

Chapter 6

Dry in the Water: The Superhydrophobic Water Fern *Salvinia* – a Model for Biomimetic Surfaces

Zdenek Cerman, Boris F. Striffler, and Wilhelm Barthlott

6.1 Superhydrophobic Biological Surfaces

Over millions of years plant surfaces evolved optimized complex multifunctional interfaces. They fulfill different functions in terrestrial plants such as limitation of uncontrolled water loss, protection against various biotic and abiotic influences, and they play a role in the attachment of insects. A recent overview on plant surface functions is presented by Jeffree (in Riederer and Müller, 2006). One of the most remarkable functions is closely linked with plant epicuticular waxes. The outermost barrier is formed by a cuticle consisting of two major components: a polyester matrix with embedded and overlaying lipids. At the cuticle the secreted lipids form thin films or complex, three-dimensional structures with various geometries of wax crystals (Barthlott and Wollenweber, 1981; Barthlott et al., 1998; Holloway, 1971; Baker, 1982). The great variability in appearance is due to the chemistry of the epicuticular waxes. Nowadays, for some wax types the relationship between chemistry and morphology is well understood. Our present knowledge is summarised by Bargel et al. (2006) and Jeffree (2006).

Epicuticular wax crystals, sometimes combined with trichomes or cuticular folds, lead to an incredible phenomenon of plant surfaces: water forming spherical droplets, bouncing and rolling off the surface even with the slightest inclinations. This amazing water-repellency is caused by hydrophobic chemistry, together with a micro- and nanostructure of the plant's surfaces. Extremely water-repellent plants were described as early as the 19th century, but detailed examinations of this plant phenomenon were not published until the work of Ziegenspeck (1942). Further publications on the wettability of plant surfaces followed from Fogg, 1944, 1948, Linskens, 1950, 1952, Adam, 1963, Günther and Wortmann, 1966, Rentschler, 1971; Hall and Burke, 1974. The most significant and comprehensive papers until that time were published by Holloway (Holloway, 1969a, b, 1970, 1971).

Z. Cerman (✉)

Nees Institute for Biodiversity of Plants, Bonn University, Bonn, Germany
e-mail: nees@uni-bonn.de

The wettability of a surface is expressed by its contact angle. This is the angle between the solid surface and a tangent drawn between the drop at the interface of the solid/liquid/gas. Surfaces having a contact angle of less than 90° are regarded as wettable or hydrophilic, whereas those with contact angles higher than 90° are non-wettable or hydrophobic (De Gennes, 1985). Today, extremely water-repellent surfaces are defined through a contact angle higher than 140° and sliding angle (the inclination when the droplet starts moving) lower than 10° (Nun et al., 2002). Commonly, these surfaces are termed superhydrophobic.

Another interesting property is linked to extreme water-repellency: most of these plant surfaces are self-cleaning (Barthlott and Neinhuis, 1997). Normally, surfaces exposed to the weather get soiled over time by inorganic and organic contaminants such as dust, exhaust soot, spores or bacteria. Negative effects of dust-covered surfaces include increased leaf temperature through higher infrared absorption and reduced photosynthesis, which can be lowered to as little as 21% of the original production (Sharifi et al., 1997). Particles deposited on superhydrophobic surfaces are, by contrast, wiped off by rain, fog or even dew. Plants having such surfaces are thus also protected from pathogenic micro-organisms (Neinhuis et al., 1992, Schwab et al., 1995).

These self-cleaning properties are based on the reduced area of contact between (plant) surface and particles or micro-organisms. Dirt only rests on top of the micro- and nanostructure, resulting in significantly decreased adhesion. If water is poured over dirty superhydrophobic surfaces, capillary forces compel the weakly-attached dirt particles to adhere to water droplets instead of sticking to the surface. This self-cleaning property allows the removal of particles independent of their chemistry, i.e. whether hydrophilic or hydrophobic, and results in a smart protection against pathogens for plants (Barthlott and Neinhuis, 1997; Neinhuis and Barthlott, 1997).

Self-cleaning properties of plant surfaces originate from the combined effect of a certain surface topography and hydrophobicity, thereby allowing transfer of this phenomenon into biomimetic self-cleaning manufactured products. The market potential for these biomimetic products is thought to be enormous (Wulf et al., 2002). But this is no longer a dream for the future. The transfer of self-cleaning properties in technical applications has already taken place. Applications for such functional materials focus on dirt-collecting surfaces that are exposed to rain or can be artificially sprayed with water, e.g. the external surfaces of buildings or vehicles. The first product, a façade paint named Lotusan[®], has already been launched successfully on the market in 1999 (Born et al., 2000). Further products having self-cleaning properties based on micro- and nanostructure are indicated with the trademark "Lotus-Effect[®]".

Although self-cleaning properties can already be transferred from biological models to technical applications, the underlying principles of superhydrophobic surfaces are quite complex and another interesting application has not yet been considered: extreme water-repellent surfaces leading to drag reduction under water. Before discussing whether *Salvinia* (Fig. 6.1) is a suitable model for technical submerged surfaces, recent advances in the interpretation of physical and chemical basics of superhydrophobicity are summarized.

Fig. 6.1 *Salvinia* water ferns – a model for the mimicking grasshopper *Paulinia acuminata*. Both larvae (shown here) and adult grasshoppers live and feed on *Salvinia*. *Paulinia* not only imitates the coloration, but also the surface structure of the superhydrophobic microstructure



6.2 Physics and Chemistry of Superhydrophobic Surfaces

One of the first to describe a model of the effect of roughness on wetting was Wenzel (1936). Starting from Young’s equation, a basic physical law describing the relationship between water, solid states and gas (6.1), he modified this equation by introducing a surface roughness coefficient.

$$\cos \theta = \gamma_{sv} - \gamma_{ls} / \gamma_{lv} \tag{6.1}$$

θ is the Young contact angle; γ_{sv} , γ_{ls} , and γ_{lv} are surface tensions at the solid/vapor, liquid/solid and liquid/vapor interfaces respectively.

Normally water drops spread on a surface, leading to hemispherical drops. For spreading, the surface tension of water has to be overcome. The energy for this process is provided by the solid state and is called ‘free surface energy’. The wettability of a surface is expressed by the contact angle, i.e. the angle between the solid surface and a tangent drawn between the drop at the interface of the solid/liquid/gas. On smooth extreme hydrophobic surfaces (e.g. monomolecular CF_3) the maximum contact angle reaches $\sim 120^\circ$ (Nishino et al., 1999). Higher contact angles can only be achieved by surface roughness. In such cases water can follow this coarseness, in which case the so called Wenzel-regime is present (Fig. 6.2a). Due to the occurrence of the rough structure, an increase of the wetted surface area amplifies the hydrophobicity of the material. Wenzel introduced a roughness factor (r) defined as the ratio between the true surface area over the apparent one (6.2).

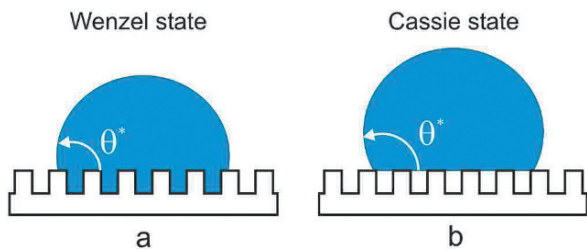


Fig. 6.2 Water droplet on a rough surface: (a) sunk into the structure (Wenzel state) (b) resting on top of the structure like a fakir on a bed of nails (Cassie state) θ^* – real measured contact angle

$$\cos \theta^* = r \cos \theta \quad (6.2)$$

θ is the Young contact angle on a smooth surface and θ^* the real measured contact angle.

In simple terms, this means that the roughness factor enhances the solid surface energy. A rough, hydrophilic material is more hydrophilic than the same material with a smooth surface. The same holds true for *hydrophobic* surfaces, where a rough surface has a distinctly higher contact angle than a smooth surface of the same material (Quéré, 2002a, b, 2005). Although this explanation for high contact angles seems self-evident, wetting on rough surfaces is far more complex.

The Wenzel model does not explain extremely high contact angles. Cassie and Baxter (1944) examined the relationship between chemical surface heterogeneity and wettability in their fundamental work on extreme water-repellency. They concluded that extreme water repellency is caused by air being enclosed between the surface structures of a rough surface. Thus a compound surface is formed which consists of a few solid portions and enclosed air. In this state (Fig. 6.2b), the liquid only contacts the solid at the top of the asperities. The perfect spherical shape of the droplets due to water surface tension (not considering gravity) is disturbed only by the fraction of the solid in contact with the droplet. The smaller the part of the solid in contact the more the contact angle trends towards 180° . Because the macroscopic contact angle is an average between the angles on the solid and on the air, such a ‘fakir’ drop is, according to Cassie and Baxter (1944):

$$\cos \theta^* = -1 + \phi_s(\cos \theta + 1) \quad (6.3)$$

θ is the Young contact angle on a smooth surface and θ^* the real measured contact angle. ϕ_s is the solid fraction in contact with the water.

Consider a surface with $\theta = 110^\circ$ and $\phi_s = 10\%$. We would measure a contact angle θ^* of about 160° . At such a surface below the drop, 90% of the corresponding area remains in contact only with air, whereby the interaction between drop and surface is extremely reduced.

Even though the contact angle predicts much about the wetting properties of a surface it is not sufficient on its own. Another important wetting effect has to be considered. The dynamics of water on water-repellent surfaces are again of interest to material scientists.

In case the droplet remains on the tips of the structure, water not only reaches very high contact angles between 140° and 174° , but also extremely low sliding angles (the inclination when the droplet starts to roll) lower than 10° are present.

For the first time Chen et al. (1999) reported that high contact angles do not automatically mean that drops move easily over the surface. They presented surfaces with contact angles of 169° and drops sticking even when the surface is held upside down. Since then, many authors reported the impact of wetting regimes on the dynamic behavior of drops on rough surfaces (Lafuma and Quéré, 2003). In summary, the dynamics of water depend on whether composite or homogenous wetting is present. If the drop wets the grooves (homogenous, the Wenzel-regime) high energy is needed to move the liquid. In the case of composite wetting – also

called the Cassie-regime – drops can move easily across the surface. Which regime occurs depends on stable equilibrium states influenced by surface geometry, how the drops are formed or external effects like pressure. To achieve advantageous properties like self-cleaning or drag-reduction the Cassie-regime must be present *and* also energetically favored.

Whether surfaces with stable Cassie-regime exist is one of the main points of debate in modern wetting physics.

Shibuichi et al. (1996) were one of the first to suppose that transition between heterogeneous and homogeneous wettings could be possible if the drop is forced to penetrate the asperities. Meanwhile, some authors suggested criteria that determine which wetting regime takes place (Lafuma and Quéré, 2003; Marmur, 2003; Alberti and DeSimone, 2005; Jopp et al., 2004; Werner et al., 2005). While Patankar (2003) proceeded with the assumption that a Wenzel-regime is always favored if the contact angle is lower than the corresponding contact angle of the Cassie-regime, Marmur (2004) and McHale et al. (2004) assumed determining factors for stabilizing the Cassie-regime. Marmur (2006) revived the factors for stable heterogeneous wetting in order to discuss the feasibility of underwater superhydrophobicity.

6.3 Superhydrophobicity and Fluid Frictional Drag

The use of superhydrophobic surfaces underwater seems to be, besides self-cleaning, another promising technical application. Since the pioneering work of McCormick and Bhattacharyya (1973) many researchers have studied air in terms of bubbles for skin friction reduction (Kodama, 1998; Kawashima et al., 1998; Kodama et al., 2001, 2003). In marine transport there is a strong demand for a reduction in fluid-frictional drag. It has been reported (Fukuda et al., 2001) that fluid-frictional drag accounts for as much as 60–70% of the total drag of a cargo ship and about 80% of that of a tanker. The first patents describing the use of air as a lubricant can be found in the early 1970s (Paffett, 1972). Although air microbubbles can increase skin friction reduction by up to 80% (Kodama et al., 2001) several problems remain. Primarily, the energy for injection of air below the ship hull reduces the net income of this technology. Also, several other problems like noise or vibration still remain unsolved. An elaborate overview on drag reduction technologies was provided by Truong (2001).

To increase the efficiency of the air bubble technique, Tokunaga et al. (1993) were the first to apply superhydrophobic surfaces to ships. The combination of super-water-repellent surfaces (SWR) and air injection (A) has been called the SWR & A technique (Fukuda et al., 2001). They showed a significant reduction of frictional drag on the SWR surface by 80% at a speed of 4 m/s and 55% at 8 m/s. Since then, several authors published articles dealing with superhydrophobic surfaces and drag-reduction. Kim and Kim showed that flow resistance in superhydrophobic microchannels could be reduced by 99% compared with a surface of the same material. Others achieved less drag reduction depending on parameters like the surface used, orientation in the flow, and the model and the flow speed (Balasubramanian

et al., 2004; Fukagata et al., 2006; Henoeh et al., 2006; Choi and Kim, 2006; Cottin-Bizonne et al., 2003). Independent of actual drag reduction, one major problem of superhydrophobic surfaces still remains. The use of these surfaces under water is limited. Although this application seems very interesting, durable water repellency under such conditions is difficult. Diffusion of gas, hydrostatic pressure and water flow past the surface have to be considered. Transition from the Cassie- to Wenzel-regime has to be avoided otherwise the rough surface increases drag reduction dramatically. In the experimental study of Balasubramanian et al. (2004) the efficiency of the drag-reducing surface drops after 15 min. due to the loss of extreme water-repellency.

Stable superhydrophobic surfaces for underwater applications, as required by Marmur (2006), need another quality other than the previously used Lotus mimicking surfaces. Over the last decade nearly all research was focused on surfaces with hierarchical structures ranging from hundreds of nanometres up to a few micrometers. Totally unappreciated were the extremely low wettable surfaces of aquatic spiders, insects, mammals and plants (Bush and Hu, 2006, Crisp, 1963, Kaul, 1976, Köhler, 1991, Suter et al., 2004) that were optimised for floating or diving as models for durable water-repellency. Their surfaces appear to be more complexly constructed than those of modern surfaces. It seems as though the physical-chemical basis of water repellency on those surfaces is quite sophisticated. Suitable as one possible model for technical surfaces, we selected the water fern of the genus *Salvinia* for our experiments.

6.4 The Water Ferns *Salvinia* – Morphology and Diversity of Superhydrophobic Floaters

In contrast to superhydrophobic plants with their micro- and nanostructured surfaces, typical surfaces of floating aquatic plants are smooth. Epicuticular waxes of these floating plants are only two-dimensional wax films without any further three-dimensional sculpture (Neinhuis and Barthlott, 1997, Kaul, 1976). There are only two exceptions of floating plants with superhydrophobic and hairy surfaces: the Aroid water lettuce *Pistia* and the floating fern *Salvinia*. The water fern genus *Azolla* is excluded here as their surface is not hairy, only covered with papillae formed from single cells (Neinhuis and Barthlott, 1997).

Both, *Pistia* and *Salvinia* are better known for their negative ecological effects as invasive or pest plants (see Room et al., 1981) than for their hairy, superhydrophobic surface structure. In *Pistia* the surface is covered with large filiform multicellular trichomes. By contrast, in *Salvinia* different types of multicellular trichomes evolved: from single hairs in *S. cucullata* (similar to those in *Pistia*), to two hairs in *S. oblongifolia*, up to four hairs in the *S. auriculata*-complex.

Hairy surface structures are exceptional in plants, but a common way to stay dry in the animal kingdom. Water repellent hairs evolved several times with several purposes in animals. These range from respiration – as in water bugs, water beetles and

the water spider – to insulation as in diving mammals (e.g. water shrews) to buoyancy control in most surface-living arthropods (water striders or fishing spiders). Mostly, hairy water-repellent surfaces serve a combination of various functions. Comparing plant and animal hairy superhydrophobic surfaces indicated that animal hairs are only filamentous, without any further branching of the hair. Though the fine sculpture of animal hairs ranges from smooth to longitudinal furrows (e.g. water shrew *Neomys fodiens*) to brush like hairs (e.g. fishing spiders *Dolomedes* and *Ancylometes*), the hairs – or trichomes – of water ferns like *Salvinia* are the most variable.

6.4.1 Morphology of the *Salvinia* Surface

The water repellency of *Salvinia* leaves, and thus the morphology of leaf surfaces with their unique trichomes ('hairs'), attracted the attention of botanists as early as the 19th century (summarized by Pringsheim, 1863).

In preceding studies, *Salvinia* trichomes were mostly used as morphological characters in taxonomic analyses (e.g. Herzog, 1935, Kopp, 1936, Sota, 1962a). No attempts were made to further investigate water repellent aspects of *Salvinia* (Fig. 6.3), though most authors mentioned this fact (e.g. Zawidzki, 1911, Kaul, 1976). Noteworthy, is that *Salvinia* trichomes were also thought to be glandular, secreting trichomes, comparable to those of the carnivorous sundew *Drosera* (Andrews and Ellis, 1913).

Although *Salvinia* surfaces and their trichomes had already been examined by the end of the 19th century, it was not until scanning electron microscopy (SEM)



Fig. 6.3 Water droplet on *Salvinia oblongifolia* leaf. The silvery shine is caused by air trapped between trichomes, resulting in a total reflection of the drop's lower surface

Table 6.1 Water repelling properties of *Salvinia*

| Species | Contact angle | Trichome type |
|------------------------------|---------------|------------------|
| <i>Salvinia cucullata</i> | 161.9° | Single |
| <i>Salvinia oblongifolia</i> | 162.3° | Double |
| <i>Salvinia minima</i> | 160.5° | Quadruple |
| <i>Salvinia biloba</i> | 159.4° | Quadruple joined |
| <i>Salvinia molesta</i> | 160.4° | Quadruple joined |

became common that the three dimensional epicuticular wax structure of its surface was studied. Initial SEM examinations of *Salvinia* (Barthlott et al., 1994) revealed these plants to have extremely thin, rodlet-shaped waxes perpendicular to the surface. These rodlets are found on the leaf surface as well as on the trichomes.

Epicuticular waxes do not vary considerably within the genus *Salvinia* although leaf shape and size, as well as trichomes, differ between species. Four different types of trichomes can be recognized within *Salvinia*:

- Single trichome (*S. cucullata*, *S. hastata*)
- Double trichome (*S. oblongifolia*)
- Quadruple trichome (*S. natans*, *S. minima*)
- Quadruple joined trichome (*S. auriculata*, *S. biloba*, *S. herzogii*, *S. molesta*)

Trichome lengths range from 200 μm (*S. oblongifolia*) to 800 μm (*S. minima*) and are found to be mostly congruent with the leaf size of the different species, which varies from 5 mm (*S. minima*) to 51 mm (*S. oblongifolia*) (Kopp, 1936). Although differently shaped, all trichomes together with their epicuticular waxes contribute to the water repellency of *Salvinia* (see Table 6.1). The question remains, why are *Salvinia* hairy and water repellent, while other aquatic floating plants have smooth and wettable surfaces?

6.4.2 The Advantages of Being Hairy

A possible function of *Salvinia* surface structures was already outlined by Kaul (1976): “A function of these trichomes, or egg-beater hairs, is clearly the prevention of wetting. Water falling on the leaf coalesces into beads on the hairs and flows off. Thus the leaf is dorsally almost unwettable. The buoyancy, water-repellency, and stability conferred by the internal architecture and the hairs, as well as the large size and rapid growth, have been factors favoring this plant to become a serious weed in the tropics”.

The combination of trichomes and waxes make *Salvinia* surfaces superhydrophobic and have a positive effect on their buoyancy through maintaining an air film underwater. This is unusual as most aquatic floating plants have wettable leaves. To prevent leaves from sinking, water lilies and other floating plants have air filled parenchyma cells, the so called aerenchyma (Kaul, 1976).

Surprisingly, *Salvinia* also have aerenchyma, which are single-layered (*S. natans*, *S. cucullata*, *S. hastata*, *S. auriculata*, *S. biloba*, *S. herzogii*, *S. molesta*), double layered (*S. oblongifolia*, *S. sprucei*, *S. martynii*) or even triple layered (*S. nymphellula*) (Herzog, 1934, Kopp, 1936, Sota, 1962b). This may indicate that positive buoyancy is not the main reason for *Salvinia* to have a water-repellent hairy surface, as other plant leaves float by means of aerenchyma alone.

Another factor to consider is that all floating aquatic plants are hyperstomatous, i.e. stomata are only on the adaxial (upper) side of the leaf (Kaul, 1976). Water-covered stomata suffer several constraints; the most obvious one being limited gas exchange. CO₂ diffusion into water is decreased 10 000 times compared to air (Nobel, 2005). Therefore continuous gas exchange might be an explanation for hairy, water-repellent *Salvinia* leaves. Even when water covers the surface, i.e. water resting as droplets on top of the trichomes, the stomata of *Salvinia* might still be able to continue gas exchange underneath the water droplets.

These factors, together with a huge growth rate, i.e. doubling its biomass within 2.3 days under optimal conditions (Jacono and Pitman, 2001), makes *Salvinia* an ecological danger for standing water bodies in most tropical and subtropical countries. The dense cover of so called *Salvinia*-mats prevents light entering the water and creates severe ecological problems. The hairy leaf surface is also one reason for the difficulties encountered in eradicating *Salvinia*-mats with herbicides (Kam-Wing and Furtado, 1977, Nelson et al., 1991). Contrasting the ecological hazards from *Salvinia*, its heavy metal fixation (Yanagimachi et al., 2005) and oil absorption (Ribeiro et al., 2003, Khan et al., 2004) are positive applications of these plants.

Recent experiments on different *Salvinia* species and their ability to retain air films underwater showed that the species with the largest leaves, *S. oblongifolia*, was the most successful in staying dry under water. An air film on a submerged *S. oblongifolia* leaf could be observed for 17 days, whereas the other examined species (*S. molesta*, *S. biloba*, *S. minima*, *S. cucullata*) only remained dry for 4–5 days. As these experiments were carried out with isolated (but living) plant leaves, it could not be excluded that the longevity of the air film was caused by physiological processes like photosynthesis. To eliminate a possible regeneration of the air film by the plant, exact replicas of the plant's surfaces were generated to overcome these problems.

6.5 Biomimetic Superhydrophobic Surfaces and Their Applications

Initial approaches towards generating replicas of superhydrophobic surfaces were carried out back in the 1950s (Crisp and Thorpe, 1950, Juniper and Bradley, 1958). The aim of these projects was not to transfer the superhydrophobic properties to a technical surface, but to produce replicas of these surfaces for examination by scanning electron microscopy.

Since the 1990s, replicas have been used to examine water-repellent properties of plant surfaces (Fürstner, 2002). Direct examinations of plants are always influenced

Table 6.2 Water-repelling properties of *Salvinia* replicas (n=10)

| Species | Contact angle | Trichome type | Molding quality (trichome) |
|--------------------------------|---------------|------------------|----------------------------|
| Replica <i>S. cucullata</i> | 146° | Single | moderate |
| Replica <i>S. oblongifolia</i> | 145° | Double | complete |
| Replica <i>S. minima</i> | 140° | Quadruple | incomplete |
| Replica <i>S. biloba</i> | 141° | Quadruple joined | incomplete |
| Replica <i>S. molesta</i> | 146° | Quadruple joined | incomplete |

by the vitality of the leaves or general physiological processes between the leaf and its environment. To eliminate these effects, exact copies of leaf surfaces have generated increasing interest (Lee and Kwon, 2006, Lee et al., 2006, Osawa et al., 2006, Vogelaar et al., 2006).

In our experiments, a silicon-based dental casting compound (President Light-body, Coltène, Switzerland) was used to generate exact acrylic copies of *Salvinia* surfaces by filling the flexible and rubber-like silicon negatives of the plants' surfaces with conventional acrylic varnish (Acryllack, seidenmatt schwarz, Karl Knauber, Germany) As the acrylic varnish itself is not hydrophobic (contact angle 68°; n=10), a fluorocarbon hydrophobing agent was used (Antispread F 2/50 FK 60, Dr. Tillwisch GmbH, Germany). The fluorocarbon forms a reticulate layer on the surface when molecules polymerize and exposes the terminal hydrophobic F₃C-groups, thus making the surface water repellent. The application of the hydrophobing agent Antispread on plain unstructured acrylic varnish increases the contact angle from 68° to 120° (n=10).

Superhydrophobic properties could thus also be observed on hydrophobic acrylic replicas (see Table 6.2, Fig. 6.5). The replica quality varied within the tested species due to different levels of complexity. *Salvinia* species with quadruple trichomes were, as expected, mostly incomplete, whereas the double trichomes of *S. oblongifolia* were almost perfectly replicated (Fig. 6.4). Interestingly the simple, filiform trichomes of *S. cucullata* were hard to mold, due to their elasticity and their tendency to bend over, if covered with the casting compound.

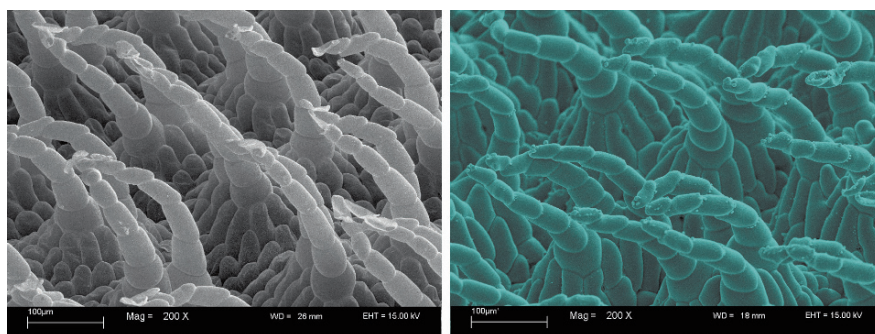
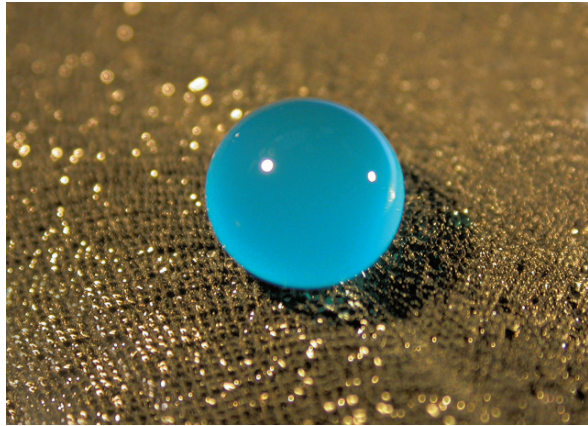


Fig. 6.4 Comparison of *Salvinia oblongifolia* trichomes (SEM; magnification 200×) *left*: plant surface; *right*: artificial microreplica

Fig. 6.5 Water droplets (stained with food dye) form a nearly perfect sphere on the acrylic replica of *Salvinia oblongifolia*



Even though in most *Salvinia* molds, except those of *S. oblongifolia*, the trichomes were only replicated incompletely, all replica surfaces were extremely water-repellent (Table 6.2).

Comparing the contact angles of original (Table 6.1) and replica, one has to note that replicas still have a distinctly lower contact angle, even though an extremely well working hydrophobing agent (Antispread) was used. It has been shown that Antispread increases the contact angle of a perfectly plain silicon surface up to 117° (Fürstner, 2002), which is close to the highest contact angle possible on a plain surface ($\sim 120^\circ$, Nishino et al., 1999).

The previously performed experiment on the durability of air films of *Salvinia* leaves was repeated with complete replicas. The artificial *S. oblongifolia* leaves successfully retained an air film for two days. There may be different factors involved – and to be tested – in the distinctive discrepancy in retaining an air film between plant (17 days) and replica (2 days): the persistence of the hydrophobing agent on the technical surface, the distinctly lower hydrophobicity (lower contact angle) and the different modes of elasticity between acrylic varnish and plant trichome. But the first and foremost reason may lie in the gas exchange by the living plant.

Based on the transfer from biological models to technical, air-retaining surfaces for underwater applications within this project a patent has been submitted outlining different fields of application, like textiles, varnishes and coatings (Cerman et al., 2006).

Future applications of superhydrophobic surfaces for underwater applications lie in the field of pipeline construction and ship building. Covering the inner wall of tubes with an underwater superhydrophobic surface, will reduce the energy needed to pump a (hydrophilic) liquid. If underwater superhydrophobic surfaces are successfully applied to large tanker ships, huge amounts of fuel could be saved due to drag reduction. It is obvious that even hairy superhydrophobic surfaces alone cannot solve the problem. The solution will lie in a combination of the microbubbles technology and optimized air retaining superhydrophobic surfaces, thus reducing the

amount of energy spent in running a compressor for microbubbles and the increasing the durability of the air films.

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