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Ultrahydrophobic and Ultralyophobic Surfaces: Some Comments and Examples

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The preparation of ultrahydrophobic and ultralyophobic surfaces using several techniques is described. Plasma polymerization of 2,2,3,3,4,4,4-heptafluorobutyl acrylate on poly(ethylene terephthalate) yields surfaces with water contact angles of $\theta_A/\theta_R = 174°/173°$. Argon plasma etching of polypropylene in the presence of poly(tetrafluoroethylene) renders surfaces with water contact angles as high as $\theta_A/\theta_R = 172°/169°$. Surfaces of compressed pellets of submicrometer, variable-diameter spherical particles of PTFE oligomers exhibit water contact angles of $\theta_A/\theta_R = 177°/177°$, methylene iodide contact angles of $\theta_A/\theta_R = 140°/138°$, and hexadecane contact angles of $\theta_A/\theta_R = 140°/125°$. We emphasize that contact angle hysteresis is more important in characterizing lyophobicity than is the maximum achievable contact angle. These surfaces are rough at the micrometer and submicrometer scales, and water drops roll easily on all of them. We make an intuitive argument that the topology of the roughness is important and controls the continuity of the three-phase contact line and thus the hysteresis. We also report smooth ultralyophobic surfaces that are prepared by silanization of silicon wafers with $Cl(SiMe_2O)_nSiMe_2Cl$ ($n = 0$, 1, 2, and 3), $(Me_3SiO)_3SiCH_2CH_2Si(CH_3)_2Cl$, and $(Me_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2Cl$. These surfaces exhibit much lower contact angles but little or no hysteresis, and droplets of water, hexadecane and methylene iodide slide easily off them. We propose that these covalently attached monolayers are flexible and liquidlike and that droplets in contact with them experience very low energy barriers between metastable states.

Introduction

The effect of surface roughness and heterogeneity on wettability and, in particular, on water contact angle has been the subject of numerous studies and theories since Wenzel's and Cassie's initial publications.[2-5] There is renewed interest in this phenomenon and there have been numerous recent reports, from a variety of research fields, of unusual wettability behavior involving very high contact angles. We site eight examples here: (1) "Super water-repellent surfaces" were prepared[6,7] from an *n*-alkylketene dimer that exhibited water contact angles "as large as 174°." The unusually high contact angles are ascribed to the fractal nature of the surfaces. (2) "Super-water-repellent alumina" coatings were formed[8,9] by hydrophobizing porous alumina gel films with fluoroalkyltrimethoxysilane; the water contact angle is reported as 165°. (3) Ion-plated poly(tetrafluoroethylene) (PTFE) coatings that had roughness dimensions of a few nanometers[10] exhibited water contact angles of 150–160°. (4) A glass plate that was roughened at the submicrometer level and hydrophobized using a fluoroalkyltrichlorosilane[11] was described as "ultrahydrophobic" and exhibited a water contact angle of 155°. (5) A composite electrode consisting of nickel and tetrafluoroethylene oligomer particles[12] exhibited a maximum contact angle with water of 173°. (6) Expanded PTFE vascular grafts that had been treated by ion-beam etching followed by oxygen glow discharge[13] exhibited water contact angles of 140–150°. (7) "Ultra water-repellent" films, with water contact angles of ~160°, were prepared using plasma-enhanced chemical vapor deposition of fluoroalkylsilanes.[14] (8) Vacuum-deposited PTFE thin films exhibited water contact angles "as high as 150°" because of nanometer-scale roughness.[15]

We make several points in this paper. First, we point out that a single "stationary" or advancing contact angle does not adequately describe the hydrophobicity or lyophobicity of a surface. Both the advancing and receding angles must be considered; consideration of the three-phase contact line is also important. This point is not original, and it is well-recognized in contact angle literature, despite the fact that the above-mentioned papers were published with just one contact angle. Second, we point out that this type of anomalous wetting behavior has significant literature precedence, although this literature is completely ignored in the papers mentioned above. Together, these papers indicate that a number of classic studies have been forgotten. Third, we make an intuitive argument that the topological nature of the surface roughness is important in determining hydrophobicity, i.e., that the continuity (or lack of continuity)

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Table 1. Calculated Contact Angles for PTFE/Air Composite Surfaces

% PTFE	$-\cos \theta_\#$	θ
100	0.342	110°
75	0.507	120°
50	0.671	132°
25	0.836	147°
10	0.934	159°
5	0.967	165°
1	0.993	173°

of the three-phase contact line (and thus the line tension) is critical. Fourth, we give several different examples of surfaces prepared in our laboratories that exhibit ultrahydrophobicity and ultralyophobicity.

Discussion

Cassie and Baxter derived eq 1[16] that can be used to

$$\cos \theta_\# = f_1 \cos \theta - f_2 \qquad (1)$$

show the relationship between the contact angle of a liquid on a smooth surface (θ) and the contact angle ($\theta_\#$) on a screen made of the same material as the smooth surface, where f_1 is the fraction of the surface area made up of material and f_2 is the fraction of open area. Rough or porous surfaces can also be analyzed with this equation, where f_1 and f_2 are the fractions of solid–liquid and air–liquid interfaces, respectively. This equation is derived for a sessile drop in equilibrium with a surface; thus, the contact angles predicted are "equilibrium contact angles" and neither advancing nor receding ones. Table 1 shows values of $\theta_\#$ calculated using eq 1 for PTFE screens of different porosity and a θ value of 110° for smooth PTFE. We emphasize that these values are calculated using an assumption of equilibrium but point out in the following paragraph that they are close to the advancing contact angle values and not the receding values for this roughness topology.

Figure 1a is a pictorial representation of a PTFE screen with 99% open area. Equation 1 predicts that this surface should exhibit a water contact angle of 173° (Table 1). The darker line in the figure describes a possible contact line between the drop and the surface. The contact line will deviate from a circular shape to maximize contact with the PTFE and minimize the noncontacting length. It is easy to imagine that if the volume of the drop is increased to advance the contact line, the drop will remain pinned until the contact angle is close to 180°, at which time the drop will jump from one metastable state to another. On the other hand, if the volume of the drop is reduced to recede the contact line, the drop will also be pinned and the receding contact angle will be as low as or lower than the value for a smooth surface. The energy barriers between metastable states will depend on the mesh size of the screen, and this will affect both the contact angles and the hysteresis. That energy barriers between metastable states are important to wettability has been discussed in the literature since 1948,[17-20] and Johnson and Dettre[21] have shown, using idealized rough surfaces of concentric troughs, that this concept is of utmost importance in determining hysteresis. These workers also described a transition to a "composite" surface: when the

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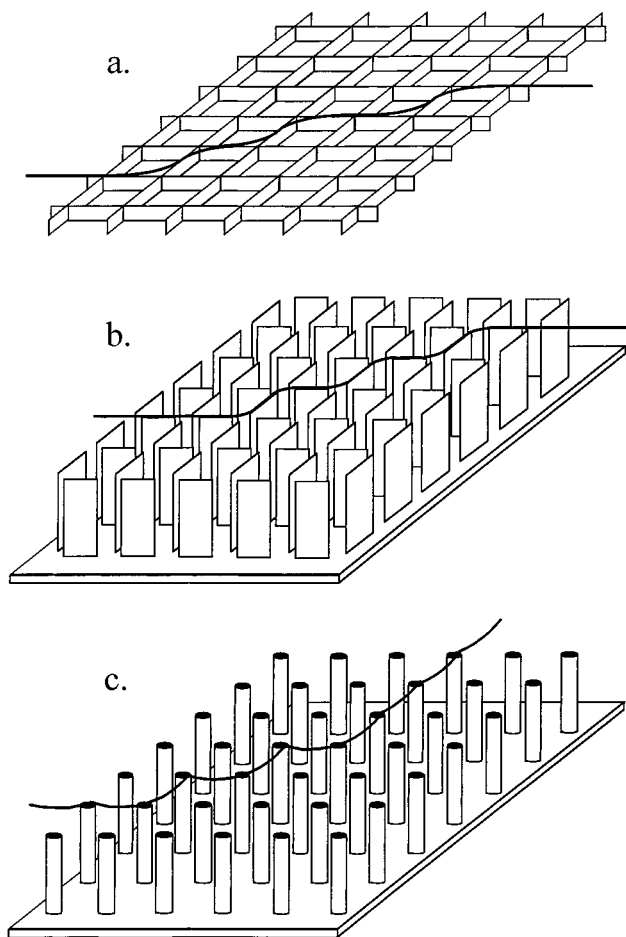(21) Johnson, R. E., Jr.; Dettre, R. H. *Adv. Chem. Ser.* **1963**, *43*, 112.

Figure 1. Pictorial representations of surfaces with three different roughness topologies. The darker lines describe possible three-phase (air–liquid–surface) contact lines for a drop of water in contact with these surfaces: (a) a screen on which a fairly continuous contact line can form, (b) separated ridges on which a discontinuous but substantial contact line can form, and (c) separated posts on which a very discontinuous contact line must form.

troughs become deep enough that water does not penetrate them, the energy barriers between metastable states decrease significantly.

Figure 1c shows a surface with a different topology roughness. The depiction is meant to describe PTFE posts that are close enough together that water does not intrude between them. In this geometry, unlike the screen or concentric grooves, the contact line cannot make continuous contact with the surface, and there is little or no difference in energy between different states; thus there are no stable metastable states. The same analysis can be done using eq 1 to predict contact angles for this system; thus a 173° water contact angle is predicted for a surface area of 1% PTFE "post-tops." In this case, however, the drop would not remain pinned (in a metastable state) before advancing or receding and would move spontaneously on the surface by small incremental advances and recessions with no contact angle hysteresis. The previous reports of roughness effects on contact angle have not described roughness in topological terms. We point out that there are a range of possible PTFE/air composite surfaces between the extremes described in parts a and c of Figure 1 that have the same composition but different topologies. Figure 1b shows one that consists of separated ridges. The line tension in this case would be intermediate between that of the surfaces in parts a and c of Figure 1.

Dettre and Johnson[22] have prepared and measured contact angles of drops on surfaces of different roughness topology but refer to them all as "porous" surfaces and do not comment on the differences in topology or contact lines.

It is clear from the above discussion that a single contact angle does not adequately describe the hydrophobicity of a surface. A drop on a surface with a high contact angle may remain pinned until the surface is tilted to a significant angle. The hysteresis is more important in determining hydrophobicity (and lyophobicity) than the maximum achievable contact angle. Equation 2[23] describes

$$F = \gamma_{LV}(\cos \theta_R - \cos \theta_A) \qquad (2)$$

the force needed to start a drop moving over a solid surface, where F is the critical line force per unit length of the drop perimeter, γ_{LV} is the surface tension of the liquid, and θ_R and θ_A are the receding and advancing contact angles, respectively. This equation indicates it is the difference between the contact angles (the hysteresis) and not their finite values that determines hydrophobicity.

We know of three literature reports of surfaces on which water drops move spontaneously and do not come to rest, with little or no apparent tilt of the surface, and we describe several new surfaces of this type below. Schreiber et al.[24] prepared plasma-polymerized hexamethyldisiloxane films using low-temperature plasma deposition and measured water contact angles "as high as 180°." The receding angles were not reported, but they must be high as the statement, "these droplets rolled off slightly inclined substrates," was made. Garbassi et al.[25] examined the wettability of oxygen plasma-treated PTFE and report contact angles of θ_A/θ_R = 170°/160° and that "water drops roll very easily on the surface." Dettre and Johnson[22] measured tilt angles (the angle of the surface, relative to horizontal, that a drop in contact with the surface moves because of gravity) as low as 2° for a series of porous surfaces. We propose that the term *ultrahydrophobic* be reserved to describe this phenomenon and that it not be used to describe surfaces with merely high advancing contact angles.

There are several other reports of surfaces that exhibit very high contact angles. The authors did not comment on whether water drops moved spontaneously or easily on these surfaces, but we expect that this is the case. Cassie and Baxter[16] made rough surfaces by coating, melting, and allowing paraffin wax to recrystallize on wire gratings. They report, for one case, water contact angles of θ_A/θ_R = 152°/148°. Johnson and Dettre[26] prepared rough fluorocarbon and paraffin wax surfaces by spraying solutions of the waxes onto glass slides; they report water contact angles of θ_A/θ_R = 159°/157° and θ_A/θ_R = 158°/157° for two fluorocarbon wax surfaces and θ_A/θ_R = 158°/153° for the paraffin wax surface. Washo[27] reports contact angles of 165–170° for plasma-polymerized tetrafluoro-ethylene films deposited in the powder region. This researcher did not report receding contact angle data, but we expect, on the basis of our experience with similar systems, that the receding values are high as well. The work of Bartell and Shepard[28] should also be mentioned;

they machined pyramid-shaped asperities into paraffin surfaces and measured contact angles. They report water contact angles as high as θ_A/θ_R = ∼160°/∼125° (and note that the values are higher with more steeply shaped pyramids) and predict that on a fibrillar surface (similar to that pictured in Figure 1c) a water contact angle of approximately 180° would be observed.

We have deliberately neglected a discussion of the size scale of roughness needed to produce ultralyophobicity and comment only that this issue remains unresolved. The reports of Schreiber et al.[24] and Garbassi et al.,[25] the results reported below, and perhaps some of the reports of single high contact angles[6–15] suggest that micron and submicrometer-scale roughness is important. On the other hand, the reports of Dettre and Johnson,[22] Cassie and Baxter,[16] and Bartell and Shepard[28] suggest that much larger scale roughness (tens to hundreds of microns) can also function to induce ultralyophobicity. We are currently addressing this issue.

Results

Ultrahydrophobic Surfaces. We have prepared a number of surfaces that meet our description of ultrahydrophobic, and here, we describe the contact angle behavior of several. Table 2 is a summary of the contact angle data for the surfaces reported here. More complete descriptions of these surfaces with atomic force micrographs, scanning electron micrographs, and X-ray photoelectron spectroscopy data will be forthcoming.

Plasma polymerization of 2,2,3,3,4,4,4-heptafluorobutyl acrylate was carried out onto smooth poly(ethylene terephthalate) (PET) film samples in a home-built inductively coupled reactor that has been described[29] elsewhere. Powder deposition was achieved at a power of 20 W, a pressure of 0.4 mm, and a flow rate of 1.7 sccm. Atomic force microscopy indicates roughness on both the 1 and 0.1 μm scales. Water contact angles[30] were θ_A/θ_R = 174°/173°, and water droplets rolled easily on horizontal surfaces.

Isotactic polypropylene (biaxially oriented, 6 μm thick, capacitor grade) was argon plasma-etched in a reactor[29] lined with PTFE film at a power of 100 W and an argon

Table 2. Contact Angles for Ultrahydrophobic and Ultralyophobic Surfaces Reported in This Work

surface	$\theta_A/\theta_R{}^a$
plasma-polymerized HFBA[b]	174°/173°
plasma-etched polypropylene	172°/169°
spherical particles of PTFE	177°/177°
	140°/138°[c]
	140°/125°[d]
Si/SiO₂ + Cl(SiMe₂O)ₙSiMe₂Cl	∼105°/∼104°
	∼74°/∼72°[c]
	∼36°/∼35°[d]
Si/SiO₂ + (Me₃SiO)₃SiCH₂CH₂Si(CH₃)₂Cl	104°/103°
	71°/66°[c]
	38°/36°[d]
Si/SiO₂ + (Me₃SiO)₂Si(CH₃)CH₂CH₂Si(CH₃)₂Cl	106°/105°
	70°/64°[c]
	30°/26°[d]

[a] Water data unless otherwise indicated. [b] Heptafluorobutyl acrylate. [c] Methylene iodide data. [d] Hexadecane data.

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(30) Contact angle measurements were made with a Ramè–Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The values reported are averages of 5–10 measurements made on different areas of the surfaces.

flow rate of ~1 sccm. Under these conditions, the PTFE is sputtered, creating a fluorocarbon plasma that reacts with the polypropylene in competition with its ablation. The micrometer and submicrometer scale roughnesses of the polypropylene increase with reaction time and the surfaces, assessed by XPS, are highly fluorinated. Water contact angles after 2, 3 and 4 h of reaction are $\theta_A/\theta_R = 164°/156°$, $169°/159°$, and $172°/169°$, respectively. Again, water droplets roll easily on horizontal surfaces of this material.

Surfaces of compressed pellets of submicrometer, variable-diameter spherical particles of PTFE oligomers[31] exhibit water contact angles of $\theta_A/\theta_R = 177°/177°$. Water drops are completely unstable on these surfaces, "dance around," and do not come to rest on horizontal surfaces. These surfaces are also lyophobic and exhibit methylene iodide contact angles of $\theta_A/\theta_R = 140°/138°$ and hexadecane contact angles of $\theta_A/\theta_R = 140°/125°$. Methylene iodide drops roll easily on these surfaces, but hexadecane drops remain pinned. The behavior of these three liquids on this surface demonstrates the importance of hysteresis on wetting, as indicated by eq 2. The hexadecane contact angle behavior is difficult to rationalize, and we can offer no explanation at this time. Hexadecane contact angles on smooth fluoropolymer surfaces are considerably lower than 90°; Wenzel's equation[2,3] predicts that they should be even lower on rough surfaces.

Scanning electron micrographs or atomic force micrographs of these three types of surfaces indicate roughness of the type described in Figure 1c. Irregular asperities jut up from the surfaces at the micrometer and submicrometer scale. It is difficult to see how a drop could form a continuous contact line without intrusion into the cavities between the asperities. Hexadecane evidently intrudes into the cavities of all of these surfaces and forms contact lines, with the plasma-derived surfaces, that are sufficiently continuous to cause low receding angles and, with the PTFE oligomer surface, that are sufficiently continuous to cause pinning.

In addition to the surfaces described above, we have prepared a number of surfaces by plasma polymerization and degradation and other "roughening" techniques that exhibit high advancing but low receding water contact angles. Examples are a 2,2,3,3,3-pentafluoropropyl acrylate plasma polymer (deposited on PET) that exhibited water contact angles of $\theta_A/\theta_R = 169°/8°$, an argon plasma-etched polypropylene sample (in a PTFE-lined reactor and reacted for 1 hour using the conditions described above) that exhibited water contact angles of $\theta_A/\theta_R = 159°/72°$, and a freeze-fractured sample of a poly(tetrafluoroethylene-*co*-hexafluoropropylene) close-celled foam[32] consisting of polygonal impinging cells (and is an experimental example of the topology represented in Figure 1a) that exhibited water contact angles of $\theta_A/\theta_R = 166°/58°$. Drops do not move spontaneously or easily on these surfaces but remain pinned. Johnson and Dettre,[26] Garbassi et al.,[25] and Bartell and Shepard[28] report surfaces with similar wettability data. A description of these surfaces in terms of the Johnson and Dettre analysis[21] is that they are not "rough enough" to be composite surfaces and have high energy barriers between metastable states. In terms of the model presented above, these surfaces exhibit roughness topologies such that the drop perimeter can make

sufficient contact to pin the drop and cause hysteresis. The recent reports of unusually hydrophobic surfaces described above,[6–15] which report only one contact angle value, may be of this type as well, rather than ultrahydrophobic in the sense meant by our restrictive definition.

Nonhysteretic Ultralyophobic Surfaces. Equation 2 indicates that lyophobicity can be controlled by contact angle hysteresis. Lyophobicity in the sense of eq 2 (and, in particular, not in the sense of maximum contact angle) indicates the ability of a surface to *not* pin a drop in contact with it. By this definition, a material that exhibits even low contact angles with probe fluids is lyophobic if drops move easily on its surface. This is a practical definition of ultralyophobic: ultralyophobic surfaces do not pin but rather repel drops in contact with them, independent of the contact angle.

We have prepared several surfaces that exhibit little or no contact angle hysteresis with various probe fluids, and indeed these surfaces exhibit ultralyophobicity: drops move easily when the surfaces are slightly tilted. These surfaces are smooth and were prepared by reacting polished silicon wafers with various silanizing agents. Reaction of silicon wafers with $Cl(SiMe_2O)_nSiMe_2Cl$ ($n = 0, 1, 2$, and 3) in the vapor phase at 60–70 °C creates surfaces that exhibit contact angles of $\theta_A/\theta_R = \sim 105°/\sim 104°$ (water), $\theta_A/\theta_R = \sim 74°/\sim 72°$ (methylene iodide), and $\theta_A/\theta_R = \sim 36°/\sim 35°$ (hexadecane). There is a literature report[33] that glass treated with dichlorodimethylsilane exhibits water contact angles of $\theta_A/\theta_R = 110°/107.5°$. Silicon wafers reacted with tris(trimethylsiloxy)silylethyldimethylchlorosilane, $(Me_3SiO)_3SiCH_2CH_2Si(CH_3)_2Cl$, in toluene at room temperature exhibit contact angles of $\theta_A/\theta_R = 104°/103°$ (water), $\theta_A/\theta_R = 71°/66°$ (methylene iodide), and $\theta_A/\theta_R = 38°/36°$ (hexadecane). Reaction of silicon wafers with bis(trimethylsiloxy)methylsilylethyldimethylchlorosilane, $(Me_3SiO)_2Si(CH_3)CH_2CH_2Si(CH_3)_2Cl$ in the vapor phase, creates surfaces that exhibit contact angles of $\theta_A/\theta_R = 106°/105°$ (water), $\theta_A/\theta_R = 70°/64°$ (methylene iodide), and $\theta_A/\theta_R = 30°/26°$ (hexadecane). We will report in detail the synthesis and characterization of these surfaces in a future publication. We believe that these covalently attached monolayers are liquid-like and that this is the reason for their lack of hysteresis. Droplets on these flexible surfaces exhibit very low energy barriers between metastable states. There have been reports of carefully prepared self-assembled monolayers,[34] flexible monolayers,[35] flexible polymers[36] and carefully prepared, extremely clean, and glossy-smooth polymers[37] that exhibit little or no contact angle hysteresis; we expect that these surfaces should exhibit ultralyophobicity as well.

Summary

We criticize recent reports of very hydrophobic surfaces that report only one contact angle and point out that both advancing and receding angles need to be reported to fully characterize wettability. We give an intuitive argument that the topology of the roughness is important and will control the continuity of the three-phase contact line and thus the hysteresis. We emphasize that the contact angle hysteresis is more important in characterizing lyophobicity

(31) This material was obtained from Central Glass Co., Ltd. and is described as a mixture of trifluoromethyl-terminated tetrafluoroethylene oligomers of molecular weight 700–4000.

(32) Electron micrographs of similar freeze-fractured foams have been reported: Arora, K. A.; Lesser, A. J.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 4614.

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than the maximum achievable contact angle and suggest that the terms ultrahydrophobic and ultralyophobic be reserved for materials upon which drops move spontaneously or easily on horizontal or near-horizontal surfaces. We give several examples of two different types of surface that, by these definitions, are ultrahydrophobic and ultralyophobic: rough surfaces that derive their low hysteresis from a discontinuous contact line and smooth surfaces that are liquidlike and exhibit very low energy barriers between metastable states.