doi:10.1246/cl.2010.482

Published on the web April 3, 2010

Removing an Air Layer from a Superhydrophobic Surface in Flowing Water

Munetoshi Sakai,*[1] Akira Nakajima,*[1,2] and Akira Fujishima[1]
[1]*Kanagawa Academy of Science and Technology, 308 East, Kanagawa Science Park, 3-2-1 Sakado, Takatsu-ku, Kawasaki 213-0012*
[2]*Department of Metallurgy and Ceramic Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552*

(Received February 12, 2010; CL-100155; E-mail: sakai@newkast.or.jp, anakajim@ceram.titech.ac.jp)

The removal of a surface air layer from a superhydrophobic coating in flowing water was evaluated using a laser beam and a high-speed camera. It proceeded via three steps: (1) removal of the top unstable air layer, (2) retention of air in the bottom of the surface microstructure, and (3) replacement of air in the microstructure with water. Different flow velocities result in different removal rates of the surface air layer.

Recently, the importance of controlling the wettability of a solid surface has been recognized in various industries.[1–6] Surfaces with water contact angles exceeding 150° (known as superhydrophobic surfaces) are currently the subject of great interest and intensive study. Superhydrophobic coatings that produce rough surfaces at the micro- and nanoscale level with low surface energies have been prepared by several methods.[1–6] Cassie's model is better than Wenzel's for achieving superhydrophobicity with high water-shedding properties.[7,8] A water droplet on a superhydrophobic coating slides down the surface when the surface is tilted at a low angle.[9] A water droplet sliding on a superhydrophobic surface exhibits almost constant acceleration.[9] Moreover, the internal fluidity of the water droplet exhibits a slipping motion.[10] Therefore, superhydrophobic coatings are a promising means of reducing the friction drag of an object in flowing water.[11] This potentiality is commonly attributed to the surface air layer of the coating. For instance, drag reduction of water flowing in a pipe with superhydrophobic walls has been experimentally clarified.[12] A laser beam is totally reflected from the air layer on a superhydrophobic coating in water; this phenomenon has been used to evaluate the surface air layers on superhydrophobic coatings with different roughnesses in a water–ethanol mixture.[13] The reflected light intensity decreased with decreasing liquid surface tension of superhydrophobic coatings with high roughnesses. A transition to the Wenzel mode was induced when a static pressure was applied to a water droplet on a superhydrophobic coating.[14]

We recently developed an image analysis system consisting of a high-speed camera[15] and an optical analysis system for evaluating air layers in liquids.[13] In the present study, we used this image analysis system with a transparent acrylic resin water tunnel to evaluate the sustainability of an air layer in flowing water.

A superhydrophobic coating was prepared by spraying a commercial paint (HIREC 450; NTT Advanced Technology Corp., Tokyo, Japan) onto glass plates (25 mm × 50 mm × 1 mm). This coating, which consists of poly(tetrafluoroethylene) particles and a fluoropolymer, has a low surface energy and a low electric permittivity (see the scanning electron microscope image in the Supporting Information).[16] Water contact angles were measured using a contact angle meter (Drop Master 500; Kyowa Interface Science Co., Ltd., Saitama, Japan). Water droplets (3 µL) were used in the contact angle measurements, and contact angles were measured at five different points on each surface. The sample surface was blown with ionized air to eliminate static electricity prior to each measurement. The mean surface roughness (*Ra*) of the sample was evaluated using a laser profile micrometer (94 µm × 130 µm measurement area, ×2500 magnification, VF-7500; Keyence Co., Tokyo, Japan). The initial contact angle of the prepared sample was 155°, and the initial surface roughness was 1900 nm.

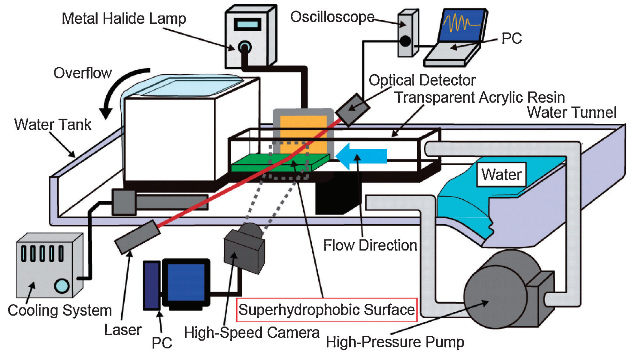

Figure 1. Schematic illustration of the system used to observe the surface air layer on superhydrophobic coatings in flowing water.

The air layer on the superhydrophobic coating in flowing water was observed using the experimental setup depicted in Figure 1. The sample was set on a stage in a transparent acrylic resin water tunnel. The cross-sectional area S above the stage in the water tunnel was 300 mm^2 (= 30 mm (width) × 10 mm (height)). Sequential images of the air layer on the superhydrophobic coating were obtained using a high-speed camera (512 PCI; Photron Ltd., Tokyo, Japan) positioned on one side of the water tunnel. In addition, a laser beam from a laser outside the water tunnel was used to irradiate the sample, and the reflected beam was detected by a photosensor on the opposite side; the intensity of the reflected signal was converted into a voltage by an external circuit.[12,16] The flow rate Q in the water tunnel was controlled by a magnetic drive pump with an inverter controller (32NWPM; Ebara Techno Serve Co., Ltd., Tokyo, Japan), allowing it to be adjusted in the range 0.36 to 20 L min^{-1}. The flow rate was monitored in real time (IR-Opflow Type 4, Tecflow International, Wijchen, Netherlands). The flow velocity V is found by dividing the flow rate by the cross-sectional area S as follows:

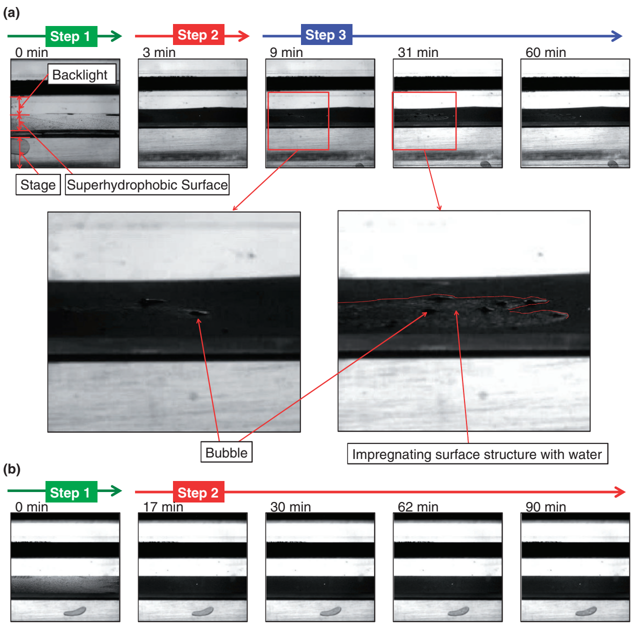

Figure 2. Sequential photographs showing removal of the surface air layer on a superhydrophobic coating in a water tunnel. Flow velocity: (a) 1.0 and (b) $0.59\,\mathrm{m\,s^{-1}}$. Dynamic Pressure: (a) 499 and (b) 174 Pa.

$$V = \frac{Q}{S} \tag{1}$$

which was in the range 0.02 to $1.0\,\mathrm{m\,s^{-1}}$. Therefore, the dynamic pressure P_d in the water flow direction was calculated as follows:

$$P_d = \frac{1}{2}\rho V^2 \tag{2}$$

where ρ was the density of water at 25 degree. The range of the dynamic pressure was 0.2 to 499 Pa. A static pressure P_s of over 800 Pa was maintained by allowing water to overflow from a height of 80 mm above the horizontal surface of the superhydrophobic coating. The water was collected in a water tank in which a cooling system maintained the temperature of the circulating water at 25 °C (ECS-50, Tokyo Rikakikai Co., Ltd., Tokyo, Japan). The dynamic viscosity ν and the surface energy of the water at this temperature were $0.893 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$ and $71.96\,\mathrm{N\,m^{-1}}$, respectively. The water contact angles of a sample were evaluated before and after observing the sample in the water tunnel.

Figure 2 shows sequential photographs of the removal of air layers from the superhydrophobic coating. The surface initially appeared silvery when the superhydrophobic coating was placed in the tunnel filled with water. Specular reflection from the superhydrophobic surface indicates the existence of an air layer on the surface structure. Three steps were observed in the process of removing the air layer from a surface immersed in water flowing with a velocity of $1.0\,\mathrm{m\,s^{-1}}$ (Figure 2a). The superhydrophobic surface became dark with time (step 1), and the specular reflection disappeared within 3 min after water flow commenced (Figure 3). The reflected light intensity I_ν in Figure 3 is defined as the ratio of the actual voltage minus the minimum voltage to the maximum voltage minus the minimum voltage.

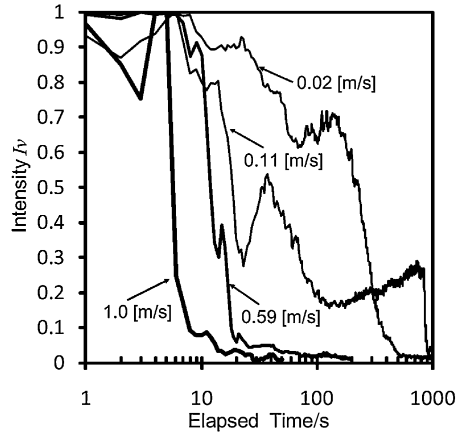

Figure 3. Dependence of the reflected light intensity and elapsed time of the superhydrophobic coating on the flow velocity in the water tunnel.

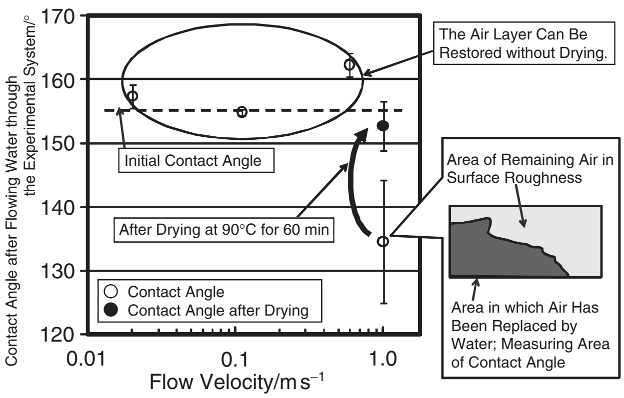

Figure 4. Contact angles of the tested samples. The broken line indicates the initial contact angle of the superhydrophobic coating of 155°.

$$I_\nu = \frac{V(t) - V_{\mathrm{Min}}}{V_{\mathrm{Max}} - V_{\mathrm{Min}}} \tag{3}$$

The superhydrophobic surface remained dark (step 2), when water flowed in the water tunnel. After 9 min, a bubble formed on the surface due to air in the surface structure being replaced with water (step 3). Steps 1 and 2 occurred at all flow velocities, whereas step 3 did not occur if the flow velocity was less than $0.59\,\mathrm{m\,s^{-1}}$ (Figures 2b, Figure S-3[16]). Progression of air-layer removal ceased in step 2 when the flow velocity was below $0.5\,\mathrm{m\,s^{-1}}$. Moreover, the time required for step 1 varied with the flow velocity (Figure 3); step 1 progressed rapidly at high flow velocities.

Figure 4 shows the contact angles of samples that had been tested in the water tunnel. The contact angle did not change from the initial contact angle of 155° when the flow velocity was below $0.59\,\mathrm{m\,s^{-1}}$. However, when the progress of air-layer removal attained step 3 on the superhydrophobic coating, the contact angle at the area where step 3 was attained became lower than the initial contact angle for samples in water flowing with a velocity of $1.0\,\mathrm{m\,s^{-1}}$. The contact angle returned to the initial angle when the sample was dried in an oven at 90 °C for 1 h. This transition in the contact angle implies that the super-

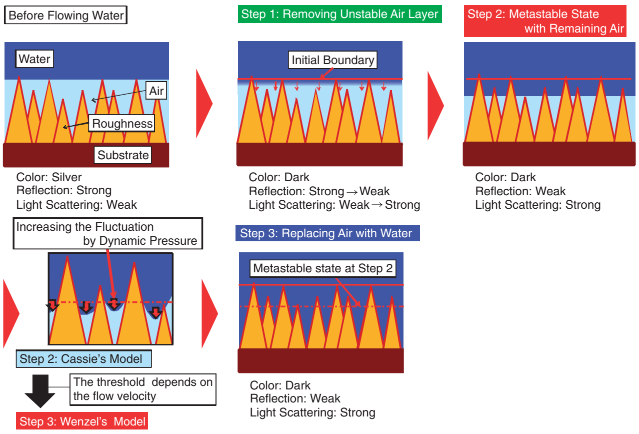

Figure 5. Schematic illustration of the expected mechanism for air layer removal from superhydrophobic surfaces by flowing water.

hydrophobic coating was not broken, but that air in the microstructure was replaced with water.

On the other hand, the air in the bottom of the surface microstructure was not replaced with water when the flow velocity was below 0.59 m s^{-1}. This finding is supported by the sequential photographs, which did not show a bubble on the surface, and the constant contact angle of the tested samples. Moreover, a large amount of air in the microstructure will not prevent scattering of the laser light when the reflected light intensity from air is low. Therefore, it will be necessary to directly observe the air layer by taking sequential photographs when investigating the replacement of air in the microstructure with water.

Figure 5 shows the expected mechanism for the three-step removal of an air layer from a superhydrophobic surface by flowing water. Step 1 progressively removed the top unstable air layer with time; it commenced immediately after water flow in the water tunnel started. The air layer entered a metastable state and air remained in the bottom of the surface microstructure (step 2). Cassie's model, in which air in the surface structure supports the liquid, is applicable to step 2. This state was sustained indefinitely at flow velocities of 0.59 m s^{-1} or less. Step 3 was attained when the flow velocity was 1.0 m s^{-1} or greater. In this state, the wettability model changed from Cassie's model to Wenzel's model, because the contact angle decreased with the air in the microstructure being replaced by water. The force that removes the air layer from the superhydrophobic surface is the shear stress τ at the gas–liquid interface:

$$\tau = \nu \frac{dv_x}{dz} \qquad (4)$$

where dv_x/dz represents the shear velocity, v_x is the velocity parallel to the x axis, and ν is the dynamic viscosity. A slip length exists at the solid–liquid interface, when water flows on the superhydrophobic surface. The slip length of water flowing with an identical velocity depends on the surface wettability when the surface is smooth in hydrodynamics. Therefore, the sustainability threshold for the air layer in flowing water was exceeded for flow velocities greater than 1.0 m s^{-1}, because the shear stress was sufficiently high to remove the air layer. In a past study, it was reported that the wettability model was converting Cassie's model to Wenzel's model, when the water droplet on a superhydrophobic coating was compressed at a few hundred Pascals.[14] Compared to that study, the air in the surface microstructure remained, when the comparable total of both static and dynamic pressure was compressed to the air layer (Figure 2). Therefore, the random surface structure, such as the closed system where the air did not leak, worked effectively. In future studies, we intend to further investigate the effects of the static/dynamic pressure of flowing water and the surface microstructure on the sustainability of air layers on superhydrophobic coatings in liquids.

The surface air layer on a superhydrophobic coating in water flow was evaluated using a laser beam and a high-speed camera. Specular reflection was observed from the superhydrophobic surface, indicating the existence of an air layer on the surface. Three steps were observed in the process of removing the air layer from the surface. The metastable state continued indefinitely, and air remained in the bottom of the surface microstructure at flow velocities of 0.59 m s^{-1} or less. However, the air in the microstructure was replaced with water at high flow velocities. The wettability model of the superhydrophobic coating changed from Cassie's model to Wenzel's model.

This study was supported by the Project to Create Photocatalyst Industry for Recycling-oriented Society of the New Energy and Industrial Technology Development Organization (NEDO).

References and Notes

1 D. Quéré, *Rep. Prog. Phys.* **2005**, *68*, 2495.
2 L. Gao, T. J. McCarthy, X. Zhang, *Langmuir* **2009**, *25*, 14100.
3 T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125.
4 K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* **1997**, *80*, 3213.
5 A. Hozumi, O. Takai, *Thin Solid Films* **1997**, *303*, 222.
6 A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, *Adv. Mater.* **1999**, *11*, 1365.
7 R. N. Wenzel, *J. Phys. Chem.* **1949**, *53*, 1466.
8 A. B. D. Cassie, *Discuss. Faraday Soc.* **1948**, *3*, 11.
9 M. Miwa, A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, *Langmuir* **2000**, *16*, 5754.
10 M. Sakai, J.-H. Song, N. Yoshida, S. Suzuki, Y. Kameshima, A. Nakajima, *Langmuir* **2006**, *22*, 4906.
11 C.-H. Choi, U. Ulmanella, J. Kim, C.-M. Ho, C.-J. Kim, *Phys. Fluids* **2006**, *18*, 087105.
12 K. Watanabe, Y. Udagawa, H. Udagawa, *J. Fluid Mech.* **1999**, *381*, 225.
13 M. Sakai, T. Yanagisawa, A. Nakajima, Y. Kameshima, K. Okada, *Langmuir* **2009**, *25*, 13.
14 A. Lafuma, D. Quéré, *Nat. Mater.* **2003**, *2*, 457.
15 M. Sakai, A. Hashimoto, N. Yoshida, S. Suzuki, Y. Kameshima, A. Nakajima, *Rev. Sci. Instrum.* **2007**, *78*, 045103.
16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

