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Unbreakable: the tough secrets of nature's glue

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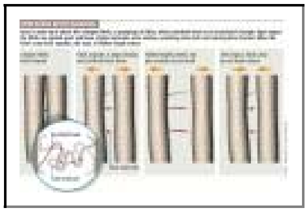

Enlarge
How bones resist breaking

When Paul Hansma looks at a zoomed-in image of a human bone, he sees nature's toughness - and its frugality. The close-up reveals bits of collagen and tiny mineral particles coated with glue, as well as lots of dark, empty spaces. In this arrangement, the biophysicist at the University of California, Santa Barbara, recognises what could be a key to creating the toughest synthetic material in the world.

The rigid parts of our bones are made up of a mixture of cells, mineral plates and collagen. It is not just these building blocks that make bones so resilient; at a molecular level it is the links, and the spaces, between them. Recently, Hansma and his team have discovered that glue is a vital feature of bones and other biomaterials, one that not only makes them able to withstand impacts without breaking, but can also repair itself. They are looking into what makes this glue so effective, in part to develop a new generation of ultra-strong, lightweight, self-healing materials.

Sure, nanomaterials and "biomimetics" have been all the rage for years, and progress has been made in everything from polymer design to artificial muscles. Now lessons are emerging about the molecular mechanisms behind toughness and self-repair, which could lead to new high-performance equipment, vehicles and even radical space hardware ranging from inflatable moon habitats to space-elevator cables.

Mimicking nature's toughness in the lab requires a major shift from traditional materials science. Engineers tend to build composite materials, like those used to make aircraft and wind turbines, where strong elements such as glass or carbon fibres make up 60 to 70 per cent of the content. Some type of resin usually fills the remaining space, acting as glue to bind the strong elements together.

State-of-the-art nanocomposites include even more filler to bolster strong elements such as ultra-thin graphene sheets or their cylindrical cousins, carbon nanotubes.

"But see, nature doesn't do that at all," Hansma says, pointing out the dark spots in his bone image. "Nature isn't afraid of voids." When all the space in a material is filled, he says, it is likely to be brittle rather than something that can take a beating.

Hansma and his colleagues started out by looking at the shiny, mother-of-pearl material in abalone shells, whose mechanical properties have been studied since at least the 1970s. Extremely thin, layered plates of calcium carbonate make up a whopping 97 per cent of the shell, with the rest consisting of organic material including adhesive protein molecules. Calcium carbonate is rather brittle on its own, yet the composite is some 3000 times more fracture-resistant than single crystals of the mineral. Why? Hansma's team reasoned that in addition to the complex layering structure of the plates, the small amount of glue - less than 3 per cent by weight - must contribute to the shells' incredible toughness.

They discovered the secret to how the glue works by building on work done in 1997 by Hermann Gaub of Ludwig-Maximilians University in Munich, Germany, and his colleagues (*Science*, vol 276, p 1109). Gaub's team showed that it was possible to use the tip of an atomic force microscope to pull and prod single protein molecules and measure their toughness by seeing how much force it took to stretch them to breaking point. They found that the force increased and then decreased, only to surge up again and then drop off with further extension of the protein.

In 1999, Hansma's group tailored the method to study networks of glue molecules in abalone shells, and clarified the mechanism behind the seemingly erratic force measurements (*Nature*, vol 399, p 761).

Hansma explains it using a long rubber tube with Velcro squares attached at points along its length. The tube represents a glue molecule's protein backbone. Hansma jostles it, jumbling and coiling up the middle portion. Then he sticks the Velcro pairs together, creating a shorter overall tube interrupted by loops of "hidden length". The Velcro represents a weak chemical bond, such as a hydrogen bond. When he tugs on the tube's ends - simulating tension in the glue - the energy breaks one of the Velcro bonds, and a loop of tubing unfurls. "These bonds sacrifice themselves for the sake of the backbone of the polymer," he says. "They break at a force that's only about a third of the force necessary to break the backbone of the polymer."

He repeats the process, breaking more "sacrificial bonds" and releasing further hidden lengths, showing how the glue molecule dissipates energy that might otherwise snap the backbone (see Diagram). Once the stretching force is removed, and as long as the backbone has not been stretched to the breaking point, its elasticity will make it bunch up again and enable bonds to reform, thereby repairing itself. To illustrate this, Hansma crumples up the tubing; when he pulls the strand back out, new Velcro connections have formed.

These principles don't just apply to bones and shells; Hansma has seen similar glue characteristics in other biomaterials such as single-celled micro-algae and spider silk (see Photo). In biologist Herbert Waite's lab across the Santa Barbara campus, the researchers have also studied the sandcastle worm, an intertidal creature that constructs a tubelike home for itself by gluing together tiny chunks of sand and shells. The tubes are tough, Waite's group found, thanks to the type of concrete the worms use. High-resolution microscope images show that their handiwork relies on sparing dabs of glue dotted carefully between the hard elements (*The Journal of Experimental Biology*, vol 210, p 1481).

So how do we harness these ideas to build better materials? Hansma has begun discussing applications with Rod Ruoff, a nanomaterials specialist at Northwestern University in Evanston, Illinois. Ruoff says he is intrigued by these "tantalising hints" that nature does the opposite to what engineers do when constructing composite materials. "Nature uses just a small amount of glue to allow the mechanical load to be distributed to these very stiff and strong elements," he says.

Nanotube glue

Earlier this year, the researchers published a description of natural adhesives and summarised how they might contribute to the construction of synthetic materials (*Nanotechnology*, vol 18, p 044026). Such glues would bind strong elements together, they say, while taking up just a few per cent of the weight of the material; they would break and dissipate energy to protect the strong elements of the material from snapping; and they would reform, or heal themselves, once they were no longer being stressed.

Hansma and Ruoff think these guidelines might make it possible to build composite materials with the enormous strength of individual nanostructures, such as nanotubes. Nanocomposites might be made tougher, for instance, by dramatically increasing the percentage of nanostructures included, and by optimising the glue binding them together. "There is, to some degree, a sentiment or even a belief on the part of materials scientists that for large structures you cannot reach the ultimate strength of the much smaller components that make up the structure," Ruoff says. "What we're suggesting is the possibility that it doesn't have to be that way."

Leonard Yowell, a specialist in nanomaterials at NASA's Johnson Space Center in Houston, Texas, calls the approach "very promising" for producing enhanced materials, but cautions that "a good deal of work must be done before such materials could become reality". Yowell points out that in the late 1990s, researchers tried to increase the percentage of carbon nanotubes in composites. As the percentage of nanostructures increased, however, so did the viscosity of the material, making the mixing process difficult and inconsistent.

To make a material tough on the macro scale means putting the nanostructures together in an optimal way, says Markus Buehler, a materials scientist at the Massachusetts Institute of Technology. Last year, Buehler showed that such a construction is at work in collagen: the particular arrangement of molecules into larger structures called fibrils, and fibrils into larger fibres, enables collagen to be both strong and resistant to snapping when stressed from the smallest to the largest scale (*Proceedings of the National Academy of Sciences*, vol 103, p 12285). "Nature takes advantage of each molecule," he says. "Implementing features at different scales is the next step in creating new biomimetic structures."

Ruoff envisions a cable built in such a hierarchical manner - by packing nanostructures such as graphene sheets closely together with the right kind of molecular glue at just the right points, thereby forming larger and larger structures. He says the team is beginning to believe that such large structures might actually retain the remarkable mechanical performance of the nanostructures. He notes that carbon nanotubes grow naturally as bundles and that it may be possible to wedge them apart to insert the optimised glue between them.

So the hunt is on for exactly the right kind of adhesive. "We need perhaps still further inspiration from nature and also likely from high-quality modelling," Ruoff says. "Then there is the approach of going into the lab and trying several different types." Still, the method seems to require flawless nanostructures, which as yet don't exist. Nor have Hansma and Ruoff yet attempted to define the types of bonds and interactions that would optimise the glue.

While Hansma is intrigued by the prospect of building an inflatable lunar base that could stand up to radiation, rocks and moondust, he insists it's still too early to talk about applications. "We're more at the stage of being able to understand a basic principle," he says. "It will require a lot of further research for people to be able to translate our discovery, together with a lot of other discoveries, into the materials of the future."

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Mussel bound

You'd be surprised what you can learn from a mollusc. The intertidal habitat of the lowly mussel is extreme, so it has evolved a remarkable structure, called a byssus, which allows it to stick to rocks despite being buffeted by strong currents and crashing waves.

Biologist Herbert Waite and his colleagues at the University of California, Santa Barbara, have found that it works by using chemical gradients. The byssal threads that keep a mussel anchored to a hard place are stiff at their attaching point for stability, and elastic closer to the animal to protect its soft parts. The protein composition gradually changes over the length of the byssal threads. That way the majority of energy from incoming waves gets dissipated along the structure, as in a shock absorber, and the mussel doesn't get swept out to sea. "Nature works with gradients," Waite says, "but these have been examined in very few systems so far."

Andrew Ruys of the University of Sydney in Australia is leading an effort to put gradients to work in synthetic materials. He has developed a process for building graded heat-shield tiles for hypersonic space planes currently under development. These tiles will have an interior metal surface that is malleable but strong, and a ceramic outer surface that resists burning but is brittle. Such tiles could help space vehicles withstand re-entry temperatures above 2000 °C.