Mass production of bio-inspired structured surfaces

S J Abbott[1*] and **P H Gaskell**[2]
[1]MacDermid Autotype Ltd, Wantage, Oxon, UK
[2]School of Mechanical Engineering, University of Leeds, Leeds, UK

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Abstract: Bio-inspired surface structures offer significant commercial potential for the creation of antireflective, self-cleaning and drag reducing surfaces, as well as new types of adhesive systems. The current article explores how the current understanding of the basic science of the biological structures occurring on the surface of moth eyes, leaves, sharkskin, and the feet of reptiles can be transferred to functional man-made materials, some of the drawbacks of which are shown to offer a long-term challenge to engineers. Explored also is the related topic of how such surfaces can be mass-produced, encompassing the important areas of current surface replication techniques and the associated acquisition of good master structures.

Keywords: biomimetics, motheye, Lotus effect, sharkskin, gecko, microreplication, nanoreplication, embossing, antireflection, self-cleaning, drag reduction, Spiderman

1 INTRODUCTION

Biomimetics [**1**] encapsulates the study and mimicry of nature's shape, form and function which on many fronts, through the process of evolution, far excel current human capabilities. Mankind has made some progress in incorporating nature's lead to improve technology [**2**]. Indeed, from an engineering standpoint, bio-inspired solutions are not new: flippers, for example, invented by Benjamin Franklin have been used as a simple swimming aid since the early eighteenth century [**3**]. However, other engineering mimicry of nature's solutions has required far greater ingenuity and scientific understanding – for example, despite birds having evolved to fly effortlessly and over long distances, for humans such a feat, whether for the purpose of travel or business, only became a reality with the advent of the jet engine and an associated deep understanding of the physics underpinning aerodynamics. Another obvious success is the progress that has occurred in relation to artificial joint and heart valve replacement together with advances in prosthetics.

In the case of aviation, mankind has surpassed nature from the standpoint of speed of flight, but not from a perspective of manoeuvrability. The latter has played a key role in the general evolutionary process and is central to both hunter and hunted – the cheetah combines both speed and manoeuvrability with a grace that can only be truly appreciated in slow-motion replay! In other areas evolution's answer is at best equalled, a good example being the invention of Velcro by George de Mestral; patented in 1955, today it forms the basis of a multi-million pound industry.

The success of the mimicry mentioned above is because of mankind's ability to manufacture engineering solutions cost effectively, either en masse (e.g. Velcro) or in small volumes to high levels of sophistication and precision (e.g. commercial and military aircraft). And as expected, as new manufacturing techniques have come on stream continued incremental improvements have emerged. Engineering solutions are of course based on the ability of engineers to design to specified tolerances which satisfy strict quality controls and customer demands; the purpose and result being exact duplication! Fish, plants, insects, etc., on the other hand, are cell-based structures that have evolved over millions of years and possess not only their own individuality but also the ability to self-replicate and in many instances self-repair – two highly desirable but equally challenging features that currently and for the foreseeable future remain firmly beyond the scientific

Corresponding author: MacDermid Autotype Ltd, Grove Road, Wantage, Oxon OX12 7BZ, UK. email: sabbott@macdermid.com

knowledge horizon. Nevertheless, although nature has never ceased to inspire the scientist and engineer alike, the emergence of new and exciting diagnostic equipment such as scanning electron microscopes, atomic force microscopes, nanoprobes, and high-speed photographic capabilities continues to push at the boundaries in the search for engineering solutions based on nature's lead. Impetus is also being provided by the advances being made in the field of nanotechnology.

The current article explores the mass production of engineered surfaces as inspired by: the moth's eye; the lotus leaf, see also reference [**4**]; sharkskin; gecko and tree-frog feet. Mass production of bio-inspired products gives rise to two sets of problems. The first is to gain a thorough understanding of the physics, chemistry, and engineering of how the biological system achieves its desirable functionality. The second is to understand the strengths and limitations of the production processes and materials which will, usually, be very different from nature's. In sections 2 to 5 it is shown how the two are intimately intertwined but above all how the route from bio-inspiration to profitable functional product is hugely multi-disciplinary. It is not too fanciful to suggest that bio-inspiration is leading to the development of new ecosystems in the world of engineering. Understanding the structures is one thing, implementing them is another; section 6 deals with the latter in the context of mass production. Conclusions are drawn in section 7.

2 NATURE'S STEALTH TECHNOLOGY

The moth has a problem. It flies in low light levels so needs large eyes to see where it is going. The laws of physics show that 4 per cent of the light hitting the surface of the moth's eye will be reflected. This reflected light is enough to alert the moth's predators. What the moth needs is stealth technology to reduce the reflectivity. The normal human approach is to create a submicron multi-layer coating using materials such as magnesium fluoride that have a low refractive index (RI). This is too hard for nature. Instead [**5**] the moth creates a graded RI on the surface of the eye that smoothly goes from RI = 1 (air) to RI = 1.5 (eye). Physicists with access to advanced optics simulations can show that a triangular structure is theoretically excellent yet too brittle to survive reality [**6**]. However, a sine-wave structure is almost as good. And that is what the moths have come up with. Regular optical structures act as diffraction gratings, which is not what the moth wants. The key trick is to make the structures significantly below the wavelength of light, which then only sees them as an average medium of a graded RI. Thus a typical motheye has a period and depth of 200–250 nm.

The above provides a considerable challenge for any mastering process. Currently, the largest motheye masters are $600 \times 800\ \text{mm}^2$ and a practical method for creating continuous rollers has still not been realized, though there is active research into alternative techniques such as growing nanoporous alumina on an aluminium drum, see for example reference [**7**]. Figure 1 shows a motheye structure as replicated into a hardcoat polymer surface.

The antireflection (AR) characteristics of the motheyes are quite attractive. Although practical implementation cannot achieve the very low reflectivities of the best sputtered multi-layers, they show very good angle dependence and colour neutrality. Typically for normal incidence the percentage of reflected light at 550 nm (the wavelength where the eye is most sensitive) is 0.8 per cent. Only above 50° angle of incidence does the reflectivity exceed 1 per cent (A. Gombert, personal communication, 2004). Motheyes can also be implemented in ways that are hard for conventional AR coatings. For example a piece of motheye film can be placed into an injection-moulding cavity and made into a thick, three-dimensional component with good AR properties [**8**]. The skills required to bring this combination together are yet another example of how the bio-inspired community is creating new ecosystems of industrial interactions.

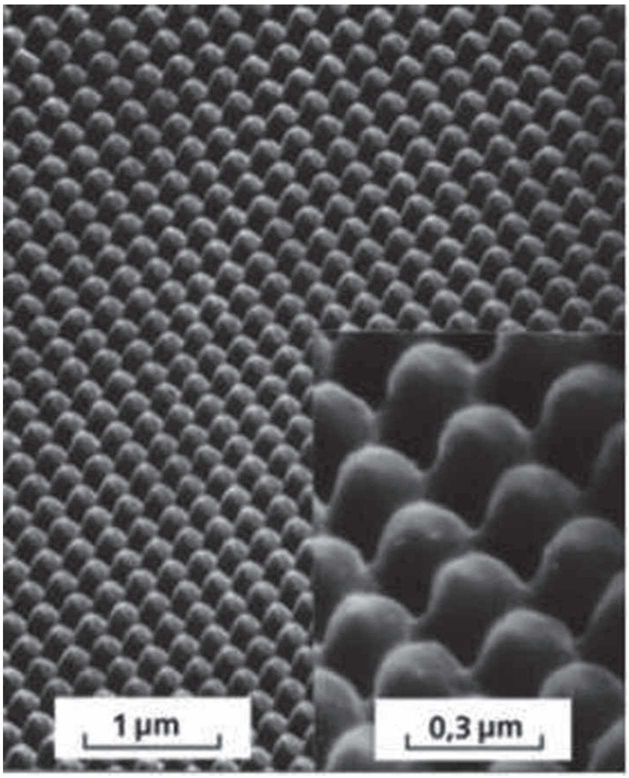

Fig. 1 Motheye structure replicated into a hardcoat polymer surface by MacDermid Autotype. (*Image courtesy of Fraunhofer ISE*)

One problem that confronts all AR coatings is the fact that a human finger-print destroys the optical system. For motheyes the problem is that finger grease gets into the structure, and therefore changes the graded RI. Because these are deep nanostructures it can be hard to wipe away the grease. One solution is to reduce the surface energy of the motheye structure. This can be via a subsequent treatment with a silicone or fluoro material, but every extra manufacturing step adds costs. An alternative method is to exploit the manufacturing method itself. A good way to produce surfaces is via UV cross-linking of systems such as acrylates. Acrylates come in a huge variety of forms, from hydrophophilic to hydrophobic. Thus one approach is to formulate the UV acrylate system with sufficient hydrophobic content so that it is naturally hydrophobic after replication. Although this works, it is still not quite good enough. The final part of the solution is to use a microfibre cloth that can reach into the depths of the motheye to help remove the finger grease.

Another problem with the motheyes is when they are used for outdoor applications such as solar cells. Although cross-linked UV acrylate systems are typically seen as being very tough they can easily lose a few tens of nanometres from the surface when exposed to sunlight. This does not matter when the systems are standard hardcoat surfaces, but, when you lose tens of nanometres from a motheye the AR performance diminishes rapidly. One approach to solving this problem is to use materials with high silica content such as sol-gels [**9**]; but the large-scale manufacture of such systems poses its own set of problems.

This digression into the practical issues of these bio-inspired films shows up an important but recurring difference between nature and human engineering. Dirt on a moth's eye or erosion of the structure is simply fixed – the moth's eye is a dynamic, growing structure, refreshing itself all the time. Finding engineering equivalents to such a self-repairing system is going to be a tough task.

3 NATURAL SELF-CLEANING

The prospect of engineering robust self-cleaning surfaces so that when it rained windows, road signs, indeed all exposed surfaces, were cleaned is a tantalizing one! Unsurprisingly nature got there first, with the lotus leaf providing the essential catalyst for work to begin on mimicking the process artificially. Not only was the chemical patterning of the leaf found to be important but also, as with motheyes, the microscale topography present. Similar findings have been exploited elsewhere in relation to understanding the motion of droplets on chemically and topographically micropatterned heterogeneous designer surfaces [**10, 11**] and on lab-on-chip devices for chemical assay [**12**]. An up-to-date description of the Lotus effect by its discoverer, Barthlott [**4**], covers the essentials, and the earlier references therein contain the biological images that inspired his work. The purpose of this short section is to provide a reminder of the unity of knowledge across diverse fields. See Fig. 2 for an example of an artificially created Lotus effect surface.

There are at least three links between motheyes and lotus surfaces.

1. They both require high aspect-ratio structures which pose similar challenges in origination and replication.
2. The partial solution to the motheye contamination issue is to make the surface highly hydrophobic. The Lotus effect requires a similar hydrophobization and the same choice exists: carry out a post-functionalization or build it in to the replication process. The same team that produced successful, practical motheye films [**8**] was also able to replicate lotus structures that were sufficiently hydrophobic and sufficiently high aspect-ratio (the two requirements) to show the effect straight off the replication machine.
3. The use of the Lotus effect in the real world is likely to be highly restricted by the ease with which the surfaces can become contaminated by oil or grease. It only needs a small reduction in the hydrophobicity of the surface (for example, a monolayer of a typical oil) or a small reduction in the depth of the structure (again by filling in with some oil) to destroy the effect entirely, taking it from a superhydrophobe to a Wenzel wetting surface [**13**]. Nature solves this problem by continually regrowing the lotus structures; indeed,

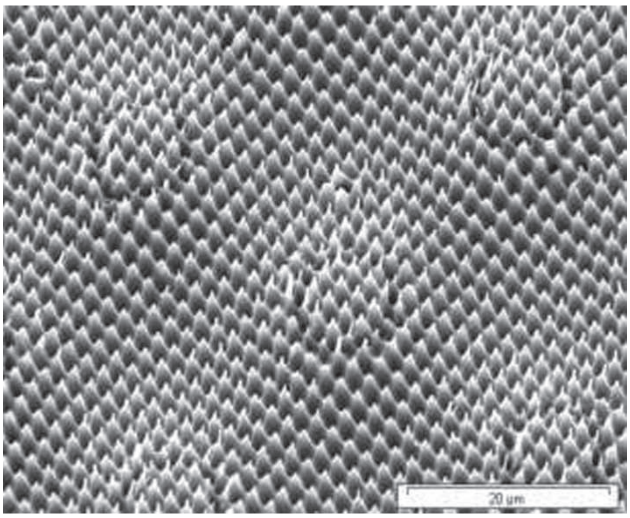

Fig. 2 Artificial Lotus effect surface created by MacDermid Autotype. (*Image courtesy of Creavis*)

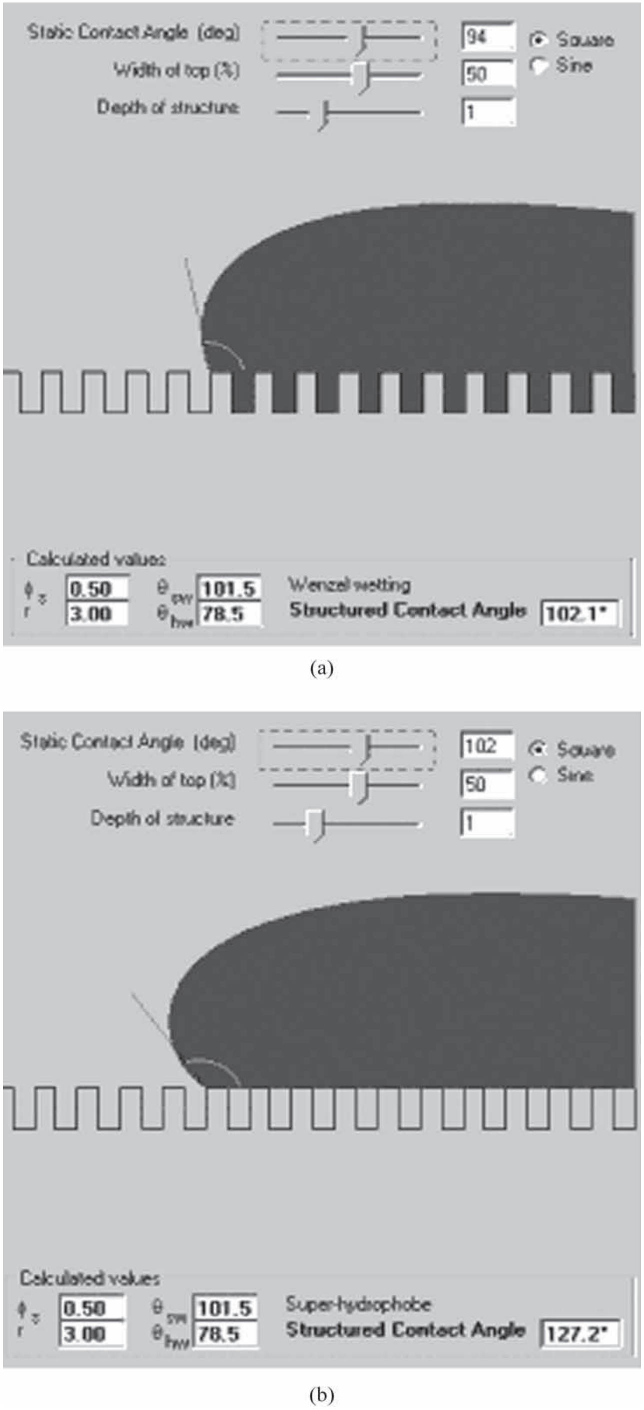

Fig. 3 (a) Almost a superhydrophobe, but not good enough. θ_{sw} and θ_{hw} are, respectively, the structured wetting and hemi-wicking critical angles. ϕ_s is the fraction of the surface on the peaks. (b) A small change in parameters makes the surface superhydrophobic

they will spontaneously pierce through a layer of low-hydrophobic contamination. Thus, as with the motheye, the challenge for the long-term future is to create dynamic self-repairing systems.

The pessimistic conclusions in 3. come from reference [**14**], the content of which is sufficient to dash many of the more näive hopes of how the Lotus effect might work. Restricting the problem to two-dimensions and treating the structured surface as one comprised of a series of crenellations (regular spikes) – see Fig. 3 – it is shown that liquid in the form of a drop on a textured (rough) surface can exist in three states. In the hemi-wicking state the liquid in the drop spontaneously flows down the structures ('wicks') beyond the edge of the drop. In the Wenzel state the liquid fills the structures below the drop. In the superhydrophobe state the liquid does not enter the structures at all. It is only in this last state that the drop is free to roll across the surface, taking dirt with it. To the casual observer, the Wenzel state looks very similar to the superhydrophobe state (high contact angle) till the observer tilts the substrate to find that the drops do not roll off.

The transitions between these states depend on: the static contact angle θ [**15**] determined on a plane surface of the same chemical composition; the fraction ϕ_s of the surface which is on top of the structure, normalized by the total surface area such that $\phi_s < 1$; the roughness r which is the ratio of the actual surface area to the apparent (zero texture) surface area, in which case for a flat surface $r = 1$. Hemi-wicking wins over Wenzel when

$$\cos\theta < \frac{1-\phi_s}{r-\phi_s} \qquad (1)$$

and superhydrophobe wins over Wenzel when

$$\cos\theta < \frac{\phi_s-1}{r-\phi_s} \qquad (2)$$

This second equation means that a small reduction in roughness (which can be thought of as a small reduction in depth) or a small decrease in ϕ_s or a small decrease in θ can transform a self-cleaning surface into one that does not self-clean at all. This is illustrated in Fig. 3, which shows inputs and outputs to the author's computer model based on the theory contained in reference [**14**]. The difference between the two images is a change of the static contact angle from 94° (Wenzel state) to 102° (super hydrophobic condition).

A subsequent paper [**16**] shows that a very modest hydrostatic pressure (200 Pa) is all it takes to flip from superhydrophobe to Wenzel. This result means that dreams of superhydrophobe surfboards are impractical. For a review of numerous other aspects of related effects see reference [**17**].

It is worth noting two more important facts with relation to the Lotus effect. First, the same effect can be found on cabbage leaves, but somehow the Cabbage effect does not sound so marketable. Second, it is likely that human ingenuity has come up with a better approach for keeping windows clean. A smooth, hydrophilic TiO_2 surface is the exact opposite of the lotus surface, yet it provides endurable self-cleaning via two mechanisms. First, the hydrophilic surface helps spread water drops into an even, thin film. Second, the TiO_2 interacts with UV and oxygen from the air to provide aggressive active oxidizing chemicals that attack dirt and bio-film to keep the window clean. This approach to cleaning also fits in with a key principle of economy in practical manufacture – the TiO_2 has to be deposited onto a hot, fresh glass surface, but that is exactly what the float glass process provides.

4 DRAG REDUCTION (WITH SELF-CLEANING FOR FREE)

Sharks, although in general feared, are the refuse collectors of the oceans and spend their whole life swimming. Their general shape and musculature has been highly optimized via evolution to make them very efficient swimmers. Indeed, in terms of shape and form there is little further that can be done to the shark to make it even more efficient. Evolution, however, found a way that seems to reduce drag by another 5–10 per cent. It is not proven that the rough nature of the sharkskin really evolved for this purpose, but as will be shown below it has been proven that the sharkskin effect can be applied to human constructions to give that 5–10 per cent improvement. Similar observations have been made with respect to dolphins [**18**]. Figure 4 shows a sharkskin surface created using screen printing – the pale coloured, elliptic shaped patterning represent regular protrusions aligned with the main direction of flow.

It seems counter-intuitive that a textured (rough) surface would have less drag than a smooth one, even in the case of creeping flow over an undulating surface [**19**]. For the relatively high Reynolds number of a swimming shark, turbulence is guaranteed. And one of those well-known, but still surprising facts is that for turbulent flow the skin drag (near wall shear stress) is not generally affected by roughness of the surface. Thus a shark's choice of skin roughness is not a simple first-order effect. The way the sharkskin provides drag reduction is complex. For the full story the reader is referred to reference [**20**].

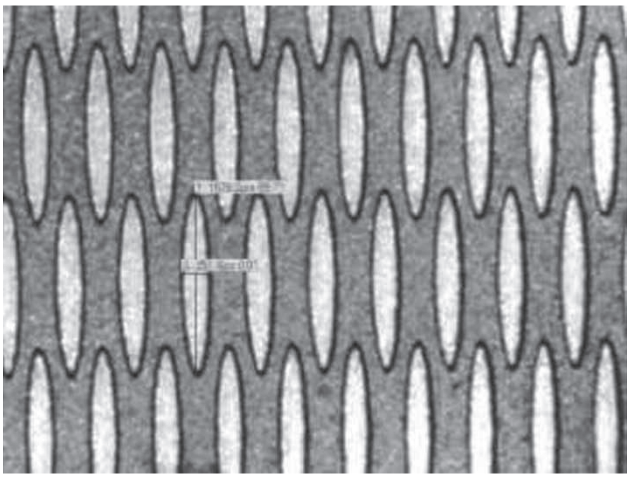

Fig. 4 An experimental screen-printed sharkskin surface designed by U. Leeds. (*Image courtesy of N. Kapur*)

In simple terms it helps to think of the shark as stationary and the bulk water as moving, with the sharkskin viewed, see Fig. 4, as a series of contiguous protrusions (riblets) aligned parallel to the local flow direction of the water. Drag comes from the exchange of momentum when high-speed water gets converted into slow-speed water by the skin and then reinjected back into the high-speed stream. Because the flow is turbulent it has both parallel and cross-flow (perpendicular) components. Although it is intuitively obvious that protrusions in the parallel direction will have little effect on turbulent flow in that direction, the protrusions influence the flows in the *cross* direction limiting the chances for momentum transfer, but, by how much does this reduce the turbulent drag? This seems to be an unanswered question.

In a series of papers [**21–23**] valiant efforts have been made to develop a fundamental theory, supported by a series of careful experiments, to quantify the effect. By considering the flow over surfaces containing grooves (ribs) running their full length and aligned with the principal direction of flow, the route to a deeper understanding came with the key observation, from experiments, that the typical size of ribs which appear to be effective is of the same order of magnitude as the height of the viscous sublayer of the turbulent mainstream flow. Within the viscous sublayer, thickness h_{vsl}, for the case of turbulent flow over a flat surface, viscosity dominates, and inertia/convection is negligible; an approximately linear velocity profile with constant slope exists. Accordingly, one can write

$$h_{vsl} = \left(\frac{\nu^2 \rho}{\tau_w}\right)^{1/2} \tag{3}$$

where υ is the kinematic viscosity of the fluid, ρ its density and τ_w the shear stress at the wall. Studying the alterations to the mean longitudinal flow produced by the presence of longitudinal ribs on a surface [**21**] gave rise to the crucial idea that the linear velocity profile in this case appears as if it originates from an equivalent flat surface located at a fixed distance, h_L, – termed a longitudinal 'protrusion height' – below the tip of the ribs. Following a similar argument, a transverse protrusion height, h_T, can be defined for the location of a corresponding virtual flat surface in the cross-flow direction. Now, if $h_T < h_L$ the viscous cross-flow will experience a higher viscous dissipation and a reduction in the level of near wall turbulence and hence drag.

What seems to be important is the difference in the protrusion heights, $\Delta h = h_L - h_T$, which gives a quantitative measure of whether and by how much ribs impede the cross-flow more than they do the longitudinal flow – the larger the difference the greater the relative drag reduction in the cross-flow direction. Of course the protrusion heights cannot be greater than the height of the ribs, so there is a natural limit to Δh. Although the calculations of Δh are precise (because they are based on the solution of Stokes equation in the viscous sublayer), in reference [**22**] the authors acknowledge that the correlation between drag reduction and Δh is not calculable, but it agrees well with a substantial body of experiments [**23**]. Proving the correlation from first principles remains a difficult challenge for the future.

What emerges from the theoretical analysis of Δh matches intuition. Very thin, vertical ribs give the best result. Broad sinusoidal ribs give an inferior result and sharp triangular ribs are intermediate. These results are important because there is a trade-off between performance and practicality (production and robustness). Triangular ribs are particularly well suited to bulk manufacture.

Another result which emerges is that a ratio of absolute rib height, h, to 'tip-to-tip' rib spacing, s, of $h/s \sim 0.5$ is the optimal value for thin ribs and that values somewhat higher are optimal for other shapes. However, higher ribs intuitively increase overall drag so the value of 0.5 is a good practical guide. For the real-world designer the ultimate question is what 'tip-to-tip' rib spacing is optimal for drag reduction (given that the preferred rib height should be half that of the rib spacing)?

The Reynolds number for the ribs can be defined as

$$s^+ = \frac{su_\tau}{\nu} \tag{4}$$

where $u_\tau = (\tau_w/\rho)^{1/2}$. By taking $\Delta\tau = \tau - \tau_w$, the difference between the shear stress on a ribbed surface and that on a flat surface under identical flow conditions, it is that negative values of $\Delta\tau/\tau_w$ will correspond to a drag reduction and positive values to an increase in drag. Plots [**23**] of $\Delta\tau/\tau_w$ against s^+ from experimental data for different rib profiles suggest that drag reduction is optimal for s^+ having a value of approximately 15. It turns out that for typical structures such as boats and aircraft s is in the 100–200 μm domain with h therefore in the 50–100 μm domain.

With the optimum structure what sort of drag reductions can you obtain? Experiments show that you can approach a drag reduction of about 10 per cent with sharp rib structures [**23**]. Mass-producible structures are more likely to provide an 8 per cent reduction in skin drag. An 8 per cent drag reduction sounds very attractive so why are not aircraft, boats (other than some rare examples of sports boats), and cars regularly covered with ribs?

An example from reference [**20**] shows the engineering thought process required before anyone would use sharkskin in practice. The skin drag from a typical aircraft is 50 per cent of the total drag. In reality you can only cover 70 per cent of an aircraft with ribs. Put these factors together and the 8 per cent drag reduction becomes a 3 per cent reduction in the total drag on the aircraft. Three per cent is still significant for an airline but so far only one Cathay Pacific Airbus 340 has been fitted with a ribbed structure as many other tradeoffs are involved [**23**].

There is another example of unity of knowledge in this field. Sharks and, as it turned out, the Cathay Pacific Airbus seem to remain cleaner in their working environment. Clearly this is not because of the Lotus effect, but the ribbed surface is making it harder for dirt and for natures contaminants (from fungae to barnacles) to stick to the surface!

5 STICKING TO WALLS

It is remarkable to see a gecko walking upside down on a plane sheet of glass and attach its body to a vertical wall using a single toe to support its entire body weight, or a tree-frog walking safely along a wet and slippery vertical leaf. There have been many theories of how these archetypal examples of animal adhesion work, with the myth of Spiderman [**24**] having made it fairly obvious that some sort of sticky adhesive must be involved. The reality, however, is both simple and complex.

The simple part is that if you put any reasonable amount of any two surfaces in intimate contact then in principle the van der Waals forces [**25**] between them are more than sufficient to bear the required load. It is surprising to many people to learn that the apparently very weak van der Waals force (which provide a low adhesion energy of 50–60 mJ/m^2 [**26**]) is sufficient so that in principle a human could hang from a smooth glass wall if only the total area of their hands were in contact.

A typical flat polymer surface in perfect contact with glass, and with no stored elastic energy can take an adhesive load of 30 000 N/m^2 simply from van der Waals forces. Thus a pair of hands of 0.03 m^2 total contact area if in perfect contact could support 900 N or about 90 kg, a typical human weight. No special adhesive bonding is required – just perfect nanometre-scale contact. And so the problem that geckos and tree-frogs have to solve is how to get perfect contact.

It is trivially the case that two planar rigid surfaces only make intimate contact at three points! Hence the actual contact area between any two real-world surfaces is usually a tiny fraction of the potential contact area. Intuition suggests that if your hand were made from a nice rubber then with a bit of pressure you could get it into intimate contact and become Spiderman.

Unfortunately, although rubber seems soft and easily deformable to make good contact with a surface, the bulk (or compression) modulus in the z-direction (perpendicular to the surface) for a rubber which is perfectly constrained in the inplane (surface) x–y directions is given by $E/[3(1-2\upsilon)]$, where E is the Young's (or elastic) modulus and υ is Poisson's ratio. For rubber $\upsilon = 0.5$ leading to an infinite compression modulus. In reality a piece of rubber is not perfectly restrained in the x–y plane so the compression modulus does not attain this pessimistic value, but nevertheless the general restriction in that plane leads to a very high-effective compression modulus. If there were no restraint in the x–y plane then the rubber is more easily compressed into contact and the compression modulus is closer to the elastic modulus. To put it another way, if one has a rubber hand and presses against a wall, the rubber at the edges can deform sideways allowing fairly good contact of the rubber with the wall, but the rubber in the centre is constrained from sideways movement and cannot effectively be pressed in intimate contact with the wall.

What the gecko does is introduce many more edges to the rubber so it can expand laterally. It sacrifices total surface area (by about 50 per cent) to give many two-dimensional fibres that can deform to be in perfect contact with the local surface, but there are two levels of deformation. The first is at the near nanometre level where the modulus effect is so helpful. The second is at a macrolevel of roughness of a wall or a tree. If the fibres are long enough they can flex to accommodate wide ranges of local roughness. In other words you want a compliant fibre.

At first it seems as though it is relatively easy to create an artificial gecko foot. Make lots of nanofibres as long, thin (for conformity) and close-packed (for maximum surface area in contact) as possible. When this is tried the result is disappointment, see for example [**27**]. The long fibres are so easily deformed that they bend towards each other and stick in a mat. They are useless as a gecko foot.

The elegant work contained in reference [**27**] and of others, shows that there is a maximum fibre length to fibre diameter ratio, which depends on the Young's modulus of the material. The maximum fibre length, l, for a fibre of radius r is given by

$$l = \frac{r^{4/3}}{l_0^{1/3}} \tag{5}$$

where l_0 is a constant, given by

$$l_0 = \frac{8F_0}{3\pi E\Delta} \tag{6}$$

where F_0 is the adhesion force of the end of the fibre normal to the surface and Δ is the spacing between the fibres.

Good adhesion requires fibres of very low radius and very small Δ, that is lots of small fibres packed close together. This intuition is backed up by the work of Arzt *et al.* [**28**], which shows that there is a log linear relationship between the number of fibres (setae) per square metre and the mass of the gecko – i.e. bigger adhesion requires more, smaller fibres. Thus formulae (5) and (6) show that to create long fibres with the necessary high compliance requires very high Young's modulus materials. The workhorse material, polydimethylsiloxane (PDMS), ($E = 0.0006$ GPa) can only create fibres $\sim 1\,\mu$m long before they mat, far too short to be useful – they could not, for example, stick on a surface with a roughness greater than 1 μm. Polyimide fibres ($E = 2$ GPa) can be grown to 16 μm, somewhat more useful but still not good enough. Carbon nanotubes are the logical materials when a pure Young's modulus ($E = 1000$ GPa for single wall and $E = 500$ GPa for multi-wall tubes) is the requirement. Recent work [**29**] shows some hope in this direction, though this particular way of producing them created matted structures. It is interesting to extrapolate the formula given in reference [**28**] to support a human body mass; fibres around 25 nm radius are required, well within the capabilities of carbon nanotubes.

Geckos do not have access to very high Young's modulus materials. Instead they gain their compliance by adding a hinged portion at the end of each of the setae. This elegant solution is, unfortunately, hard to implement by standard nanoreplication techniques.

The definitive image, shown in Fig. 5, that encapsulates the hierarchy of structures is taken from reference [**30**].

There is another important element to the gecko-foot story. Adhesion is not just about pure adhesive force. It is also about resistance to concentrated stresses. With modern adhesives it is rare to get failure simply through lack of van der Waals forces. Failures tend to occur at stress points, for example when one carries out a cross-hatch tape adhesion test. All the energy is concentrated at one point. If the adhesive interface is smooth then the crack which starts to form simply propagates along the interface and all strength is lost in an instant.

Anything which relieves stress concentration adds to practical adhesive strength. The gaps between the fibres on the gecko structure are natural blocks to crack propagation.

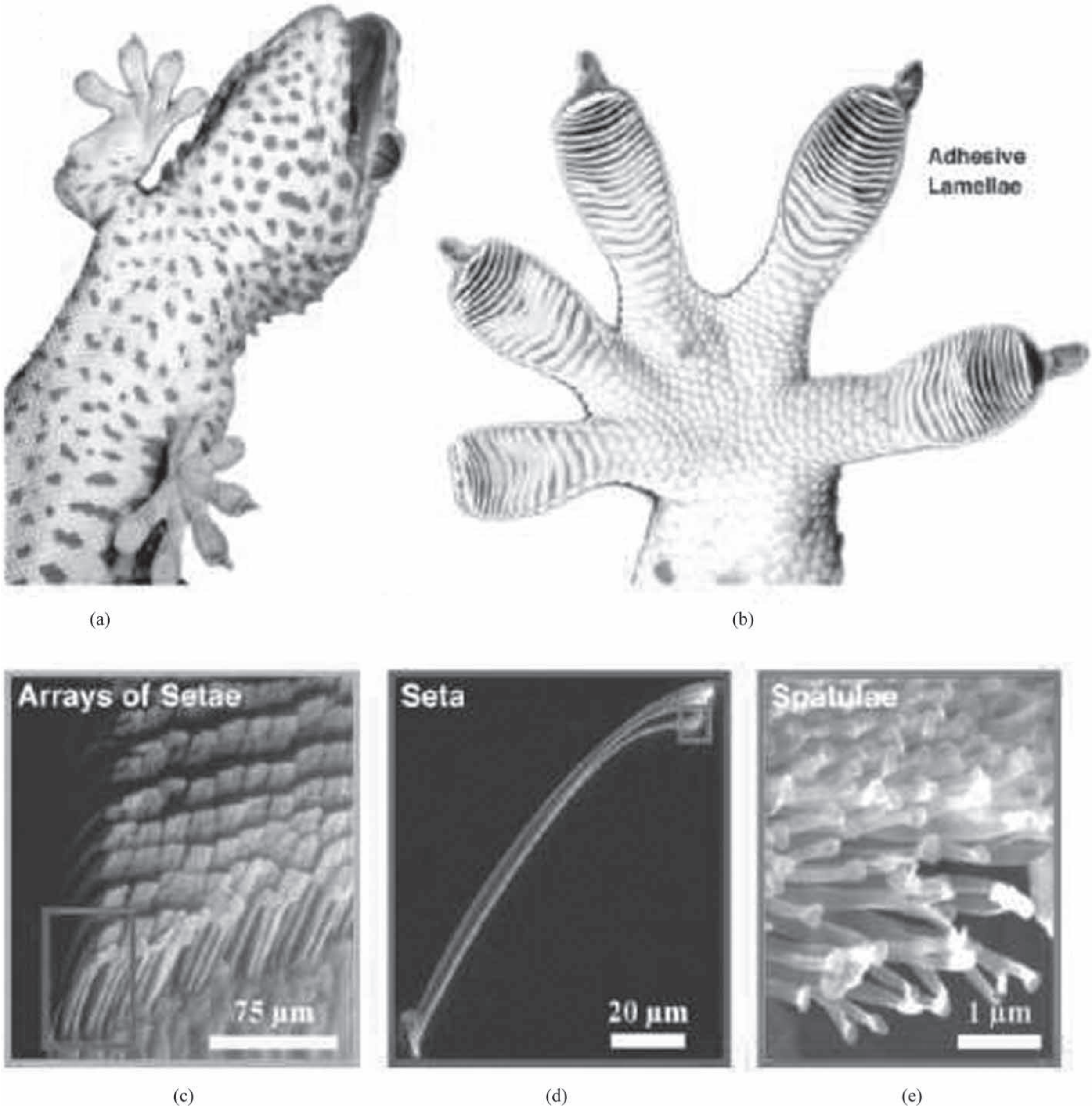

Fig. 5 The hierarchy of structures in the gecko effect. (*Image Copyright ©2005 PNAS from reference* [**30**])

Finally, it seems as though you can get an extra adhesion boost through the stretching of the individual fibres before separation. This elastic energy contribution can typically be a factor of two compared with a solid surface so although the total adhesive strength is halved by having only a 50 per cent fill factor the extra energy compensates for that reduction. This is the counterpart to the starting discussion on compressing rubbers. If you force a surface into contact then all that energy is stored in the rubber and aids release from the surface, yet another reason why plain rubbers are not suitable.

The interplay between the various effects of surface energies, compliancy, crack propagation, and elastic energy is complex. Different authors [**31–33**] tend to stress different aspects of the same story. What is clear is that the gecko has evolved a sophisticated system that provides more than enough adhesion, is resistant to sudden shocks and which, importantly, is easy for them to unstick when they walk. The problem of unsticking is one of applying concentrate forces at one part of the foot. The gecko's gait delivers these forces effectively. It looks unlikely that any simple prosthetic addition to a human body would make it easy for a human to climb a wall with the ease of a gecko – our geometry is optimised for other activities.

It is no surprise to discover two other aspects of the gecko foot. It tends to keep clean in the way the sharkskin does. And if you remove setae from a gecko's foot ('harvesting') they rapidly grow back, a self-healing ability engineers are very far from emulating.

The self-cleaning aspect is discussed in detail in reference [**30**]. It turns out that after only a few steps a gecko's foot gets clean after severe soiling. The evidence shows that the cleaning is not due to anything to do with the motion of the foot itself. Instead it is a balance of adhesion forces between the foot and the dirt and between the dirt and the substrate. By putting in plausible assumptions of number of setae in contact with a dirt particle it becomes clear that the dirt is preferentially attracted to the wall, provided the dirt particles show high local curvature as in the microspheres used in the experiments. The work provides further insights into the problem of matting. It may well be a good trade-off to reduce the surface energy of the setae. Although this decreases the adhesion to the wall it also decreases adhesion to the dirt and given that van der Waals force provides more than enough total adhesion, the gecko can sacrifice total adhesion in order to keep its feet clean.

This leads to the topic of the tree-frogs. As the frogs secrete mucus onto their feet it seemed obvious that this was some sort of aid to adhesion; perhaps this was a real Spiderman fluid. The elegant work in reference [**34**] has shown that the viscosity of the mucus is close to that of water. There is no way it provides any special adhesive force. Indeed the truth is the opposite. The distinctive pattern on a tree-frog's foot seems to serve exactly the same function as the tread on a tyre. The water gets squeezed out from the contact between foot and leaf so they make perfect van der Waals contact. The structures on the foot are the channels along which the water can flow out of the way. In one way it is comforting to know that humans invented the 'tyre tread effect' before it was discovered in tree-frogs. The tree-frogs got there first, but at least this time engineers were smart enough to discover the principle themselves rather than have to discover it in nature.

Before abandoning Spiderman entirely it is good to know that the tarantula borrows some of his techniques [**35**]. A tarantula is sufficiently heavy that it can seriously damage itself if it falls. Hence in addition to adhesion via spatulae (that is the normal gecko effect) and hooks (for clinging onto rough parts of the surface) the tarantula has a web gun in each of its feet. If it feels itself slipping it ejects some sticky web to help it stay in control.

6 MASS PRODUCTION OF SURFACE STRUCTURES

6.1 Surface replication techniques

A good technical review of various issues of surface replication can be found in reference [**36**]. Probably the best-known surface replication technique is that of hot-embossing, used in decorative and security holograms. This is done by pressing a master structure into a polymer that has been softened by heat, and takes place as a discontinuous process in a press or as a continuous roll-to-roll process. For both process the problems are the same. If the temperature of the process is far above the softening point of the polymer low pressures can be used. However, unless the replica is cooled in contact with the master it is likely that the polymer will carry on flowing and precision replication will be lost. With low temperatures much higher pressures are required, but high pressures increase the chance of damage to the master and many polymers relax after high-pressure deformation, once again losing good definition.

A related technique is that of injection moulding, in which a hot polymer is injected into a mould containing the master structure on one surface. A good example is that of CD and DVD presses. Hot polycarbonate is forced against a nickel master structure containing the digital information. Because the information on these disks is submicron it is natural to assume that injection moulding can be used for a large variety of nanostructures. The reality is that structures with high aspect-ratios (depth/width) are very difficult to produce in this way. The hot polymer is cooled very quickly by the peaks of the master structure and it can take unrealistically high mould temperatures and pressures, plus very long moulding cycles to be able to replicate these structures very accurately.

A further limitation of embossing/moulding processes is that there is a relatively limited number of thermally processable polymers so it is hard to produce such a replicated surface with all the other properties the product requires such as the correct hardness, surface energy, UV resistance, etc.

The obvious alternative is to use curable polymer systems. The system most often used in research labs is PDMS. Although PDMS is a wonderful research material it unfortunately does not stand up too well to real-world applications partly because the cure times are typically rather long. Another favourite is epoxy curing systems. Here there is a massive range of potential materials and epoxies can meet just about any requirement one might wish. However, the downside is that the curing times are often too long to be practical for large volume manufacture, which is the core interest of this review.

This leads to the method that seems to have the most long-term potential. UV curing (typically using acrylate-based resins) allows a huge range of properties in the final product. It can be done (i) on flat surfaces using precision presses, (ii) semiflat (with a flexible polymer master and a rigid substrate), and (iii) as a continuous roll-to-roll technique. However, in all three methods the challenges are the same:

- to formulate a UV lacquer which will give the required balance of properties;
- to get the UV lacquer (usually low viscosity) sandwiched between the substrate and the master, fully filling the master without air bubbles;
- to cure the lacquer quickly *in situ*;
- to get 100 per cent release of the cured structure from the master;

all of which requires a good mixture of engineering and chemistry expertise.

It is easy to show that the roll-to-roll process is highly attractive for mass production. A typical machine can operate 1 m wide at 10 m/min. It can truly make 'nanostructures by the kilometre'. For example it takes 100 min to make 1 km of motheye AR material, which consists of 250 nm peaks and troughs.

However, for the replication of very high aspect-ratio materials such as are needed for the gecko effect, discussed in section 5, there is still a major challenge for this sort of process. It is probably not too hard to fill the master structure with the liquid. Removing the cured structure from the master is going to be the hard part. For a detailed discussion on the effects of shrinkage and aspect ratio on release, see reference [**37**].

6.2 Making a master

Although implementing a replication technique is hard, it is no less hard to get hold of good master structures that can be used to replicate. The most usual technique is to create a structure in a photoresist via conventional imaging, e-beam writing, direct laser writing (including new excimer laser techniques), and interference techniques (holograms).

The pattern in the resist is then copied into (usually) nickel by an electroforming process. The process is attractive because from one nickel master made from the photoresist, a number of submasters and sub-submasters can be made so the replicator has access to multiple low-cost replication masters from a usually very expensive photoresist original. Alternatively for roll-based production the structure can be cut with a diamond tool or etched by a variety of techniques.

The skills required to make good masters are often very different from those required to make good replicas so a network of alliances of the differing skills is usually required.

7 CONCLUDING REMARKS

As the current article shows, bio-inspiration can be a great starting point. Real-world AR structures, drag reduction films, specialist self-cleaning surfaces, and novel adhesives are gradually emerging. However, it is clear that the scientific and engineering community has to work across a wide range of skills in order to transfer the basic insights offered by bio-systems into bulk manufacturable products. Although the next few years will see bio-inspired engineering solutions in wider use, it will be a much longer wait before our community can deliver the like with the added biological feature of self-repair. Now, there is a real bio-inspired challenge for the brave of heart!

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