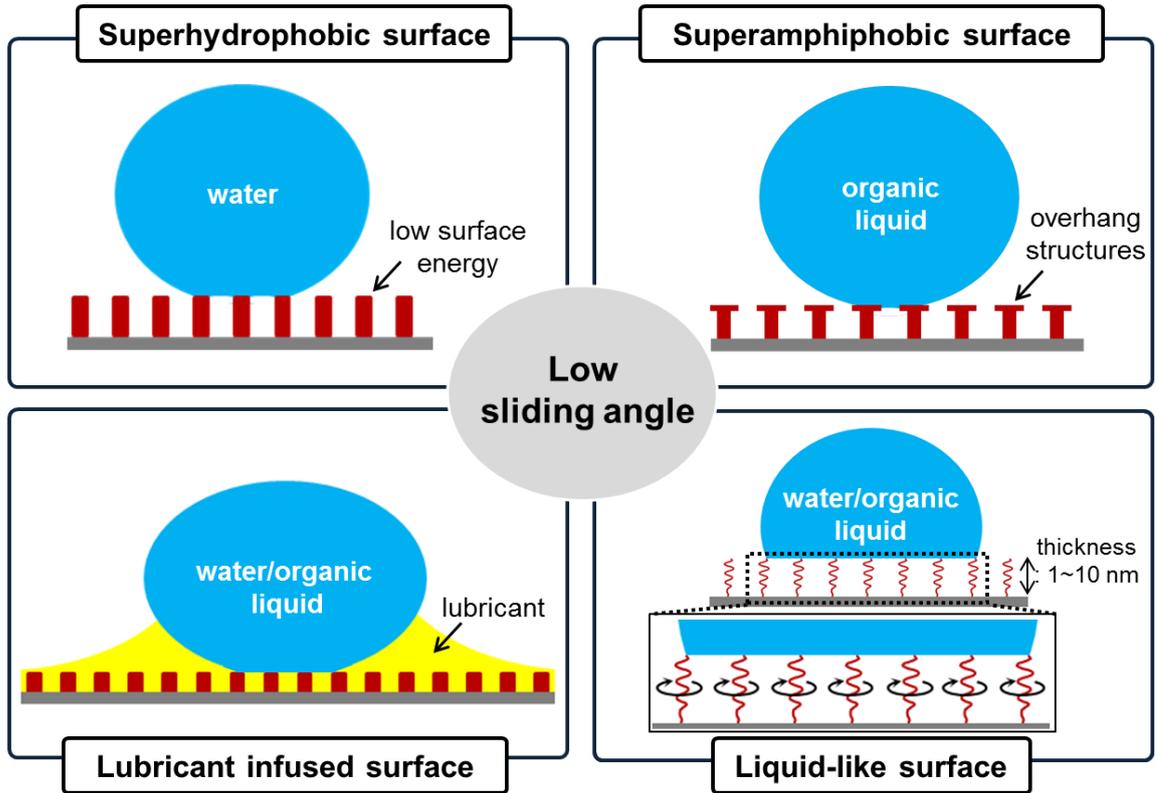
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Liquid droplets are omnipresent. This has inspired numerous studies on the wetting behavior of liquid droplets under static and dynamic conditions. Insights from these studies have led to improvements in the efficiency, energy consumption and environmental friendliness of various industrial processes. Prominent examples include efficient distribution of pesticides on leaves, spray cooling and painting and heat transfer. Detailed investigations have been conducted into drop nucleation and growth and a great deal of research has gone into developing novel surfaces to optimize the wetting behavior for specific applications. In particular, super-liquid-repellent surfaces have been investigated extensively.<sup>[1]</sup>

The wetting behavior of smooth and rough surfaces is characterized by the static contact angle, also termed material's contact angle. However, its value depends on how the drop is deposited. In practice a droplet has two contact angles for every material, an advancing ( $\theta_{adv}$ ) and a receding ( $\theta_{rec}$ ) contact angle. The reason is that even the tiniest topographical or chemical inhomogeneity provides pinning sites for the droplet. The strength of pinning is reflected in the difference between the advancing and receding contact angles, i.e. the contact angle hysteresis (Scheme 1).<sup>[2]</sup>



**Scheme 1.** a) Schematic illustration of a liquid drop resting on a horizontal surface.  $\theta$  is the static contact angle, also termed the material's contact angle. b) A drop on a tilted surface. The advancing contact angle denotes the maximum angle just before the drop advances. The receding contact angle denotes the minimum angle just before the drop recedes. The tilting  $\alpha$  denotes the angle at which the gravitational force overcomes the lateral adhesion force and induces sliding or rolling of the drop.



**Scheme 2.** Low sliding angle surfaces. Superhydrophobic and superamphiphobic surfaces show contact angles above  $150^\circ$  and roll-off angles below  $10^\circ$  for water and for both water and organic liquid drops, respectively. Liquid drops deposited on a lubricant-infused surface typically have a contact angle above  $150^\circ$  and a sliding angle below  $3^\circ$ . Liquid-like surfaces can show a sliding angle below  $8^\circ$  for water and  $1\text{--}2^\circ$  for non-polar organic liquids.

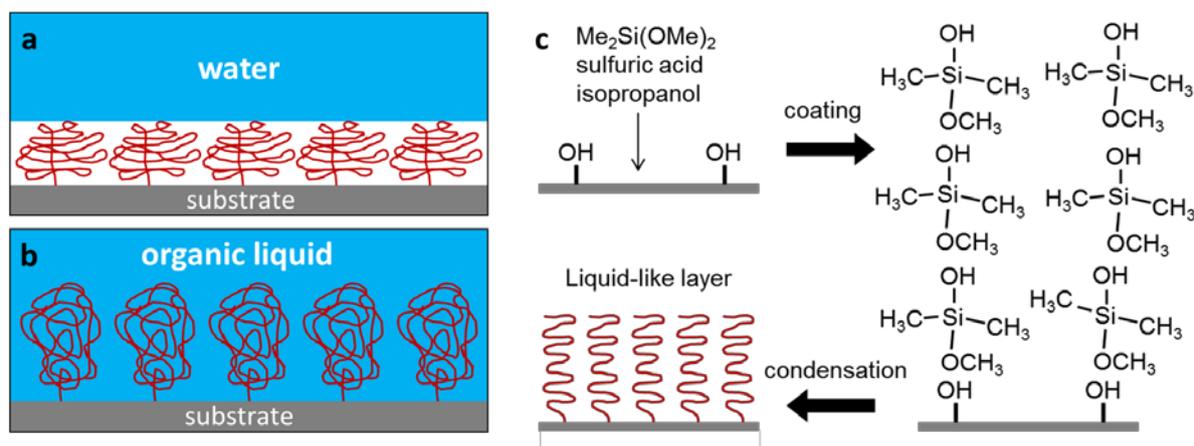
A low contact angle hysteresis is essential for easy removal of droplets from the surface, as defined by the lateral adhesion force  $F_{LA} = k\gamma L (\cos\theta_{rec} - \cos\theta_{adv})$ , where  $\gamma$  is the surface tension,  $L$  is the contact width of the drop with the surface, and  $k$  is a dimensionless factor that accounts for the precise shape of the solid-liquid-air three phase contact line.<sup>[3]</sup> A low lateral adhesion force implies a low sliding or rolling angle  $\alpha$ , which is the tilt angle required for the gravitational force,  $F = \rho V g \sin\alpha$ , to overcome the adhesion force. Equating these two forces leads to the critical angle required for droplet sliding or rolling:

$$\sin\alpha = \frac{k\gamma L}{\rho V g} (\cos\theta_{rec} - \cos\theta_{adv})$$

where  $V$  is the volume of the drop,  $\rho$  is the density of the liquid, and  $g=9.81 \text{ m/s}^2$  is the acceleration due to gravity.<sup>[4]</sup> Note that for rough surfaces, the receding and advancing contact angles need to be replaced by their apparent values, – the values observed on a length scale much larger than the scale of the microstructures.

Super-liquid-repellent surfaces were expected to show very low contact angle hysteresis and tilting angles below  $10^\circ$ . A model example of a superhydrophobic surface is composed of hydrophobic nano- or micro-sized posts (Scheme 2) – water droplets partially rest on an air cushion between the posts.<sup>[5]</sup> The high apparent contact angles and the presence of the air cushions leads to greatly reduced solid-liquid contact areas and thus to low contact angle hysteresis and low tilting (here roll-off) angles. To extend the concept of superhydrophobicity towards low surface tension, non-polar liquids, Tuteja et al. developed a so called superamphiphobic surface.<sup>[6]</sup> Essential for superamphiphobicity is that the typically fluorinated, micro-rough surface possesses overhangs, which prevent or slow down wetting of the surface. To date, however, poor durability, high fabrication costs and difficulties in maintaining the air cushions restrict large-scale applications of superhydrophobic and superamphiphobic surfaces.

An alternative strategy to achieve surfaces with low sliding angles is to infuse textured or porous surfaces with lubricant. (Scheme 2).<sup>[7]</sup> The lubricant needs to be chemically compatible with the surface so that it fully wets the substrate and capillary forces can keep the lubricant in place. However, the drops are always surrounded by an annular wetting ridge. In addition, the drops are sometimes cloaked by a thin layer of lubricant. Whether the drops are cloaked by lubricant depends on the interplay of liquid-air, liquid-lubricant and lubricant-air interfacial tensions.<sup>[8]</sup> In practice, most droplets wet the top faces of the textured surface. Still, the high mobility of the lubricant layer combined with the large apparent contact angles typically result in a sliding angle below  $3^\circ$ .



**Scheme 3.** Liquid-like surfaces. a) water and b) non-polar organic liquid drops resting on PDMS-grafted liquid-like surface.<sup>[9c]</sup> c) Formation of liquid-like omniphobic surface by covalently grafted PDMS via rapid acid-catalyzed polycondensation<sup>[10]</sup>.

Lubricant-infused surfaces suffer from depletion of lubricant with time, either by evaporation or by the removal of lubricant along with the moving drops. This leads to the question: Can flexible, lubricating molecules that are chemically grafted to a surface provide similar wetting behavior? Recently, brush-like polydimethylsiloxane (PDMS) grafted surfaces were created to address this question (Scheme 3).<sup>[9]</sup> The siloxane repeating group (-O-Si-O-) adds high flexibility to the grafted molecules, and thus the surfaces could be

considered liquid-like. Characteristic of brushes is that only one end of the PDMS is covalently grafted on the substrate; the remaining part of the PDMS keeps its high mobility from rotational and/or bending motion. Notably, these grafted PDMS brushes can show a contact angle hysteresis for water below  $5^\circ$ . This low value results from the smoothness of the surface and the high mobility of the grafted PDMS brushes (Scheme 3a). In contrast, a contact angle hysteresis above  $50^\circ$  is typically observed for water drops deposited on crosslinked PDMS surfaces. The main reason for this large value is that the mobility of the siloxane bonds decreases with increased crosslinking. The grafted PDMS brushes on the surface become even more mobile in the presence of non-polar liquids because most non-polar liquids are miscible with PDMS, leading to contact angle hysteresis below  $2^\circ$  (Scheme 3b). Therefore the brush-like PDMS surfaces show a low contact angle hysteresis and thus a low sliding angle for both polar and non-polar liquids, i.e. these surfaces are not only amphiphobic but also omniphobic as they repel liquids of extremely low surface tension such as hexane too.

For application of liquid-like surfaces on a large scale, the fabrication procedure needs to be fast and simple. Two previously reported strategies to graft PDMS to surfaces are as follows:

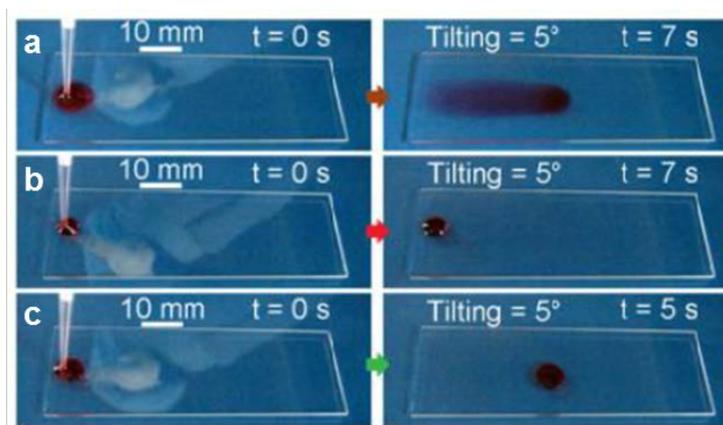
1) PDMS is grafted by heat treatment to a metal-oxide surface (such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{O}_3$ ).<sup>[9a, 9b]</sup> Heating silicone oil above  $100^\circ$  activates it so that it can react with the hydroxyl group of the metal-oxide. It was demonstrated that PDMS grafted to flat glass showed a contact angle hysteresis below  $2^\circ$  for both water and non-polar liquids.

2) PDMS is covalently grafted to a surface by using functional groups containing PDMS (e.g. vinyl-terminated PDMS).<sup>[9c]</sup> In this grafting-to approach, the vinyl-end group covalently binds with the Si-H moieties of a 1,3,5,7-tetramethylcyclotetrasiloxane pre-coated monomeric layer through Pt-catalyzed hydrosilylation. After the grafting reaction, the surface also showed omniphobic character with contact angle hysteresis below  $5^\circ$  for water ( $3\ \mu\text{L}$ ) and below  $2^\circ$  for non-polar low surface tension liquids. This grafting-to method requires a layer with as-prepared Si-H moieties and reaction times up to few days.

Recently, Wang and McCarthy introduced a new grafting-from method using acid-catalyzed polycondensation of dimethyldimethoxysilane monomers.<sup>[10]</sup> PDMS was grown from the hydroxyl group of the substrate by polycondensation of monomers with sulfuric acid, making use of a catalytic reaction. Smooth, chemically-grafted PDMS, liquid-like surfaces were obtained within a few seconds. The coated surfaces showed contact angle hysteresis below  $1^\circ$  for most liquids and sliding angles below  $8^\circ$  for water and below  $0.5^\circ$  for non-polar liquid drops ( $3\ \mu\text{L}$ ) (Table 1). These extremely low sliding angles are even more notable because it was assumed that easy removal of droplets would require a high receding contact angle. However, even though these liquid-like, PDMS-grafted surfaces provide low receding contact angles, e.g.  $\theta_{\text{rec}} \approx 19^\circ$  for decane (Table 1), most liquids still slide off more easily than from any other surfaces because of the mobility of grafted PDMS brushes (Scheme 4).

**Table 1.** Advancing / receding contact angles ( $\theta_{adv} / \theta_{rec}$ ), contact angle hysteresis ( $\Delta\theta$ ), and sliding angles ( $\alpha$ ) of liquid drops with different volumes (3 / 20  $\mu\text{L}$ ) on the PDMS-grafted liquid-like omniphobic surface.<sup>[10]</sup>

Liquid	Surface tension (mN/m)	Contact angle ( $\theta_{adv} / \theta_{rec}$ )	Contact angle hysteresis ( $\Delta\theta$ )	Sliding angle (3 / 20 $\mu\text{L}$ )
Water	72.8	104.6°/103.6°	1.0°	8° / 4°
Toluene	28.4	32.0°/31.8°	0.2°	2° / 1°
Decane	23.8	19.6°/19.6°	0°	1° / 1°



**Scheme 4.** Images for comparison of mobility of 20  $\mu\text{L}$  toluene drops (containing Oil Red O) with 5° tilting angle on a) a clean hydrophilic glass, b) a hydrophobic glass modified with  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$  molecules, c) a liquid-like omniphobic surface.<sup>[10]</sup>

This fabrication concept of PDMS-grafted, omniphobic, liquid-like surfaces produced using acid-catalyzed graft polycondensation of dimethyldimethoxysilane introduces a novel strategy to rapidly realize omniphobic surfaces of low contact angle hysteresis and low sliding angle. The proposed reaction takes just a few minutes and is performed at room temperature, making the process suitable for large-scale, fast manufacturing. No energy is required for grafting PDMS. In addition, the few-nanometer-thick, covalently attached layer of PDMS is not easily washed away or depleted by evaporation. However, this approach of PDMS-grafted surfaces has one limitation: Once the layer is damaged or contaminated, the contact angle hysteresis increases due to pinning of droplets at the damaged or contaminated site. The problem of defect-induced pinning may be reduced in the case of discontinuous contact lines, for example by applying an acid-catalyzed graft polycondensation method to roughened metal-oxide structures such as silicon glass or hierarchical etched aluminum. We expect that this combination of topography and a new PDMS grafting method will offer a novel avenue towards next-generation super-liquid-repelling surfaces.

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