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Invited Review

Recent Studies on Super-Hydrophobic Films

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Summary. Films whose water contact angle is higher than 150° have been the subject of great interest and enthusiastic study in recent years. These films, which are called super-hydrophobic, are fabricated by combining appropriate surface roughness with surfaces of low surface energy. Here we briefly review the fundamental theories on the wettability of a hydrophobic rough solid surface, together with recent works on the processing and properties of super-hydrophobic films. Though the practical application of these films is still limited, the obstacles to application are gradually being surmounted, providing a great opportunity for the development of various industrial products.

Keywords. Surface; Wetting reaction; Hydrophobic; Contact angle; Photocatalyst.

Introduction

Wettability and repellency are important properties of solid surfaces from both fundamental and practical aspects. When the effects of surface stains or adsorption of molecular substances can be ignored, the wettability of the solid surface is a characteristic property of materials and strongly depends on both the surface energy and the surface roughness. Since the surface energy is an intrinsic property of each material, it is generally difficult to control the wettability of the solid surface for a long exposure period. Significant interest has been stirred by a recent series of experiments showing that UV illumination generates a super-hydrophilic TiO_2 surface with a water contact angle of 0° [1–6]. Since TiO_2 is transparent in the visible wavelength range, this material has already been successfully applied for antifogging and self-cleaning usage as a transparent super-hydrophilic coating [7].

However, various industrial products require not only hydrophilicity but also hydrophobicity. Currently, a surface with a water contact angle above 150° (*i.e.* a super-hydrophobic surface) is attracting great attention [8]. Given the limited contact area between solid surface and water, chemical reactions or bonding formation through water are limited on a super-hydrophobic surface. Accordingly, various phenomena such as the adherence of snow, oxidation, and current conduction are expected to be inhibited on such a surface. The present paper is a short

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review of recent progress in the processing and properties of super-hydrophobic films.

Requirements for the Processing of a Super-Hydrophobic Surface

When the surface energy is lowered, the hydrophobicity is enhanced. For the simplest case, the wettability of the solid surface is commonly evaluated by the contact angle [9] given by *Young*'s equation (Eq. (1)):

$$\cos\theta = (\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})/\gamma_{\mathrm{LV}} \tag{1}$$

where γ_{SL}, γ_{SV}, and γ_{LV} are the interfacial free energies per unit area of the solid-liquid, solid-gas, and liquid-gas interfaces, respectively. This equation is applicable only to flat surfaces and not to rough ones. Based on the theories of *Dupre* and *Girifalco-Good* in their work on adhesion [10, 11], the maximum contact angle that can be attained on a flat surface merely by lowering the surface energy (the lowest surface energy value yet recorded, 6.7 mJ/m^2, was obtained for a surface with regularly aligned closest-hexagonal-packed CF_3 groups [12]) can be calculated to amount to about 120° [13].

Wenzel proposed a model describing the contact angle θ' at a rough surface [14]. He modified *Young*'s equation as follows (Eq. (2)):

$$\cos\theta' = r(\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}})/\gamma_{\mathrm{LV}} = r\cos\theta \tag{2}$$

In Eq. (2), r is a roughness factor, defined as the ratio of the actual area of a rough surface to the geometric projected area. Since r is always larger than unity, the surface roughness enhances both the hydrophilicity of hydrophilic surfaces and the hydrophobicity of hydrophobic ones.

Cassie proposed an equation describing the contact angle θ' at a surface composed of solid and air. When a unit area of the surface has a wetted solid surface area fraction f (defined as $\Sigma a/\Sigma(a+b)$ in Fig. 1) with a water contact angle θ, the contact angle on the surface can be expressed by Eq. (3), assuming a water contact angle for air of 180° [15]. The concepts of *Wenzel* [14] and *Cassie* [15] are outlined in Fig. 1.

$$\cos\theta' = f\cos\theta + (1-f)\cos180^\circ = f\cos\theta + f - 1 \tag{3}$$

Johnson Jr. and *Dettre* have simulated the contact angle of a water droplet on idealized sinusoidal surfaces [16]. During the regime where the *Wenzel* mode is dominant, they could show that the contact angle and its hysteresis (the difference between the cosine of a receding contact angle and that of an advancing contact angle for a water droplet on a tilted surface) on hydrophobic rough surfaces increase as the roughness factor increases. They also demonstrated that the contact angle continues to increase when the roughness factor exceeds a certain level ($\sim$1.7), whereas the hysteresis starts to decrease. This decrease in hysteresis occurs as a consequence of the switching of the dominant hydrophobicity mode from *Wenzel* to *Cassie* due to the increase of the air fraction at the interface between the solid and water.

In addition, various theoretical works were carried out on the hydrophobicity of rough surfaces [17–25]. *Hazlett* discussed a theoretical analysis of the effect of fractal structure on the hydrophobicity [17]. Recently, *Onda* and *Tsujii* have

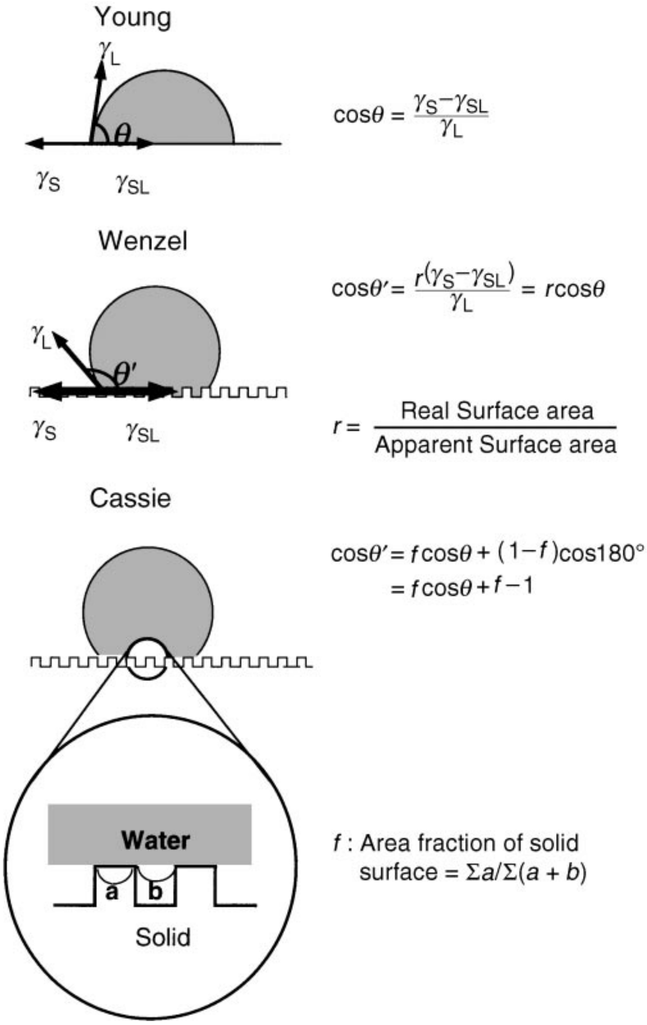

Fig. 1. Effect of roughness on the hydrophobicity of solid surface

prepared a super-hydrophobic surface by solidifying a wax (alkylketene dimer) from a melt and demonstrated that the practical contact angles were in good agreement with the calculated values based on their fractal analysis [18]. *Drelich* discussed molecular level heterogeneity and revised the *Cassie* equation by considering the line tension (the excess energy in the region of the three-phase (liquid-solid-air) contact line associated with intermolecular and surface-free energy) and contact angle hysteresis [19, 20]. *Wolansky* and *Marmur* presented a general equation for the actual contact angle on a solid surface with roughness in a three-dimensional setting by considering the effects of line tension and the variation in line with the position of the contact line [21]. *Yamauchi et al.* applied *Wenzel*'s and *Cassie*'s equations for their poly-tetrafluoroethylene (PTFE) based particulate composites by considering particle shape, number, and distribution [22]. *Chow* used the long-range noise correlation function to derive functional relationships that show the effect of surface roughness on contact angle, surface tension, and pinning of the contact line [23]. *Sakai* and *Fujii* studied the theoretical effect of gravity on rough solid-liquid interfaces and showed that the tension of the interface is enhanced by gravity when gas is adsorbed on it [24]. *Swain* and *Lipowsky* consider a three-dimensional liquid drop sitting on a rough and chemically heterogeneous substrate under the presence of gravity and line tension [25]. In any case, both the low surface energy and proper surface roughness are indispensable for the processing of super-hydrophobic surfaces.

Recent Studies of Super-Hydrophobic Films and Surfaces

Process and starting materials

Studies on super-hydrophobic films or surfaces are listed in Table 1 [17, 26–51, 55–57, 61, 63, 65, 66, 78] together with details concerning materials and processes. Basic research on the processing of super-hydrophobic surfaces started in the 1950's [26], and the processing method has been enthusiastically studied from the 1990's

Table 1. Recent studies on the processing of super-hydrophobic surfaces and films; *: cf. text

Authors	Process	References
Bartell et al.	Machining paraffin surface	[26]
Dettre et al.	Glass beads with fluorocarbon wax	[27]
Washo	Plasma polymerization of PTFE	[28]
Morra et al.	Plasma etching of PTFE	[29]
Kunigi et al.	Simultaneous plating of Ni and graphite-fluoride	[30]
**Ogawa et al.*	RF plasma etching of glass surface + F-silane coating	[31]
Murase et al.	Water repellent silica particle and polymers with F-groups	[61]
Onda et al.	Fractal surface of wax by natural cooling	[18, 32, 34] [57]
	Anodically oxidized aluminum surface + Fluorinated monoalkyl phosphates or F-silane	[36, 43]
**Tadanaga et al.*	Sol-gel alumina + hot water immersion + F-silane coating	[37, 40]
Yamauchi et al.	Organic paint with PTFE particles	[33, 56, 78]
Saiki et al.	Air blast roughening of PTFE surface	[35]
**Hozumi et al.*	Plasma-enhanced CVD of F-silane	[38, 39, 44] [50]
Tokuumi et al.	Spray of PTFE particles on organic paint surface	[41]
Sasaki et al.	Phase separation of organic paint with silica particles	[42, 51]
**Nakajima et al.*	Mixture of sublimation material with silica or boehmite + F-silane coating	[46, 55, 63]
	Phase separation + colloidal silica + F-silane coating	[48, 49]
Youngblood et al.	Plasma etching of PP	[47]
Bico et al.	Molding of silicate gel + F-silane	[65]
Matsumoto et al.	Plasma polymerization of CH_4/CF_4 gas mixture	[66]

[30–51, 55–57, 61, 63, 65, 66, 78]. The methods so far developed to impart roughness to solid surfaces include the addition of fillers (silica particles [42, 51, 61], PTFE particles [35, 41, 56, 73], glass beads [27]), etching [26, 31, 35, 47], plasma polymerization [28, 66], simultaneous plating with fluoride particles [30], wax solidification [18, 32, 34, 57], anode oxidation of metal surfaces [36, 43], solution-precipitation reaction in hot water [37, 40], chemical vapour deposition (CVD) [38, 39, 44, 50], addition of a sublimation material [46, 55, 63], phase separation [42, 48, 49, 51], and molding [65]. The low surface energy is produced by using, coating, mixing, or polymerizing low-surface-energy materials such as fluoroalkylsilane (heptadecafluorodecyltrichlorosilane [31], perfluorooctyltrichlorosilane [36, 43], heptadecafluorodecyltrimethoxysilane [37, 38, 39, 40, 44, 46, 48, 49, 50, 55, 63] perfluorododecyltrichlorosilane [65]), fluoropolymers (PTFE [28, 29, 33, 35, 41, 56, 78], polyvinyliden fluoride [33, 56, 78], polyperfluoroalkyl acrylate [61]), organic polymers (polypropylene [47]), wax (paraffin [26], fluorocarbon wax [27], alkylketene dimer [18, 32, 34, 57]), and fluorine compounds (graphite fluoride [30], fluorinated monoalkyl phosphates [36, 43], C_4F_8 gas [66]).

Properties

Whereas the preparation of super-hydrophobic surfaces has been extensively studied, only a few methods have been reported for transparent films so far. The methods marked with an asterisk in Table 1 concern transparent super-hydrophobic thin films or surfaces. From the viewpoint of surface roughness, hydrophobicity and transparency are competitive properties. Providing surface roughness means introducing sources of light scattering. When the roughness increases, the hydrophobicity also increases, whereas the transparency decreases. Therefore, precise roughness control is required to satisfy both properties. Since the visible light wavelength is *ca.* 400–750 nm, the surface roughness for transparent films should be less than 100 nm. *Ogawa et al.* developed a method for producing a transparent super-hydrophobic surface on glass plates by RF plasma etching and subsequent coating by heptadecafluorodecyltrichlorosilane [31]. By controlling the gas pressure and substrate temperature during the preparation of hydrophobic films by CVD, *Hozumi et al.* kept the surface roughness in a range from 9.4 to 60.8 nm, and through the use of various fluoroalkylsilanes they could attain nearly transparent super-hydrophobic films in their experiments [38, 39, 44, 50]. *Tadanaga et al.* prepared transparent boehmite (AlOOH) films by the sol-gel method with subsequent immersion into hot water [37, 40]. By varying the immersion time, they were able to precisely control the surface roughness within a range from 20 to 50 nm. Then, by coating the boehmite with heptadecafluorodecyl trimethoxysilane, they were able to produce a transparent super-hydrophobic film. *Nakajima et al.* imparted surface roughness to boehmite or silica films by the sublimation of aluminum acetylacetonate ($Al(C_5H_7O_2)_3$) during calcination, and subsequently they were able to prepare transparent super-hydrophobic films from these materials by coating them with heptadecafluorodecyl trimethoxysilane [46].

Over long periods of outdoor exposure, the excellent hydrophobicity of an artificially constructed super-hydrophobic surface gradually degrades due to the accumulation of stains that adhere to the surface. However, natural super-hydro-

Fig. 2. Transparent super-hydrophobic thin film with TiO_2 photocatalyst

phobic surfaces such as the surfaces of lotus leaves avoid this problem by continuous metabolism of their surface wax layer, which makes it possible to maintain hydrophobicity throughout their lifetimes [52–54]. Since the proper metabolic mechanism of a lotus leaf is impossible to mimic, practical applications of super-hydrophobic surfaces have not been successful. Recently, *Nakajima et al.* [55] and *Yamauchi et al.* [56] discovered that the addition of a few percent of TiO_2 photocatalyst effectively provides a self-cleaning property to super-hydrophobic films and maintains high contact angles during long periods of outdoor exposure (Figs. 2 and 3). Although various factors affect the result of outdoor exposure, several mechanisms that might be responsible for the overall self-cleaning performance have been proposed. These include: 1) a long diffusion distance of the radical species on the fluorine-coated surface, 2) effective stain collection to the TiO_2 surface and subsequent photocatalytic decomposition or washing out by water due to the high surface energy or photo-induced hydrophilic property of the surface

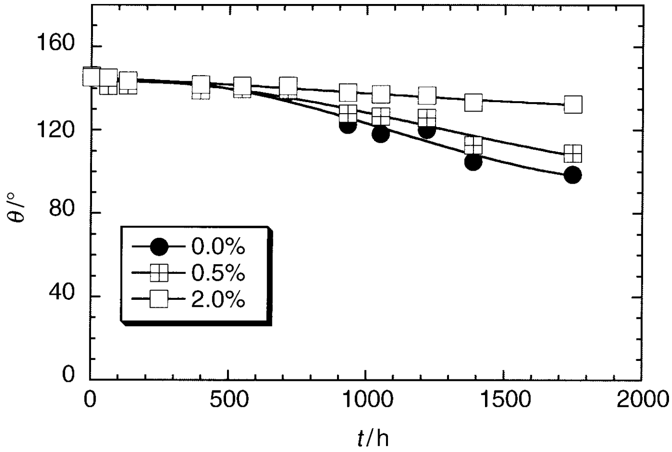

Fig. 3. Effect of TiO_2 addition on the hydrophobicity of a super-hydrophobic thin film during outdoor exposure; the numbers refer to TiO_2 concentration (%(w/w))

of TiO_2, and 3) reduction of static electricity by the photo-induced hydrophilicity of TiO_2 [55].

Surfaces with a high roughness commonly show fewer mechanical properties than flat surfaces, and this is a crucial problem for the application of super-hydrophobic surfaces. A needle-like structure is known to constitute an ideal surface for super-hydrophobicity [57]. However, this structure is not applicable for practical use because its hardness is generally insufficient. To increase the hardness of super-hydrophobic surfaces, a crater-like structure is thought to be preferable to a needle-like one. In the case of a crater-like structure, however, it is difficult to obtain a super-hydrophobic state on the surface due to the increase of the contact area between solid and liquid. Very recently, *Nakajima et al.* have prepared a hard super-hydrophobic silica film with visible light transmission by combining two different roughness dimensions [48, 49]. They combined a crater-like roughness (~800 nm) prepared by a phase separation achieved by the sol-gel method and a fine roughness (~20 nm) provided by colloidal silica. Although the transmittance in the visible range is slightly lower than that of previous transparent super-hydrophobic films (85–90%), this film is harder. The concept of roughness combination might be important for the design of super-hydrophobic films with high durability.

Whereas the contact angle of water has been commonly used as a criterion for the evaluation of hydrophobicity of the surface, this alone is inadequate for the evaluation of the sliding properties of water droplets on surfaces. The sliding angle, *i.e.* the angle when a droplet of water of a certain weight begins to slide down an inclined plate, is not always low on a surface with a high contact angle. Together with the various studies on static contact angles, there has also been extensive investigation of the sliding behavior of water droplets on rough surfaces [45, 47, 48, 58–64]. In an investigation of sliding angles on stainless plates with different finishes and contact angles of about 90°, *Bikerman* showed that the surface roughness provides resistance against the sliding of water droplets [58]. This result suggests that *Wenzel*'s mode is a dominant mechanism for the hydrophobicity of the surface. *Youngblood et al.* insisted that a rough hydrophobic surface with poor continuity of the three-phase line is suitable for an excellent water sliding behavior [45, 47]. *Miwa et al.* produced an equation to describe a direct relationship between the contact angle and the sliding angle of a water droplet on a super-hydrophobic surface with a needle-like surface morphology [63]. They showed that a small (7 mg) water droplet slid down from a super-hydrophobic film with a water contact angle of 162° with almost no sliding resistance at a tilt of only 1°. Their study revealed that water droplets slide down by constant accelerations on the super-hydrophobic films. *Richard* and *Quere* also investigated liquid droplets rolling on tilted super-hydrophobic surfaces and showed that viscous species such as glycerol slide down on the super-hydrophobic surface with constant velocities [67]. Moreover, they demonstrated that a water drop fully bounces when impinging a super-hydrophobic surface [68]. *Murase et al.* demonstrated that a polyperfluoroalkyl acrylate with a water contact angle of 117° showed a higher sliding angle than a poly-dimethylsiloxane with a water contact angle of 102° [61, 62, 64]. Based on the energy calculation, they proposed that this phenomenon was due to the rigidity of fluoropolymer segments and enhancement of an ice-like molecular arrangement in water [62].

Besides structures and chemical species on the surface, the electric field is known to be an important factor for both the hydrophobicity and water sliding behavior on solid surfaces [69–76]. Whereas water contact angles on hydrophobic solid surfaces have been shown to decrease, it is known that the droplet motion is controllable under an electric field. Although relatively few studies have dealt with this feature of super-hydrophobic surfaces [77], it might be important for their practical application.

Applications of Super-Hydrophobic Thin Films

By applying a super-hydrophobic film to the surface of a satellite antenna, *Yamauchi et al.* succeeded in reducing the disruption of communication by the adherence of snow to the antenna [56, 78]. *Murase* demonstrated that snow was less likely to adhere to a surface with a high water angle contact because of the large amount of air between solid and snow [79]. Their result portends well for techniques to apply super-hydrophobic film coatings to buildings, signs, and roofs in areas with heavy snowfall.

Tokunaga et al. investigated the friction drag on super-hydrophobic films [80, 81]. When supplying a small amount of air to the super-hydrophobic film surface, the air adsorbs on the film, forming a filmy air flow along the surface in water. This phenomenon removed 55–80% of the friction drag under their experimental conditions. These reports suggest that super-hydrophobic film coatings are effective not only for building glass and the windshields of cars, but also the hulls of ships and tubes or pipes.

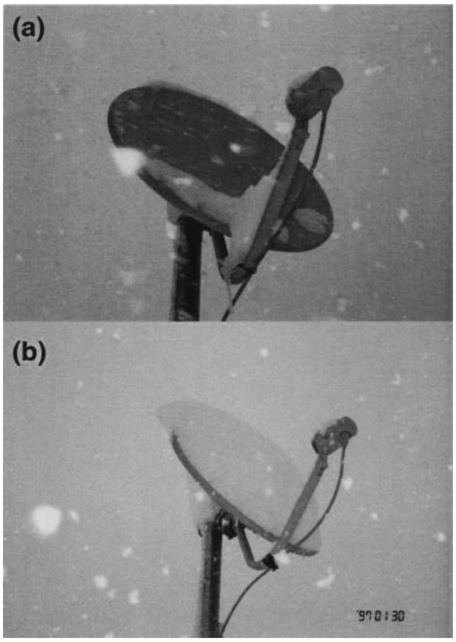

Fig. 4. Effect of super-hydrophobic coating on the snow adherence on metal plates (a) with and (b) without coating (courtesy by NTT Advanced Technology Corporation)

Under rainy conditions, subconductors of transmission lines generate audible noise due to corona discharge by water droplets on their surfaces. In general, this problem is avoided by reducing the electric field using a bundle of conductors. Recently, *Miyajima* and *Tanabe* reported that conductors coated with super-hydrophobic film drastically decrease corona activity because water droplets do not remain on the surface [82].

In addition to these properties, super-hydrophobic coatings are also expected to offer beneficial properties for anti-oxidation or anti-current conduction.

Conclusions and Outlook

This paper gives a brief overview of recent studies on super-hydrophobic thin films which offer great promise for the development of various industrial products. Although practical application of these films is still limited, the obstacles to application are being surmounted. The wettability of a solid surface is a complex property and affects various other surface properties. Basic research on the control of the wettability of solid materials has just started. This is a key technology for industries, and further investigations are expected in this field.

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