Wetting Behavior of Water and Oil Droplets in Three-Phase Interfaces for Hydrophobic/philicity and Oleophobic/philicity†

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Biomimetics, mimicking nature for engineering solutions, provides a model for the development of superhydrophobic/superoleophobic and self-cleaning surfaces. A number of biomimetic superhydrophobic surfaces have been developed by using a hydrophobic coating, surface roughness, and the ability to form air pockets between solid and water. Oleophobic surfaces that have the potential for self-cleaning and antifouling from biological and organic contaminants in both air and water need to be studied. The surface tension of oil and organic liquids is lower than that of water, so to create a superoleophobic surface, the surface energy of the solid surface in air should be lower than that of oil. The wetting behavior of water and oil droplets for hydrophobic/philic and oleophobic/philic surfaces in three-phase interfaces was studied. In order to make the surface oleophobic at a solid—air—oil interface, a material with a surface energy lower than that of oil was used. In underwater applications, the oleophobic/philicity of an oil droplet in water was studied on the surfaces with different surface energies of various interfaces and contact angles of water and oil droplets in air. A model for predicting the contact angles of water and oil droplets was proposed. To validate the model, the wetting behavior of flat and micropatterned surfaces with varying pitch values were studied. Furthermore, the wetting behavior of the nano- and hierarchical structures found in Lotus plant surfaces and the shark skin replica as an example of aquatic animal were also studied. On the basis of the experimental data and the model, the trends were explained.

1. Introduction

One of the crucial surface properties for various surfaces and interfaces in wet environments is nonwetting or hydrophobic/oleophobic. Wetting is characterized by the contact angle, which is the angle between the solid and liquid surfaces.1–4 If the liquid or oil wets the surface (referred to as a hydrophilic/oleophilic surface), the value of the contact angle is 0 ≤ θ ≤ 90°, whereas, if the liquid or oil does not wet the surface (referred to as a hydrophobic/oleophobic surface), the value of the contact angle is 90° < θ ≤ 180°. The term hydrophobic/philic, which was originally applied only to water, is often used to describe the contact of a solid surface with any liquid. The term “oleophobic/philic” is used with regard to wetting by oil and organic liquids. A surface is considered superhydrophobic/superoleophobic if θ is greater than 150°. These surfaces should have low contact angle hysteresis and tilt angle in order to be self-cleaning and to have low drag for fluid flow. Self-cleaning surfaces are of interest in various applications, including self-cleaning windows, windshields, exterior paints for buildings, navigation ships, utensils, roof tiles, textiles, solar panels, and applications requiring antifouling from biological and organic contaminants and a reduction of drag in fluid flow, e.g., in micro/nanochannels and ships.5–6

The study and simulation of biological objects with desired properties is referred to as “biomimetics.” Biomimetics involves taking engineering solutions from nature, mimicking them, and implementing them in an application.7 A model surface for superhydrophobicity and self-cleaning is provided by the leaves of the Lotus plant (Nelumbo nucifera), which have an intrinsic hierarchical structure, built by convex cell papillae and randomly oriented hydrophobic wax tubules.8–10 The Lotus plant surface with hierarchical structure has a very low water contact angle hysteresis (the difference between the advancing and receding contact angles), on the order of 3°, which is responsible for water droplets rolling off (with some slip) of the surface and taking contaminants with them, providing self-cleaning ability, known as the Lotus effect. Water on such a surface forms a spherical droplet, and both the contact area and the adhesion to the surface are dramatically reduced.

On the basis of the understanding of nature, a number of artificial hydrophobic surfaces have been fabricated with hierarchical structures using electrodeposition, colloidal particles, photolithography, soft lithography, plasma treatment, self-assembly, and imprinting.6,11–21

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A model surface for superoleophobicity and self-cleaning is provided by fish, which are known to be well protected from contamination by oil pollution although they are wetted by water. Fish scales have a hierarchical structure consisting of sector-like scales with diameters of 4–5 mm covered by papillae 100–300 μm in length and 30–40 μm in width. Shark skin, which is a model from nature for a low drag surface, is covered by very small individual tooth-like scales called dental denticles (little skin teeth), ribbed with longitudinal grooves (aligned parallel to the local flow direction of the water). These grooved scales reduce vortices formation present on a smooth surface, resulting in water moving efficiently over their surface. The water surrounding these complex structures can lead to protection from marine fouling and play a role in the defense against adhesion and growth of marine organisms, e.g., bacteria and algae. If oil is present on the surfaces in air or water, surfaces are known to be oleophobic and may provide self-cleaning and antifouling. Many sea animals including fish and shark are known to be oleophobic under water. Superoleophobic surfaces can also reduce significant losses of residual fuel in fuel tanks and pipes.

The surface tension of oil and organic liquids is lower than that of water, so to create a superoleophobic surface, the surface energy of the solid surface in air should be lower than that of oil. For underwater applications, if an oil droplet is placed on a solid surface in water, the solid–water–oil interface exists. The nature of oleophobicity/philicity of an oil droplet in water can be determined from the values of surface energies of various interfaces and contact angles of water and oil in air.

Many superoleophobic surfaces have been developed by modifying the surface chemistry with a coating of extreme low surface energy materials. Tutela et al. showed that surface curvature, in conjunction with chemical composition and roughened texture, can be used for liquids with low surface tension, including alkanes such as decane and octane. Liu et al. performed experiments at a solid–water–oil interface. They found that hydrophobic and oleophilic surfaces (solid–air–water interface and solid–air–oil interface) can switch into an oleophobic surface in water (solid–water–oil interface). As a result, oil contaminants are washed away when immersed in water. This effect can be employed for underwater oleophobicity and self-cleaning that can be used against marine ship fouling. Wetting behavior in three phase interfaces for hydrophobic and oleophilic surfaces needs to be carried out. Additionally, the geometrical effects in three phase interfaces for synthetic patterned surfaces, where geometric parameters can be varied, have not yet been studied. In this paper, a model for predicting the oleophobic/philic nature of the surfaces was proposed. To validate the model, it was investigated how the water and oil droplets in three-phase interfaces influence the wetting behavior on flat surfaces as well as micropatterned surfaces with varying pitch values. Micropatterned surfaces were selected to study the effect of geometry. For creating hydrophobic and oleophobic surfaces, n-pentfluoroecosane (C₅F₁₂) with surface energy lower than that of oil was deposited on flat and micropatterned surfaces, and the trends were explained in terms of the measured contact angle and the predicted values of models. The wetting behavior of the nano- and hierarchical structures found in Lotus plant surfaces and the shark skin replica as an example of aquatic animal were also studied.

2. Theoretical Background

In this section, we first develop expressions for contact angles for various interfaces: solid–air–water interface, solid–air–oil interface, and solid–water–oil interface. Then, we present the Wenzel and Cassie–Baxter equations for an interface with and without air pockets and the application of these equations to micropatterned surfaces. In general, if an oil droplet is placed on a solid surface in air, the solid–air–water interfaces come together with a static contact angle, \( \theta_W \). The value of \( \theta_W \) can be determined from the condition of the total energy of the system being minimized and is given by Young’s equation for the contact angle, \( \theta_W \):

\[
\cos \theta_W = \frac{\gamma_{SA} - \gamma_{SW}}{\gamma_{WA}}
\]

where \( \gamma_{SW} \), \( \gamma_{SA} \), and \( \gamma_{WA} \) are the surface tensions of the solid–water, solid–air, and water–air interfaces, respectively. If an oil droplet is placed on a solid surface in water, Young’s equation for the contact angle, \( \theta_O \), can be expressed by

\[
\cos \theta_O = \frac{\gamma_{SO} - \gamma_{SA}}{\gamma_{OA}}
\]

where \( \gamma_{SO} \), \( \gamma_{SA} \), and \( \gamma_{OA} \) are the surface tensions of the solid–oil, solid–air, and oil–air interfaces, respectively. As predicted by eq 2, if \( \gamma_{SO} \) is higher than \( \gamma_{SA} \), an oleophobic surface can be achieved.

To create an oleophobic surface in water, let us consider the solid–water–oil interface. If an oil droplet is placed on a solid surface in water, the contact angle of an oil droplet in water, \( \theta_{OW} \), is given by Young’s equation:

\[
\cos \theta_{OW} = \frac{\gamma_{SW} - \gamma_{SO}}{\gamma_{OW}}
\]

where \( \gamma_{SO} \), \( \gamma_{SW} \), and \( \gamma_{OW} \) are surface tensions of the solid–oil, solid–water, and oil–water surfaces, respectively. Combining eqs 1, 2, and 3, the equation for the contact angle, \( \theta_{OW} \), of an oil droplet in water is given as

\[
\cos \theta_{OW} = \frac{\gamma_{SO} \cos \theta_O - \gamma_{SW} \cos \theta_W}{\gamma_{OW}}
\]

As predicted by eq 4, for a hydrophilic surface (\( \gamma_{SA} > \gamma_{SW} \)), an oleophobic surface at the solid–water–oil interface can be created if \( \gamma_{SO} \cos \theta_O \) is lower than \( \gamma_{SW} \cos \theta_W \). Since the surface tension of oil and organic liquids is much lower than that of water, most hydrophobic surfaces can be made oleophobic at the solid–water–oil interface. For a hydrophobic surface (\( \gamma_{SA} < \gamma_{SW} \)) and an oleophobic surface at a solid–air–oil interface (\( \gamma_{SA} < \gamma_{SO} \)), an
oleophobic surface at a solid-water-oil interface can be created if $\gamma_{OA} \cos \theta_O$ is higher than $\gamma_{WA} \cos \theta_W$ and vice versa. For a hydrophobic and an oleophilic surface at a solid-air-oil interface, an oleophobic surface at a solid-water-oil interface cannot be created. Schematics are shown in Figure 1, and the summary of the philic/phobic nature at various interfaces is shown in Table 1. For an oleophobic surface, oil contaminants are washed away when immersed in water. This effect leads to self-cleaning that can be used against marine ship fouling.

2.2. Wenzel and Cassie–Baxter Equations. Consider a rough solid surface with a typical size of roughness details smaller than the size of the droplet. For a droplet in contact with a rough surface without air pockets, the contact angle, $\theta$, is given by the Wenzel\textsuperscript{34} equation:

$$\cos \theta = R_f \cos \theta_f$$  (5)

where $\theta_l$ is the contact angle of the liquid droplet on a solid surface ($\theta_{w}$, $\theta_o$, or $\theta_{OW}$), and $R_f$ is a roughness factor defined as

$$R_f = \frac{A_{SL}}{A_F}$$

(6)

$A_F$ is the flat solid–liquid contact area or a projection of the solid–liquid area $A_{SL}$ on the horizontal plane. For a composite interface with air pockets with fractional solid–liquid contact area $f_{SL}$, the contact angle is given by the Cassie–Baxter equation:

$$\cos \theta = R_f \cos \theta_l - 1 + f_{SL}$$

(7)

To show an application example of the Wenzel and Cassie–Baxter equations, we consider a geometry of flat-top, cylindrical pillars of diameter $D$, height $H$, and pitch $P$ distributed in a regular square array. For the special case where the droplet size is much larger than $P$, a droplet only contacts the flat-top of the pillars in the composite interface, and the cavities are filled with air. For this case, $f_{LA} = 1 - \left(\pi D^2/4P^2\right) = f_{SL}$. Let us further assume that the flat tops are smooth with $R_f = 1$. Equations 5 and 7 for this case reduce to

$$Wenzel: \quad \cos \theta = \left(1 + \frac{\pi DH}{P^2}\right) \cos \theta_l$$

(8)

$$Cassie–Baxter: \quad \cos \theta = \frac{\pi D^2}{4P^2} (\cos \theta_l + 1) - 1$$

(9)

The Wenzel and Cassie–Baxter equations present two possible equilibrium states for a liquid on the surface. This indicates that there is a critical pitch below which the composite interface dominates and above which the homogeneous interface dominates the wetting behavior. It should also be noted that, even in cases where the liquid droplet does not contact the bottom of the cavities, the liquid droplet in a metastable state becomes unstable, and the transition from the Cassie–Baxter regime to the Wenzel regime occurs if the pitch is large.4

### 3. Experimental Details

#### 3.1. Instrumentation

For the measurement of static contact angle, deionized water was used for water droplets and hexadecane was used for oil droplets. The surface tensions of the water–air interface ($\gamma_{WA}$), oil–air interface ($\gamma_{OA}$), and oil–water interface ($\gamma_{OW}$) are 73, 27.5, and 51.4 mN/m, respectively.3738 The mass densities are 1000 and 773 kg/m$^3$ for water and hexadecane, respectively. Water and oil droplets of about 5 μL in volume

### Table 1. Summary of Philic/Phobic Nature at Various Interfaces

<table>
<thead>
<tr>
<th>Solid-air-water interface</th>
<th>Solid-water-oil interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophilic ($\gamma_{WL} &gt; \gamma_{WO}$)</td>
<td>Oleophilic if $\gamma_{OL} \cos \theta_L &lt; \gamma_{WO} \cos \theta_L$</td>
</tr>
<tr>
<td>Oleophilic if $\gamma_{OL} \cos \theta_L \geq \gamma_{WO} \cos \theta_L$</td>
<td>Oleophilic if $\gamma_{OL} \cos \theta_L &gt; \gamma_{WO} \cos \theta_L$</td>
</tr>
</tbody>
</table>

Figure 2. Schematics of a solid–water–oil interface system. A specimen is first immersed in water phase, and then an oil droplet is gently deposited using a microsyringe, and the static contact angle in the system is measured.

(with radius of a spherical droplet about 1 mm) in air environment were gently deposited on the specimen using a microsyringe. The process of wetting behavior of an oil droplet in water was obtained in a solid–water–oil interface system as shown in Figure 2. A specimen was first immersed in water phase. Then an oil droplet was gently deposited using a microsyringe from the bottom of the system because the density of oil (hexadecane) is lower than that of water. The image of the droplet was obtained by a digital camcorder (Sony, DCRSR100, Tokyo, Japan) with a 10x optical and 120x digital zoom. Images obtained were analyzed for the contact angle using ImageTool software (University of Texas Health Science Center). The measurements were reproducible to within $\pm 2^\circ$.

For surface roughness, a commercial atomic force microscope (AFM; D3100, Nanoscope IIIa controller, Digital Instruments, Santa Barbara, CA) was used. In order to measure surface roughness, experiments were performed using a square pyramidal Si(100) tip with a native oxide layer which has a nominal radius of 20 nm on a rectangular Si(100) cantilever with a spring constant of 3 N m$^{-1}$ and a natural frequency of 82 kHz in tapping mode. The scan size used in these measurements was 50 μm.

#### 3.2. Samples

A two-step molding process was used to replicate the microstructures with varying pitch values. In this technique, first a negative is generated and then a positive.6 As a master template for the flat and micropatterned surfaces, a flat Si surface and micropatterned Si surfaces with pillars of 14 μm diameter and 30 μm height with different pitch values (21, 23, 26, 35, 70, 105, 126, 168, and 210 μm), fabricated by photolithography, were used. A polyvinylsiloxane dental wax (President Light Body Gel, ISO 4823, Polyvinylsiloxan (PLB), Coltene Whaledent, Hamburg, Germany) was applied via a dispenser on the surface and immediately pressed down with a glass plate. After complete hardening of the molding mass (3–5 min at room temperature), the silicon master surface and the mold (negative) were separated. After a relaxation time of 30 min for the molding material, the negative replicas were filled with a liquid epoxy resin (Epoxydharz L, No. 236349, Conrad Electronics, Hirschau, Germany) with the

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hardener (Harter S, Nr 236365, Conrad Electronics, Hirschau, Germany). Specimens with microstructures were immediately transferred into a vacuum chamber at 750 mTorr (100 Pa) pressure for 10 s to remove trapped air and to increase the resin infiltration through the structures. After hardening at room temperature (24 h at 22 °C), the positive replica was separated from the negative replica. To generate several replicas, the second step of replication was repeated 20 times for each surface type.

To study the surfaces with some oleophobicity, a surface coating that has a lower surface tension than that of oil is needed. For this purpose, n-perfluoroeicosane (C$_{20}F_{42}$) (268828, Sigma-Aldrich, USA) was deposited on the specimen surfaces by thermal evaporation. The surface energy of n-perfluoroeicosane is 6.7 mJ/m$^2$ (6.7 mN/m). The specimens were mounted on a specimen holder with double-sided tape and placed in a vacuum chamber at 30 mTorr (4 kPa pressure), 2 cm above a heating plate loaded with 6000 μg n-perfluoroeicosane. The n-perfluoroeicosane was evaporated by heating it up to 170 °C. In a vacuum chamber, the evaporation from the point source to the substrate occurs in straight line; thus, the amount of sublimated material is equal in a hemispherical region over the point of source. In order to estimate the amount of sublimated mass, the surface area of the half sphere was calculated by using the formula $2\pi r^2$, whereby the radius ($r$) represents the distance between the specimen to be covered and the heating plate with the substance to be evaporated. The calculated amount of n-perfluoroeicosane deposited on the surfaces was 2.4 μg/mm$^2$ (amount of n-perfluoroeicosane loaded on a heating plate divided by surface area).

Hierarchical structures were fabricated using a two-step fabrication process, including the production of microstructured surfaces by soft lithography and subsequent development of nanostructures on top by self-assembly of n-hexatriacontane with amounts of 0.2 μg/mm$^2$ deposited by thermal evaporation, as described above.

A shark ($Squalus acanthias$, L., Squalidae) was used for creating a shark skin replica. The shark was conserved in formaldehyde–acetic acid–ethanol (FAA) solution. A shark is an aquatic animal, and its skin is permanently exposed to contamination from marine organisms, e.g., bacteria and algae. Before replicating the conserved shark skin, the area of interest was first cleaned with acetone and then washed with deionized water. This process was repeated twice. The cleaned skin was placed in air for 1 h for drying. For the negative replica, a polyvinylsiloxane dental wax was applied via a dispenser on the upper side of the shark skin and immediately pressed down with a glass plate. After complete hardening of the molding mass (at room temperature 3–5 min), the master surface and the mold (negative) were separated. The first negative replica was made only to remove any remaining contaminations from the shark surface by embedding the dirt into the replica material. A second and third replica of the same area was made to obtain negatives without contamination. For the positive replica, the process was followed as described above, and epoxy was used.

Figure 3a shows the scanning electron microscopy (SEM) micrographs taken at a 45° tilt angle, showing two magnifications of the micropatterned surface. Figure 3b shows the hierarchical structures and nanostructures fabricated with n-hexatriacontane platelets. The nanostructure is formed by three-dimensional platelets of n-hexatriacontane. Platelets are flat crystals, grown perpendicular to the substrate surface. The platelet thickness varied between 50 and 100 nm, and their length varied between 500 and 1000 nm. As shown in Figure 3c, the shark skin replica shows only three ribs on each scale. It is clearly visible that the V-shaped riblets’ height varies between 200 and 500 μm and their space varies between 100 and 300 μm.

V-shaped riblets’ height varies between 200 and 500 μm, and their space varies between 100 and 300 μm.

To characterize the surface coated with n-perfluoroeicosane (C$_{20}F_{42}$), AFM height maps of the flat epoxy resin and flat epoxy resin with C$_{20}F_{42}$ were obtained with a scan size of 50 μm × 50 μm as shown in Figure 4. Statistical parameters of the surfaces (root-mean-square (rms) height, peak to valley height, and summit density ($\eta$)) were calculated and are presented in Table 2.

A summit is defined as a point whose height is greater than that of its...
four nearest neighboring points where the height difference is greater than a threshold value of 10% of rms height to avoid measurement errors.

### Table 2. Roughness Statistics for Flat Epoxy Resin with C$_{20}$F$_{42}$ Measured Using an AFM (Scan Size 50 μm × 50 μm)*

<table>
<thead>
<tr>
<th></th>
<th>rms height (nm)</th>
<th>peak to valley height (nm)</th>
<th>( \eta ) (μm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat epoxy resin</td>
<td>1.4</td>
<td>9.2</td>
<td>1.1</td>
</tr>
<tr>
<td>flat epoxy resin with C$<em>{20}$F$</em>{42}$</td>
<td>4.3</td>
<td>34</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* rms = root mean square; \( \eta \) = summit density.

### Table 3. Summary of the Static Contact Angle for Droplets at Three-Phase Interfaces on Flat Epoxy Resin and Micropatterned Surfaces (14 μm Diameter, 30 μm Height Pillars) with Varying Pitch Values* 

<table>
<thead>
<tr>
<th>pitch (μm)</th>
<th>contact angle of water droplet in air (deg)</th>
<th>contact angle of oil droplet in air (deg)</th>
<th>contact angle of oil droplet in water (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>76 ± 0.9</td>
<td>13 ± 1.7</td>
<td>109 ± 1.9</td>
</tr>
<tr>
<td>21</td>
<td>150 ± 0.9</td>
<td>4 ± 0.8</td>
<td>146 ± 1.3</td>
</tr>
<tr>
<td>23</td>
<td>155 ± 0.8</td>
<td>5 ± 1.6</td>
<td>151 ± 1.3</td>
</tr>
<tr>
<td>26</td>
<td>160 ± 0.6</td>
<td>7 ± 1.3</td>
<td>155 ± 1.7</td>
</tr>
<tr>
<td>35</td>
<td>111 ± 2.2</td>
<td>9 ± 1.3</td>
<td>115 ± 0.9</td>
</tr>
<tr>
<td>70</td>
<td>93 ± 0.8</td>
<td>8 ± 1.0</td>
<td>111 ± 0.9</td>
</tr>
<tr>
<td>105</td>
<td>87 ± 0.9</td>
<td>10 ± 1.6</td>
<td>107 ± 0.8</td>
</tr>
<tr>
<td>126</td>
<td>83 ± 0.8</td>
<td>10 ± 0.5</td>
<td>105 ± 1.3</td>
</tr>
<tr>
<td>168</td>
<td>81 ± 1.3</td>
<td>12 ± 1.3</td>
<td>96 ± 1.3</td>
</tr>
<tr>
<td>210</td>
<td>80 ± 0.5</td>
<td>12 ± 0.9</td>
<td>104 ± 2.6</td>
</tr>
</tbody>
</table>

*The variation represents ±1 standard deviation.

### 4. Results and Discussion

#### 4.1. Wetting Behavior on Flat and Micropatterned Surfaces

To observe the wetting behavior of water and oil droplets for philic/phobic nature in three phase interfaces, experiments with the droplets on both hydrophilic and hydrophobic and oleophilic surfaces in air were performed. Figure 5 shows the optical micrographs of droplets in three different phase interfaces on flat epoxy resin and micropatterned surfaces. At a solid–air–water interface, the water droplet was hydrophilic for the flat epoxy resin and was superhydrophobic for the micropatterned surface with 23 μm pitch. It is known that air pocket formation between the pillars makes a high static contact angle for micropatterned surface. However, at a solid–air–oil interface, the oil droplet was oleophilic for both surfaces. In the solid–water–oil interface system, in which the oil droplet sits on water trapped in the pillars, it is observed that the oil droplet in water was oleophobic and had contact angles of 109° and 151° for flat epoxy resin and a micropatterned surface with 23 μm pitch, respectively.

To study optimization of oleophobicity at both the solid–air–water and solid–air–oil interfaces, the static contact angles for water and oil droplets were measured on the micropatterned surfaces and are summarized in Table 3. Figure 6 shows the measured static contact angle as a function of pitch between the...
pillars for a water droplet (circle) and an oil droplet (cross) in air. The data are compared with predicted static contact angle values obtained using Wenzel and Cassie–Baxter equations (solid lines) with a measured value of $\theta_W$ for the micropatterned surfaces. At a solid–air–water interface for a water droplet, the flat epoxy resin showed a static contact angle of 76°. The static contact angle on micropatterned surfaces is higher than that on flat surfaces. It first increases with an increase in the pitch values, then starts to drop rapidly to a value slightly higher than that of the flat surfaces. In the first portion, it jumps to a high value of 150° corresponding to a superhydrophobic surface and continues to increase to 160° at a pitch of 26 μm because open air space increases with an increase in pitch responsible for propensity of air pocket formation. The sudden drop at a pitch value of about 30 μm corresponds to the transition from the Cassie–Baxter to the Wenzel regime. The experimental observations for the transition are comparable to the value predicted from Wenzel and Cassie–Baxter equations.

At a solid–air–oil interface for an oil droplet, the flat epoxy resin showed a static contact angle of 13°. As shown in Figure 6, the oil droplets on all micropatterned surfaces were oleophilic, and the contact angle was lower than that on the flat surfaces. It increases with an increase in the pitch values, as predicted from the Wenzel equation. As mentioned earlier, the surface tension of the oil–air interface is very low for hexadecane. Therefore, it is observed that from eq 2 the surface tension of the solid–oil interface ($\gamma_{SO}$) is lower than that of the solid–water interface ($\gamma_{SW}$), resulting in oleophic state for all micropatterned surfaces.

To study optimization of oleophobicity at a solid–water–oil interface, the static contact angles for oil droplets in water were measured on the micropatterned surfaces and are summarized in Table 3. Figure 6 shows the measured static contact angle as a function of pitch between the pillars for an oil droplet in water (triangle). The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie–Baxter equations (solid lines), with a measured value of $\theta_W$ for the micropatterned surfaces. At a solid–water–oil interface, the oil droplet on the flat epoxy resin was oleophilic and had a static contact angle of 109°. The static contact angle of micropatterned surfaces at the solid–water–oil interface showed a similar trend to that at the solid–air–water interface. As the pitch increases up to 26 μm, the static contact angle first increases gradually from 146° to 155° because the oil droplet sits on water trapped in the pillars, and open space increases with an increase in pitch. Then, the contact angle starts decreasing rapidly due to the transition from the Cassie–Baxter to the Wenzel regime. The experimental observations for the transition are comparable to the values predicted from Wenzel and Cassie–Baxter equations. The micropatterned surfaces studied here were either hydrophilic or hydrophobic and both were oleophobic. At the solid–water–oil interface, they were oleophilic. As shown in Figure 1 and Table 1, it is observed that the data are not consistent with the model for hydrophilic surfaces. However, hydrophilic surfaces became oleophobic at the solid–water–oil interface because $\gamma_{WA} \cos \theta_W$ is higher than $\gamma_{WO} \cos \theta_W$.

### 4.2 Wetting Behavior on Flat and Micropatterned Surfaces with C$_{20}$F$_{42}$

To study the surfaces with some oleophobicity, $n$-perfluorooctane (C$_{20}$F$_{34}$), which has lower surface tension than that of oil, was deposited on the surfaces, and experiments with droplets on hydrophobic and both oleophilic and oleophobic in air were performed. Figure 5 shows the optical micrographs of droplets in three different phase interfaces on a flat epoxy resin and a micropatterned surface with C$_{20}$F$_{42}$. At a solid–air–water interface and a solid–air–oil interface, the water droplet and oil droplet showed contact angles of 122° and 76° for the flat epoxy resin with C$_{20}$F$_{42}$ and contact angles of 162° and 133° for the micropatterned surface with 23 μm pitch with C$_{20}$F$_{42}$, respectively. However, at a solid–water–oil interface, the oil droplet in water was oleophilic and has contact angles of 4° and 9° for both surfaces, respectively. To explain why the oleophobic surfaces in air became oleophilic in water, the theoretical values for both surfaces were calculated using eq 4. For calculations, the surface tensions of the water–air interface ($\gamma_{WA}$), oil–air interface ($\gamma_{OA}$), and oil–water interface ($\gamma_{OW}$) were taken to be 73, 27.5, and 51.4 mN/m, respectively, and the contact angles for water and oil droplets in air were taken from the measured values. The theoretical values for the flat epoxy resin and the micropatterned surface with 23 μm pitch with C$_{20}$F$_{42}$ are 28° and 10°, respectively. These values are similar to those from the experiments. This indicates that the oleophobic surfaces become oleophilic in water.

To study optimization of oleophobicity in both solid–air–water and solid–air–oil interfaces, the static contact angles for water and oil droplets were measured on the micropatterned surfaces with different pitch values and with C$_{20}$F$_{42}$ and are summarized in Table 4. Figure 7 shows the measured static contact angle as a function of pitch between the pillars for a water droplet (circle) and an oil droplet (cross) in air. The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie–Baxter equations (solid lines) with a measured value of $\theta_W$ for the micropatterned surfaces with C$_{20}$F$_{42}$. At a solid–air–water interface for the water droplet, the flat epoxy resin with C$_{20}$F$_{42}$ showed a static contact angle of 122°. The static contact angle of micropatterned surfaces with C$_{20}$F$_{42}$ first increases from 158° to 169° with an increase in the pitch values, then starts to drop rapidly at a pitch value of 110 μm. From comparison of the experimental data to the Wenzel and Cassie–Baxter equations, this corresponds to the transition from the Cassie–Baxter to the Wenzel regime. All surfaces with C$_{20}$F$_{42}$ had an increase in contact angle, and the transition took place at higher pitch value than that of the micropatterned surfaces (Figure 6).

At a solid–air–oil interface for an oil droplet, the flat epoxy resin with C$_{20}$F$_{42}$ showed a static contact angle of 76°. As shown in Figure 7, the highest contact angle of micropatterned surfaces with C$_{20}$F$_{42}$ was 133° at a pitch value of 23 μm. Then, it decreases with an increase in the pitch values, and these values are comparable with the values predicted Wenzel equations. The contact angles of all micropatterned surfaces with C$_{20}$F$_{42}$ are higher than that of the flat surfaces.

To study optimization of oleophobicity at a solid–water–oil interface, the static contact angles for oil droplets in water were

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**Table 4. Summary of the Static Contact Angle for Droplets in Three-Phase Interfaces on Flat Epoxy Resin and Micropatterned Surfaces (14 μm Diameter, 30 μm Height Pillars) with Varying Pitch Values with C$_{20}$F$_{42}$**

<table>
<thead>
<tr>
<th>Pitch (μm)</th>
<th>Contact Angle of Water Droplet in Air (deg)</th>
<th>Contact Angle of Oil Droplet in Air (deg)</th>
<th>Contact Angle of Oil Droplet in Water (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>122 ± 1.3</td>
<td>76 ± 0.8</td>
<td>4 ± 0.8</td>
</tr>
<tr>
<td>21</td>
<td>158 ± 0.5</td>
<td>129 ± 1.2</td>
<td>11 ± 0.5</td>
</tr>
<tr>
<td>23</td>
<td>160 ± 0.8</td>
<td>133 ± 2.6</td>
<td>9 ± 1.3</td>
</tr>
<tr>
<td>26</td>
<td>162 ± 1.0</td>
<td>113 ± 1.5</td>
<td>10 ± 1.3</td>
</tr>
<tr>
<td>35</td>
<td>163 ± 0.9</td>
<td>107 ± 1.1</td>
<td>9 ± 1.0</td>
</tr>
<tr>
<td>70</td>
<td>166 ± 1.0</td>
<td>99 ± 1.0</td>
<td>8 ± 0.8</td>
</tr>
<tr>
<td>105</td>
<td>169 ± 0.8</td>
<td>96 ± 0.9</td>
<td>6 ± 0.5</td>
</tr>
<tr>
<td>126</td>
<td>129 ± 1.5</td>
<td>89 ± 1.2</td>
<td>6 ± 0.5</td>
</tr>
<tr>
<td>168</td>
<td>124 ± 1.7</td>
<td>88 ± 1.3</td>
<td>5 ± 0.8</td>
</tr>
<tr>
<td>210</td>
<td>123 ± 0.5</td>
<td>84 ± 1.3</td>
<td>5 ± 0.5</td>
</tr>
</tbody>
</table>

*The variation represents ±1 standard deviation.*
measured on the micropatterned surfaces with different pitch values and with C_{20}F_{42} and are summarized in Table 4. Figure 7 shows the measured static contact angle as a function of pitch between the pillars for an oil droplet in water (triangle). The data are compared with the predicted static contact angle values obtained using the Wenzel and Cassie–Baxter equations (solid lines) with a measured value of $\theta_0$ for the micropatterned surfaces with C_{20}F_{42}. At a solid–water–oil interface, the flat epoxy resin with C_{20}F_{42} was oleophilic and had a static contact angle of 4°. All micropatterned surfaces with C_{20}F_{42} were oleophilic and had contact angles lower than 10°. The reason why hydrophobic and oleophilic surfaces in air became oleophilic in water can be explained from Figure 1 and Table 1. The contact angle for a water droplet is higher than that for an oil droplet on all surfaces with C_{20}F_{42}, and the surface tension of the water–air interface ($\gamma_{WA}$) is higher than that of the oil–air interface ($\gamma_{OA}$). Therefore, it is observed that $\gamma_{WA}\cos\theta_W$ is higher than $\gamma_{OA}\cos\theta_O$, and then the surfaces become oleophilic at the solid–water–oil interface.

4.3. Wetting Behavior on Nano- and Hierarchical Structures, and Shark Skin Replica. To observe the wetting behavior of water and oil droplets for nano- and hierarchical structures found from Lotus plant surfaces, experiments with the droplets on the surfaces were performed in the three-phase interface, and the data are summarized in Table 5. Figure 8 shows the optical micrographs of droplets in three different phase interfaces on a nanostructure and a hierarchical structure fabricated with a 0.2 μg/mm$^2$ mass of n-hexatriacontane and Shark Skin Replica with and without C_{20}F_{42}.

Table 5. Summary of the Static Contact Angle for Droplets at Three-Phase Interfaces on Nanostructure and Hierarchical Structure Fabricated with a 0.2 μg/mm$^2$ Mass of n-Hexatriacontane and Shark Skin Replica with and without C_{20}F_{42}.

<table>
<thead>
<tr>
<th>Contact angle of water droplet</th>
<th>Contact angle of oil droplet</th>
<th>Contact angle of oil droplet in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (deg)</td>
<td>Contact angle (deg)</td>
<td>Contact angle (deg)</td>
</tr>
<tr>
<td>in air</td>
<td>in air</td>
<td>in water</td>
</tr>
<tr>
<td>Nanostructure</td>
<td>Hierarchical structure</td>
<td>Shark skin replica</td>
</tr>
<tr>
<td>without C_{20}F_{42}</td>
<td>158 ± 0.5</td>
<td>8 ± 1.3</td>
</tr>
<tr>
<td>with C_{20}F_{42}</td>
<td>169 ± 0.8</td>
<td>3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>142 ± 0.5</td>
<td>5 ± 0.5</td>
</tr>
</tbody>
</table>

*The variation represents ±1 standard deviation.

(31.4 mN/m), and this value is higher than that of an oil droplet (hexadecane). At the solid–water–oil interface, nano- and hierarchical structures had a static contact angles of 10° and 5°, respectively. As shown in Figure 1 and Table 1, it is observed that both surfaces are oleophilic at a solid–water–oil interface.

To study the surface structure on an aquatic animal, experiments with water and oil droplets on the shark skin replica were performed at a three-phase interface, and the data are summarized in Table 5. Figure 9 shows the optical micrographs of droplets in three different phase interfaces on a shark skin replica without and with C_{20}F_{42}. First, the shark skin replica had contact angles of 89° and ~0° for water and oil droplets, respectively. After the surface was coated with C_{20}F_{42}, the contact angles of water and oil droplets became 142° and 115°, respectively. At the solid–water–oil interface, the oil droplet in water on the shark skin replica became oleophilic and had a contact angle of 109°.

On the basis of eq 4, the calculated value was 59° for the oil droplet in water on a shark skin replica. This difference may come from the open space under the scales of the shark skin replica responsible for the propensity of trapped water pocket formation, as shown in Figure 3. Shark skin replica with C_{20}F_{42} was


Figure 7. Static contact angle as a function of geometric parameters for water droplet (circle) and oil droplet (cross) in air, and oil droplet in water (triangle) compared with predicted static contact angle values obtained using Wenzel and Cassie–Baxter equations (solid lines) with a measured value of $\theta_0$ for the micropatterned surfaces with C_{20}F_{42}.

Figure 8. Optical micrographs of droplets in three different phase interfaces on nanostructure and hierarchical structure fabricated with a 0.2 μg/mm$^2$ mass of n-hexatriacontane and Shark Skin Replica with and without C_{20}F_{42}. Left image: a water droplet is placed on a surface in air. Middle image: an oil droplet is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water.

Figure 9. Optical micrographs of droplets in three different phase interfaces on a shark skin replica without and with C_{20}F_{42}. Left image: a water droplet (158°) is placed on a surface in air. Middle image: an oil droplet (6°) is placed on a surface in air. Right image: an oil droplet is placed on a solid surface in water.
oleophilic and had a contact angle of $\sim 0^\circ$. This state is the same as
the micropatterned surfaces with $C_{20}F_{42}$ as shown in Figure 1 and
Table 1.

5. Conclusions

Superhydrophobic/superoleophobic and self-cleaning surfaces are
desirable for many industrial applications. Oleophobic surfaces
have the potential for self-cleaning and antifouling from
biological and organic contaminants in both air and underwater
applications. A model for predicting the contact angle of water
and oil droplets was proposed. The surface tension of oil and
organic liquids is lower than that of water. So to make the surface
oleophobic at a solid–air–oil interface, a material with surface
energy lower than that of oil was used. The wetting behavior of
water and oil droplets for hydrophobic/philic and oleophobic/
philic surfaces in three phase interfaces was studied. In under-
water applications, the oleophobicity/philicity of an oil droplet in
water was studied on surfaces with different surface energies of
different interfaces and contact angles of water and oil droplets in
air. On the basis of the proposed model, it is found that, for a
hydrophilic surface, an oleophobic surface at the solid–water–oil
interface can be created if $\gamma_{OA} \cos \theta_O$ is lower than $\gamma_{WA} \cos \theta_W$
$j$. For a hydrophobic surface and an oleophobic surface at the
solid–air–oil interface, an oleophobic surface at the solid–
water–oil interface can be created if $\gamma_{OA} \cos \theta_O$ is higher than
$\gamma_{WA} \cos \theta_W$.

To validate the model for predicting the oleophobic/philic
nature of the surfaces, flat and micropatterned surfaces with
varying pitch values were produced by soft lithography.
$n$-Pentafluoroeicosane ($C_{20}F_{42}$) with low surface energy (6.7 mN/m)
was deposited by thermal evaporation to produce superhydro-
phobic and oleophobic flat and micropatterned surfaces. For
water and oil droplets in three phase interfaces, the experimental
observations showed that there is a good agreement between the
measured contact angle and the predicted values of models. It is
also found that the transition can occur for hydrophobic and
oleophobic micropatterned surfaces with a larger distance be-
 tween pillars. The wetting behavior of the nano- and hierar-
chical structures found in Lotus plant surfaces and the shark
skin replica as an example of aquatic animal was also investigated.
It is found that the nano- and hierarchical structures with
$n$-hexadecyltriacontane were oleophilic as a result of the high surface
energy of $n$-hexadecyltriacontane. The structure of the shark skin
replica showed a higher propensity for trapped water pocket
formation, resulting in a higher contact angle than the theoretical
value, whereas the shark skin replica with $C_{20}F_{42}$ had a contact
angle of $\sim 0^\circ$ at the solid–water–oil interface, as predicted by
the model. For self-cleaning and antifouling from biological
and organic contaminants, an oleophobic surface can be created
based on this study.

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