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The strong yet flexible shell of the armadillo is helping biomedical scientists to devise super-materials.

STRUCTURE

Artificial armour

Researchers are borrowing tricks from armadillo shells and mother-of-pearl to create replacements for human bone and to develop a new generation of protective clothing.

BY KATHARINE SANDERSON

Would you put such trust in your bones to hold you up and move you around if you knew they were made from jelly and chalk? Hydroxyapatite is the inorganic, mineral component — a brittle, white, calcium-based, chalky material. Collagen, the organic, carbon-based part of bone, "is very similar to gelatine", says André Studart, a materials scientist at the Swiss Federal Institute of Technology in Zürich.

Yet from these weak raw materials, nature produces a strong, flexible, self-healing structure. Living cells guide the growth of a complex, rigid frame that houses blood vessels and supports the entire body. Trying to better understand this complex structure and how it works has kept teams of scientists busy for many years. And bone is not the only natural structure worth investigating. Nacre, also known as mother-of-pearl, is extraordinarily fracture-resistant. Dentin in the teeth is similar to bone, and is comprised mostly of calcium minerals, water and organics in an intricate structure that, beneath the enamel layer, is strong enough to worry steak or crack nutshells. Armour plates seen on fish and armadillos are models of materials that are flexible, puncture-proof and water-resistant. Research reported in February 2015 suggests that limpets' teeth, endowed with nanometre-scale fibres intertwined with minerals, may be the strongest material that nature has crafted[1].

The hope: if scientists could learn some of the tricks used to make these types of materials, perhaps people, too, could make self-healing, super-strong items from cheap and abundant ingredients, or biological implants that work as well as the body parts they want to replace. Humans, of course, need not be limited to particular substances found in living things. Perhaps the tricks nature has perfected over millions of years might be applied to graphene, Kevlar, titanium or glass, to create even more advanced materials.

Researchers are making steady progress towards recreating what has been honed over thousands of years of evolution. It is now possible to make artificial nacre, although a fully synthetic bone replacement is still a distant goal. Borrowing tricks from bone has enabled the manufacture of shatterproof glass, however. Materials scientists are working with the military to develop armour based on some of the principles that fish use to protect themselves. But evolution has had one luxury that humans lack: "Nature doesn't have the time restraints we have," says materials scientist Eduardo Saiz from Imperial College London.

TWISTED TALES

The first part of the challenge is to understand how these materials are built. Bone, nacre and other tough, natural materials have complex structures at the atomic and molecular level, at the nanometre scale, which in turn influences their micrometre-scale structure — and so on up to a whole shin bone or left molar. Working out what all these intricacies are at each scale requires a wide range of state-of-the art techniques, including atomic force microscopy, X-ray analysis and tomography (which looks at materials slice by slice) says Christine Ortiz, a materials scientist from Massachusetts Institute of Technology in Cambridge. She hopes to borrow tricks from these materials — but that will only be possible by properly understanding them at each level of the structural hierarchy.

In bone, this hierarchy is well understood. It begins with long molecules of collagen: three chains twist into nanometre-sized helices, which then come together to form fibrils about one millimetre thick. The fibrils weave together to make filaments that are around ten times as thick, leaving just enough room for the hydroxyapatite to fill the holes, adding stiffness. The thicker filaments organize into a flat, foil-like structure and roll up to form tubes, called osteons, that allow blood vessels to run through bone's interior. Many osteons together make a fully formed piece of bone.

The cells alter the chemistry around the collagen fibres to dictate what kind of structure, or what level of mineralization, occurs at each site. Studart's aim is to mimic this level of intricacy, but that is a long way off. "We're far from being able to reach the organization of building blocks we have in nature," he says. "We lack a deep understanding of what the cell really does."

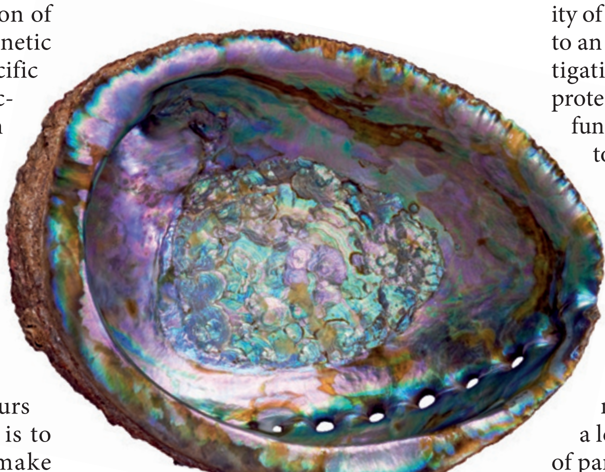
Nevertheless, researchers are starting to borrow ideas from this hierarchical complexity to try and create their own super-materials. Studart, for one, is seeking other ways to control how materials organize themselves, in a crude version of what happens in bone. "I take the engineering approach," he says — which in his case, has led to magnets. He and his team add small amounts of strongly magnetic nano-sized particles to composite materials made from tiny flakes and rods of alumina, polyurethane and other polymers with varying elastic properties, all of which are swimming in a solvent. Application of a weak magnetic field causes the magnetic nanoparticles to drag the fibres in specific directions to create an organized structure — much like collagen fibrils in bone. Once the flakes and rods are in position, they can be frozen in place by evaporating the solvent. Studart has used this method to make composite materials that are tough and durable and have some memory of their shape when deformed.

But the alignment of molecules to provide a material with stability is only one small part of what occurs in the natural world. Another trick is to use the same building blocks to make materials with different physical properties. Think of tendons attached to a bone: many of the same starting materials, particularly collagen, combine in different quantities and with different structures to have opposite functions in a joint. At the bone end, they are calcified and very hard. At the tendon end, the collagen is much less calcified, and forms soft, flexible tissue. Studart is trying to work out how to make materials with a compositional gradient in the laboratory[2] and has made onewith elasticity that varies by five orders of magnitude. That is a large improvement on natural bone–tendon connections, where the elasticity spans a mere two orders of magnitude. In nature, the range in physical properties alters depending on how much hydroxyapatite reinforces collagen fibrils. Studart, similarly, gets his wide range of elasticity by reinforcing polyurethane with differently sized particles of tougher aluminium oxide or a synthetic clay.

It will be a while before artificial materials replace worn out vertebrae or tendons. Capturing the intricacies of bone and nacre in one step is "very complicated", says Saiz. He pins some hope on the advent of three-dimensional (3D) printing, which can, in theory, print any structure when supplied with a range of materials. But he notes that machines capable of printing structures with nanometre-scale features are not currently available.

SMALL DETAILS MATTER

The nanoscale structure of bone, nacre and teeth consists of flake-like mineral pieces, arranged like bricks in a wall, with the organic component making up the mortar. In nature, specialized proteins inside bone cells are responsible for getting the mineral molecules to form in the right places in that wall-like pattern — a process called biomineralization. This bottom-up way of building is difficult to recreate in the lab, says François Barthelat, a materials engineer from McGill University in Montreal, Canada, not only because of the physical challenge of manipulating nanoscale bricks, but also because the nature of the forces on the surface of the materials radically changes at such a small scale.



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The microstructure of nacre has inspired researchers to develop low-cost, strong materials.

Some materials scientists, including Saiz, think that to make a synthetic mimic of bone it is essential to recreate all the features at each level in the structural hierarchy: nano, micro and macro. But others believe it might be possible to skip the tiniest level of the hierarchy. "You don't have to work at the nanoscale to get good properties," says Barthelat. Instead of building up a wall nanobrick-by-nanobrick, Barthelet approached the problem from another angle. His team etched into glass a 3D brick wall pattern similar to that in bone, but with the bricks about 200 micrometres wide rather than nanometres[3]. The team used a laser that could penetrate the glass and etch not only on the surface, but inside the glass sheet as well. Even these micrometre patterns have an effect. "It totally changes the way the material works," Barthelat says of this bio-inspired technique. The resulting glass was 200 times tougher than non-etched glass, and could even be bent out of shape. The reason, Barthelet says, is that patterns etched into the glass are conduits for the destructive energy carried in a propagating crack, and give that energy a route of escape out of the material without shattering it. He hopes that using his approach, artificial materials such as glass or ceramics could be made tougher or more durable than they currently are, and perhaps even superior to natural materials.

"We're far from being able to reach the organization of building blocks we have in nature."

FISH OUT OF WATER

To truly make the most of these super-strong natural materials means mimicking not only their structures, but also the way they are used. Take fish scales, which offer tough armour for the animal even as it is flexing, flipping and squirming. Intrigued by this ability of fish skin to offer such good protection to an uneven surface, Ortiz has been investigating how the structure of such natural protective surfaces is related to the way they function, and in doing so she is finding ways to make some remarkably effective protective clothing for humans.

Her team examined how scales of different species of fish provided armour against bite attacks. They found that fish have scales arranged in many layers, with scales of different sizes, each layer having its own unique deformation mechanism, mechanical properties and ability to bear a load. They made scaled-up 3D models of parts of the fishy armour. They also created a computational model that they used to design custom armour for a human body, which would offer protection to vulnerable joints parts, including shoulders, knees and elbows, as well as the flatter areas such as the torso. Actual armour made for use in the field is some way off. Ortiz has a patent on the shape of such armour, but she says that the patent and the computer design are just the first steps to actually making the armour with all its intricacies.

The artificial structural materials made so far are not yet as sophisticated as bone, fish scales or nacre — but perhaps they don't need to be. Graphene, a form of carbon consisting of single-atom sheets of molecules laid out in a honeycomb pattern, is the strongest material ever measured — and so once graphene production has been mastered, crafting intricate 3D arrangements from it might turn it into the toughest, strongest, most flexible material by a factor of hundreds. By combining natural building processes with synthetic materials, lightweight, sensitive, responsive, self-healing and tough structures will be the future of super-materials. "We should surpass nature," says Studart. The difficult part is to first understand nature. ■

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