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Wettability of natural superhydrophobic surfaces

Hayden K. Webb, Russell J. Crawford, Elena P. Ivanova *

Faculty of Life and Social Sciences, Swinburne University of Technology, Hawthorn, Australia

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ABSTRACT

Since the description of the 'Lotus Effect' by Barthlott and Neinhuis in 1997, the existence of superhydrophobic surfaces in the natural world has become common knowledge. Superhydrophobicity is associated with a number of possible evolutionary benefits that may be bestowed upon an organism, ranging from the ease of dewetting of their surfaces and therefore prevention of encumbrance by water droplets, self-cleaning and removal of particulates and potential pathogens, and even to antimicrobial activity. The superhydrophobic properties of natural surfaces have been attributed to the presence of hierarchical microscale (>1 μm) and nanoscale (typically below 200 nm) structures on the surface, and as a result, the generation of topographical hierarchy is usually considered of high importance in the fabrication of synthetic superhydrophobic surfaces. When one surveys the breadth of data available on naturally existing superhydrophobic surfaces, however, it can be observed that topographical hierarchy is not present on all naturally superhydrophobic surfaces; in fact, the only universal feature of these surfaces is the presence of a sophisticated nanoscale structure. Additionally, several natural surfaces, e.g. those present on rose petals and gecko feet, display high water contact angles and high adhesion of droplets, due to the pinning effect. These surfaces are not truly superhydrophobic, and lack significant degrees of nanoscale roughness. Here, we discuss the phenomena of superhydrophobicity and pseudo-superhydrophobicity in nature, and present an argument that while hierarchical surface roughness may aid in the stability of the superhydrophobic effect, it is nanoscale surface architecture alone that is the true determinant of superhydrophobicity.

Contents

1. Introduction

The wetting behaviour of natural superhydrophobic surfaces has been studied for well over half a century [1–4]. Many organisms have now been identified to possess superhydrophobic structures, most notably a large number of plants and insects [5–15]. The most famous of these, and perhaps the archetype for natural superhydrophobic surfaces, is the lotus leaf [16]. Natural surfaces such as this have inspired the fabrication of countless synthetic analogues in an attempt to reproduce the extremely low wettability and other associated desirable properties of these substrata [17–21]. Given their significance as the templates on which new superhydrophobic materials are based, it is the intention of this review to discuss the mechanisms of superhydrophobicity with respect to natural surfaces, and identify the factors that make them extremely effective at repelling water.

* Corresponding author. Tel.: +61 3 9214 5137; fax: +61 3 9214 5921.
E-mail address: eivanova@swin.edu.au (E.P. Ivanova).

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1.1. Evolutionary benefits associated with low wettability

From an evolutionary perspective, there are several benefits associated with the ability to repel water. First and foremost, the ability to easily shed droplets prevents an organism from becoming encumbered by water [13,22]. This is highly relevant to many insects, especially those that live in or near aquatic environments. Adhesion of water droplets increases the load an insect must bear, and therefore increases the energy that needs to be expended for locomotion. The associated consequences are obvious, ranging from the inability to evade predators to the inability for the insect to successfully forage.

The second major benefit is the 'self-cleaning' effect that is bestowed through the condition of superhydrophobicity. The low adhesion of water to a superhydrophobic surface enables the droplet to roll/slide across the surface with ease, and in the process sweep away contaminating particles through adsorption or absorption [10,23]. The archetype lotus leaf is the prime example of this effect; it has long been renowned for its ability to stay clean under a range of environmental conditions [16,24]. This means that in addition to repelling water, superhydrophobicity allows an organism to repel foreign particles, such as dirt, dust and fungal spores.

2. Contributing factors that determine hydrophobicity

The hydrophobicity of a surface can be measured as a function of the water contact angle [25–27]. It is a continuous scale that ranges from a contact angle of 0° for a surface that is able to be completely wet by water, to 180° for a surface that is completely non-wetting in nature. Therefore, the classification of surfaces as being superhydrophobic, hydrophobic, hydrophilic or superhydrophilic is somewhat arbitrary. Nevertheless, for the sake of an intuitive understanding of these definitions, it is useful to define the range of water contact angles that apply for each category. It is generally accepted that the water contact angle on a superhydrophilic surface is between 0° and 10°, a hydrophilic surface between 10° and 90°, a hydrophobic surface between 90° and 150°, and for superhydrophobic surfaces, a contact angle in excess of 150° is observed [28–32]. It has been suggested that 65° may be a more appropriate boundary to distinguish hydrophobicity from hydrophilicity [32], however 90° is the more commonly adopted contact angle for this definition. In addition, it is generally accepted that to be categorised as a superhydrophobic surface, a surface should also display low degrees of contact angle hysteresis together with a low sliding angle [33,34].

Two main wetting regimes have been accepted throughout the literature, i.e. the Wenzel and Cassie–Baxter wetting regimes [2,3]. Briefly, in the Wenzel regime, a water droplet is said to penetrate and wet the spaces between the features on a rough surface. In this case, the cosine of the observed contact angle, θ, is expressed as a function of the Wenzel roughness factor, r, and the theoretical contact angle of a water droplet on an ideal smooth surface of the same component material, θ_{smooth}:

$$\cos\theta = r\cos\theta_{\text{smooth}}.$$

In the Cassie–Baxter regime, the inability of water to fully penetrate between the surface features leads to the entrapment of air pockets, which in turn increases the observed water contact angle. In this case, the cosine of the observed angle is described as a function of the area fraction of the solid/liquid interface on the contact line, f, and θ_{smooth}:

$$\cos\theta = f(\cos\theta_{\text{smooth}} + 1) - 1.$$

The Wenzel and Cassie–Baxter wetting regimes have both been extensively utilised and reported throughout the literature, and it is generally assumed that any water droplet on a rough surface is in either the Wenzel or Cassie–Baxter state, or an intermediate between the two, sometimes referred to as a 'Cassie-impregnating' state [35,36].

The chemical composition of a surface is also well known to be the second contributing factor in determining the wettability of a surface [2,3,37,38]. Its effects are substantial when the wettability of a smooth surface is being considered, however with increasing surface roughness, the physical structure plays an increasingly important role in the determination of the observed contact angle [1,2]. When considering surface wetting in the Cassie–Baxter state, it is at least theoretically possible to achieve a water contact angle of 150° on a material that, if smooth, would otherwise be wet completely, provided that the solid/liquid interface fraction is limited to approximately 0.07 (Fig. 1). While this is likely to be impossible to achieve in practice, it serves to demonstrate the important contribution of surface structure to the superhydrophobicity of a surface. It is notable that in the case of the feet of water striders in contact with water, the solid/liquid interface fraction has been reported to be as low as 0.03 [39]. For these reasons, the surface structure and topography of natural superhydrophobic surfaces will be the primary focus of this review.

3. Superhydrophobic structures found in nature

3.1. Plants

Plants are by far the best-characterized of all the organisms that have been identified to possess superhydrophobic surfaces. The works of Neinhuis, Barthlott, Bhushan and Koch have provided a great insight, together with a systematic analysis, into the various surface structures amongst plants from diverse habitats [5,7,16,24,40–44]. Generally speaking, the structure of the outer surface of plants is determined by a combination of two factors: the morphology of the epidermal cells in question, and the layer of cuticular waxes and lipids usually present on the external extremity of the surface [5,30]. Both the epidermal cells and cuticular waxes can exhibit a variety of morphologies, the combination of which can result in a diverse range of surface architectures.

In 1998, Barthlott et al. developed a classification system for the description of plant cuticular wax structures [5]. According to this system, cuticle wax morphologies can be grouped into two main categories, each containing several sub-groupings. The first category is the layers and films, which generally consist of relatively flat, homogeneous coatings on the surfaces of plants (Fig. 2a–d). These structures can be further sub-classified as films, smooth layers, fissured layers and crusts, primarily according to the thickness of the wax layer and its tendency to form cracks and fissures on drying. The second category of wax structures, however, is far more relevant to superhydrophobic phenomena, as all known superhydrophobic plant structures belong to this group. They are the wax crystals, and many different crystal morphologies have been described in the literature [41–43,45–47]. The wax crystals can be further divided into plates/platelets, and rodlets/tubules. Platelets are flat and thin structures that are attached to the underlying substrate via one edge (Fig. 2e). They may be rounded with entire margins that can be either irregular or membranous in nature. Plates, as opposed to platelets, are often polygonal and usually have distinct edges. Rodlets, on the other hand are relatively cylindrical or slightly conical in shape (Fig. 2g). They can have a variety of cross-sections, e.g. circular or polygonal in shape, and sometimes possess transverse ridges or form coils. Tubules are similar to rodlets in terms of their size and aspect ratios, however as the name suggests, they resemble hollow cylinders (Fig. 2f). Threads are another wax crystal structure similar to rodlets, differing primarily in that they are much longer, with higher aspect ratios (Fig. 2h).

The vast majority of plants with superhydrophobic surfaces exhibit hierarchical surface features, consisting of microscale roughness (i.e. features greater than 1 μm in diameter), as a result of epidermal cell morphology, supplemented with nanoscale roughness (features less than 1 μm, typically 200 nm or less) resulting from the presence of wax crystals. The best-known example of a superhydrophobic plant surface, the lotus leaf, possesses microscale (~10 μm) papillae covered