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# Biomimetics for next generation materials

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Billions of years of evolution have produced extremely efficient natural materials, which are increasingly becoming a source of inspiration for engineers. Biomimetics—the science of imitating nature—is a growing multidisciplinary field which is now leading to the fabrication of novel materials with remarkable mechanical properties. This article discusses the mechanics of hard biological materials, and more specifically of nacre and bone. These high-performance natural composites are made up of relatively weak components (brittle minerals and soft proteins) arranged in intricate ways to achieve specific combinations of stiffness, strength and toughness (resistance to cracking). Determining which features control the performance of these materials is the first step in biomimetics. These 'key features' can then be implemented into artificial bio-inspired synthetic materials, using innovative techniques such as layer-by-layer assembly or ice-templated crystallization. The most promising approaches, however, are self-assembly and biomineralization because they will enable tight control of structures at the nanoscale. In this 'bottom-up' fabrication, also inspired from nature, molecular structures and crystals are assembled with a little or no external intervention. The resulting materials will offer new combinations of low weight, stiffness and toughness, with added functionalities such as self-healing. Only tight collaborations between engineers, chemists, materials scientists and biologists will make these 'next-generation' materials a reality.

**Keywords: biomimetics; hard biological materials; deformation; fracture**

## 1. Natural materials and biomimetics

Many biological tissues and devices boast remarkable engineering properties. The toughness of spider silk, the strength and lightweight of bamboos or the adhesion abilities of the gecko's feet are a few of the many examples of high-performance natural materials. In recent years, more and more of these materials have been systematically studied with the objective of duplicating their properties in artificial man-made materials. This 'technology transfer' from nature to engineering is most often called biomimetics, and also sometimes biomimicry or bionics (Vincent *et al.* 2006).

There are several reasons why engineers and scientists are now turning to natural materials for inspiration. As researchers strive to develop better and better materials and devices, there is a lot to learn from nature. In many cases, the types

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of design requirements for materials (stiffness and strength for example) are similar in the engineering realm and in nature. However, it appears that natural and man-made materials often use different routes to solve similar engineering problems (Vincent *et al.* 2006). For example, while engineers use a wide variety of material chemistries to achieve various properties (a car, for example, contains at least 30 different materials), natural materials are made up of a relatively limited number of 'base components'. A molecule like type I collagen serves as the building block for a variety of tissues in the human body: bone; cartilage; skin; or eye cornea (Sanchez *et al.* 2005). Nature can therefore inspire alternative approaches to solving design problems. Moreover, natural materials possess qualities which would be highly beneficial to duplicate in their man-made counterparts: miniaturization; adaptability; and multifunctionality.

## 2. Hard biological materials

Within the realm of materials produced by natural organisms, 'hard' biological tissues are attracting a lot of attention from researchers for their unique combinations of stiffness and strength. Hard tissues can serve a variety of functions: mechanical support (bones); cutting, tearing and crushing tools (teeth); or armoured protection (seashells). Over millions of years of evolution, these materials have been finely tuned to enhance their mechanical capabilities. There is a great diversity in properties and structures across hard biological materials, from which engineers can 'tap' for inspiration.

The main mechanical feature of hard biological tissues is of course their 'hardness', although 'stiffness' (resistance to deformation) may generally be a more accurate term (Currey 1999). Resistance to cracking (toughness) is another important property which controls the tensile strength of hard materials. How natural materials combine stiffness and toughness will now be elaborated. In nature, the most common route taken to make stiff materials out of soft protein networks and tissues is to incorporate minerals, which are much stiffer (Currey 1999). To this day, approximately 60 biogenic minerals (i.e. generated through biological processes) have been identified (Giraud-Guille *et al.* 2004). The most common are calcium carbonate (in seashells), hydroxyapatite (in teeth and bones) and silica (in radiolarians and diatoms, which are sub-millimetre marine organisms; Meyers *et al.* 2006). These minerals come in various sizes, concentrations and shapes. For example, the hydroxyapatite crystals embedded in the collagen fibrils that form the building block of bones are nanometres in size (one billionth of a metre; Weiner & Wagner 1998), while a sea urchin spine is one single crystal of calcium carbonate which can reach 10–50 mm in length.

The effect of combining soft proteins with stiff minerals can be seen in figure 1, which is a material properties map for a selection of natural ceramics, biopolymers and their composites (Wegst & Ashby 2004). On the horizontal axis, the modulus is a measure of the stiffness, while the vertical axis represents toughness. At the upper left of the diagram is the realm of the 'soft', natural elastomers such as skin; they are compliant and tough materials that tear rather than crack. At the lower right is the domain of the hard, with minerals that are not only much stiffer than elastomers but also much more fragile (low toughness). At the upper right of the diagram in figure 1 are the hard biological tissues, which incorporate

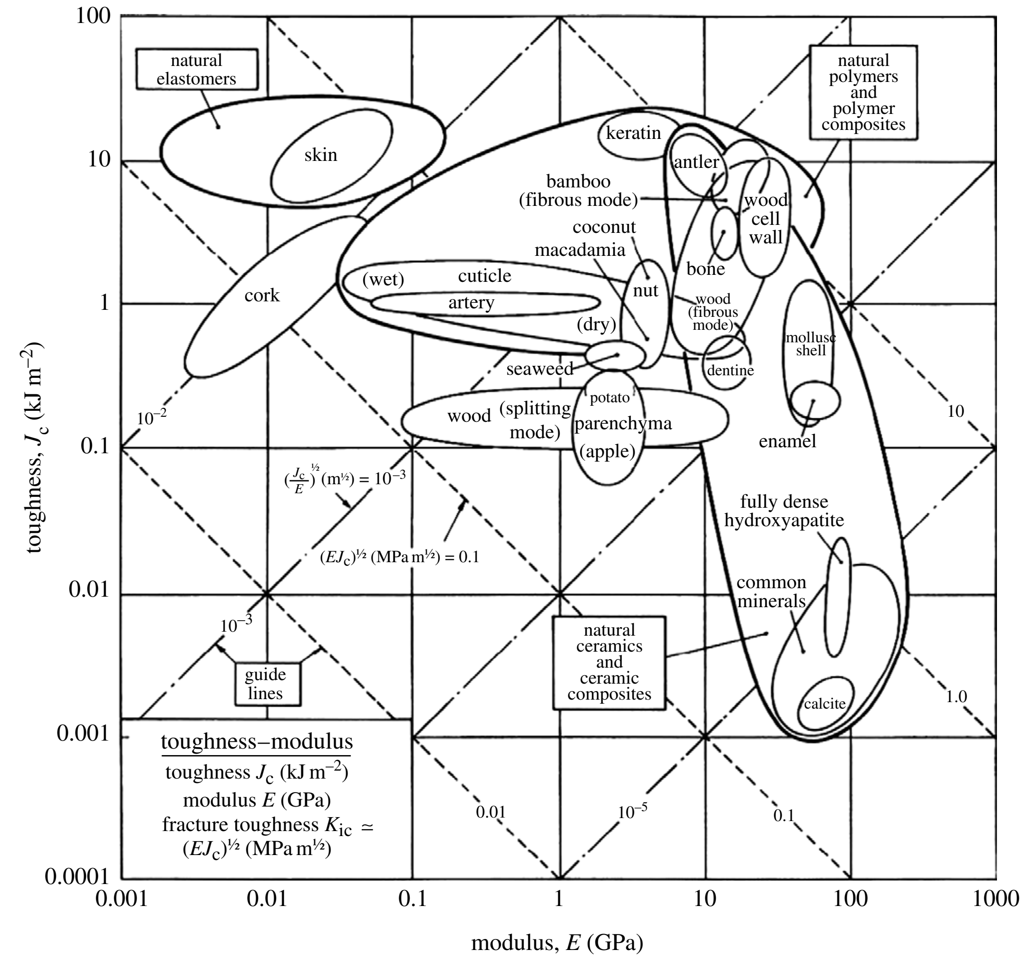


Figure 1. Material properties map for a variety of ceramics, soft natural tissues and their composites. The vertical axis (toughness) is a measure of the ability of the material to resist cracking, while the horizontal axis (modulus) is a measure of the stiffness of the material. (Adapted from Wegst & Ashby (2004).)

both natural elastomers and minerals. Their mineral content makes them 100–5000 times stiffer than soft proteins. For example, antler bone is composed of approximately 30% of mineral and is 100 times stiffer than collagen. Higher mineralization leads to a higher stiffness: tooth enamel, with 99% mineral content (the highest degree of mineralization in the human body) is 1000 times stiffer than collagen.

One could expect that the large amounts of minerals contained within these natural materials would make them fragile, yet figure 1 shows that materials like bone, mollusc shells or teeth are several orders of magnitude tougher than the minerals they contain. Note that these degrees of improvement are currently unmatched by man-made ceramic composites. The key behind this mechanical performance is how soft and stiff materials are arranged to form the structure of these materials. In natural composites, a powerful strategy has emerged over

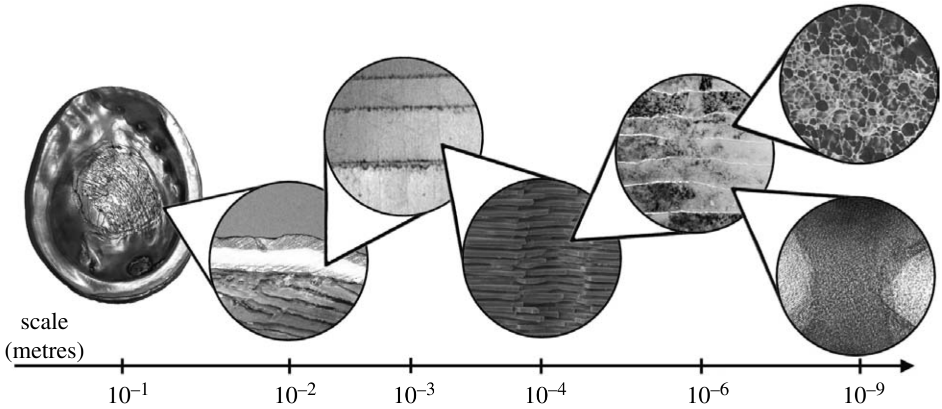


Figure 2. The hierarchical structure of nacre (growth line image from Menig *et al.* (2000), nanograins from Rousseau *et al.* (2005)).

evolution: specific features can be found over several distinct length-scales, from macro- to micro- to nano scale. The mechanical performance measured at the macroscale is the result of the synergy of mechanisms that act over several scales to transfer loads and stresses, dissipate energy, distribute damage and resist cracking. These include nanoscale mechanisms (Smith *et al.* 1999; Gao 2006; Gupta *et al.* 2006; Tai *et al.* 2006) as well as microscale mechanisms (Nalla *et al.* 2005; Barthelat *et al.* 2007). These so-called hierarchical structures seem to be the general rule for hard biological materials (Sanchez *et al.* 2005). In §§3 and 4, two hard biological tissues are examined in detail: nacre (mother-of-pearl) from seashells and bone.

## 3. Nacreous shells

Within the mollusc family, bivalve and gastropods grow a hard shell in order to protect their soft body against external aggression from predators, rocks or debris displaced by currents or waves. The protective shells are mostly made up of calcium carbonate, with a small fraction of organic materials (not exceeding 5% in mass). Several types of structures emerged from evolutionary processes, and among them it appears that nacre is the strongest and toughest (Currey & Taylor 1974).

### (*a*) *The hierarchical structure of nacre*

The structure of a typical nacreous shell is shown in figure 2 for the shell of red abalone, a marine gastropod. At the largest scale (figure 2, macroscale, $10^{-1}$ m), the adult shell is approximately 15–20 cm in diameter. It is composed of two layers (figure 2, $10^{-2}$ m scale): the outside (red) layer is made up of large crystals of calcite, which makes a hard, but brittle, material. The inner layer, nacre, is composed of 95% volume of aragonite (one of the crystallographic forms of calcium carbonate) and 5% volume of organic materials (proteins and polysaccharides; Sarikaya & Aksay 1995). Nacre has a finer structure than the outer layer and is capable of relatively large inelastic deformations. While the

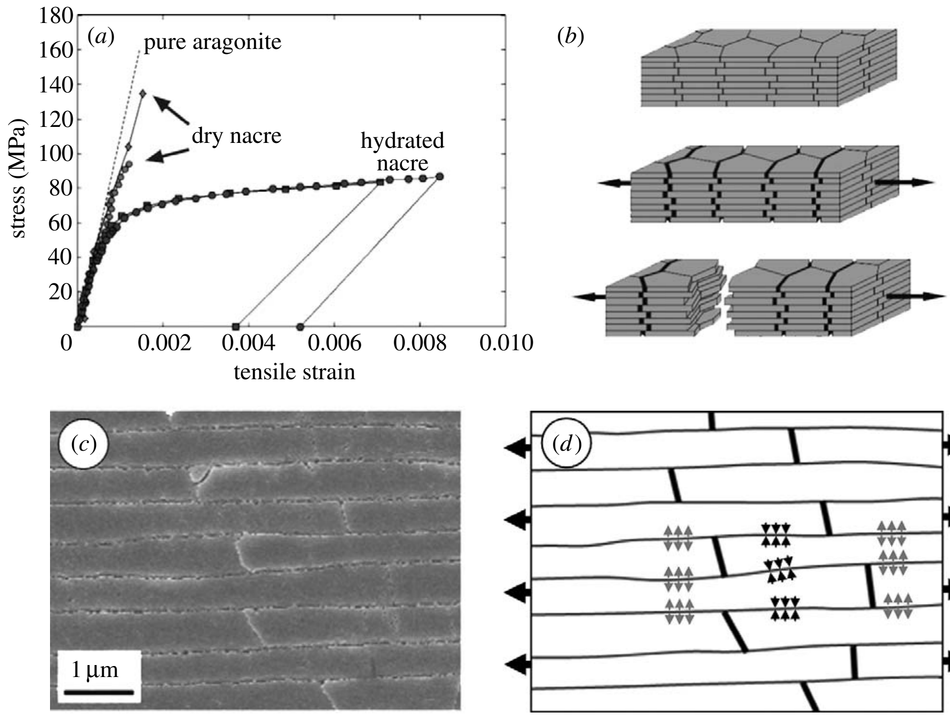


Figure 3. The deformation of nacre. (*a*) Stress–strain curve in tension along the tablets for pure aragonite, dry nacre and hydrated nacre. (*b*) Collective tablet sliding generates the relatively large deformations up to failure. (*c*) SEM image showing a dove-tail tablet ends. (*d*) Mechanism associated with the waviness: under tension, compressive stress builds up (black arrows), balanced by a tensile stress (grey arrows) outside of the sliding area. The result is progressive locking and local hardening.

hardness of the outer layer makes it suitable to arrest projectile and prevent penetration of the shell, the inside layer (nacre) is capable of dissipating mechanical energy through inelastic deformation. This two-layer arrangement is believed to be an ideal armour design (Sarikaya & Aksay 1995). Nacre has been at the focus of several studies, as this material exemplifies many of the traits of hard biological tissues: remarkable mechanical properties resulting from a hierarchical structure and mechanisms operating across several length-scales (Mayer 2005). Observations at higher magnification (figure 2, millimetre scale, $10^{-3}$ m) reveal a few lines that partition the nacreous layer. These so-called ‘growth lines’ mark pauses during the growth of the shell (Lin & Meyers 2005).

The bulk of nacre is made up of 0.5 μm thick layers (figure 2, mesoscale, $10^{-4}$ m), each layer being composed of a tiling of polygonal aragonite tablets approximately 5–8 μm in diameter. In nacre from red abalone, there is some degree of organization across layers: tablets are stacked in columns (columnar nacre) with some overlap between tablets from adjacent columns. While they are often described as flat, the tablets actually show a rather convoluted surface, with a waviness that can reach up to half of the tablet thickness in amplitude (figure 2, $10^{-6}$ m scale). This waviness can also be observed in other species (Sarikaya & Aksay 1995; Feng *et al.* 2000; Song *et al.* 2002*a*,*b*; Bruet *et al.* 2005). The interface between the tablets is a 30 nm thick complex system including several layers of organic materials (Schäffer *et al.* 1997), nanoasperities (Wang *et al.* 2001) and direct mineral connections from one tablet to the next (Song *et al.* 2002*a*,*b*; figure 2, $10^{-9}$ m scale). The tablets themselves are composed of aragonite nanograins delimited by a fine three-dimensional network of organic material (Li *et al.* 2004; Rousseau *et al.* 2005). The shell structure therefore contains six levels of hierarchy.

### (*b*) *The deformation and fracture of nacre*

Nacre exhibits remarkable mechanical properties, which have been probed using a variety of techniques including tension (Currey 1977; Barthelat *et al.* 2007), three and four point bending (Jackson *et al.* 1988; Wang *et al.* 2001), shear (Menig *et al.* 2000; Wang *et al.* 2001; Barthelat *et al.* 2007) and compression (Menig *et al.* 2000; Barthelat *et al.* 2006). The individual components of nacre have also been probed, using nanoindentation on individual tablets (Li *et al.* 2004; Bruet *et al.* 2005; Barthelat *et al.* 2006). However, it appeared that their mechanical properties are similar to single crystal aragonite (Barthelat *et al.* 2006), which is a stiff (100 GPa), but brittle ($J_c = 2$–$3\ \mathrm{J\ m^{-2}}$), material.

Nacre is made up of 95% of that material, yet it can exhibit relatively large inelastic deformation in tension along the direction of the tablets. The tensile stress–strain curve for nacre (figure 3*a*) shows an initial linear region, followed by relatively large deformation accompanied by hardening up to almost 1% strain at failure (locally, the strain can reach 1.5%; Barthelat *et al.* 2007). These levels of strains are achieved by a unique mechanism: at a tensile stress of approximately 60 MPa, thousands of microscopic tablets will slide on one another, generating large tensile deformations (figure 3*b*). In this mechanism, the tablets remain essentially linear elastic, while the nonlinearity and large deformations are provided by significant shearing of the interfaces. Such deformations involve viscoplastic deformation of the organic materials, which can withstand tremendous stretches while dissipating energy in the process (Jackson *et al.* 1988; Smith *et al.* 1999). This process is only possible if the interfaces and the organic materials are hydrated, and dry nacre behaves very much like pure aragonite (figure 3*a*). This is because the organic material at the interface becomes brittle when dried. In addition to the organic, other nanoscale features such as nanoasperities may also provide resistance to tablet sliding (Evans *et al.* 2001; Wang *et al.* 2001).

While these mechanisms are necessary to tablet sliding, they are not sufficient. In order to spread tablet sliding over large volume, a hardening mechanism must operate at the interface: as tablets begin to slide on one another, it must become more and more difficult to slide them further so that other sliding sites will be ‘activated’, thus spreading the inelastic deformations over large volumes of materials. This hardening mechanism is actually found in a larger scale: the waviness of the tablets is such that in some locations the tablets are thicker at their periphery, generating low-angle dovetails (figure 3*c*). These dovetails are the critical features that will progressively lock the tablets as they are pulled apart (figure 3*d*).

The energy dissipation associated with tablet sliding and the hardening generated by their waviness has significant implications on the fracture of nacre. The inelastic deformation will initiate and spread where the stresses are highest

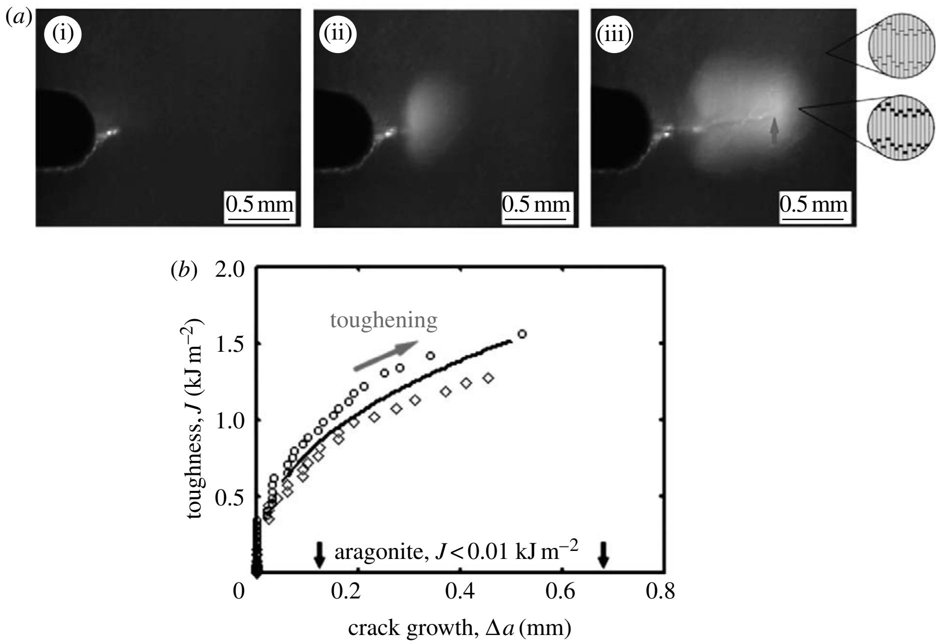


Figure 4. The fracture of nacre. (*a*) Crack emanating from a notch (dark area). The white area is an indication of nonlinear deformations due to tablets sliding. (*b*) Crack resistance curve (or *R*-curve) for nacre.

within the material, around defects and cracks. This can be observed during a fracture test, where a crack is propagated in a pre-notched specimen (figure 4*a*). A white area appears ahead of the loaded notch, which is an indication of inelastic deformation and tablet sliding (this effect is similar to stress-whitening in polymers). Once the crack propagates through this region, it will 'activate' fresh material ahead, which implies dissipation of energy. The energy required to grow cracks in nacre will therefore be augmented by the energy dissipated by the generation of these inelastic regions. This increase of toughness as a crack advances can actually be measured from fracture experiments (figure 4*b*): the more the crack extends, the more difficult it gets (the more energy it requires) to grow further. This property is critical to the reliability of the material, because it will stabilize cracks emanating from existing flaws within the materials.

### (*c*) *Artificial nacres*

With such remarkable properties, nacre has started to inspire novel composite designs, and several mimics of this material have actually been fabricated. For example, layer by layer deposition was used to generate a nanostructured nacre with similar strength and a deformation mode dominated by the sliding of layers on one another (figure 5*a*; Tang *et al.* 2003). More recently, the microscopic layers formed by ice crystals were used as a template for a fine ceramic structure, which could then be infiltrated with softer materials such as aluminium (Deville *et al.* 2006). The result resembles nacre (figure 5*b*) and shows improved mechanical properties, mostly from crack deflection. More and more of the fine

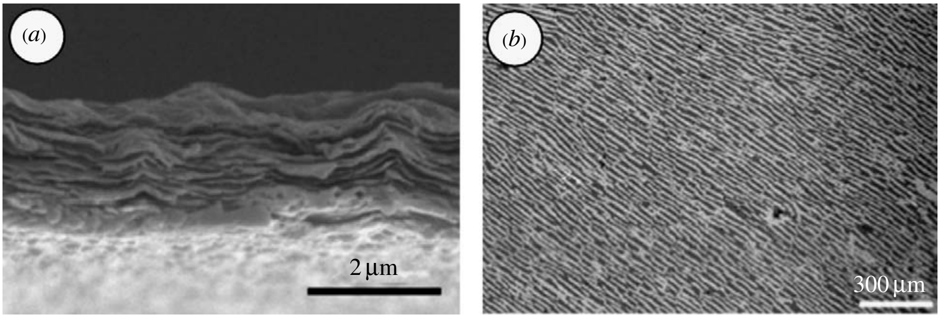


Figure 5. Two examples of 'artificial' nacres. (*a*) Clay/polyelectrolyte layered material (Tang *et al.* 2003). (*b*) Ice-templated alumina infiltrated with aluminium (Deville *et al.* 2006).

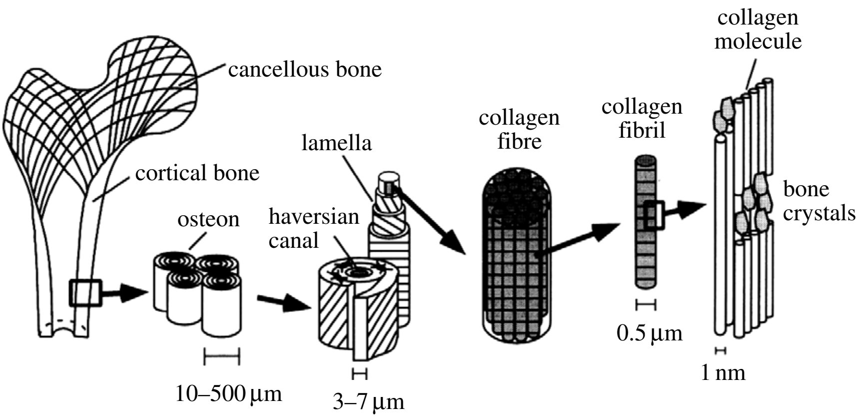


Figure 6. The hierarchical structure of bone. (Adapted from Rho *et al.* (1998).)

structures of nacre are being duplicated using innovative fabrication techniques. To this day, however, the highly controlled collective tablet sliding and their associated energy dissipation could not be reproduced in an artificial material.

## 4. Bone

Bone is another example of a high-performance biological material, which combines a soft material (collagen) with a mineral (hydroxyapatite) to achieve stiffness. As with nacre the structure of bone is organized over several length-scales (figure 6), with six to seven levels of hierarchy (Rho *et al.* 1998; Weiner & Wagner 1998). Nanoscopic mineral crystals are embedded into collagen fibrils, and their relative displacement serves as the basic deformation mechanism of the collagen fibril (Gupta *et al.* 2006; Tai *et al.* 2006). The three-dimensional arrangement of these fibrils (woven, plywood and aligned) is an important factor in the properties of bones (Weiner & Wagner 1998). When aligned, the collagen fibrils form collagen fibre which serves as the building block for larger structures: lamellae and osteons (figure 6). Although it is not clear how cracks interact with these features, mechanisms at these larger scales seem to be at least as important as the nanoscale mechanisms. Recent observation showed a variety of toughening

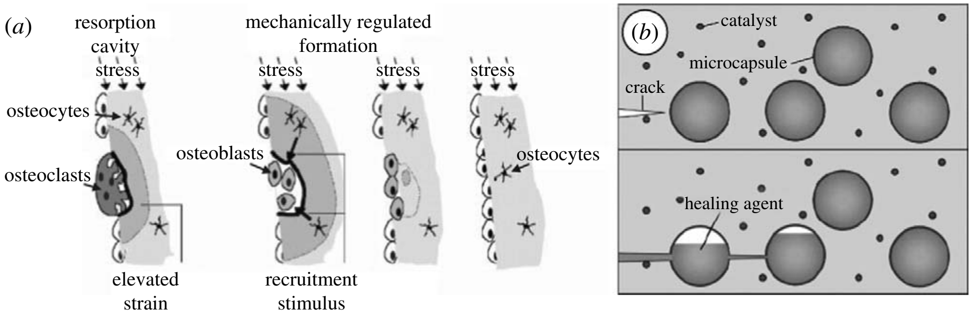


Figure 7. Self-healing in (*a*) bone (adapted from Huiskes *et al.* (2000)) and (*b*) a bio-inspired polymer (adapted from White *et al.* (2001)).

mechanisms at the microscale such as viscoplastic flow, crack deflection, microcracking and crack bridging (Nalla *et al.* 2005; Peterlik *et al.* 2006). The latter mechanism, which seems to be predominant, consists of ligament of intact bone material bridging the crack, pulling the crack faces together and therefore impeding crack advance (Nalla *et al.* 2005).

In addition to being a stiff and tough material, bone exhibits remarkable functionalities: bone material continuously regenerates, can adapt to local stress and can heal itself. This is made possible by specialized cells that fulfil various functions and vastly expand the capabilities of the material. Osteoclasts are cells which specialize in dissolving bone (mineral and collagen), leaving cavities within the material. When bone is subjected to mechanical loads, higher strains will develop around these cavities (figure 7*a*). This excess strain is detected by another type of cells, the osteocytes, which are embedded within bone and act like strain gauges (Huiskes *et al.* 2000). Osteocytes then release chemicals to recruit osteoblasts, a third type of cell which produces collagen networks which are mineralized to form hard bone material (calcification). The activity of these specialized cells is therefore largely regulated by mechanical stimuli (figure 7*a*). Bone growth, and the associated stiffening, is thus promoted in regions of high mechanical strain, while in the absence of mechanical load, osteoclasts are prevalent and bone density decreases.

The process of bone generation and elimination is continuous, so that for a healthy individual approximately 25% of the skeleton is regenerated every year (Huiskes *et al.* 2000). This mechanism has important implications: bone basically adapts its density to mechanical stress. In addition, through the same processes, bone can heal microscopic damage and major cracks. A synthetic material with similar properties would solve a lot of reliability problems and would probably find numerous applications.

The self-healing capability has recently been duplicated in bio-inspired, self-healing polymers. These polymers contain pockets of a healing agent and a catalyst. A crack propagating through the material will puncture these pockets and release, mix and cure these agents, effectively healing the crack by filling it with glue. The original load-carrying capability of the material could be restored and, in some cases, even improved (White *et al.* 2001). While this mechanism is not as sophisticated as bone, is it a promising example of a self-healing artificial material.

## 5. Summary and future directions

Hard natural materials such as nacre and bone are made up of relatively weak components, yet exhibit remarkable mechanical performances. From an engineering point of view, they have the potential to inspire a next generation of composites with enhanced strength and toughness. However, total replication of these natural materials for engineering purposes would not make much sense for several reasons. First, not every single microstructural feature observed in these materials serves a structural purpose. It is therefore critical to identify the exact microstructural features and mechanisms which control the overall performance of the material. This is even more relevant in the context of technical limitations in fabrication—natural features which would be very hard to duplicate in artificial material may not actually be needed from a mechanistic point of view. Second, the rules for material selection are different in engineering and nature. There are severe restrictions on material selection in nature (limited availability, biocompatibility, etc.) that do not necessarily apply in engineering. Engineers have more freedom in the choice of materials and can, for example, use advanced ceramics where nature uses fragile minerals. Again a good understanding of the mechanics of the natural materials is critical there, because in order to swap materials in the design of composites one must understand and predict the overall effect on the performance. For example, the aspect ratio for the aragonite tablets in nacre may have to be different in an artificial composite made up of alumina tablets.

The characterization of hard biological materials is therefore the key in biomimetics. This is a very active research area, with discoveries made possible by modern tools, such as electron microscopy, scanning probe microscopy and small-scale mechanical testing. Modelling also plays a significant part, and in this area the emerging multiscale models are the most promising for their ability to capture and integrate mechanisms over several length-scales.

The duplication of key features in artificial materials remains a challenge. While innovative fabrication approaches have recently been proposed, no techniques can currently generate small-scale features and integrate them into larger structure with a sufficient degree of control. The most promising route in this area is actually also inspired by nature and consists in assembling elements from small scale to form larger and larger structures through chemistry ('bottom-up' approach). The controlled growth of crystals (inspired by biomineralization) and the building of structures from molecules (self-assembly) are powerful techniques, which once harnessed will allow a greater control over shapes and patterns over multiple length-scales (Mann 2000). Moreover, compared with traditional fabrication techniques self-assembly uses very little energy and, therefore, offers a sustainable approach to fabricating materials.

More sophisticated hard tissues such as bone yield their unique capabilities (adaptation and repair) from complex cellular activities, including strain detection, release of chemical signals and morphing capabilities. The duplication of such functions in artificial materials will require development of small smart devices that duplicate the function of bone cells. A possible route is synthetic biology, where the DNA of micro-organisms can be 'reprogrammed' to perform specific tasks. This approach has already been successful, to produce antimalarial drugs for example (Silver & Way 2004). From the engineering point of view, a material that self-heals and adapts its microstructure to load would revolutionize the way engineers design mechanical components. The traditional failure and reliability criteria and the design approach would have to be revised. How to design a mechanical component when the material it is made up of adapts to stresses and self-repair? These 'next-generation' materials will only be made possible by close collaborations between structural and mechanical engineers, materials scientists, chemists and biologists.

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# AUTHOR PROFILE

**Francois Barthelat**

Francois Barthelat grew up in the north suburb of Paris. He obtained his BSc in mechanical engineering at the Ecole Nationale Supérieure d'Electricité et de Mécanique in Nancy, France. A student exchange programme took him to the University of Rochester (New York State, USA), where he obtained his Master's degree in mechanical engineering. For the next 2 years, he worked as a development engineer at Datapointlabs (Ithaca, NY), in the area of polymers mechanical modelling and testing. He then joined Northwestern University as a PhD student in 2000 under the supervision of Horacio D. Espinosa, where he worked on a variety of projects (multilayered ceramics, metal foams, dynamic testing on ceramics coatings, for which he and co-workers won the Hetenyi awards for the best experimental mechanics paper of the year). His main PhD topic was the mechanical behaviour of nacre (mother-of-pearl) from seashells. At 32 years of age, he is currently an Assistant Professor in the Department of Mechanical Engineering at McGill University, Montreal. His research focuses on the deformation and fracture of hard biological materials and the development of bio-inspired composites.