Synthetic sea shell

Michael Rubner

The mechanical properties of natural substances such as bone and shell are envied by those involved in the fabrication of materials. A 'bricks-and-mortar' structure, assembled layer by layer, is the key to making sea shells.

For a materials scientist, cross-sectional images of the complex microstructures of naturally occurring hard materials such as bones and sea shells are awe-inspiring. Over many millions of years, nature has devised schemes to combine seemingly incompatible building-blocks — 'soft' organic proteins and 'hard' inorganic particles of calcium carbonate — in a manner that produces composite materials with the unusual combination of high strength, hardness and toughness. Imagine, however, that you could build such a structure as a mason would, one layer at a time, from the bottom up. Writing in *Nature Materials*, Tang and colleagues[1] explain how it can be done, using a molecular-level processing scheme known as layer-by-layer assembly[2,3].

Flexible soft materials that can undergo energy-absorbing molecular rearrangements during deformation are tough, but also very compliant. In contrast, rigid hard materials are stiff but often also very brittle, and they have little ability to absorb energy, so their toughness is low. To be strong, hard and tough, a material must be able to absorb a large amount of energy during mechanical deformation and also maintain high stiffness. In bone or shell, this desirable combination of properties is made possible by one key attribute — a bricks-and-mortar-like structure, made up of strongly interacting, nanometre-size building-blocks. The 'hard' bricks and 'soft' mortar are complementary in their response to stress and strain.

So far, attempts to mimic these structures with synthetic building-blocks have failed to produce a material with similarly impressive mechanical properties, because most conventional processing techniques simply do not offer the nanoscale level of control needed to create a highly regular bricks-and-mortar-type arrangement. Nature has no such difficulty with nanoengineering: it can assemble, in a regular manner, building-blocks of the right dimensions that interact strongly enough at their interfaces to allow the transfer of deformation energy between the rigid bricks and the softer mortar. Reproducing these elements synthetically is a challenge.

But this is exactly what Tang *et al.*[1] have achieved, through the alternating sequential deposition of negatively charged, nanometre-thick clay platelets (the bricks) and a positively charged polymer (the mortar).

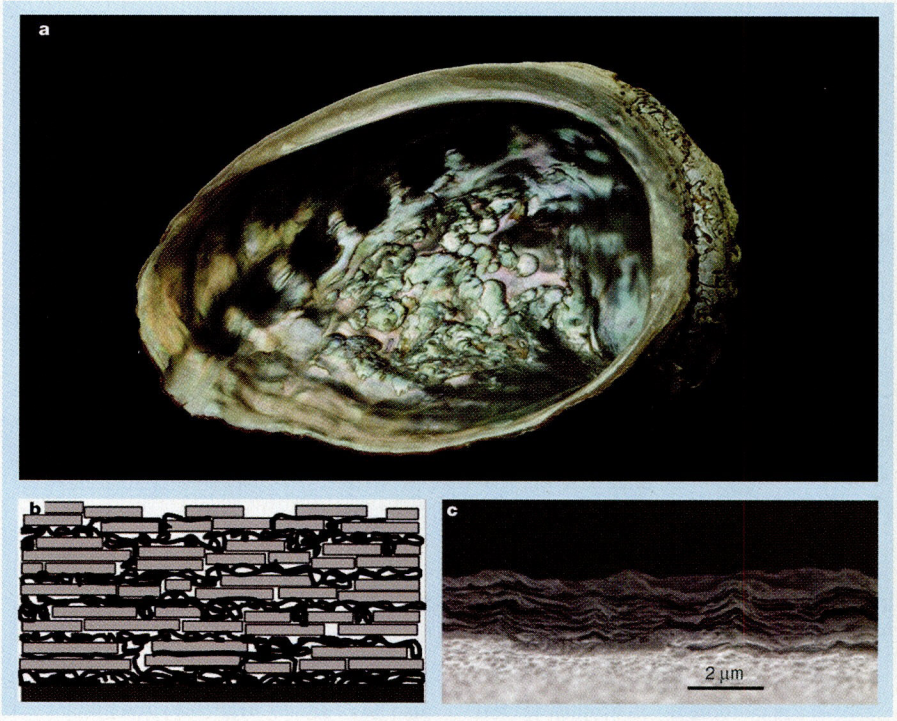

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Figure 1 **The 'bricks-and-mortar' approach.** a, **The natural strength, hardness and toughness of bone and shell are attributable to their nanoscale structure of calcium carbonate bricks and mortar-like protein layers. By mimicking this structure, Tang *et al.*[1] have created a new material with mechanical properties similar to nacre, or mother-of-pearl.** b, **Montmorillonite bricks (0.9 nm thick) are deposited layer by layer above a silicon-wafer substrate, alternating with polymer chains of mortar.** c, **Structures that are many layers deep can be built — this one has 100 brick and polymer layers — although the process is slow.**

The primary driving force for this adsorption-based assembly, which is carried out entirely from dilute aqueous solutions of the materials, is electrostatic: the positively charged polymer chains are attracted to the negatively charged clay platelets, and vice versa. By assembling the clay platelets (in this case, a material called montmorillonite) and polymer chains one deposition step at a time, the authors are able to create a bricks-and-mortar-type arrangement that mimics the natural structure of nacre, the material known as mother-of-pearl (Fig. 1).

The polymer chains are arranged in coils and folds, physically pinned by relatively weak electrostatic interactions. As the material is deformed and the clay platelets begin to slide over each other, the polymer chains can undergo molecular rearrangements, through the breaking of 'sacrificial' ionic bonds and the concomitant unfolding of the coiled polymer chains. And this process, in turn, allows the material to absorb a lot of deformation energy. The authors report that thin films assembled in this way have tensile strength and stiffness that approach those of seashell nacre. Their stiffness is significantly higher than the more disordered composites previously fabricated from similar materials using conventional methods.

As a step towards creating synthetic materials that truly mimic the mechanical behaviour of naturally occurring materials, this is an important advance. The true potential of this approach — to construct more complicated layered structures containing many types of building-blocks — has yet to be pursued. But, for example, this group has also shown that layer-by-layer assembled films containing carbon nanotubes have exceptional mechanical properties[4]. So this seems a promising way of fabricating multilayered, multi-component thin films, with molecular architectures designed to take full advantage of the complex interactions possible between many different types of materials. And as this

assembly process simply involves alternately dipping a substrate into dilute aqueous solutions of oppositely charged materials, it is easy to control the number, type and sequence of layers added to the film[5].

There is a price to pay, however, for assembling the building-blocks one layer at a time. Such structures, particularly if they need to reach thicknesses in the micrometre range, require far longer fabrication times than more conventional processes such as spin-coating. Indeed, it is impressive that Tang *et al.*[1] have succeeded in creating free-standing, micrometre-thick films in this way (Fig. 1c).

Another challenge in working with charged polymers is that they are capable of adsorbing a lot of water, which in turn can degrade the mechanical properties by screening the ionic interactions that lend strength to the material. Tang *et al.* show that there is a significant decrease in mechanical performance when films are tested in high-humidity environments. But this problem can be addressed, as many different types of materials can be assembled in these multilayer films, including those that are hydrophobic (water resistant) or that can be rendered hydrophobic by subsequent chemical or thermal treatments.

In any event, these model structures are sure to provide new insight into the behaviour of naturally occurring materials. Their applications could be widespread, from synthetic engineering of biological hard tissue to thin-film protective coatings. ■

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Telomeres

Taking the measure

Vicki Lundblad

Telomeres — the tips of chromosomes — need to be preserved, and this involves replenishing telomeric DNA when it has been eroded. But telomeres must not become too long, and one aspect of length control is now revealed.

In every organism, maintaining the integrity of the genome is a crucial endeavour. One aspect of genome maintenance involves protecting telomeres, the natural ends of linear chromosomes. This task is achieved by a suite of specialized protein complexes, which are anchored to chromosome ends through their association with further proteins that bind directly to telomeric DNA. The resulting structure prevents events that would be catastrophic for the genome, such as the loss of terminal DNA sequences or end-to-end chromosome fusions.

One of the complexes involved in telomere maintenance is an enzyme called telomerase, which adds DNA back to telomeres that have become eroded. Several other proteins also regulate this complex. But how the different proteins talk to one another — to keep telomeres the right length, to protect them, and to replicate them during cell division — is poorly understood. Writing on page 1013 of this issue and in *Current Biology*, respectively, Loayza and de Lange[1] and Colgin *et al.*[2] describe a crucial feature of the process by which telomerase can sense, and thus regulate, the length of individual chromosome ends.

Telomeric DNA is composed of G-rich repeats — reiterations of a short DNA sequence that does not code for protein and is high in guanine (G) nucleic-acid bases. It also has a single-stranded stretch that overhangs the end of the double-stranded (duplex) telomeric region. This overhang is the substrate for telomerase, which elongates chromosome ends by adding G-rich repeats. The importance of telomerase is evident from studies of yeast and human cells in which reductions in telomerase levels produce a steady decline in telomere length that eventually blocks cell division. Not surprisingly, then, telomerase is highly active in systems such as the blood and reproductive system, which rely on continuous replenishment through cell proliferation[3]. Much to the interest of cancer biologists, telomerase levels are also increased in most human tumours, providing a potential target for the development of anticancer drugs[4].

In normal cells, telomerase activity is carefully controlled by several mechanisms. For instance, subunits that are part of the telomerase complex itself can positively regulate the enzyme, for example by mediating recruitment of the complex to chromosome ends[5]. Surprisingly, proteins that bind to the duplex region of the telomere can also be potent regulators, even though they do not appear to associate physically with telomerase. These duplex-binding proteins — which include Rap1 in budding yeast and the TRF1 and TRF2 proteins in human cells — can 'count' the number of G-rich repeats and, when telomeres become overly long, inhibit further telomerase activity[6,7].

Missing from this elegant proposal for telomere-length regulation, however, is an explanation for how information from the duplex portion of the telomere is relayed to the very tip of the chromosome — the site of telomerase action. To address this, Loayza and de Lange[1] and Colgin *et al.*[2] turned to a recently discovered human protein called

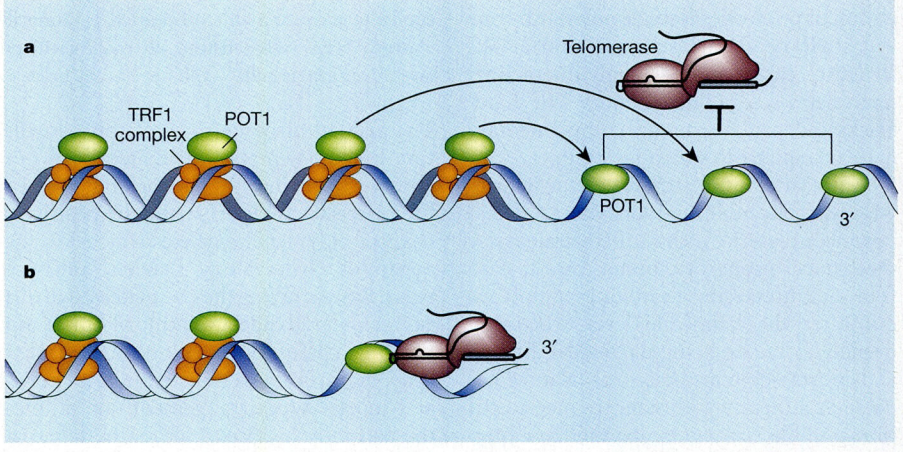

Figure 1 **Model for telomere length control. Telomeres are found at the end of linear chromosomes, and their length must be precisely regulated — a process that involves the POT1 protein in human cells[1,2]. Loayza and de Lange[1] have shown that POT1 binds to the TRF1 complex on the double-stranded (duplex) portion of telomeres. TRF1 complexes sense the length of the telomere, and the authors propose that this information is transmitted to telomerase (an enzyme that extends telomeres) via POT1, by transferring POT1 to the single-stranded overhang at the telomere tip.** a, **When the telomere is long enough, the levels of POT1 on the overhang are high, and telomerase is inhibited.** b, **When the telomere is too short, little or no POT1 is transferred to the end, and telomerase is no longer inhibited, allowing it to add DNA back to the telomere. Colgin *et al.*[2] have proposed that POT1 may also act as a positive regulator of telomerase when present at the single-stranded terminus. It might do so via a direct interaction with telomerase, in an analogous way to how the yeast Cdc13 protein regulates telomerase[5,11].**