The Superhydrophobicity of Polymer Surfaces: Recent Developments

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Abstract

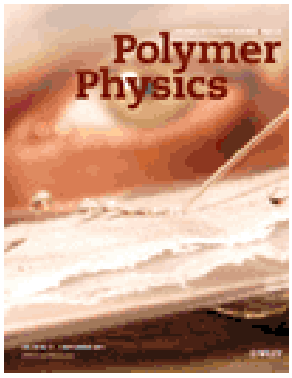
Superhydrophobicity is the extreme water repellence of highly textured surfaces. The field of superhydrophobicity research has reached a stage where huge numbers of candidate treatments have been proposed and jumps have been made in theoretically describing them. There now seems to be a move to more practical concerns and to considering the demands of individual applications instead of more general cases. With these developments polymeric surfaces, with their huge variety of properties have come to the fore and are fast becoming the method of choice for designing, developing and producing superhydrophobic surfaces.

Keywords

anti-reflection; fog collection; ice resistance; Lotus effect®; micromolding; plastron; polymers; self-cleaning; superhydrophobicity; superoloephobicity.

Front Cover Story

SUPERHYDROPHOBIC SURFACES



Superhydrophobicity is where roughness, or surface topography, modifies the surface interaction with a liquid to enhance the apparent hydrophobicity relative to a smooth surface. Droplets on such surfaces can sometimes move extremely easily, leaving the surface dry as shown in the cover image where a fibrous polymer repels a stream of water. As research into superhydrophobic surfaces reaches a degree of maturity where approaches are numerous and theoretical understanding is well-formed, focus shifts towards more practical concerns for individual applications and the role of polymers has come to the fore. On page 1203 of this issue, Neil Shirtcliffe, Glen McHale and Michael Newton review progress in this field and consider how polymers allow research to move out of the laboratory and add value to superhydrophobicity by providing suitable properties.

TOC Entry

Superhydrophobicity is undergoing a transition from a freshly exciting research area to application. Research has moved from generating surfaces and understanding, to planning complex structures and structure-liquid interactions. It is often no longer enough to just have a superhydrophobic or superoleophobic surface - it must now also fulfil other practical performance requirements. This review considers how polymers allow research to move out of the laboratory and add value to superhydrophobicity by providing those extra properties.

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1. Introduction

Superhydrophobicity is where the roughness, or surface topography, modifies the surface interaction with a liquid to enhance the apparent hydrophobicity over that of a smooth surface of the same material. In general, small water droplets on flat surfaces form spherical shapes truncated by the surface. The angle at the edge of a water drop on a polymer will be up to 120° for polytetrafluoroethylene (PTFE) but not much greater for a flat surface. Roughened surfaces can achieve angles that are difficult to measure because they approach 180°. Some such drops can also move over the surface extremely easily because the stickiness is determined by the difference between the advancing and receding angles, which can be very high or very low on roughened surfaces. In a recent review we suggested reserving the title of superhydrophobic for those surfaces with low contact angle hysteresis.[1]

Increasing the roughness of a wettable surface increases its wettability, increasing the roughness of a non-wettable surface increases its repellence. As a water repellent surface is roughened the contact angle between water drops and the surface increases, but they adhere more strongly, because the roughness increases the interaction area under the drop. Eventually the roughness becomes so great that bridging over the roughness, leaving gas pockets under the liquid, is lower in energy than wetting the whole surface. If this is taken to extremes the interfacial contact area between solid and liquid becomes very low. In this case drops of liquid will roll over the surface if it is slightly tilted, carrying particulate contamination away and leaving no residue.

These possibilities have been covered in great detail before[2,3]. The theories date back to early studies of textiles, showing that the shape and degree of roughness combined with the contact angles on a flat surface can be used to predict how different surfaces will behave.[4,5] Although the beginnings of the theory were decades ago, refinements are still being made.

The sizes for superhydrophobicity vary from tens of micrometers down[6]. The smallest dimension where superhydrophobcity functions is unknown, some studies show that structures on a unitary nanometre scale may behave differently[7] but few surfaces can be prepared with nanometre scale roughness that are flat on a micrometer and millimetre scale. Many effective artificial and natural superhydrophobic surfaces have roughness on both length scales.

Superhydrophobic surfaces have been produced in a bewildering variety of ways, reviewed in many publications recently[3,8,9,10,11,12,13,14,15,16,17,18,19,20]. The roughness shape and size can vary widely from ordered pillars to chaotic roughness, from particles to fibers, and from materials such as metals to inorganic and organic compounds. Owing to the number of reviews recently published, this one will be confined to polymeric surfaces and some of the unique properties offered by them.

The high roughness used for superhydrophobicity has made them difficult to integrate into daily life. Roughened surfaces are fragile so become damaged and surfaces that are designed to repel one liquid are often easily wet by another. Natural superhydrophobic surfaces have an advantage over artificial ones in that they can regenerate continuously. Artificial surfaces are more difficult to regenerate and therefore applied research has concentrated on areas where damage is low, lifetime is short or reapplication is cost effective. Inorganic materials can be made harder and stiffer than polymers, but even the stiffest materials are easily damaged when very small and most inorganic surfaces must be coated to render them hydrophobic. Because of this, polymer materials with their versatility, surface properties and ease of forming have proved to be good substrates for producing superhydrophobic surfaces despite usually being softer than inorganic materials.

Although polymers have lower hardness than some inorganic compounds their toughness, particularly when combined with inorganic fillers, can be very high. Tough superhydrophobic surfaces are a must because of the high aspect ratio features making them fragile and any particles

that become embedded in the surface must be removed without damaging the structures.

Recent publications show that elastomer surfaces[21] and hybrid materials[22] can stand up to large amounts of wear and still be superhydrophobic. The behaviour depends on a combination of relatively rounded features and either hardness or flexibility so that the surface returns to its original state after the deforming forces are removed.

In a previous review we showed the variety of methods that could be used to produce superhydrophobic surfaces. Here we consider methods used for polymers since that time, the effect of the shape of the topography and a few effects that are particularly suited to polymers that allow superhydrophobicity to progress from being an interesting phenomenon to being a versatile tool.

2. Generation of Polymeric Superhydrophobic Surfaces

2.1 Paint Technology

The most commercially successful route to superhydrophobicity so far has been to modify existing paint technology. Paints typically contain particles, solvent and a polymeric binder. If the particle loading is high and binder content is low as the solvent evaporates particles or aggregates distort the binder to generate a roughened surface, such as that shown in Figure 1a. This is the most common method used in commercial products. Methods like this can generate very effective superhydrophobic surfaces with mostly random texture. With careful choice of binders and filler the surface morphology can be varied and some mixtures can be produced cheaply enough that nature's continual repairs can be approximated by occasional reapplication of paint.

An interesting extension of this is to use carbon nano-fibers and PTFE to generate a conductive and superhydrophobic coating that can shield low and high frequency electric fields. The binder in this case was a mixture of polyvinylidenefluoride (PVDF) and polymehtylmethacrylate (PMMA), a useful compromise to impart adhesion, hydrophobicity and resistance.[23]

Another common method is to take an existing rough surface, such as that of concrete and treating it with a thin hydrophobising agent. These are typically surface adherent molecules such as silanes, but fluorocarbon block copolymers are also common with the other block attaching to the substrate. As these are only slightly linked with polymer technology they are not discussed in depth here.

2.2 Layer-by-layer Deposition

This is a method where positive and negative polyions are coated onto surfaces in sequence. Roughness can develop if one of the components contains solid particles (often inorganic) or a third component (Figure 1b).[24,25] As long as the last layer is hydrophobic, or a hydrophobic capping layer is used, superhydrophobicity will appear after enough cycles. This is a simple method for research, being useable wherever the starting materials can be obtained. It is suitable for covering complex objects, but becomes difficult when large areas or large numbers of parts are desired and the types of topography possible are limited. It is very effective, however, for adding a small scale roughness and hydrophobicity to a surface that is already rough.

2.3 Electrodeposition/Electropolymerisation

Rough surfaces for superhydrophobicity have been electrodeposited in metals[26], but polymers are more interesting as they can be deposited with hydrophobicity already present, allowing single stage deposition as long as the polymer deposited becomes hydrophobic(Figure 1c).[27,28,29] Such surfaces can coat complex objects and can be used to post-treat conductive areas, leaving the rest of a substrate clear. There has been recent attention on the formation of oil repellent surfaces using this route.[30] There is quite a bit of choice in polymer that can be used as the electrodeposition backbone. Roughness can be developed by diffusion limited growth, crystallisation or patterned by arranging conducting areas[31] depending on the system.

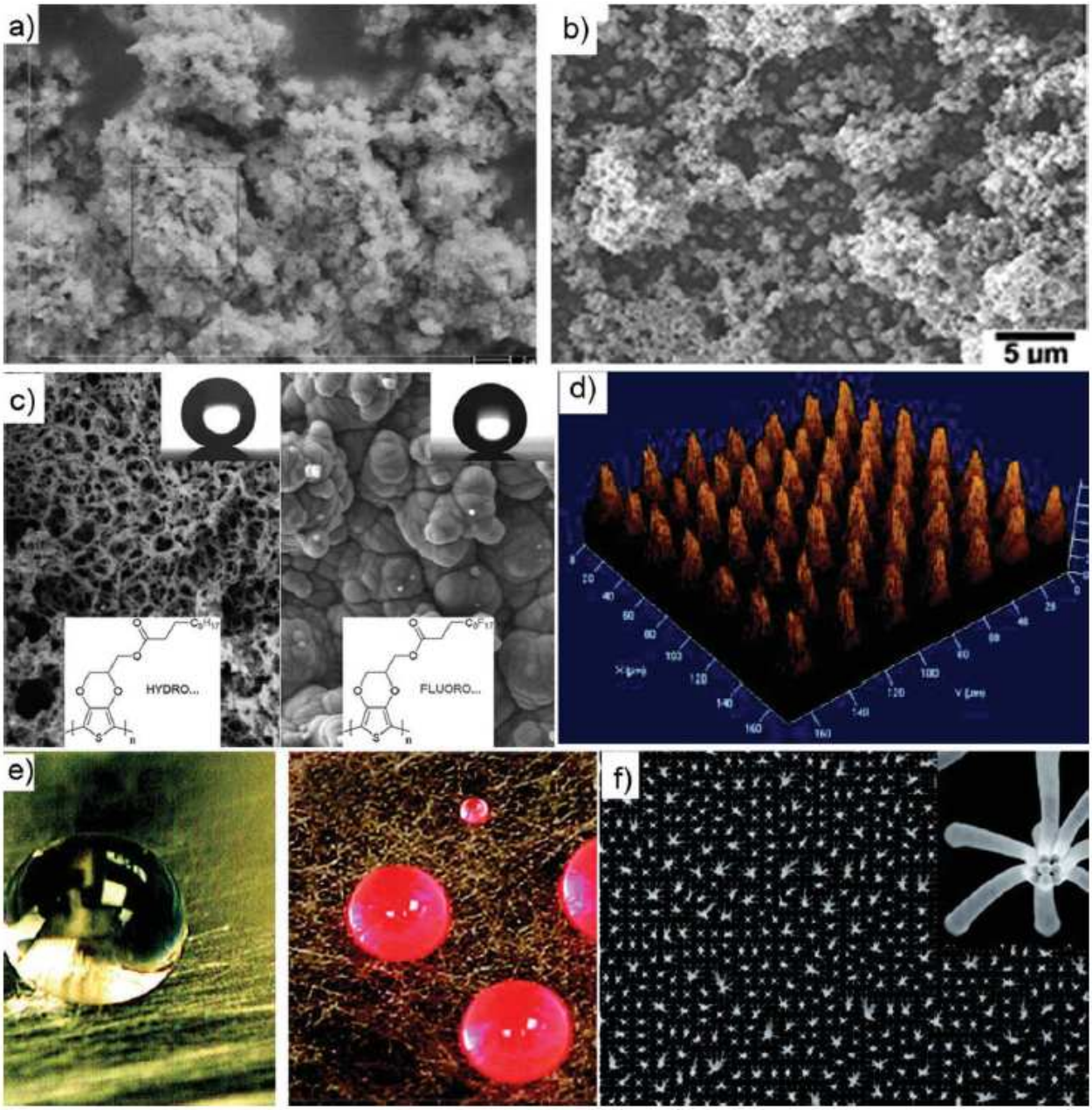

Figure 1 Superhydrophobic polymers with the topography produced in various manners, a) paint (From J. Yang et al., Appl. Surf. Sci. **255**, 3507-3512, 2009, ©Elsevier, reproduced by permission), b) layer-by-layer deposit (From X. Liu et al., J. Mater. Chem., 2009, **19**, 497-504, The Royal Society of Chemistry, reproduced by permission), c) electrodeposited polymer (From T. Darmanin et al., Langmuir **26**, 17596-17602, 2010, ©American Chemical Society, reproduced by permission), d) Laser sculpted (From C. Wohl et al., Langmuir **26**, 11469–11478, 2010. ©American Chemical Society, reproduced by permission), e) Electrospun polymer with water and oil drops (From D. Han and A. Steckl Langmuir **25**, 9454-9462, 2009, ©American Chemical Society, reproduced by permission) and f) nanocast polymer (From S. Kang et al., ACSNano **4**, 6323-6331, 2010, ©American Chemical Society, reproduced by permission).

2.4 Plasma and Laser Treatment

When polymers are treated with a plasma or laser, structures that are superhydrophobic can be generated directly. Plasma treatment leads to polymer shrinkage and the generation of random roughness or the roughness can be directed by applying a resistant mask. Often it is necessary to hydrophobise the surface of the polymer again after treatment, but some methods, such as the treatment of silicone in CF_4,[32] can produce roughness and maintain hydrophobicity in a single step. Laser treatment is less random and allows the formation of designed structures(Figure 1d), but is

less suited for large surfaces.[33] Laser treatment is often more effective at producing superhydrophobic surfaces than anticipated due to re-deposition of vaporised material in clusters on the treated surfaces. Plasma deposition is also highly effective and leads to a hard, dense polymer which is relatively resistant to damage.[34,35] The structures formed in a depositing plasma usually arise from diffusion limited growth.

2.5 Electrospinning

Electrospun fibers are particularly effective at repelling water due to their very large surface area and high curvature. Asmatulu et al.[36] for example used polystyrene and PVC fibers and showed that the repellence depended upon the diameter of the fibers. Earlier studies demonstrated the effectiveness of allowing the fibers to partially retract or adding particles, forming structures they called "strings of beads". These methods break the contact line of an adherent liquid into smaller sections. The smallest fibers produced by electrospinning are a few tens of nanometres in diameter and are therefore especially suited for superhydrophobicity.

As discussed above, if oil is to be repelled or even it if is to be prevented from being drawn into the structures of a superhydrophobic surface it is usually necessary to use a fluoropolymer. This has particular problems for electrospinning as fluoropolymers do not hold charge and therefore do not spin well. One way around this is not to spin at all, but to add other materials and rely solely on electrospray to produce a blobby surface. This has been achieved in various ways[37] with great success, but the surface is not fibrous and so some of the potential benefits are lost.

It is possible to form mats of fluoropolymers, by spinning a blend of polymers as a mixture[38], through co-axial needles[39] or attaching the fluorocarbon to another polymer[40,41]. It is also possible to use functionalised solvents to carry charge.[42] All of these routes allow the formation of perfluorinated fibers on one step, although any other fibers can be treated in a second step coating a finished mat[43]. Such fiber structures are then highly hydrophobic and also oleophobic.(Figure 1e) The materials are very effective medically[44], possibly due to their high surface area and pore volume, possibly also due to their superhydrophobic nature.

2.6 Other Fiber Surfaces

Other methods for producing fibrous coatings include conventional spinning, which can produce fibers down to a micrometer in size. These have traditionally been used to produce superhydrophobicity, although weaving usually generates relatively adhesive surfaces because liquid drops can form long contact lines. As debated by McCarthy et al[45] and McHale among others[46] it is important to remember that the structures in the immediate vicinity of the contact line determine its behaviour, not the average across the entire surface or under the droplet. If a contact line can align or pin with features or groups of features, this will alter the liquid shedding and wet adhesion behavior.

Carbon fibers and nano-tubes have been used for superhydrophobic surfaces for some time, but usually these have been grown on a surface at temperatures incompatible with polymers. They can be used without modification, depending upon the location of catalyst and fiber structure, or can be coated with fluorocarbons.[47,48]

More recently carbon fibers have been applied to polymers and allowed to sink into the surface. This has proved very effective and is very simple[49]. An interesting variation on this has been to coat cotton fibers with carbon nano-fibers with a polymer linkage[50]. This has shown good properties against washing and similar surfaces have resisted hot water[51], factors often causing problems for superhydrophobic textiles. This extreme resistance is probably due to the multiple length scale overhanging fiber structure for reasons described later.

A simple and relatively low cost method has been described more recently where short fibers are accelerated into a polymer in a softened state.[52] The fibers align hydrodynamically in flight so that they are mostly perpendicular to the surface and are trapped when the polymer hardens. The density of the fibers can be altered and relatively large surface areas can be treated.

2.7 Casting and Molding

Polymers lend themselves particularly to molding, although to replicate superhydrophobic surfaces micro- or nano- casting is required and mould fabrication can be a problem.

Polydimethylsiloxane (PDMS) is often used to copy small patterns due to its flow characteristics and ease of mould removal. The technique is known as nano-imprint lithography (NIL). It is still a challenge to copy natural superhydrophobic surfaces with features of 5 nm or less, although application of high electric fields has been found to improve copy fidelity in both the negative and the positive copy.[53] Other possibilities include increased pressure and the application of ultrasound.[54]

Other polymers have also been cast against harder, more heat resistant substrates and have shown some success. Some studies have used nanoporous aluminium oxide as templates and have been able to generate aligned fiber forests, these tend to form into bunches and behave as dual size structures, and are particularly effective superhydrophobic surfaces(Figure 1f).[55] Usually the fibers are brought together during the drying of the solvent content. They are initially held by capillary forces and then by solid-solid interactions as the liquid dries, which can lead to interesting arrangements and rearrangements[56] Typical fibers produced have a diameter of 50-200 nm and a high aspect ratio.

Other types of imprint lithography have been developed to reach small scales and are suitable for the generation of superhydrophobic surfaces. These include capillary lithography, where the polymer is deposited in a layer on the substrate, a mould is applied and the features in the mould filled by capillary action[57] and electrostatic structure formation[58]. These techniques usually require the formation of large areas of patterned mould, but can form complex multilevel structures in a single step using polymers. This is of major interest in microfluidics, where the generation of superhydrophobic structures inside channels allows gating through electrowetting and reduction of pumping pressure through interfacial slip.[59,60,61]

Phase separation, crystal growth, coating other surfaces and other methods have also been used to generate superhydrophobic polymers, these possibilities have been covered in the other reviews cited above.

3. Value Added Superhydrophobicity using Polymers

Simple superhydrophobicity is not robust enough or effective enough to warrant its use in more than niche areas. There are, however, far more potential applications for surfaces that are capable of a little more than just repelling water[62], some example areas are described here.

3.1 Waterproof, Breathable Surfaces

Breathable waterproof jackets have been produced for some time[63]. An ideal breathable waterproof surface has a superhydrophobic top layer to prevent the pores becoming blocked by a film of water. A natural analogy is the surface of some lichen, which probably use the effect to maintain access to air while it is raining[64]. As the main technical use is for clothing, polymers have been the material of choice, despite problems with washing and maintaining a water repellent, rough surface.

3.2 Antireflective Superhydrophobic Surfaces

One of the possible ways for antireflective coatings to function it by providing a gradient of

effective optical density for light to enter a material instead of a single sudden jump. This can be achieved by depositing different materials, but rough surfaces smaller than the wavelength of the light and typically conical in structure allow the effective density of the material to increase smoothly from air to bulk so also have the potential to function as antireflective layers and if hydrophobic will be superhydrophobic as well. This mimics the eyes of moths, that have to have large relative size and low reflection to avoid attracting predators.

This dual function was recognised some time ago and, despite a mismatch between the ideal structures for each function a dual function coating of this type is highly desirable, particularly for solar cells. This is because solar cells are often placed in inaccessible locations and, therefore, would ideally be self cleaning and maintenance free to enhance their long term efficiency and viability. Other light gathering devices, such as large lenses also have the same problems of reflection, and dust and waterborne contamination that can be solved by an antireflective, superhydrophobic coating.

Initially coatings suggested for this purpose were predominantly inorganic with a hydrophobic surface[65], but recently some organic suggestions have been put forward, partly due to current research into polymeric solar cells. These include layer by layer materials[66] and PDMS microstructures[67]. Polymeric coatings can be made flexible and cheap and, because of the relatively low refractive index of many polymers it is easier to get antireflective properties with them than with inorganic coatings.

3.3 Ice Resistance

Many surfaces are affected by ice deposition, in addition to the wings of aircraft, bridges, ships and power cables are affected, costing considerable sums. Although superhydrophobic surfaces cannot prevent the eventual formation of ice, a reduction on the ice adhesion strength leads to significant advantages, as the size and weight of equilibrium build-up and pieces breaking off can be reduced, thus improving safety and reducing maintenance.

Simple treatments, such as thin coatings of PTFE on roughened surfaces[68] have shown reduced adhesion but few studies have investigated longer term stability. The same team looked at three surfaces and showed that they degraded over icing cycles and became worse than smooth surfaces. They postulated that asperities become chiselled away by icing cycles, eventually resulting in Wenzel wetting and enhanced adhesion[69]. This may be because condensing frost forms in a wetting mode inside the roughness of the surface, circumventing its protective value[70] but more advanced topographies have not always been investigated. Where structure has been investigated, polymeric complex topographies have come out on top.[71] Even surfaces that do not reduce adhesion of ice can depress the nucleation point significantly by increasing the free energy of nucleation.[72,73]

Research has so far concentrated on treatments that can be easily applied to large technical surfaces and on PTFE, which has shown the lowest ice adhesion on flat surfaces, due to its low polarisability. The high polarity of water molecules means that induced dipoles are a major part of attachment forces on non polar surfaces. Future research may concentrate on the details of topography.

Fibrous superhydrophobic surfaces with their increased robustness and resistance to condensation induced full wetting would seem to be the ideal substrates for resisting ice adhesion, assuming they can be made robust enough not to be damaged.

3.4 Oil Super-absorbance

Porous hydrophobic materials have superhydrophobic surfaces, but they also have large internal volumes that can be accessed by non-polar molecules. This makes them useful for absorbing non-

polar liquids, particularly from water. Additionally the high surface for interaction also functions as an emulsion breaker. These effects were initially shown on coated surfaces or porous materials[74,75,76,77] with fibrous mats showing water or oil sorbtive properties depending upon surface chemistry[78] but more recently the use of microporous conjugated polymers has been shown to allow the absorption of large volumes of non-polar liquid in macro and micro-pores of a low mass sponge.[79,80] Another approach has been to use polyelectrolytes with large ions and hydrocarbon side chains to allow the polarity of the solvent that will cause maximum swelling to be varied over a wide range.[81, 82]

3.5 Complex Geometries and Superoleophobicity

The shape of the roughness is of great importance under certain circumstances. On smooth, vertical-walled pillars a surface can only support a liquid against which it has a contact angle of greater than 90°, but liquids with a lower contact angle than this will penetrate into the gaps between the pillars. The addition of even a small overhang allows liquid to balance on the tops of the pillars even when it has a lower contact angle with the surface (Figure 2)[83,84]. This is particularly important when hydrocarbons are to be supported as the highest achievable contact angle is not always very high. Recent research shows that polyhedral oligomeric sesquisiloxanes (POSS) when tagged with fluorocarbon chains are extremely low in surface energy. They reproduce surfaces with very high contact angles and low hysteresis, but even they must be used with re-entrant surfaces to generate superoleophobicity[84]. They are used as a surface coating agent, but can also be added to a polymer and self segregate to the surface, allowing hydrophilic polymers to be converted to hydrophobic polymer surfaces without extra processing steps.[85] This method also adds a roughness on a nanometre scale to the surface, due to the aggregation of the POSS molecules, which could be considered to be molecular particles.

Re-entrant features are challenging to generate in many materials, with even a relatively simple method involving deep reactive ion etching[86]. Overhanging geometries are relatively simple to produce with polymers, with various casting and lithographic techniques described later in this review. Additionally, non-woven mats, such as those formed by electrospinning, form naturally overhanging structures and are superoleophobic if made with fluorocarbons.

3.6 Gecko Feet, Passive Attachment, and Superhydrophobicity

Wall running lizards and many other small climbing creatures have adhesive pads on their feet that are covered with flexible hair-like setae. The structures are remarkably similar to those that appear in superhydrophobic surfaces and indeed gecko feet turn out to be superhydrophobic(Figure 3)[87]. This is useful to the animal because water between the setae and surface can allow slip to occur and reduce adhesion. Some animals, such as snails and some insects use liquids for adhesion, but these are non-Newtonian and high viscosity (unlike water).

Gecko setae work by maintaining intimate contact with both flat and rough surfaces of all types, increasing the van der Waals-London interaction. The setae have flat ends that align with the surface, forming a much larger area of contact than is available between normal surfaces and their flexibility allows them to conform to the surface without storing much elastic energy, that would push the animal away from the surface. The interaction loses its strength if dust becomes attached to the surfaces so the lizard must be able to clean them in some manner and they are found to be superhydrophobic, preventing water from entering the gap between them and a surface and possibly also allowing cleaning.

When producing artificial analogues both functions of the surface are facilitated by using polymers, producing structures surfaces with high hydrophobicity and local softness to conform with the target surface. Various studies have shown that surfaces can be both temporary adhesives and super water repellent and various methods for producing soft polymer spatulae including microcasting

followed by dip coating[88] and irradiation of PMMA (polymethylmethacrylate, Perspex) through a mask in a novel photolithographic step, also copied onto a softer polymer[89]. The plate on a stick surfaces shown here are strikingly similar to those shown in Figure 2 that allow superoleophobicity meaning that the hydrophobicity of the polymers can be lower and self cleaning will still occur.

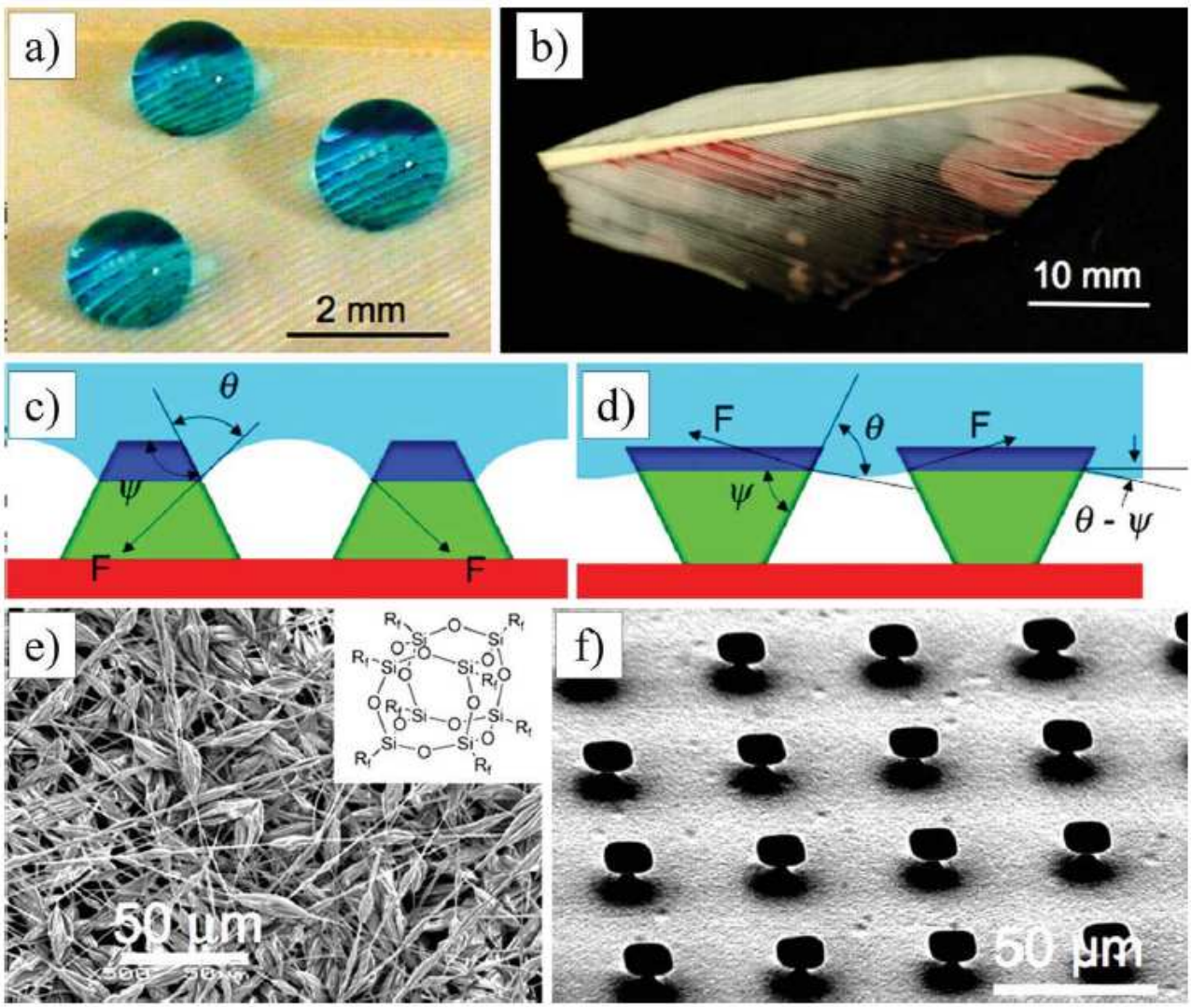

Figure 2 a) and b) Water and oil on feathers showing oil is absorbed c) and d), the meniscus at negatively and positively sloping pillars showing that for the same intrinsic contact angle the liquid is drawn into the structure of c) but held out of d) e) and f) show re-entrant structures electrospun and lithographic and the structure of a POSS with R being a fluorocarbon for oleophobicity (From A. Tuteja et al., PNAS **105**, 18200-18205, 2008, ©National Academy of Sciences, U.S.A. Reproduced by permission).

3.7 Maintaining an Air Layer Underwater (Plastrons)

One of the features of natural plastrons, the superhydrophobic surfaces used for underwater respiration[90] and whose functional behaviour can be reproduced using artificial superhydrophobic surfaces[91], is bent hair-like structures (Figure 4a). The bending increases the interfacial area and introduces re-entrant curvature, thereby reducing the tendency of the surface to dewet and expel the creature into the air or to pop down and wet the surface of the animal. In a type of water weed hydrophilic patches at the tips of the structures add to this effect.[92] It also acts as a spring to help the layer to survive against small pressure waves. The flexibility of the hair absorbs the pulse of pressure preventing loss of gas from the features of the surface, particularly if the tops of the hairs are hydrophilic.[92] This reduces the tendency for the gas film to lose volume and eventually collapse. Similar structures can be produced in polymer micro and nanostructures by treating one side of the features to shorten them. Both electron beam irradiation[93] and metal deposition[94] have

been shown to produce similar features(Figure 4b).

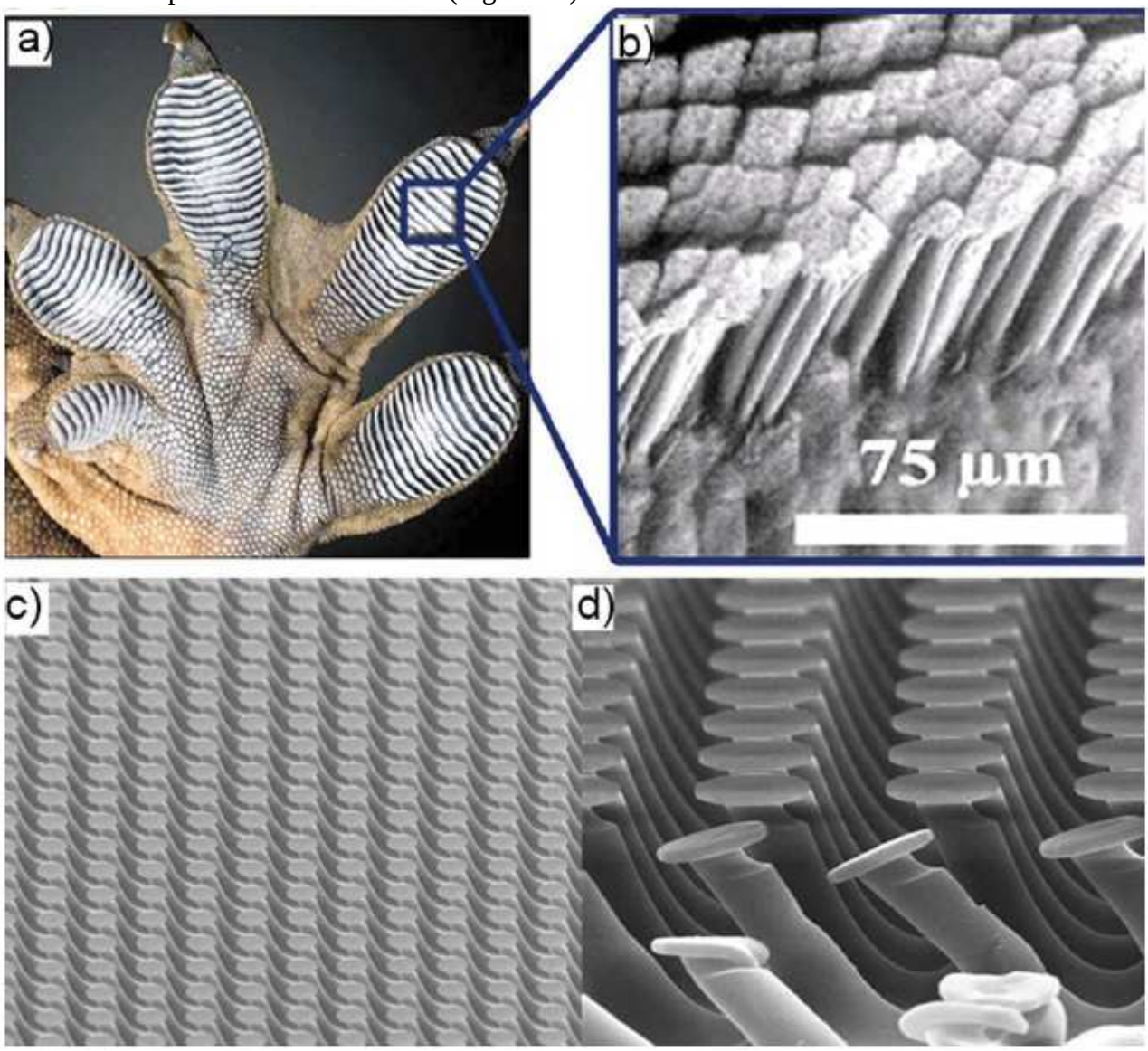

Figure 3 Gecko Feet Showing Structure and polymeric analogues a) Gecko foot b) setae (From L. Ge et al., PNAS **104**, 10792-10795, 2007). c) and d) polymeric analogues (From D. Sameoto and C. Menon, J. Micromech. Microeng. **20**, 115037, 2010, IOP publishing, reproduced by permission.

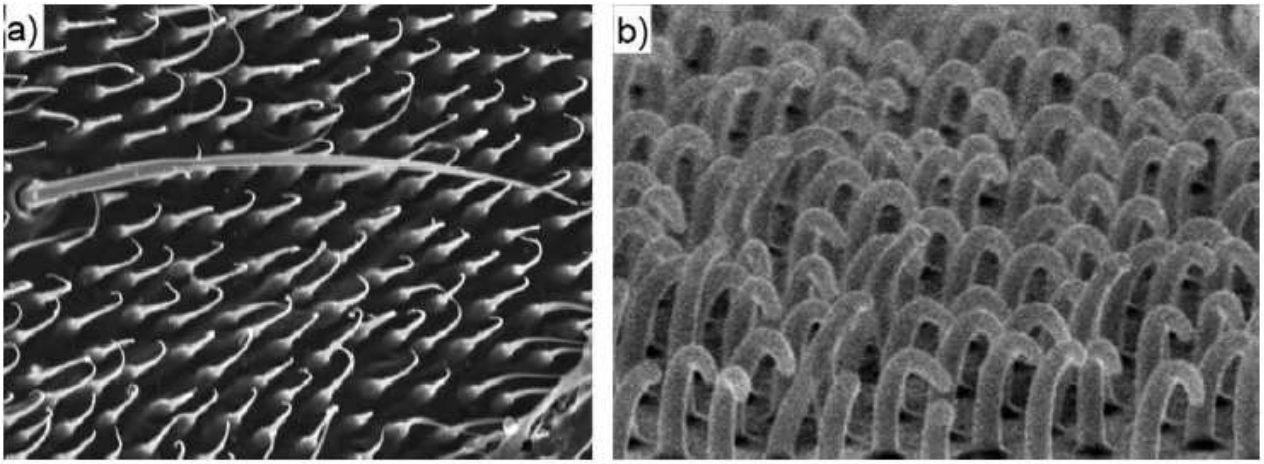

Figure 4 a) Image of diving beetle surface (from Natures Raincoats: www.naturesraincoats.com) and b) bent polymer pillars (From T. Kim et al., Langmuir **25**, 16, 8879-8882, 2009, ©American Chemical Society, reproduced by permission).

3.8 Flexible Superhydrophobic Structures

In a recent review Guo at al.[9] argued that natural superhydrophobic surfaces have two main formats, hierarchical roughness and single size fibrous structures. The second type is particularly interesting for polymeric materials as the sizes required are larger and the shapes are more robust.

Kusumaatmaja and Yeomans[95] have simulated hairs and show that moderate flexibility allows them to partially align with the interface, stabilising the bridging state. Our research has shown that such hairy surfaces are more resistant to condensation driven drop penetration than other superhydrophobic surfaces. Usually liquid condensing on a superhydrophobic surface enters the fully wetting Wenzel state and it is often difficult to remove it as this state is "sticky".[96] Condensate on hairy surfaces rarely reaches the true surface of the substrate, instead condensing on the upper areas of the hairs. This leads to the formation of nuclei in the outer portions of the surface, preventing condensation lower inside the surface. A similar intermediate stage of partial penetration also allows reversible electrowetting on some of these surfaces[97],[98]. There is some evidence that this is also the case on natural superhydrophobic surfaces, indeed the well known Alchemilla (*Alchemilla mollis*), which fascinated the alchemists with its tendency to collect dew drops is one such surface has been shown to collect and transport dew drops across its leaves using this mechanism.[99] Interestingly the hairlike structures of the Alchimilla are relatively hydrophilic, probably because a contact angle close to 90° aids fixation of flexible features into the liquid interface.[100] Research has shown that the Lotus leaf (*Nelumbo nucifera*), an example of natural multi-scale superhydrophobicity, is not resistant to condensation as it does not have fibrous surface structures and therefore becomes fully wetted by condensation.[101] These combined effects make the formation of polymeric fibrous surfaces very attractive as a method for generating superhydrophobicity, such surfaces can be formed by electrospinning, conventional spinning and molding methods as described earlier.

3.9 Sticky and Slippery Repellent Surfaces

Although the most common aim of superhydrophobicity research is to generate surfaces where the liquid is repelled as much as possible, other types of surface are possible depending upon the details of the shape and chemistry of the surface. There are several ways to generate surfaces on which water drops stick but their contact angle is high. In other words their advancing contact angle is high but receding contact angle is low.

The simplest is a Wenzel type fully wetted rough surface, this can generate high hysteresis. This difference to a bridging type of surface was highlighted by Quere et al.[102]. The advancing angle achievable in this way is limited because if a high advancing contact angle is present the wetting can switch to a bridging type of wetting and become less adhesive. A more targeted approach is to use a partially Wenzel, partially Cassie-Baxter surface[103], this is observed in some plants and has been called the "petal effect" as some flowers exhibit this behaviour. This type of surface can be relatively easily produced in polymeric materials and can be made very stable.[104],[105] See figure 5a for a diagram of this type of wetting, although an alternative explanation is that the tops are in a Wenzel wetting state and the bases are not wetted, which would produce a similar mixed state and the same result.

A second way is to provide a netlike or grid-like surface. Although the area fraction of the surface can be low, so the advancing angle of a drop of liquid can be high the contact line shapes itself to contact a large proportion of solid by following the lines of the net. This allows the receding angle to be low as the contact line sticks on the structures (Figure 5b). The principle was described in early publications by Oner and McCarthy[106], who proposed that if the contact line lies on a length of solid hysteresis will be higher than for an equivalent surface with interrupted solid under the contact line. The method has been more recently used to generate surfaces with variable stickiness[107] and is applicable to all materials.

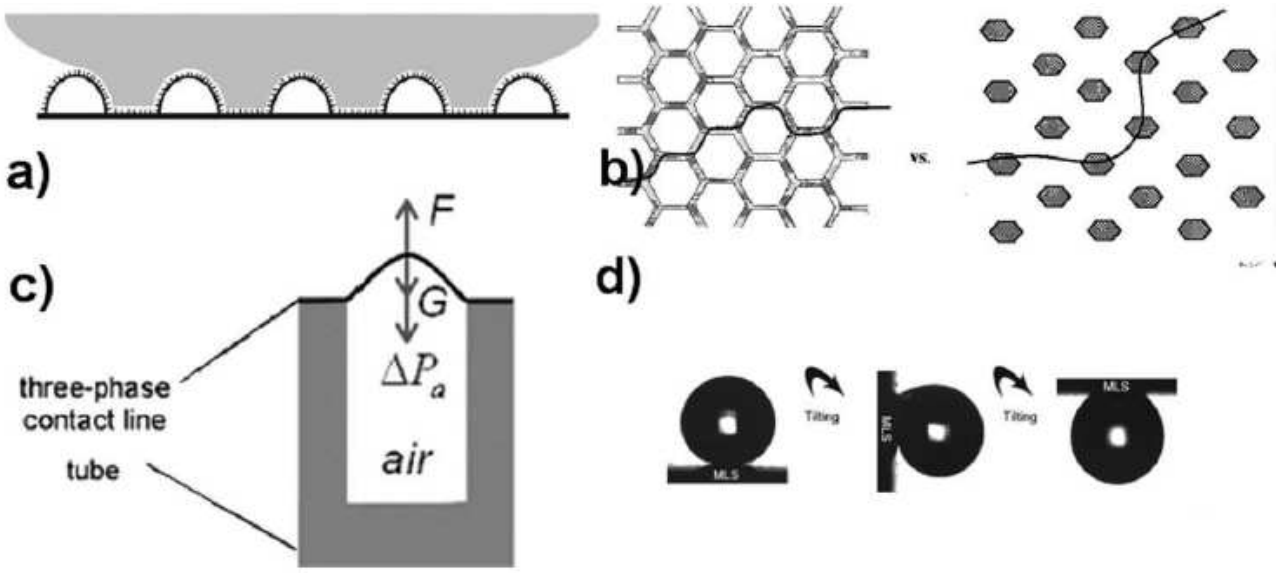

Figure 5 a) "petal" type wetting (From B. Bhushan et al., Langmuir **26**, 8207–8217 , 2010, ©American Chemical Society, reproduced by permission), b) Connected or fragmented contact line (From D. Öner and T. McCarthy, Langmuir **16**, 2000, 7777–7782, ©American Chemical Society, reproduced by permission), c) "suction" type adhesion (From Y. Lai et al., Adv. Mater. **21**, 3799–3803, 2009, ©Wiley, reproduced by permission), d) example of a sticky superhydrophobic surface with a drop at various angles (From X. Zhao et al., Langmuir **27**, 3224–3228, 2011, ©American Chemical Society).

The third possibility is to use a material for the roughened surface that has a high intrinsic contact angle hysteresis. This can be accomplished by generating domains of hydrophilic and hydrophobic surface chemistry on a single surface. This can then be roughened to increase the contact angle but the hysteresis remains.[108,109]

Another method is to have concave structures or open tubes, like microscopic chimneys. Liquid drops adhere on these surfaces because a negative pressure can develop in the cavity, adhering the liquid to the top of the pillars but not pulling it down their outsides.[110,111,112]. Krumpfer and McCarthy suggest that negative pressure is not required for this type of surface to show high hysteresis; the inward curve of the surface is sufficient to generate a low receding contact angle.[113]

3.10 Positional and Directional Anisotropy

It is often advantageous to steer drops of water passively using a surface. This can be done by varying the surface shape, forming rills and gutters, but the formation of superhydrophobic and hydrophilic regions can generate flat areas where drops are contained(Figure 6a, b)[114], incidentally the natural surfaces on which these are modelled use different shaped structures to generate adhesive and slippery areas. If the contact angle of a superhydrophobic surface can be varied across the surface any drops will tend to move towards the lower contact angle regions[115,116,117]. Also of interest, drops can be elongated different ways by patterning the roughness of the surface anisotropically, some examples relevant to this review are aligned fibers[118], and anisotropically structured polymer surfaces[119,120].

In the study by Bordorouglu et al[121], polyxylylene was deposited by angled vapour deposition and produced a carpet of angled fibers. This proved highly superhydrophobic and stable when treated to render it more hydrophobic. This is a promising mechanism for producing highly ordered arrays and has been used to generate directional wetting. A possible mechanism was postulated by Kusumaatmaja and Yeomans[122] in response to reports of directional wetting on butterfly wings (Figure 6c, d)[123]. The shape of the surface allows a wetting state between Wenzel and Cassie-Baxter that has angled menisci and, therefore, a directional pinning component.

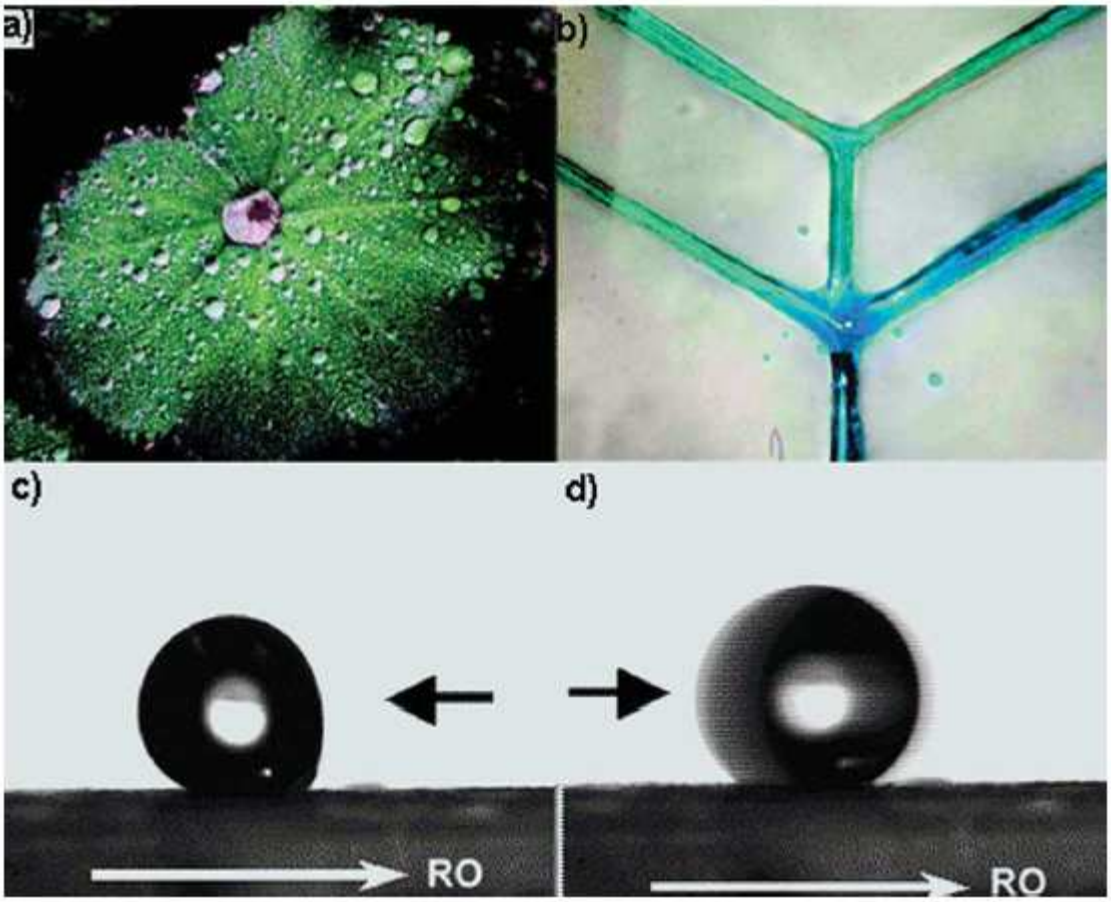

Figure 6 a) *Alchimilla mollis* leaf b) patterned superhydrophobic surface (From N.J. Shirtcliffe et al., Langmuir **25**, 14121-14128, 2009, ©American Chemical Society, reproduced by permission) and c) and d) directional anisotropy of butterfly wings, the drop moves to the right but not to the left even though the driving force is the same (From Y. Zheng et al., Soft Matter **3**, 178-182, 2007, The Royal Society of Chemistry, reproduced by permission).

3.11 Mimicking the Stenocara Beetle/ Gathering Water from Fog

The Stenocara beetle of Namibia uses a superhydrophobic surface with hydrophillic raised patches to enhance droplet capture from fog[124]. The hydrophilic patches capture small droplets which, when they grow too large slip off their single attachment point and rollaway. This is important for a variety of applications, water recovery is energy intensive and any passive assistance is very beneficial. Small features with topography and local variation in chemistry are difficult to produce on a large scale. Polymers are ideal for forming this type of surface, depending upon the scale of the features required different printing methods can be used to generate the features by depositing a second material or the polymer can be modified to render it hydrophilic in patches (Figure 7).[125,126,127]

Other natural structures gather water, some spiders' webs use variations in surface structure and surface energy along the fiber to cause water droplets to form at hydrophilic points. The edges of the drop become pinned to the junction between the hydrophilic and hydrophobic regions of the fiber. As the hydrophilic region is longer than a typical drop it coils inside it and the drop can be deformed on pulling the thread, forming a spring using the surface tension of the water.[128]

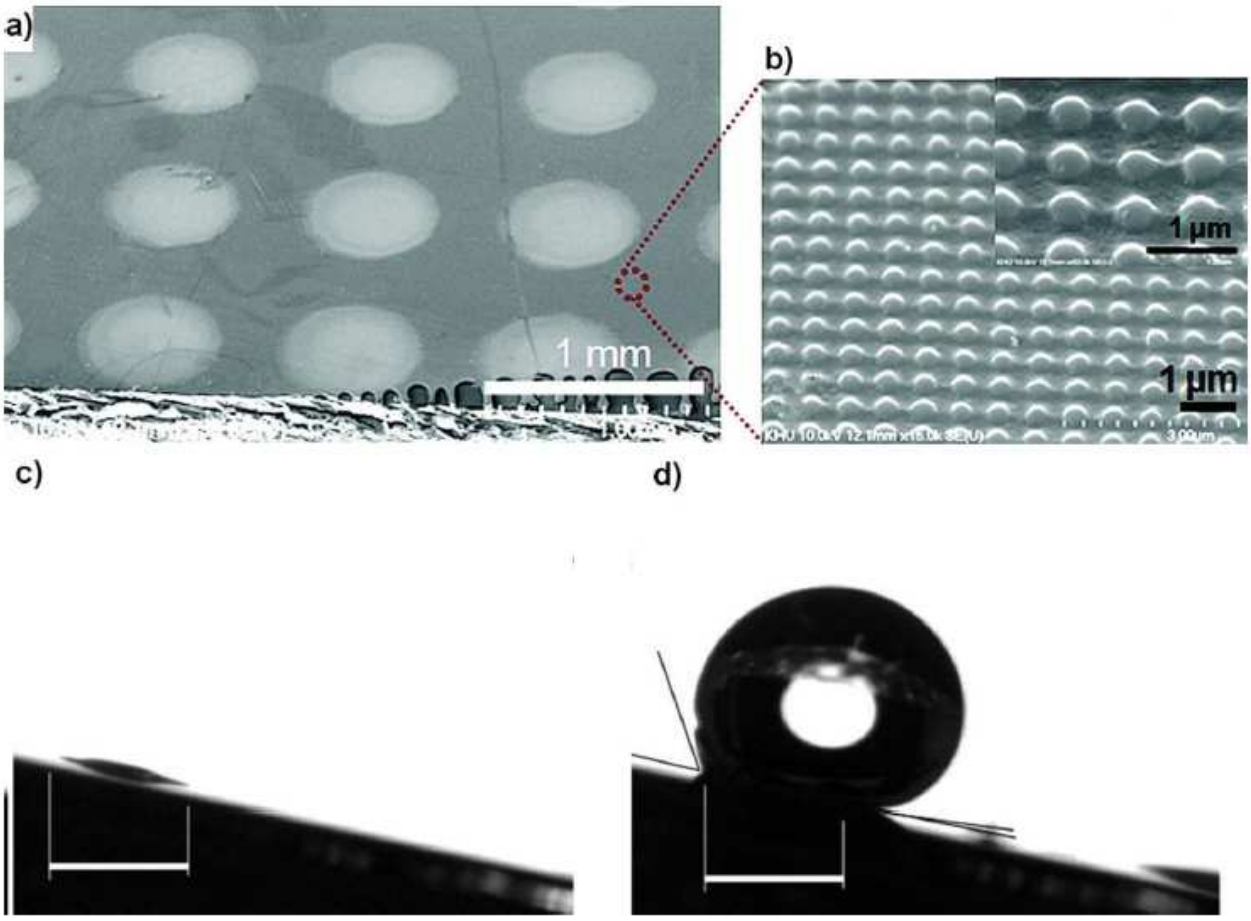

Figure 7 Polymeric fog capture surfaces a) low magnification image showing hydrophilic spots b) high magnification image showing superhydrophobic structure (From J. Choi et al., Langmuir **25**, 7156-7160, 2009, ©American Chemical Society[129]), c) and d) dewetting of drops from a patterned superhydrophobic surface (From C. Dorrer and J. Ruhe, Langmuir **24**, 6154-6158, 2008, ©American Chemical Society).

3.12 Switching Wetting States

Changing the chemical contact angle at a rough surface by a small amount can change its apparent contact angle by a large amount (Figure 8b and c). [99] We showed that a small change near 90° can switch the sample from repelling water to absorbing it[129,130]. This type of change is very attractive as it could allow water to be controlled on a surface or function as a valve with no moving parts. Interest is high enough that two reviews were published recently.[131,132] Almost all of these methods involve polymers, as their properties can be controlled most effectively. Even our work on sol-gel materials utilised the polymeric structure of an inorganic-organic macromolecule[133].

Polymers that can change contact angle can be used to switch superhydrophobic surfaces from one state to another simply by roughening them in some manner; particularly if they can be switched around 90° as the contact angle is magnified the most in this region by roughening the surface. The switching can be carried out chemically, by having a rearrangement in the polymer, in the simplest case a switching from a conductive to a non-conductive state, for example polypyrrole[134] but also by using thermal[135], pH[136] (poly(N-isopropylacrylamide for both thermal and pH) and poly(dimethylamino)ethyl methacrylate (PDMAEMA) became protonated and switched configuration on exposure to acid) and light (in the form of photoreactive inorganic-organic hybrids[137] and conformational changes as in spyropyrans[138]). Other examples include ionisation of a carboxylic or amine ligand on an inorganic particle[139], using PDPAEMA, brushes and switching with a gas[140] A block copolymer of PAA and PS can be switched by long exposure to water/dry heat from a patchy PAA surface to a hydrophobic PS surface[141]. Using a copolymer of 3-(acryloylthioureido) phenylboronic acid (ATPBA) allowed switching to be carried out using sugar

molecules[142]. An interesting variation is the use of ultrasound to switch cholesterol based gels[143]

Nadermann et al[144] recently showed a flat PDMS film on a pillared surface that could be collapsed over the pillars to generate a rough surface and inflated away from the base to generate a flat one. This continues earlier similar work[145] and shows simple micromechanical switching. The flexibility, natural hydrophobicity and toughness of the polymer are key to this functioning.

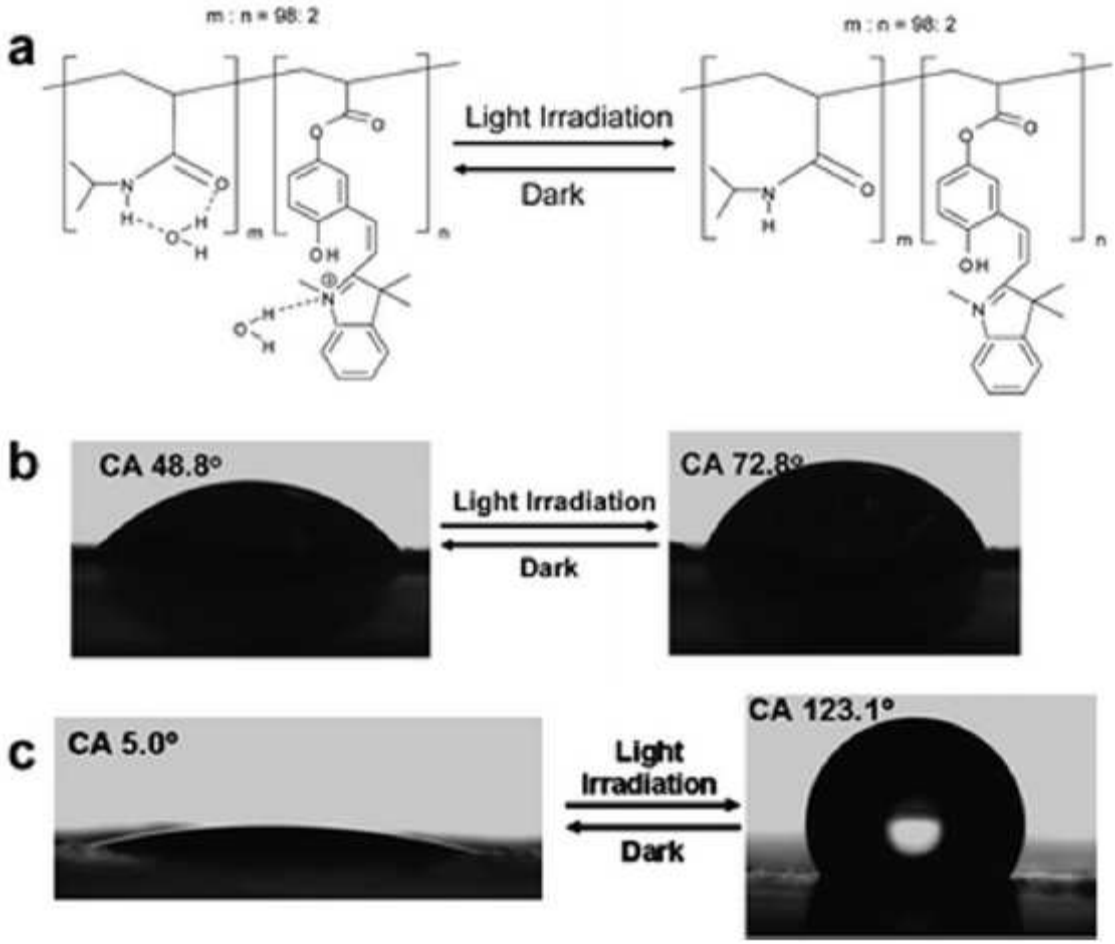

Figure 8 a) Chemical switch activated by light b) flat contact angle change c) rough contact angle change (From G. Joseph et al., Analyst **135**, 2303-2308, 2010, The Royal Society of Chemistry, reproduced by permission).

4. Summary

Since our last review in 2008 the field of superhydrophobicity has moved away from simply generating surfaces to finding more complex applications and searching for additional advantages that can be achieved.

Simple surfaces, such as those that can be deposited with paints have been available now for some time, but still remain rare. This is mostly due to the cost of the coatings and their relatively low tolerance to abuse. There is little call for an anti-graffiti coating that is expensive or that cannot withstand pressure washing.

More recent research has focussed on ways to reduce costs, increase toughness or to increase the utility of superhydrophobic surfaces by adding other functionality.

Polymeric surfaces are ideally placed to fill the special requirements of many of these new applications. The complex topography and various physical properties that polymers allow

combined with their ease of use and relatively low cost means that they have become the material of choice for new applications.

Included in this is toughness for maintaining topography, flexibility to absorb pressure waves and other potential damage, ability to switch surface wetability in various ways to allow active patterning, softness to allow gecko sticking and crucially the ability to form complex patterns.

5. Outlook

As the science of superhydrophobicity matures, costs must decline to enter the consumer market and compete with existing products. Most recent developments have been in adding functionality to simple superhydrophobicity to increase the value and to develop smarter materials and surfaces. These developments mean that polymers are becoming the material of choice for generating superhydrophobic surfaces both due to their low cost and ease of formation into complex shapes but also for their chemistry, softness, variable thermal conductivity and chemical variability. The advantages polymers offer are beginning to allow superhydrophobic technology to escape from the laboratory and niche use to fulfil its potential; it is not an accident that so many natural surfaces are superhydrophobic and that they are almost all polymers.

Acknowledgements

The authors' acknowledge financial assistance from the U.K. Engineering and Physical Sciences Research Council (Grant No. EP/E063489/1).

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