

MATERIALS SCIENCE

Biology Reveals New Ways To Hold on Tight

Researchers are figuring out the chemistry behind natural adhesives—useful data for developing synthetic glues

Sticking can be nature's way of moving as well as of staying put. The comic-book character Spiderman gets his inspiration from the spider that effortlessly dashes up walls and across ceilings. Contrast this arachnid's lifestyle with that of many mollusks, which put down adhesive roots that withstand the roughest surf. Even blood cells alternately stick and roll as they navigate their way through the human circulatory system.

At an unusual recent meeting,* biologists and materials scientists swapped notes about how natural and artificial adhesives work. The materials scientists discussed physical or chemical properties that biologists should consider as they try to figure out how nature performs its sticky tricks. The biologists described how various organisms—from octopi to limpets—stay put. By bringing the two disciplines together, the Defense Advanced Research Projects Agency, which funded the symposium, hoped to stimulate insights that might one day lead to more effective adhesives.

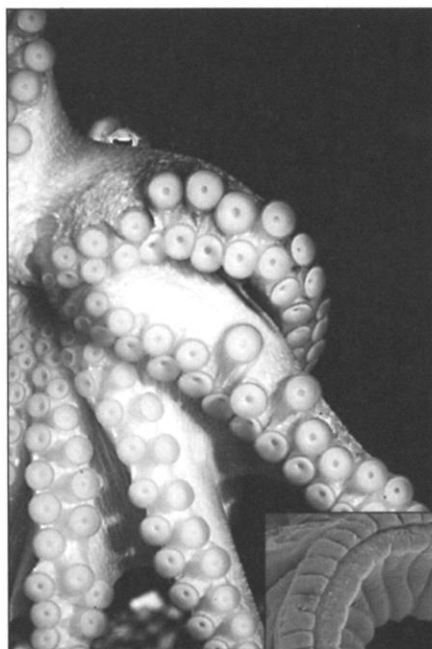
If materials scientists can indeed take their cues from nature, the payoffs could be numerous: Think better suction cups, non-toxic and quick-acting marine adhesives, strong but temporary glues, extraterrestrial rovers—even new drug-delivery systems that stick to the target cell. But designing adhesives based on nature's own glues will be tough, says Anand Jagota, a materials scientist at DuPont in Wilmington, Delaware. "The art is to find the one critical thing that you need to mimic."

Microscopic handholds

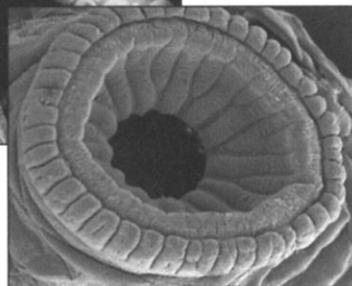
Although nature has a multitude of ways to ensure that organisms get a solid foothold, they share some common elements. "Over many different scales—from cells to geckos to mussels—the mechanisms [of adhesion] have great similarity," noted Dan Hammer, a bioengineer at the University of Pennsylvania in Philadelphia. For example, several very different species employ tiny extensions—variously called fibrils, denticles, pili, or setae—on their stick-to-it sur-

faces. These so-called microstructures result in better-than-average adhesion and attachment by providing a slightly rough surface, says Jagota.

Take the octopus. New research is rewriting the book on this animal's incredible maneuverability, which depends in large part on rows of muscular suckers along its arms and tentacles. Biologist William Kier of the University of North Carolina, Chapel



Tight seals. Electron micrograph (right) reveals the complex sucker structure that enables the octopus (top) to be so agile.



Hill, recently found that there's more to the story. Octopus suckers' tiny projections called denticles are 3-micrometer-diameter pegs that provide more intimate contact with the surface underneath. With these denticles, the suckers "can grip a remarkable range of objects, including objects smaller than the suckers [themselves]," Kier said.

Suction cup manufacturers should take note, suggests Kellar Autumn, one of the symposium organizers and a biologist at Lewis and Clark College in Portland, Oregon. "We have suction cups all over, and not

a single one has anything but a flat surface." Adding microstructures would be "a revolution" for these devices, he said.

Gecko history is also under revision—again, with potential practical applications. For years, researchers suspected that the gecko's sticking power came from friction between its toes and the surface. But 2 years ago, engineers developed the technology to actually measure the microscale forces behind gecko attachment—and they, Robert Full, an integrative biologist at the University of California, Berkeley, and Autumn found that the attachment force exceeded the frictional forces by a factor of 600. At about the same time, Full's team determined that the pads of these acrobatic creatures contained thousands of branching hairs that create a tremendous surface area (*Science*, 9 June 2000, p. 1717).

Autumn and Full suspected that when these split ends get close enough to a surface, each generates a weak intermolecular force, called a van der Waals force; they add up to guarantee a secure foothold. At the meeting, Autumn reported that they had demonstrated that is indeed the case.

Anthony Russell, a functional morphologist at the University of Calgary, Alberta, wants to find out how geckos attach and release their toes so incredibly quickly. To do so, he is comparing footpads and setae structure on as many of the dozens of species of geckos as he can. "He's giving us the principles by which you can build the [artificial gecko pad]," says Full, who already has a prototype in his lab. One day, he speculates, the pad might be used to design rovers that can move more easily across the rough terrains of other planets.

Molecular stick and go

Hammer is probing a system far removed from planetary explorers: white blood cells. Typically, white blood cells roll their way through the bloodstream, yet they are able to anchor themselves where they are needed to defend against foreign in-

vaders, heal wounds, or form blood clots. Hammer hopes that if he can devise materials that mimic that roll-and-stick ability, he'll be able to devise a new targeted drug-delivery system.

Like gecko feet and octopus suckers, white blood cells also gain their acrobatic and adhesive abilities through projections—in this case, surface proteins called selectins that stick out of the cell surface. The white cells use these selectins to grab onto the inner surface of the blood vessel; as the current of blood pushes against the cell, its

* The Society for Integrative and Comparative Biology annual meeting, Anaheim, California, 2–6 January.

rear bonds release and it tumbles forward, establishing new links, thereby cartwheeling down the vessel.

This rolling requires “dynamic regulation of binding and unbinding between molecules in fluid [and the surface],” Hammer explains. “The fluid is pushing the cell along; bonds are forming in front and breaking in the back.”

Hammer and his colleagues have coated microscopic beads with various selectins and followed their start-and-stop tumbling in an artificial blood vessel. Just a slight difference in the starchy components of the selectins “can have large effects on the dynamics of rolling,” he reported. “These cells make protein backbones [selectins] and with great precision modify them to get the adhesion that they want,” giving them “remarkable” control over how fast they move and where they attach.

As a first step toward harnessing this transport system, Hammer and his colleagues have switched to porous, biodegradable beads that one day can be filled with drugs. By changing the starchy components of the selectin coat, he hopes to control exactly where the sphere docks in the body—for instance, delivering an anti-inflammatory medicine to sites undergoing inflammatory responses.

Nature's glues

Whereas some creatures rely on projections to stay put, others secrete glue, either permanent or temporary. New studies are showing how each adhesive's properties depend in part on modifications of proteins that make up their constituents. “When and how these transformations occur and to what degree is quintessentially linked to the organism's life history and what it needs to adhere [to],” explains Herbert Waite, a marine biochemist at the University of California, Santa Barbara.

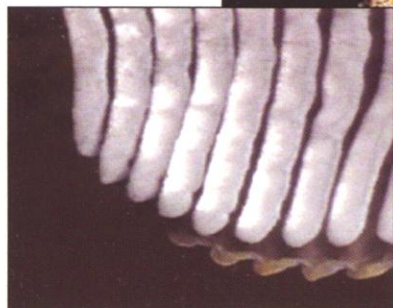
For example, Andrew Smith, a biologist at Ithaca College in New York, is learning how limpets make glue strong enough to keep them from being washed away at high tide but temporary enough to let the limpet resume its foraging when the tide recedes. By studying several limpet species, he has found that the animals secrete mucus that is full of short proteins, with a small percentage of carbohydrates. The critical factor appears to be an activating protein that prompts the carbohydrates and proteins to intertwine.

What's surprising, he reported, is that

this oozing goo traps moisture in its network of proteins. Smith had expected that the opposite would happen, as most glues harden only after expelling any water they contain. But for the limpet, water accounts for 90% of its adhesive.



Touch and go. Rows of tiny hairs called setae (left) use van der Waals forces to help the gecko (top) scoot up walls and along ceilings.



Smith has been tinkering with the natural chemical mix to create his own glue. Success, he has found, depends on the lengths of the protein polymers, the degree to which they branch, and the mix of protein and carbohydrate. At this point the stickiness of his concoctions is “not impressive compared to what limpets do,” he reported. Smith is surveying the makeup of these glues in a variety of other snails for tips about what works best.

Waite has been probing the secrets of a different mollusk, one that glues itself permanently to a rock. Mussels extrude thin threads to attach themselves to rocks. “The biochemistry of [their] adhesion is still in-

complete,” says Waite, yet he's fairly certain that mussel glue works something like epoxy, a two-part glue created by mixing hardener and resin together. Mussel threads have two isolated compartments, one containing resinlike proteins that have a lot of reactive branches and the other full of chemicals, including enzymatic factors, that act as the hardeners. As the thread exits the mussel, the hardening chemicals mix with the proteins; this glue takes a mere 5 minutes to set. Mussel glue, Smith points out, works quite differently from limpet glue. “You wouldn't put epoxy glue on your feet if you wanted to keep moving about,” he explains.

Some of these insights from mussels have already been put to use, Waite adds. One automaker now treats the raw steel auto body with mussel-inspired compounds that make paint stick better. Waite predicts a variety of applications, because “sticking opportunistically to all kinds of surfaces underwater is a useful capability for dentistry, surgery, and the manufacture of things that have regular contact with moisture, such as roads and the exteriors of cars, houses, and ships.”

The sea cucumber, a relative of the starfish, produces a distinctly different type of thread. A few species of this cylindrical invertebrate protect themselves from predators by ejecting, in a matter of seconds, fine, sticky threads that entangle an attacker and enable the sea cucumber to sneak away. Before they are ejected, the threads, which consist of an outer and an inner layer of cells, are quite short and not sticky at all, says Patrick Flammang, a marine biologist at the University of Mons, Belgium. But as the cucumber ejects them, the emerging threads shed their outer cell layer, enabling the inner cell layer to spring open and elongate. At the same time, the inner cells secrete granules of insoluble proteins that stick together and adhere to whatever they come in contact

with in the water, he explains. Such quick-acting, underwater glues are tempting alternatives to existing marine adhesives, which tend to take longer to cure, says Flammang.

Autumn expects that nature holds many more adhesion secrets that can be put to work. “Biodiversity is a library of engineering applications,” says Autumn, “and while we don't yet have the right model for designing the best adhesive, it's out there.”

—ELIZABETH PENNISI



Sticky defense. Sea cucumbers eject sticky threads that entrap predators, enabling the sea cucumber a leisurely escape.