Smart, clean surfaces

by Paula Gould

Fed up with cleaning dusty windows, soiled shoes, and dirty paintwork? A series of products are now emerging on the market that claim to have self-cleaning surfaces, apparently removing the need for regular washing, scrubbing, and polishing with chemical agents. But consumers should refrain from throwing away all their cloths and detergents just yet. Questions regarding the longevity of such products, the optimal technology, and the most suitable applications have yet to be settled.

Two apparently contradictory principles lie behind the realization of so-called self-cleaning materials: an unrivaled love of water (superhydrophilicity), and an extreme repugnance for the very same liquid (superhydrophobicity)[1]. The fate of water landing on any surface is described by Young's equation, which relates surface tensions between the solid surface, liquid droplets, and surrounding air to the contact angle between the water/air interface and the solid (Fig. 1). Water droplets consequently assume a cap-like shape when sitting on a solid substrate. The smaller the contact angle, the flatter the droplets and the wetter the surface. By the same token, large contact angles mean reduced area at the liquid/solid interface, and the substrate is not wetted as easily.

Self-cleaning materials exploit what happens at the extreme ends of this situation, where the contact angle either tends to zero (superhydrophilic situation) or approaches 180° (superhydrophobic situation). Water coming into contact with a superhydrophilic surface spreads out and forms a thin film, while on the superhydrophobic surface, water forms into spherical bead-like drops, minimizing the solid/liquid contact area. In the first scenario, cleaning can occur when a thin sheet of water running off a surface washes away loose dust. The second scenario relies on the spherical droplets rolling off the surface and picking up particulate dirt in their path.

Two contrasting approaches, but the same result: a surface that exploits the dynamics of drop formation and wetting to maximize dirt removal when doused with water. If the water

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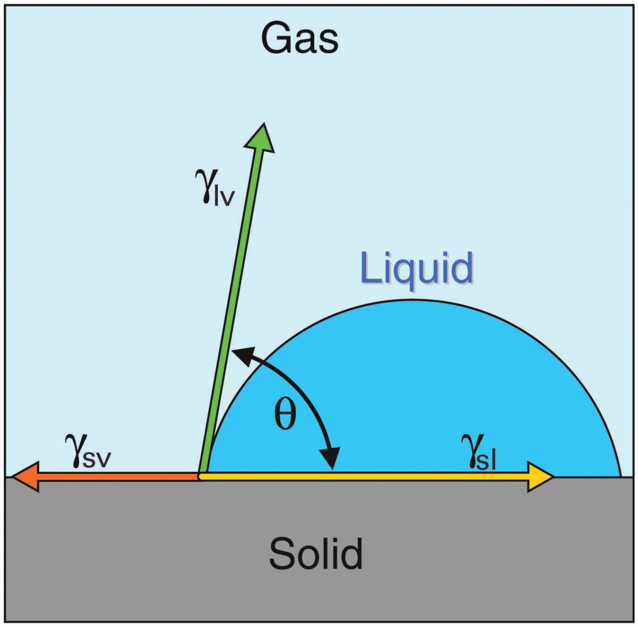

Fig. 1 Wetting of solid surfaces according to Young's equation: $\gamma_{sv} - \gamma_{sl} = \gamma_{lv}\cos\theta$*, where* γ *= surface tensions between the three phases. Schematic shows a water drop on a 'normal' surface. For the lotus effect,* $\theta > 90°$*. (Credit: BASF.)*

comes from rainfall, then no external intervention is needed to keep the surfaces free from dust and dirt, hence the term *self*-cleaning.

The concepts underpinning both methods of water-based, self-cleaning sound simple. However, creating a synthetic material capable of ridding itself of residual dust during a rainstorm requires more detailed knowledge about the surface itself. Rainwater may be repelled from a superhydrophobic surface, but what if the drops slide or stick? If light rain falling on a superhydrophilic surface evaporates instead of providing an all-over rinse, what happens to the dirt? And is water alone sufficient to shift the organic growths and oily grime that amass over time?

Proponents of the superdry, beading-and-rolling approach have a pair of botanists to thank for revealing the basic principles of superhydrophobic, self-cleaning surfaces. Wilhelm Barthlott and Christoph Neinhuis, both from the University of Bonn, noticed how certain leaves seem to protect themselves from external contamination. This was particularly true of the sacred lotus plant, a wetland species native to Asia and revered as a symbol of purity (Fig. 2).

Barthlott and Neinhuis characterized the structure of the lotus leaf and deduced the link between its surface appearance and self-cleaning functionality[2]. They dubbed the phenomenon the 'Lotus Effect' and with one eye on future business opportunities, trademarked the term. The expression has now become synonymous with superhydrophobic self-cleaning, though lotus leaves are by no means the only natural surface to exhibit this behavior. We could easily have been talking about the 'reed effect', the 'tulip effect' or the 'dragonfly effect' had Barthlott and Neinhuis' studies not led them to the lotus plant. Marketing executives should perhaps be thankful they are not being asked to whip up enthusiasm for materials displaying the 'cabbage effect'.

The botanists' chief observation was that the spotless leaves of the lotus plant are, in fact, rough. Each leaf surface is covered in an array of tiny bumps, 5-10 µm high and about 10-15 µm apart. This uneven surface is itself covered with waxy, hydrophobic crystals, measuring around 1 nm in diameter. This discovery was a great surprise at the time, Barthlott says. "We were first able to help scientists and engineers in the coatings industry by moving them away from the thought that smooth surfaces mean clean surfaces," he explains.

The two-tier roughness on the leaf's surface is particularly important to its self-cleaning properties, according to David Quéré, applied physicist at the Laboratoire de Physique de la Matière Condensée, Collège de France and scientific advisor to the French glass company, Saint-Gobain. Water droplets meeting a superhydrophobic material effectively perch on high points on the rough surface, minimizing their contact with the solid and forming spherical drops. "You trap air below your drop, so the drop sits on the patchwork of solid

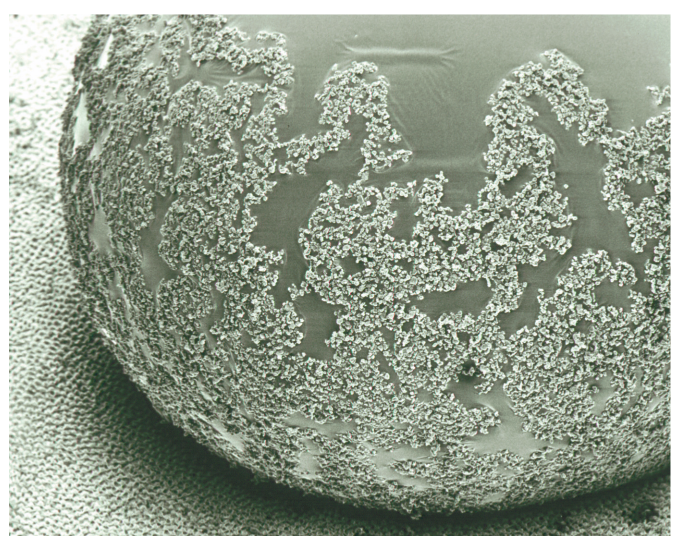

Fig. 2. The pristine leaves of the lotus plant have inspired studies into the superhydrophobic mechanism of self-cleaning. (Credit: BASF.)

and air," explains Quéré. "The image I like is that of a fakir carpet, where the drop is the fakir sitting on a bed of nails. Below the fakir you have nails, but you also have air."

Dual levels of texture on the lotus leaf increase the overall surface roughness, which correspondingly boosts its hydrophobicity. But the two-tier setup also reduces the likelihood of surface air spaces being invaded by water, for instance, from condensation, evaporation, or high-impact rain storms[3]. Drops sat atop the 'fakir carpet' roll away easily, Quéré says. Any water landing on a 'clogged' surface would be more inclined to smear out across the surface before evaporating, or simply stick where it landed. "If the drop is adhesive, it does not move, so it does not take any dust away. As the drop evaporates, it concentrates the dust close to the contact line, and so at the place where the drop was pinned, you have a concentration of dust, and the surface looks dirtier than before it rained," he says.

Efforts to produce a robust, anti-adhesive, superhydrophobic surface should consequently concentrate on engineering materials with these two scales of roughness, just as nature does, he says. "Many materials are naturally superhydrophobic, and if you look at them carefully, you see bumps of the order of 20 µm in size, and on each bump you see smaller bumps that are approximately 1 µm in size," he says.

Clear view

Quéré is reluctant to use the term 'self-cleaning' for superdry materials with anti-adhesive properties. These surfaces do not really clean themselves, he says, but simply benefit from the motion of unpinned drops. The true *self*-cleaning materials, in Quéré's view, are those that use coatings with combined photocatalytic and superhydrophilic behavior to break down dirt and give surfaces an all-over wash.

Coatings containing the semiconductor TiO_2 have been shown to fit the bill. UV light is absorbed by the TiO_2, which reacts with oxygen and moisture in the air to form activated oxygen. This helps oxidize and decompose organic debris and gases, and kill bacteria. Any water falling on the activated surface spreads out into a continuous film and washes away any remnants of loose dirt. "These properties allow continual cleaning and prevention of contamination of the surface when exposed to sun (or artificial light) or rain," explains Tim Kemmitt, member of the materials technology group at Industrial Research Limited, New Zealand.

Commercial products exploiting the dual cleaning and wetting behavior of TiO_2-based coatings are already available. Pilkington started the gradual roll-out of its self-cleaning glass two years ago. The photocatalytic, superhydrophilic Pilkington Activ™ is now offered in the US and in many European countries as a standard option for windows. Saint-Gobain has also now launched a self-cleaning glass with similar dual-action functionality (SGG Bioclean).

The transparent coating on Pilkington Activ is just 40 nm thick, and is applied to the glass by a process of chemical vapor deposition during the manufacturing process at temperatures of 600°C. This ensures that the self-cleaning functionality will last the lifetime of the glass, says Chris Gill, marketing communications manager for Pilkington.

Gill accepts that the self-cleaning tag is only applicable to the external window surface. Home-owners will still have to use a sponge and soapy water to keep the internal surfaces dirt-free. If windows are sheltered from the elements, or in periods of little or no rainfall, the panes can be cleaned with water from a spray jet or hosepipe. However, he rejects suggestions that the windows' hydrophilic behavior would be detrimental to their optical properties, and that consumers would object to viewing the outside world through a sheet of water. "It does look visually different, but what we've been told is that it actually improves vision through the window when it is raining," he says.

Researchers elsewhere are investigating the use of photocatalytic, superwetting surfaces inside the home. Surfaces coated with a hydrophilic substance, which causes water to spread out, will naturally dry out quickly too. This could prevent windows, mirrors, shower screens, or even lenses from fogging up when in contact with steam or condensation (Fig. 3). Additional applications already suggested include easy-clean household goods and road signs, anti-condensation air conditioners, and anti-fouling paints. Japanese company TOTO, for example, currently has 350 patents pending in this area.

Manufacturing self-cleaning, rapid-drying surfaces is relatively straightforward, says Kemmitt, whose group has patented much of its work in this field. The researchers are using modified sol-gel methods to apply the coating, rather than chemical vapor deposition. These techniques are generally cost-effective and easily adapted to the application being considered. "We can, for example, apply clear, hard coatings to glass, plastics, painted surfaces, metals, and

Fig. 3 Superhydrophilic coatings may be used to eliminate fogging from mirrors, lenses, and shower screens. (Courtesy of Tim Kemmitt.)

ceramics," he says. "We have developed alternative methods of coating to suit the specific application."

One of the main development issues is producing an active coating on substrates that cannot be heated, according to Kemmitt. Early prototypes required the films to be heated up to 650°C, though the active structure can now be produced in solution. "A second issue has been the abrasion resistance," he says. "In areas regularly subject to high wear, the coating can be scratched or damaged. Advances in our formulation have improved this, although the low temperature coatings still have limitations."

Aging process

Longevity is also going to be a significant issue for companies developing the superhydrophobic class of self-cleaning materials, according to Ralf Blossey, research director of the biological nanosystems group at the Interdisciplinary Research Institute in Lille, France. The superdry materials will, by definition, have microscopically rough surfaces. This essentially increases both the area to be cleaned and the complexity of dirt removal. Gradual accumulation of trapped debris would not only counteract the material's anti-adhesion properties, but could also make the surface harder to clean than before it was treated. "Whenever you have a greater surface area there are more possibilities for matter to get stuck, and if it gets into these corrugations then it is especially difficult to get out," Blossey says.

Axel Ebenau, project manager for BASF Future Business, appreciates the potential difficulties in producing a long-lasting, synthetic material with a superhydrophobic and anti-adhesive nature. BASF is one of several organizations currently working with the University of Bonn botanists to create materials capable of mimicking the 'Lotus Effect'. The company showcased its so-called Lotus Spray last year, a prototype, demonstration product containing a mixture of silica or alumina nanoparticles, hydrophobic polymers, and a propellant gas (Figs. 4 and 5)[4]. The spray has proven to be 20 times more water-repellent than a smooth, wax coating,

Fig 4. Wood treated with BASF's 'Lotus Spray' exhibits superhydrophobic behavior. Water landing on the wood forms spherical drops to minimize its surface contact area. (Credit: BASF.)

Fig. 5 Superhydrophobic coatings could also improve the waterproofing on textile goods, such as this umbrella. (Credit: BASF.)

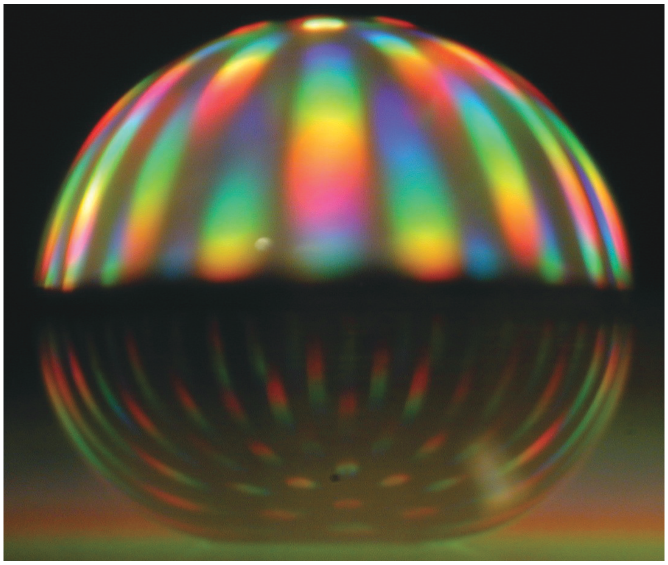

Fig. 6 Millimetric water drop on a hydrophobic, microtextured substrate. The microtexture enhances the chemical hydrophobicity, inducing superhydrophobic behavior. It also provides the colors which reflect inside the drop. This same effect explains the coloring on some butterfly wings. (Credit: Aurélie Lafuma and David Quéré.)

but still only 50% as hydrophobic as a lotus leaf. Surfaces treated with the aerosol product also lose their shine and the coating rubs off too easily.

BASF researchers are now using the same spray technology to develop a marketable, liquid formulation that can be applied to external building materials, such as stone, wood, or textiles. "We know from the chemists that hydrophobic surfaces are not so stable," Ebenau says. "At the moment we have some long-term tests running, and what we actually see is that surfaces in the outdoor tests, on which our product has been applied, are cleaner than the same surfaces that have not been treated."

But Blossey remains unconvinced of the suitability of superhydrophobic, self-cleaning technology for building applications. "There are surfaces where you can live with a bit of dirt, like roof tiles, for example," he says. He suggests that the technology would be better suited to single-use, disposable applications where degradation and aging are not an issue. For example, the controlled patterning of hydrophilic areas on superhydrophobic substrates using lithography could improve existing techniques for spotting and analyzing small volumes of liquid DNA. The same principle could be used in the expanding area of microfluidics, generating open structures on which liquids could be guided through channels by surface tension.

The optical properties of superhydrophobic coatings could also lead to applications in the microelectronics industry (Fig. 6). Researchers from the Kanagawa Academy of Science and Technology, Japan, have produced a self-assembling, water-repellent film that reflects different colors depending on the distance between air gaps in the microstructure. The colorful coating combines uniformly-spaced silica nanoparticles with a layer of fluoroalkylsilane. This same technique could be used to create self-cleaning photonic crystals, either for decoration or optical circuitry[5].

Self-assembly fabrication may help researchers get closer to the hierarchical microtexture seen on natural superdry surfaces. Yet there is still another important lesson to be learned from nature, says Blossey. Biological superhydrophobic surfaces might get damaged by the elements or predators, but the system copes with this by new growth and regeneration. One option under consideration is the addition of self-healing functionality, such as a built-in reservoir of hydrophobic polymer, for example. A synthetic self-cleaning material might then respond to surface abrasion by releasing additional polymeric coating where required.

"People who are working in applied research now want to make surfaces that are truly smart, biomimetic if you like, and this is the most interesting avenue in this field," Blossey says. "The superhydrophobic self-cleaning mechanism is only closer to nature when the surfaces have this element of self-renewal." MT

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