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A lichen protected by a super-hydrophobic and breathable structure

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Summary

A species of lichen, Lecanora conizaeoides, is shown to be super-hydrophobic. It uses a combination of hydrophobic compounds and multi-layered roughness to shed water effectively. This is combined with gas channels to produce a biological analogue of a waterproof, breathable garment. The particular lichen grows mostly during wet seasons and is unusually resistant to acid rain [Hauck, M., 2003. The Bryologist **106** (2), 257–269; Honegger, R., 1998. Lichenologist **30** (3), 193–212]. The waterproof, breathable surface allows this lichen to photosynthesise when other species are covered with a layer of water. In addition, rainwater runs off the surface of the organism, reducing its intake of water from above and probably contributing to its resistance to acid rain.

Key Words: Acid rain, breathable, fungus, lichen, super-hydrophobic

Introduction

Lichens are symbiotic organisms consisting of a fungus and an alga. They can live on hard surfaces without penetrating them, extracting most of their water and nutrients from the atmospheric environment. Most lichens are particularly susceptible to airborne pollution, their open structure and tendency to dry and re-hydrate in response to drought mean that alga and fungus are exposed to large quantities of unbuffered rainwater. Additionally, algae are intrinsically sensitive to pollution. Lichens growing on basic surfaces are more resistant as some of their water is buffered by the surface (Hauck, 2003).

Super-hydrophobicity has been observed on natural and synthetic surfaces (Barthlott and Neinhuis, 1997; Shibuichi *et. al.*, 1996), it occurs when a surface is both hydrophobic and very rough. The roughness increases the surface area of the hydrophobic material, increasing the interfacial energy required to wet the same geometric area. This increase in interfacial energy causes an increase in the angle between a drop of water and the surface. If the roughness is slight, liquid can follow the contours of the surface but if it is very high, water tends to bridge the tops of peaks of the roughness. Both cases can lead to increases in contact angle for small droplets of liquid deposited on the surface. When liquid bridges the peaks of a very rough surface it tends to follow the Cassie-Baxter model (Quéré, 2002); this relates the contact angle to the relative proportions of contacted solid and liquid bridges. A diagram showing this type of non-wetting is shown in Fig. 1. If the surface causing the Cassie-Baxter super-hydrophobicity is made up of pillars, gas exchange to the outside air will be possible through the channels formed underneath a drop of water. Cassie-Baxter super-hydrophobicity also tends to cause drops of water to roll off more readily than ones on a flat surface; unlike super-hydrophobic surfaces with increased interfacial contact, which cause drops to stick (Quéré *et. al*., 2003). This is an obvious advantage and the plant surfaces that show super-hydrophobicity that have been analysed are all of this type (Neinhuis and Barthlott, 1997).

Gore-Tex® membranes are micro-porous and allow water vapour to pass through but act as a barrier to liquid water. The micro-pores are hydrophobic, so entry of liquid water is prevented by capillary forces. The outside layer of a breathable garment, on top of the micro-porous membrane, is made super-hydrophobic to prevent the formation of a film of water and blockage of gas transport. Even when drops of water are present on the surface of the garment they only contact the tops of its rough surface, so no pores are blocked entirely (Fig. 1).

Materials and Methods

Lichen were collected from sites close to Nottingham, U.K.. Samples were taken from a site close to a road and near farmland to compare the effect of pollution (none was observed). Scanning electron micrographs were made on samples that were flash frozen in liquid nitrogen and then freeze-dried. They were sputter coated with gold and viewed in a Jeol JSM 840A scanning electron microscope at an acceleration voltage of 10 kV. Contact angle measurements were carried out using a Krüss DSA10 MKII. Multiple measurements were taken using 6 μL drops of deionised water on different parts of the samples.

Results and Discussion

Investigation of samples of *Leconora. conizaeoides* reveals that it is super-hydrophobic (Fig. 2A inset), with a water contact angle of around 160°. Electron micrographs of the lichen (Fig. 2A) show that it is rough, with structures of different sizes layered on one-another (unlike *Flavoparmelia caperata*, which is not super-hydrophobic (Fig. 2B)). This type of structure tends to cause water bridging (Cassie-Baxter) super-hydrophobicity (Feng *et al*., 2002; Herminghaus, 2000; Shirtcliffe *et al.*, 2004).

Gas transport to and from the algal cells in lichens takes place through a network of open channels. These have been shown to be hydrophobic on their inner surfaces (Honegger, 1998), which will prevent them from flooding when the outer surface of the lichen is exposed to water. When the outer surface of the lichen is super-hydrophobic these channels will behave like those in Gore-Tex® and similar membranes, allowing gas exchange even during rainfall. This will allow these lichens to photosynthesise when others cannot but will reduce the total amount of water available to them by causing water to roll off their surface.

A related but different mechanism prevents the entry of water into the gas exchange pores of land plants including angiosperms (Schönherr and Bukovac, 1972) and mosses (Schönherr and Ziegler, 1975). Protrusions in the stomata create bottlenecks that halt further ingress of water by acting as a local energy minimum. Water enters down to these protrusions but to move further would increase air/water interfacial area and therefore cost surface energy. In this case gas exchange is severely reduced as water blocks the pores, unlike on super-hydrophobic lichen and other leaves where there is always a path for gas to enter the plant. Unlike many plants crustose lichens have no faces that are sheltered from rainfall over which gas exchange can occur if their top face becomes blocked.

Promoting water runoff from the top surface of the lichen will also reduce direct exposure to rainwater; most of the water absorbed by *L. conizaeoides* thalli will therefore be through their lower surface and hence buffered and filtered by the substrate. This may contribute to their resistance to acid rain.

Higher plants use the super-hydrophobic effect to maintain clean and dry leaves. Drops of water falling onto a super-hydrophobic surface roll off, carrying dust particles with them. This factor may also protect *L. conizaeoides* from dust and may also contribute to its resistance to acid rain.

In lichens the algal partner is embedded in the fungal partner (Honegger, 1998), the fungal partner is therefore most likely to be responsible for the super-hydrophobicity observed in *L. conizaeoides* as the algal cells are embedded in a fungal matrix and only fungal cells are exposed to the environment. Some other fungi are super-hydrophobic; *Penicillium expansum* exhibits a similar contact angle to *L. conizaeoides* as shown in Fig. 3. The structure and hydrophobicity of these fungi are thought to arise from their mechanism for escaping the surface tension of water and grow vertical filaments (Kershaw and Talbot, 1998). The fungi synthesise surface active proteins which end up on the surface of the aerial parts of the fungus with their hydrophobic parts outward. The filamentous structure, combined with the hydrophobic coating, produces a material similar to the Gore-Tex® membrane in Fig. 1 and the fungal hyphae of the *L. conizaeoides* in Fig. 2a. Super-hydrophobicity in fungi has not been studied, but may have evolved as a mechanism for remaining at the surface of water. As with super-hydrophobic foams (Shirtcliffe *et. al.*, 2003), these super-hydrophobic fungi have no closed pores but will float on water, aided by the buoyancy of air trapped in their rough surfaces. The spores of *P. expansum* are situated on the ends of the branched structures visible in Fig. 3. Drops of water rolling across the fungus surface collect them and are converted into "liquid marbles" (Aussillous *et. al.* 2001), see Fig. 3 lower insert. Water drops coated with particles like this can roll across solid surfaces, carrying the fungal spores with them.

Conclusions

The lichen *Lecanora conizoides* shows bridging super-hydrophobicity producing very high water contact angles on its surface. Like all lichen it is full of hydrophobic pores for gas exchange. The combination is very similar to that of breathable garments, where a super-hydrophobic surface protects a system of small pores from becoming blocked by a film of water. We postulate that the lichen uses this super-hydrophobic breathable surface to allow gas exchange during and soon after rainfall. The super-hydrophobic outer surface may also act to protect the lichen from pollution by reducing direct exposure to rainwater and promoting dust removal.

Acknowledgements

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Figures

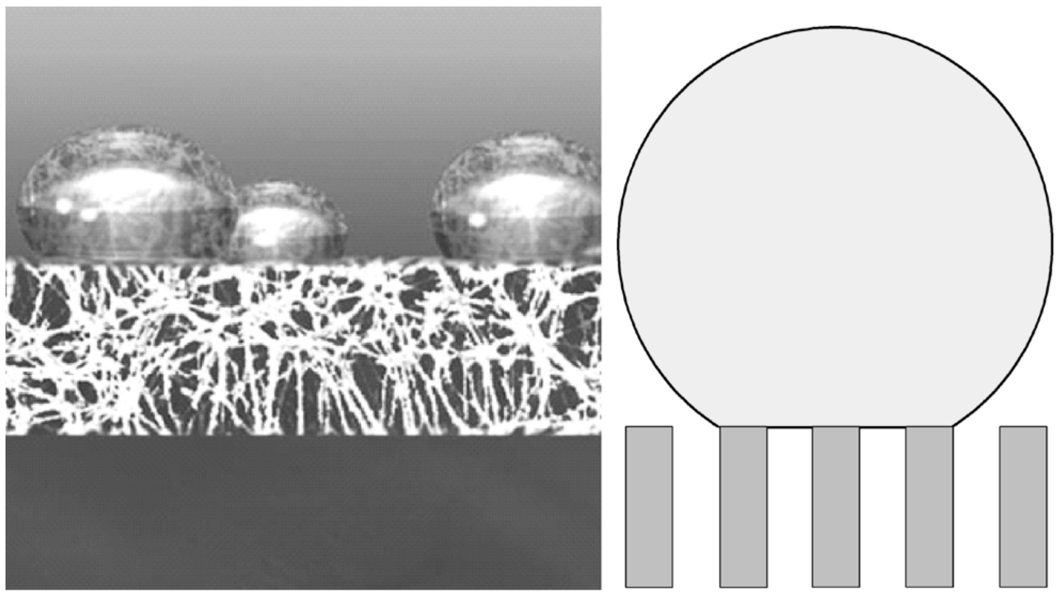

Figure 1. Left Gore-Tex® breathable membrane reproduced with permission from W L Gore & Associates, pore size 0.2-2 µm (left) and right a diagram of bridging super-hydrophobicity.

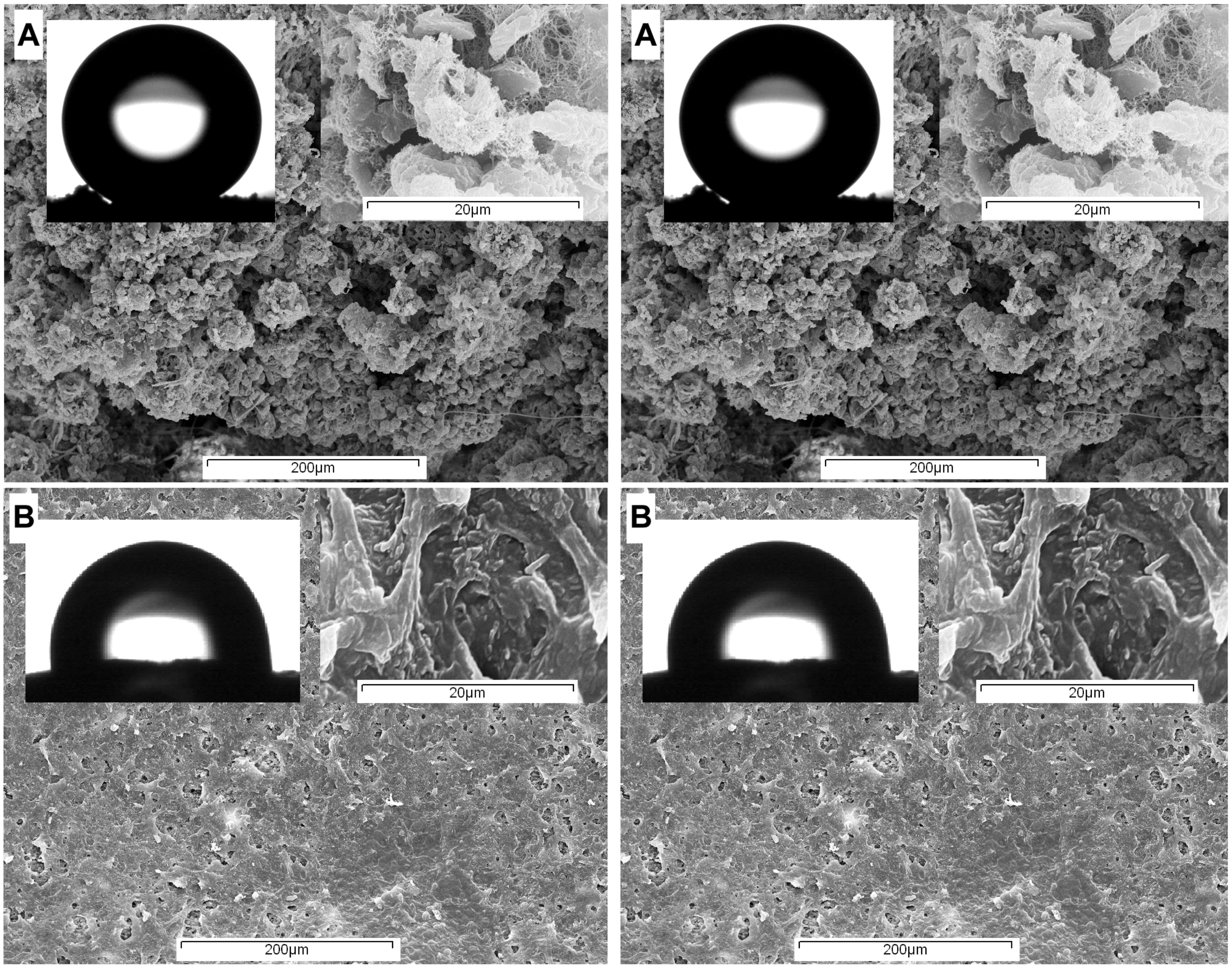

Figure 2. (A) main and inset right electron micrographs of *Lecanora conizaeoides* showing high roughness with photograph of water drop inset left, contact angle 155±4°. (B) Main and inset right electron micrographs of a lichen, *Flavoparmelia caperata (Parmelia* spp*)*, and inset left a photograph of a drop of water on its surface, contact angle 89±4°. SEM scale bars 200 µm (outer pictures) and 20 µm (insets).

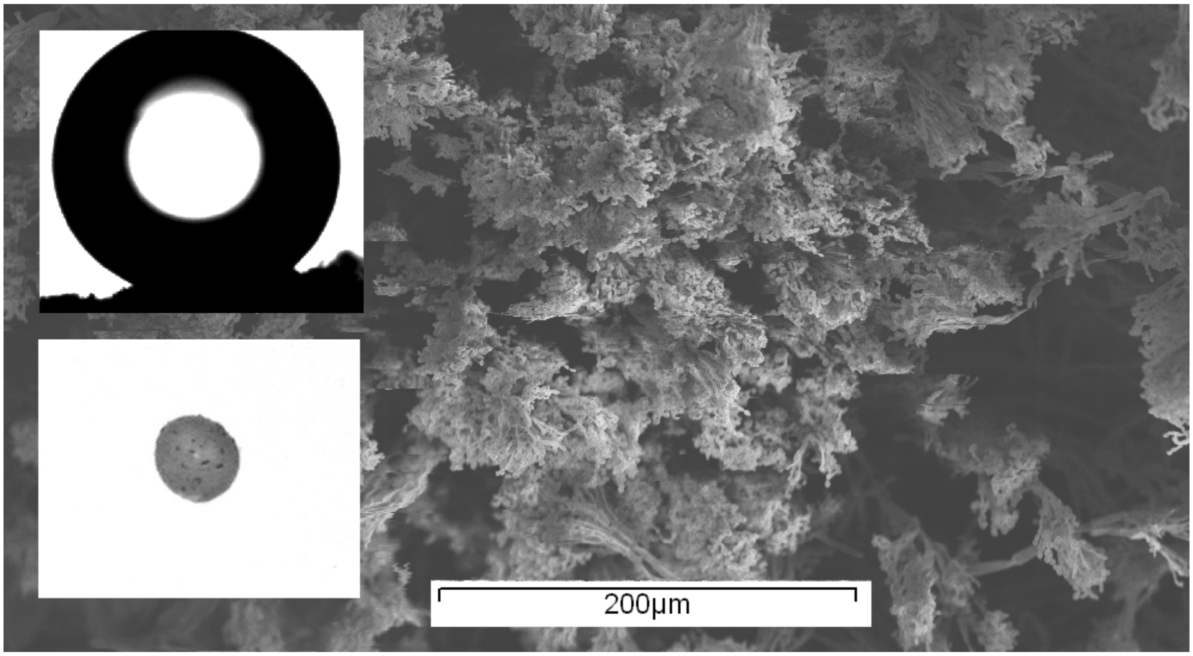

Figure 3. Electron micrograph of the mould *Penicillium expansum* and inset water drop showing high contact angle and drop coated with spores after being rolled over the colony. SEM scale bar 200 µm, drop size approx. 4 mm diameter.