MITCH DIAMOND/GETTY

Ivy produces one of nature's strongest adhesives; by studying the plant's attributes, researchers are developing advanced surgical glue.

SYNTHETIC COATINGS

Super surfaces

Characteristics adapted from lizards, ivy and other natural materials could help to engineer everyday objects with remarkable properties.

BY NEIL SAVAGE

For millennia, people looked at birds and wished for the gift of flight — and finally the Wright Brothers made it so. Similarly, some scientists have gazed at geckos walking up walls and wondered whether humans could do the same. Now they can. In June 2014, a 100-kilogram man wearing a heavy pack climbed up a vertical sheet of glass using only a pair of hand-held paddles made from an advanced material inspired by geckos.

The synthetic gecko skin on the paddles has plenty of company in the world of materials science. Researchers are increasingly looking towards plants and animals for ideas on how to design coatings and textures that imbue surfaces with special properties. The adhesive that ivy uses to cling to walls, for example, has inspired a material that might help damaged tissues to regenerate. Molecules taken from mussel adhesives could provide a way to target cancer cells. And the veins on nasturtium leaves have led to the development of a synthetic surface that could prevent rain from freezing on aeroplane wings or keep grimy fingerprints off smartphone screens. The trick is to take ideas sparked by nature — some of them long in development, others brand new — and make them practical and durable.

THE LIZARD'S SECRET

Biologists had long believed that the secret to geckos' residue-free, sticky feet was a series of microscopic fibres called setae. Setae, which cover the pads of the lizards' feet, were thought to increase the contact area between each foot pad and the surface it is trying to climb, thereby allowing the attraction between atoms (known as van der Waals forces) to overcome other forces, such as gravity. But researchers who tried to duplicate the effect using artificial setae were not successful.

That is because the setae are not the whole story. "These fibrils are interesting, but they're not enabling," says Al Crosby, a polymer scientist and engineer at the University of Massachusetts Amherst, who helped to develop the Geckskin that the US Defense Advanced Research Projects Agency used in its June 2014 demonstration. A piece of Geckskin measuring 10 x 10 centimetres can hold about 318 kg. Whereas other researchers had focused on surface features of the gecko's foot, Crosby and his colleagues turned their attention to underlying questions of how the foot behaved when it came into contact with a wall.

The researchers made mathematical models of the forces at play — principally the van der Waals forces created by the contact between the gecko's foot and whatever it touched, and

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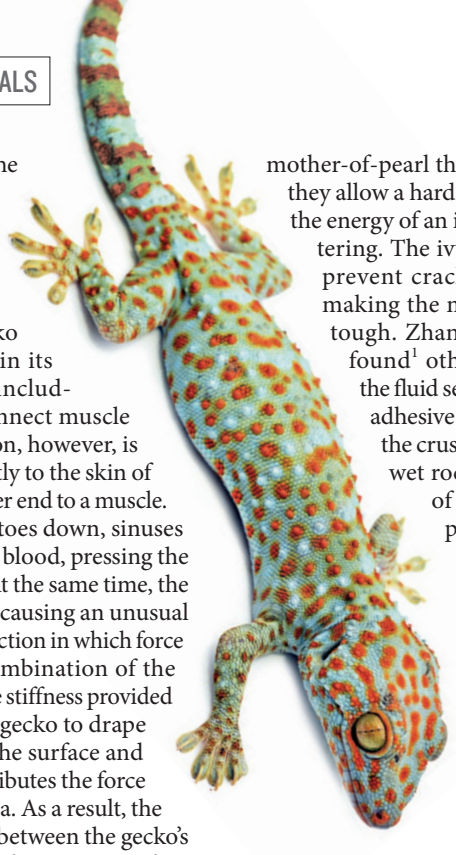
the gravitational tug on the lizard's body. The models led the team to examine how the gecko's anatomy interacted with those forces.

In particular, the gecko has an unusual tendon in its foot. In most animals, including humans, tendons connect muscle to bone. The gecko tendon, however, is attached at one end directly to the skin of its foot pad, and at the other end to a muscle. When the gecko puts its toes down, sinuses in the foot pad swell with blood, pressing the skin against the surface. At the same time, the tendon pulls on the skin, causing an unusual level of stiffness in the direction in which force is being applied. The combination of the softness of the skin and the stiffness provided by the tendon allows the gecko to drape and conform its skin to the surface and hold it in place. This distributes the force of gravity over a larger area. As a result, the van der Waals attraction between the gecko's feet and the surface it is climbing is greater than the opposing force of gravity. When the gecko wants to take a step, it curls its foot. That action releases tension on the tendon and diminishes the stiffness, letting the animal peel its foot away from the surface.

Geckskin mimics geckos' feet by using a soft, rubber-like material such as polyurethane for the pad, combined with a stiff fabric such as Kevlar or carbon fibre to provide the stiffness of the tendon. And the material forgoes the setae. "It's not a requirement that we do things exactly the way nature did," says Duncan Irschick, a biologist and Crosby's colleague in developing Geckskin. "We just sort of took inspiration from the gecko and went further."



THAWATS/THINKSTOCK

The anatomy of geckos such as the tokay (above) helps them to hold on to walls.

CLIMBERS AND CREEPERS

Unlike the gecko, ivy's adhesive seems more conventionally glue-like. Ivy produces a sticky, yellowish liquid that lets it cling to walls and which dries into a material that can withstand forces equivalent to two million times its own weight. "It's one of the strongest adhesives in nature," says Mingjun Zhang, a biomedical engineer at Ohio State University in Columbus, who hopes that he can apply what he is learning about the plant's properties to new surgical adhesives.

Zhang found that the yellow fluid was a mix of water, polysaccharides and organic particles about 70 nanometres in diameter. These tiny particles reduce the viscosity of the liquid, which helps it to spread across the surface that the ivy wants to cling to, and thus maximizes contact. The nanoparticles also form a molecular bond with the polymer in the adhesive. This renders the final product strong and elastic, not hard and brittle the way some glues become when they dry. Zhang thinks that the material uses sacrificial bonds, in which molecules break apart and rejoin; such bonds give bones and mother-of-pearl their strength because they allow a hard material to dissipate the energy of an impact without shattering. The ivy nanoparticles also prevent cracks from spreading, making the material particularly tough. Zhang has subsequently found[1] other nanoparticles in the fluid secreted by mussels, an adhesive that famously allows the crustaceans to remain on wet rocks despite the force of waves pushing and pulling them — something that is beyond the capacity of most artificial glues (see page S12). Other researchers have found similar structures in adhesives produced by starfish and barnacles.

Some scientists say that for nanoparticles to fulfil their technological promise they will need to be better understood. "It would be interesting to know more information about specific amino acids and protein structures as well as the underlying adhesion mechanism," says Chao Zhong, a professor of bio-inspired engineering at ShanghaiTech University in China. Phillip Messersmith, a materials scientist and bioengineer at the University of California, Berkeley, stresses that the research is still at an early stage and the results are inconclusive. "I do not think I have seen convincing evidence that the nanoparticles within the ivy adhesive are responsible for adhesion," he says.

But if they are, the combination of toughness, adhesion and biologically based components would make ivy nanoparticles attractive for a variety of uses, says Zhang, who is trying to develop ways to repair damaged tissues using ivy adhesive. In theory, a bandage made with ivy adhesive could provide an environment that would encourage new cells to grow, allowing an organ such as the heart to heal itself. It might also be seeded with stem cells to help the process along. In tests in a Petri dish, Zhang has shown that the adhesive helps cells to grow and attach to a surface. "It's not a simple mechanical bond," he says. "It's a biomaterial to help create a biological environment for wound healing." Zhang is starting animal studies on this application, although he says that it may be quite some time before it is ready for use in humans.

A different kind of coating based on ivy nanoparticles might be ready sooner. Zhang proposes using them in sunscreen, replacing the titanium oxide or zinc oxide now used. Zhang has found that the sizes of the ivy nanoparticles do not vary as much as the sizes of their metal counterparts, which means that they scatter light more uniformly. So a liquid laced with ivy nanoparticles would appear clearer than conventional sunscreens, and block a wider range of ultraviolet wavelengths[2]. Zhang is also trying to take what he has learned about ivy's mechanisms and apply it to other materials. He is synthesizing nanoparticles with different chemical compositions and trying them in different polymer matrices. That should lead to a variety of adhesives for different situations, he says; perhaps one would be very strong, whereas another would be more elastic. "I'm trying to go beyond what nature does."

Many other researchers are also taking inspiration from nature and pushing it in new directions. Messersmith studies mussel adhesive, which is ideal for securing objects underwater. But he hopes to use engineered versions of mussel adhesive in different environments, possibly even in a space probe. "If you were to simply mimic a natural material, you would get something that would work and perform well only under the conditions in which that natural material has evolved," says Messersmith. "Nature never evolved materials to have to survive interplanetary travel."

Messersmith has focused on a key component of mussel adhesives: the amino acid L-3,4-dihydroxyphenylalanine (DOPA). It turns out that DOPA makes a useful coating that helps attachments — such as antibodies — to stick to the surface. "In paint terminology, it's essentially a primer," he says. Messersmith's proprietary DOPA coating method involves dissolving DOPA in water, making sure the solution has the same acidity as the ocean, and then immersing the object to be coated. Advanced Hydro of Austin, Texas, licenses Messersmith's coating technique to make filters for wastewater treatment and desalination plants. Advanced Hydro coats its filters with DOPA, then attaches molecules of polyethylene glycol to make the filters resistant to fouling, improving their efficiency and reducing maintenance costs.

At the Materials Research Society's meeting in December 2014 in Boston, Massachusetts, Messersmith described the latest application of the technique. He put a coating of polydopamine, a molecular cousin of DOPA, on gold nanorods, which allowed him to add an antibody that targets cancer cells. The antibodies carry the nanorods to the cancer. The rods would then be heated with near-infrared light, killing the tumour. He reported using the method to kill cancer cells in a culture.

"We just sort of took inspiration from the gecko and went further."

Messersmith is looking beyond DOPA to sticky chemicals known as polyphenols, found in cacao, green tea and red wine[3]. Such compounds have similar chemical properties to DOPA and can be more cheaply extracted, he says. "These molecules, because they're found in tissue, have biological properties one could exploit in the

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BOTH IMAGES: POWER AND SYRED/SPL

form of a coating," he explains. Specifically, he adds, their antioxidant and antibacterial properties would make such coatings useful for medical instruments or food-preparation surfaces.

DROP ZONE

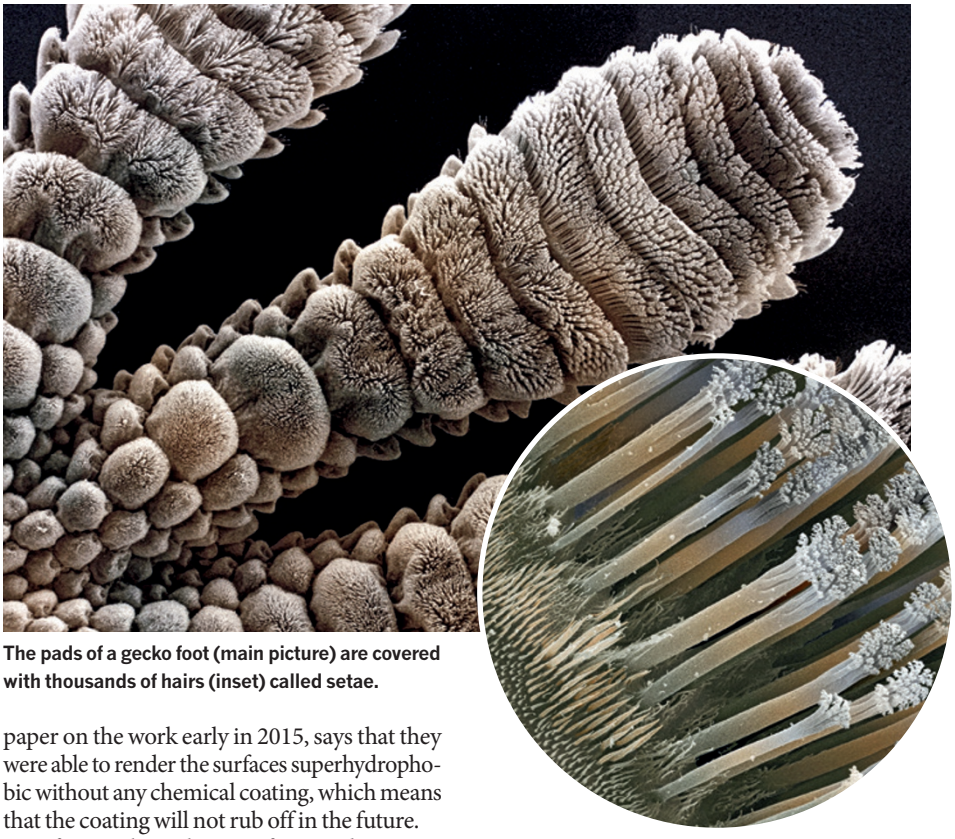
Although getting things to stick to surfaces is useful, there is also value in making surfaces more slippery — for instance to keep them clean or dry or to reduce drag. Mechanical engineer Kripa Varanasi develops nano-engineered surfaces to be hydrophobic so that water runs off. Varanasi found inspiration in a nasturtium plant in his office at the Massachusetts Institute of Technology in Cambridge. "I was one day struck by the fact that the veins were on the top of the leaf, not the bottom," he says.

Until then, plant scientists thought that nature's most water-repellent — also called superhydrophobic — surface belonged to the lotus leaf. Lotus leaves are coated with wax, which chemically repels the water. The wax is arranged in microscopic bumps; the roughness means that there is less contact between the water and the leaf, so a droplet stays rounder and rolls off more easily. Such a surface is also self-cleaning, because the water carries away contaminants; this makes the lotus effect popular among researchers developing surfaces that need to resist moisture or bacterial build-up. But Varanasi wondered whether the nasturtium had veins on the top of its leaves to do the same job as the lotus leaf's waxy bumps.

Varanasi had a reason for studying his office plant. He wanted to see whether he could increase the speed at which water bounces off a surface — specifically, he wanted it to bounce off so quickly that it would not have time to freeze on a plane's wing or to start the process of rusting a metal part. Reduced contact time could also decrease drag for wind turbines in the rain, making them more efficient. Normally when a drop hits a superhydrophobic surface, it briefly flattens out, then recoils into a ball shape and bounces off. On a surface using the lotus effect, Varanasi measured the recoil time at 12.4 microseconds. Then he took pieces of aluminium and milled thin ridges into them, 100 micrometres (μm) high and 200 μm wide, to mimic the nasturtium's veins. Drops that hit the ridges broke into smaller bits, and recoiled in 7.8 microseconds. Those few microseconds can mean the difference between freezing and not[4].

Varanasi guesses that plants may have evolved superhydrophobic properties because droplets that bounce away quickly have less opportunity to deposit bacteria or viruses. He says that butterflies, which need to resist the effects of rain, have even more complicated vein structures on their wings, and he is exploring those to see what effects he can mimic.

Two laser specialists at the University of Rochester in New York have used a laser to mill ridges into pieces of brass, platinum and titanium, and got a similar bouncing effect. Chunlei Guo, one of the physicists who published a paper on the work early in 2015, says that they were able to render the surfaces superhydrophobic without any chemical coating, which means that the coating will not rub off in the future.



The pads of a gecko foot (main picture) are covered with thousands of hairs (inset) called setae.

In fact, making these surfaces and coatings strong enough to stand up to the wear and tear of use is a challenge for scientists trying to take their ideas out of the laboratory and into manufacturing. "We have to find a way to make this material robust," says Ajay Malshe, a professor of materials and manufacturing processes at the University of Arkansas in Fayetteville. "In biology there's always a constant self-healing process going on, whereas we don't have that" in materials engineered for oil pipelines or plane wings.

Water-repellent surfaces are one challenge for researchers, but surfaces that repel oil (superoleophobic), which would be valuable in arenas from energy to consumer electronics, are even harder to realize, says Bharat Bhushan, a mechanical engineer whose laboratory at Ohio State University analyses the microscopic structures on the surfaces of living things. Because oil has a lower surface tension than water, it is more prone to spreading across a surface, so applying a repellent lotus-like effect requires different chemistries and surface structures. Bhushan makes a surface superoleophobic by covering it with a series of tiny pillars, 14 μm in diameter and 30 μm tall, and coating the surface with a fluorine compound (such compounds are well known for their anti-stick properties; Teflon is a prime example). The set-up traps air pockets beneath any oil near the surface, so the oil cannot stick. Bhushan says that Sony, which makes touch screens for mobile phones, has enquired about using the technique to prevent smudging on its screens. Treating the inside of an oil pipeline in this way could let oil flow more smoothly, reducing the need for higher pressures that push the oil along but can promote leaks.

Bhushan is also tackling the problem of biofouling[5], where bacteria and other organisms form hard-to-remove colonies on a surface. The US Navy estimates that it spends US$56 million a year dealing with biofouling, from cleaning hulls to the extra fuel used to counteract drag. Bhushan covers a surface with pillars of different heights and spacings. Because of the spacing, an individual bacterium is either isolated on top of the pillars or falls into the gaps between, and is unable to link up with its fellows to form a film. "If you have a structured surface, bacteria cannot spread very easily," Bhushan says.

Evolution has produced an endless variety of materials and techniques that might be exploited, so there is no danger of running out of ideas. When faced with an engineering puzzle, Varanasi says he always starts by asking a simple question: "In that situation, what would an insect or what would some other kind of living thing do?" ■

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