Omniphobic Surfaces

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Silicone Brushes: Omniphobic Surfaces with Low Sliding Angles

*Sanghyuk Wooh and Doris Vollmer**

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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 the efficient distribution of pesticides on leaves, spray cooling and painting, as well as 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 wetting behavior for specific applications. In particular, super-liquid-repellent surfaces have been investigated extensively.[1]

The wetting behavior of smooth and rough surfaces is characterized by the static contact angle, also termed the contact angle of the material. However, its value depends on how the droplet is deposited. In practice a droplet has two contact angles for every material, an advancing (θ_{adv}) and a receding (θ_{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 ($\Delta\theta = \theta_{\text{adv}} - \theta_{\text{rec}}$), that is, the hysteresis of the contact angle (Figure 1).[2] A low contact angle hysteresis is essential for easy removal of droplets from a surface, as the contact angle hysteresis relates to the lateral adhesion force $F_{LA} = k\gamma L(\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}})$, where γ is the surface tension, L is the contact width of the droplet with the surface, and k is a dimensionless factor that accounts for the precise shape of the solid–liquid–air three-phase contact line.[3] A low lateral adhesion force implies a low sliding or rolling angle α, 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 sliding or rolling of a droplet [Eq. (1)], where V is the volume of the droplet, ρ is the density of the liquid, and $g = 9.81\ \text{m s}^{-2}$ is the acceleration due to gravity.[4] Note that the receding and advancing contact angles need to be replaced by their apparent values for rough surfaces.

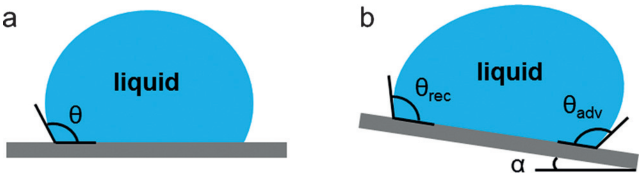

Figure 1. a) Schematic illustration of a liquid droplet resting on a horizontal surface. θ is the static contact angle, also termed the contact angle of the material. b) A droplet on a tilted surface. The advancing contact angle denotes the maximum angle just before the droplet advances. The receding contact angle denotes the minimum angle just before the droplet recedes. The sliding or rolling angle α denotes the tilting angle at which the gravitational force overcomes the lateral adhesion force and induces sliding or rolling of the droplet.

$$\sin\alpha = \frac{k\gamma L}{\rho V g}(\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}}) \qquad (1)$$

Super-liquid-repellent surfaces were expected to show very low contact angle hysteresis as well as tilting angles below 10°. A model example of a superhydrophobic surface is composed of hydrophobic nano- or microsized posts (Figure 2). Water droplets partially rest on an air cushion between the posts.[5] 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 to low surface tension, nonpolar liquids, Tuteja et al. developed a so-called superamphiphobic surface.[6] Essential for superamphiphobicity is that the typically fluorinated 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 have restricted 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 a lubricant (Figure 2).[7] The lubricant needs to be chemically compatible with the surface so that it fully wets the substrate, with capillary forces keeping the lubricant in place. The droplets are always surrounded by an annular wetting ridge and sometimes cloaked by a thin layer of lubricant. Whether the droplets are cloaked by lubricant depends on the interplay

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[*] Dr. S. Wooh, Prof. D. Vollmer
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
E-mail: vollmerd@mpip-mainz.mpg.de

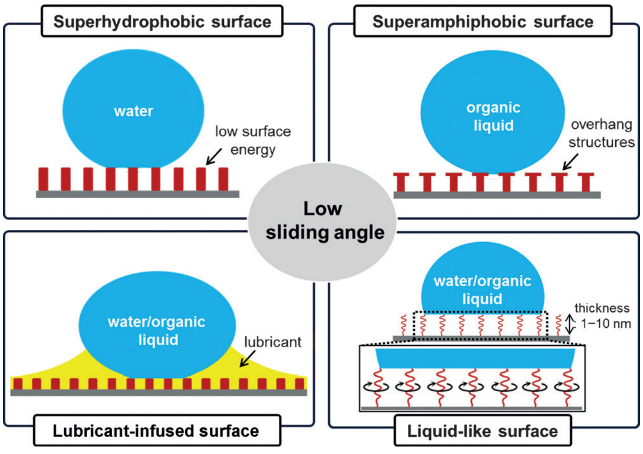

Figure 2. Surfaces with low sliding angles. Superhydrophobic and superamphiphobic surfaces show contact angles above 150° and roll-off angles below 10° for water (< 10 µL superhydrophobic) and for mixed water and organic liquid droplets (< 10 µL superamphiphobic). Liquid droplets deposited on a lubricant-infused surface typically have a contact angle above 140° and a sliding angle below 10°. Liquid-like surfaces can show sliding angles below 8° for 10 µL sized water droplets and 1–2° for 10 µL sized droplets of nonpolar organic liquids.

of liquid–air, liquid—lubricant, and lubricant–air interfacial tensions.[8] In practice, most droplets wet the top faces of the textured surface. However, the high mobility of the lubricant layer combined with the large apparent contact angles typically result in a sliding angle below 3°.

Lubricant-infused surfaces suffer from depletion of lubricant over time, either by evaporation or by the removal of lubricant along with the moving droplets. This leads to the question: Can flexible, lubricating molecules that are chemically grafted to a surface provide similar wetting behavior? Recently, surfaces grafted with brushlike polydimethylsiloxane (PDMS) were created to address this question (Figure 3).[9] The siloxane repeating group (-O-Si-O-) adds high flexibility to the grafted molecules, and thus the surfaces could be considered liquid-like. A characteristic of the brushes is that only one end of the PDMS is covalently grafted to the substrate; the remaining part of the PDMS maintains its high mobility through rotational and/or bending motions. Notably, these grafted PDMS brushes can show a contact angle hysteresis for water below 5°.

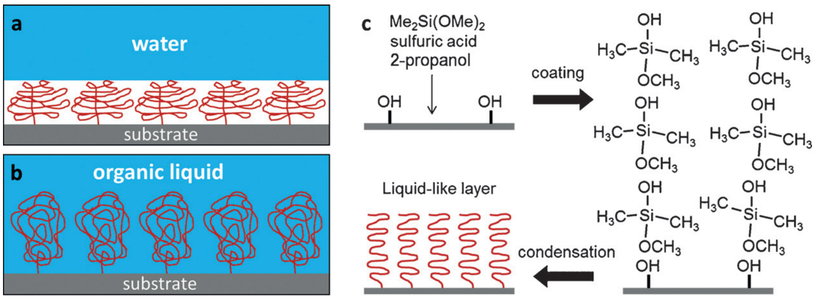

Figure 3. Liquid-like surfaces. a) Water and b) nonpolar organic liquid droplets resting on a PDMS-grafted liquid-like surface.[9c] c) Formation of a liquid-like omniphobic surface by covalently grafting PDMS by rapid acid-catalyzed polycondensation.[10]

This low value likely results from the smoothness of the surface and the high mobility of the grafted PDMS brushes (Figure 3a). In contrast, a contact angle hysteresis above 50° is typically observed for water droplets deposited on cross-linked PDMS surfaces. The main reason for this large value is that the mobility of the siloxane bonds decreases with increased cross-linking. The grafted PDMS brushes on the surface become even more mobile in the presence of nonpolar liquids because most nonpolar liquids are miscible with PDMS, thereby leading to a contact angle hysteresis below 2° (Figure 3b). Therefore, the brushlike PDMS surfaces show a low contact angle hysteresis and thus a low sliding angle for both polar and nonpolar liquids, that is, these surfaces are not only amphiphobic but also omniphobic as they also repel liquids with an extremely low surface tension, such as hexane.

The fabrication procedure needs to be fast and simple for application of liquid-like surfaces on a large scale. Two previously reported strategies to graft PDMS to surfaces are:

1) PDMS is grafted by heat treatment to a metal-oxide surface (such as SiO_2, TiO_2, or Al_2O_3).[9a,b] Heating silicone oil above 100° activates it so that it can react with the hydroxy group of the metal oxide. It was demonstrated that PDMS grafted to flat glass showed a contact angle hysteresis below 2° for both water and nonpolar liquids.
2) PDMS is covalently grafted to a surface by using functional groups containing PDMS (e.g. vinyl-terminated PDMS).[9c] In this grafting-to approach, the vinyl end group covalently binds with the Si-H moieties of a 1,3,5,7-tetramethylcyclotetrasiloxane precoated monomeric layer through Pt-catalyzed hydrosilylation. After the grafting reaction, the surface also showed omniphobic character with a contact angle hysteresis below 5° for water (3 µL) and below 2° for nonpolar low surface tension liquids. This grafting-to method requires a layer with as-prepared Si-H moieties and reaction times up to a few days.

Recently, Wang and McCarthy introduced a new grafting-from method by the acid-catalyzed polycondensation of dimethyldimethoxysilane monomers.[10] PDMS was grown from the hydroxy group of the substrate by polycondensation of monomers with sulfuric acid through a catalytic reaction. Smooth, chemically grafted, liquid-like surfaces of PDMS were obtained within a few seconds. The coated surfaces showed contact angle hysteresis below 1° for most liquids and sliding angles below 8° for water and below 0.5° for nonpolar liquid droplets (3 µL; 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, for example, $\theta_{rec} \approx 19°$ for decane (Table 1), most liquids still slide off more easily than from any other surfaces because of the mobility of the grafted PDMS brushes (Figure 4).

This fabrication concept of PDMS-grafted, omniphobic, liquid-like surfaces produced by the acid-catalyzed graft polycondensation

Table 1: Surface tension (γ), advancing/receding contact angles (θ_{adv}/θ_{rec}), contact angle hysteresis ($\Delta\theta$), and sliding angles (α) of liquid droplets with different volumes (3/20 μL) on the PDMS-grafted liquid-like omniphobic surface.[10]

Liquid	γ [mN m^{-1}]	$\theta_{adv}/\theta_{rec}$	$\Delta\theta$	α (3/20 μL)
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°	0.0°	1°/1°

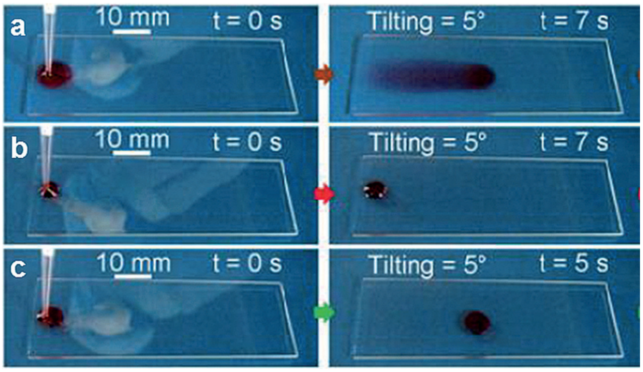

Figure 4. Images for comparison of the mobility of 20 μL toluene droplets (containing Oil Red O) with a 5° tilting angle on a) a clean hydrophilic glass, b) a hydrophobic glass modified with $CF_3(CF_2)_5CH_2CH_2SiMe_2Cl$ molecules, and c) a liquid-like omniphobic surface.[10]

of dimethyldimethoxysilane introduces a novel strategy to rapidly realize omniphobic surfaces with a low contact angle hysteresis and low sliding angle. The proposed reaction takes just a few minutes and is performed at room temperature, thereby making the process suitable for fast, large-scale 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 as a result of the pinning of the drop 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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