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Nacre from mollusk shells: a model for high-performance structural materials

Francois Barthelat

Department of Mechanical Engineering, McGill University, 817 Sherbrooke Street West, Montreal,
QC H3A 2K6, Canada

E-mail: francois.barthelat@mcgill.ca

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Abstract

Nacre is the iridescent layer found inside a large number of mollusk shells. This natural composite has a very high mineral content, which makes it hard and stiff. However it is the toughness of nacre which is the most impressive: it is three orders of magnitude tougher than the mineral it is made of. No manmade composite material can boast such amplification in toughness, and for this reason nacre has become a biomimetic model material. The mineral in nacre comes in the form of microscopic polygonal tablets, which have the ability to 'slide' on one another in large numbers when the material is loaded in tension. This key mechanism makes nacre a quasi-ductile material, which in turn greatly increases its toughness and makes it damage tolerant. Numerous 'artificial nacres' were developed in the past but none of them can truly duplicate the remarkable mechanism of tablet sliding. In this work selected structural features of nacre were implemented in a PMMA-based composite, which for the first time could replicate the collective tablet sliding mechanism. This material demonstrates that the powerful toughening mechanism operating in natural nacre can be duplicated and harnessed in engineering materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Natural designs can be extremely efficient in terms of fulfilling specific functions, and offer a vast reservoir of solved engineering problems [1]. For this reason engineers and researchers are increasingly turning to nature for novel designs and inspiration. In particular, high-performance structural materials produced by nature are attracting more and more attention [2, 3]. While their mechanical properties cannot compare one on one with engineering materials (except for a few extreme cases such as spider silk), what makes them attractive is how they combine building blocks and amplify properties. In the area of hard materials, the shells of mollusks have been intriguing zoologists and engineers for a long time [4–9]. In particular nacre, the iridescent layer found as an inner layer in the shell is now serving as a biomimetic model for a new generation of composite materials [10–12]. The primary function of the mollusk shell is to protect the soft body of the animal against predators or foreign objects (rocks propelled by tide currents for example). Mollusks shells are highly mineralized tissues (at least 95% mineral content) and as a direct result have high stiffness and hardness [4]. Their most impressive property however is their toughness (their ability to resist the propagation of cracks), which is two to three orders of magnitude higher than the minerals they are made of (in terms of J_{IC}). Toughness is critical here, so that cracks emanating from initial defects in the shell can be resisted, effectively making the material damage tolerant.

The motivation for mimicking mollusk shells is to increase of the toughness of ceramics to unprecedented levels. Compared to metals, ceramics offer many advantages: they are stiffer, harder, can be used at higher temperatures and display superior wear properties. The only obstacle to using more ceramics in engineering is their inherent brittleness. Tremendous efforts were therefore deployed (mostly in the 1970s and 1980s) to overcome this limitation, drawing on then recent fracture mechanics theories. New concepts such as toughening mechanisms, damage tolerance, crack bridging or transformation toughening emerged. High-performance

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ceramics with built-in toughening mechanisms are the product of these efforts, with partially stabilized zirconia or fiber ceramic–ceramic composites as the best representatives [13]. These advanced ceramics can be up to ten times tougher than traditional ceramics (in terms of K_{IC}), and are now used for special applications in engineering. Their toughness and reliability remain however lower than engineering metals such as steel, which limits their range of applications. Biomimetics is now revisiting this problem with a new promise: duplicating the mechanisms of deformation and fracture of mollusk shells (and of nacre in particular) could lead to ceramics 50 times tougher than traditional ceramics, thereby greatly expanding their range of application.

It is useful to review the concepts and processes involved in biomimetics. A successful biomimetic transfer of technology from nature to actual engineering materials can be decomposed into three steps, each of which must be brought to a reasonable level of completion to ensure a successful technology transfer.

Step 1 is the identification of a high performance natural model. There is a great variety of natural materials and it is not always obvious which should serve as models for manmade designs. In particular, structure–performance–function relationships must always be kept in mind when examining natural materials. While traditional engineering materials can be studied independently of their intended application, it does not make sense to study a natural material without specifying its function. In fact, the most successful biomimetic designs have a similar function in nature and in the engineering application. To further complicate this process a large number of natural materials are actually multifunctional, so this identification process can become difficult. Design theories such as TRIZ have helped in this regard [1].

Step 2 is the abstraction of key mechanisms, structures and design principles. Mimicking is not copying. The features that give a natural material its attractive properties must be identified, understood and abstracted from the natural model so they can be successfully implemented into engineering designs. This process is not always straightforward: natural materials can be extremely complex and organized over several length scales. This is what gives them attractive properties, but it also makes it difficult to fully understand how they deform, fracture or react to stresses. For example, it is still not clear how bone fractures, despite hundreds of articles published each year on this topic.

Step 3 is the actual fabrication of a biomimetic material. Once the previous two steps are achieved to a reasonable degree, an actual biomimetic material remains to be fabricated. Considering the complexity of natural materials this step can be either extremely difficult, or in the worst case there is simply no technology available to duplicate the key features identified in natural materials.

This paper presents recent development in our understanding of what makes nacre from mollusk shells so tough. Recent biomimetic 'artificial nacres' are then discussed. The three-step biomimetic process permeates this discussion. In particular, mimicking this remarkable material has only been moderately successful so far, because each of the three steps above has only been partially completed.

2. Mollusk shells overview

Mollusk shells are dense and acellular tissues which contain at least 95% mineral and 5% proteins and polysaccharides. In engineering terms mollusk shells are therefore composite materials (most biological materials are actually composites). Their high mineral contents position mollusk shells among the stiffest materials found in nature [2]. Their modulus of elasticity falls within 40 to 70 GPa [2], which is two to four times the modulus of cortical bone. Seashells are also hard materials, a highly desirable property for resisting penetration from foreign objects or predators. The tensile strength of seashells falls within the 40–100 MPa range and, as with all ceramics, their compressive strength can be up to ten times the tensile strength. Shell materials are brittle or quasi-brittle materials (their strain at failure does not exceed 5%). For this reason, the tensile strength of shells is sensitive to initial flaws (defects, pores or contaminants) in their structures. When the shell is stressed these flaws will give rise to stress concentrations, which may generate cracks and catastrophic failure of the shell. It is therefore critical for the shell to also possess a high toughness, so that cracks propagating from the initial defects can be resisted. While stiffness and hardness are easily explained by high mineral content, the toughness of shells is less understood. This represents a significant gap since toughness is arguably the most spectacular property. With a range of $K_{IC} = 3$ to 10 MPa $m^{1/2}$ and $J_{IC} = 0.2$ to 2 kJ m^{-2} [2], shells approach the toughness of advanced engineering ceramic and ceramic–metal composites (cermets). Even more impressive is the improvement in toughness in those materials: made of 95% extremely brittle minerals, mollusk shells are 100 to 1000 tougher than those minerals (in J_{IC} terms) [2]. No manmade composite material can currently boast a toughness amplification of this magnitude, which has motivated further studies on the structure and mechanics of shells over the past 30 years.

While the composition of mollusk shells does not vary much across species, a great variety of microstructures exist (figure 1). How the mineral and organic phases are arranged dictate, to a great extent, the mechanical properties.

Assessing the mechanical performance of various mollusk shells represents the first of the three 'biomimetic steps' described above. Currey [4] compared the mechanical properties of shells from 19 species and concluded that nacre was the strongest [4], and more recent studies showed that it was also the toughest [14]. Over the years nacre has therefore emerged as a perfect model for biomimetic hard and tough materials.

3. The structure of nacre

Nacre is composed of 95% mineral calcium carbonate ($CaCO_3$) in the aragonite form. This mineral is in the form of polygonal microscopic tablets 5 to 15 μm in diameter and

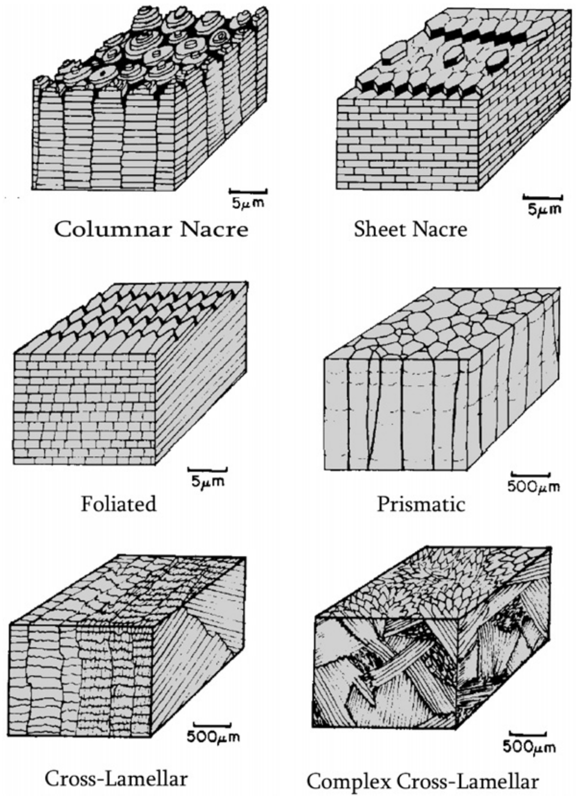


Figure 1. Various mollusk shell microstructures (adapted from Currey [4]). All these materials are made of at least 95% of mineral.

with a thickness of 0.5 to 1 μm. These tablets are tightly arranged into three-dimensional brick walls. In some species the tablets are arranged in columns (columnar nacre, figure 1), while in others the arrangement is more random (sheet nacre, figure 1).

For a long time, the tablets were believed to be composed of a few twinned microscopic crystals [15]. However, recent studies using atomic force microscopy revealed that the tablets are in fact composed of nanograins with a consistent crystallographic texture and separated by a fine network of organic materials [16, 17]. The impact of this nanostructure on the modulus and strength of the mineral seems minimal [18], although it was suggested that their nanostructure could confer some ductility upon the tablets [19].

The remaining 5% of the composite of nacre consists of proteins and polysaccharides mostly located at the interface between tablets. This softer organic phase plays an important role by maintaining the cohesion of the tablets over large separation distances, by forming tough ligaments [6]. This high extensibility is the result of the uncoiling of modules along the chain of some proteins [20]. Other features are also present at the interface between tablets: nanoasperities form a nanoscale roughness on the surface of the tablets, which provide a frictional resistance to sliding [8]. Mineral bridges also connect tablets across the interfaces to reinforce them [21]. Finally, while for a long time the tablets in nacre were assumed to be flat, in all species a significant waviness can actually be observed [9]. Its wavelength is in the order of one half to one tablet length, and its amplitude is about one fourth of the tablet thickness. This feature has important implications which are discussed below. This sophisticated structure, summarized in figure 2, grows through complex chemical processes: organic scaffolds are first self-assembled, to then guide the biomineralization of the microscopic tablets [22]. The complexity of the structure of nacre emphasizes the need to identify which features should be transferred to a successful biomimetic material. Trying to implement all of these features would be extremely difficult and would actually be copying rather than mimicking.

4. Nacre in tension

While examining the mechanical behavior and performance of a specific natural material, it is important to keep its function in mind. A mollusk shell loaded from the exterior will experience bending, which translates into tension in the inner nacreous layer. More severe loads may lead to the cracking of the outer brittle layer from contact stresses. In that case it is the nacreous layer that will ensure the integrity of the shell. For these two situations tensile stresses along the tablets are prominent in nacre, and nacre is probably constructed to maximize strength along that direction. The rest of this paper therefore focuses on tension along the tablets. The stress–strain curves of nacre from red abalone in tension are shown in figure 3. Dry

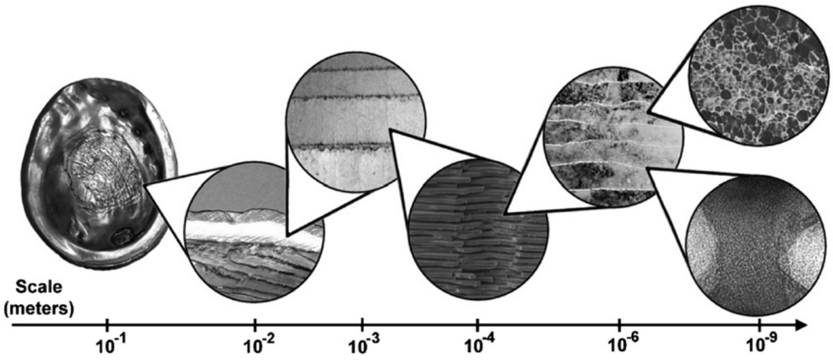
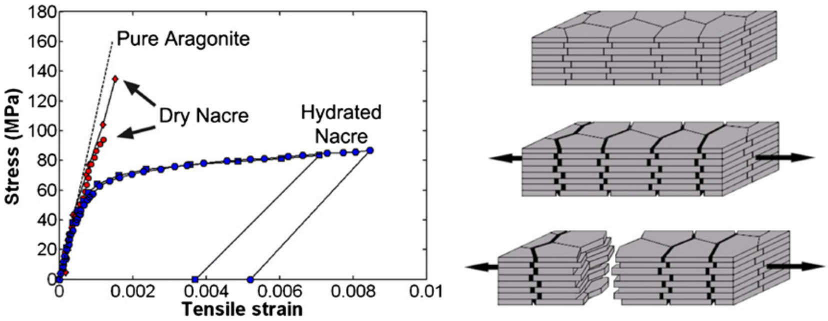
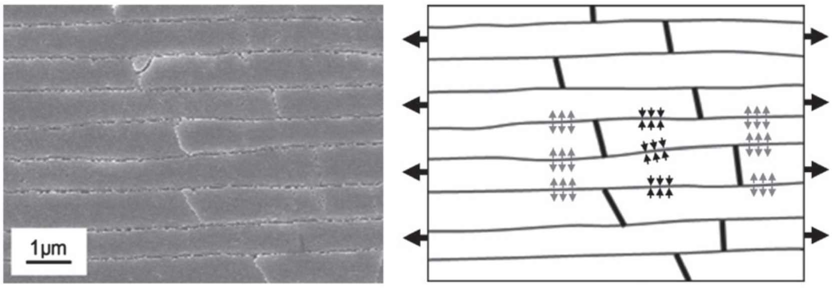


Figure 2. The structure of nacre over several length scales (shown for red abalone *Haliotis rufescens*). Reproduced from [3].



(*a*) (*b*)

Figure 3. (*a*) Stress–strain curve in tension along the tablets for pure aragonite, dry nacre and hydrated nacre. (*b*) The relatively large strains measured in the hydrated case are the result of collective tablet sliding at the microscale.



(*a*) (*b*)

Figure 4. (*a*) SEM showing nacre tablets with dovetail ends; (*b*) under tension transverse compressive stresses are generated at the dovetail, generating resistance to pullout. These stresses are balanced by transverse tensile stresses in other regions (gray arrows).

nacre exhibits a behavior similar to bulk aragonite: linearly elastic up to brittle failure. Hydrated nacre on the other hand displays a totally different response, that can almost be qualified as ductile. Large strains develop at tensile stresses of 60–70 MPa, and strain hardening is observed up to failure at almost 1% strain. Note that this strain at failure is modest compared to many engineering metals, but it is ten times the strain at failure of aragonite. This makes a significant difference in the area under the stress–strain curve, which is related to the energy required to break the material.

The mechanism responsible for these relatively large strains is shown in figure 3(*b*). The applied tensile load is transmitted through the material by tensile stress in the tablets and shear stresses at the interfaces. When the applied load is increased these stresses will increase accordingly, until one of several possible failure modes is activated. In natural nacre the prominent failure mode is shearing of the interfaces (this requires less tensile stress than tablet fracture). The tablets then start to slide on one another, generating large strains in the process. Interestingly this sliding mechanism was also observed in bone and tendon in tension [23]. In nacre tablets sliding spreads throughout the material so that at failure all of the sliding sites are ‘activated’. Each of the local extensions generated at the sliding site add up, contributing to the relatively high strains measured at the macroscale. In order to achieve this behavior there must be a hardening mechanism taking place at the interfaces to make it increasingly difficult to slide tablets further, in order to activate an increasing number of sliding sites. Without hardening, sliding would lead to localization, i.e. the tablets would only slide along a single band perpendicular to the loading direction, leading to small failure strains. The mechanism behind this hardening was recently shown to be progressive tablet locking, generated by the waviness of the tablets [9]. Figure 4 shows that in some areas in the microstructure the waviness makes the tablets thicker at their periphery, effectively generating geometric ‘dovetails’. Upon sliding, the end of the tablet will be pulled out and the dovetail will generate progressive locking and hardening. In turn, the spreading of these deformations over large volumes will increase toughness, as described in the next section.

5. The fracture of nacre

Ultimately, it is the ability to resist cracking (toughness) which is of interest in nacre. A crack in nacre will be subjected to high stresses, so that tablet sliding will be triggered in regions ahead and behind the crack tip called ‘process zones’. These regions can be observed macroscopically, because tablet sliding tends to whiten the material (an optical phenomenon similar to stress-whitening in polymers). It was recently shown that the high toughness of nacre was the result of the energy dissipated in this process zone [14]. Interestingly, more recent results also show that the extent of the process zone varies across mollusk species [24]. Figure 5 shows the result of fracture tests performed on nacres from four different mollusk

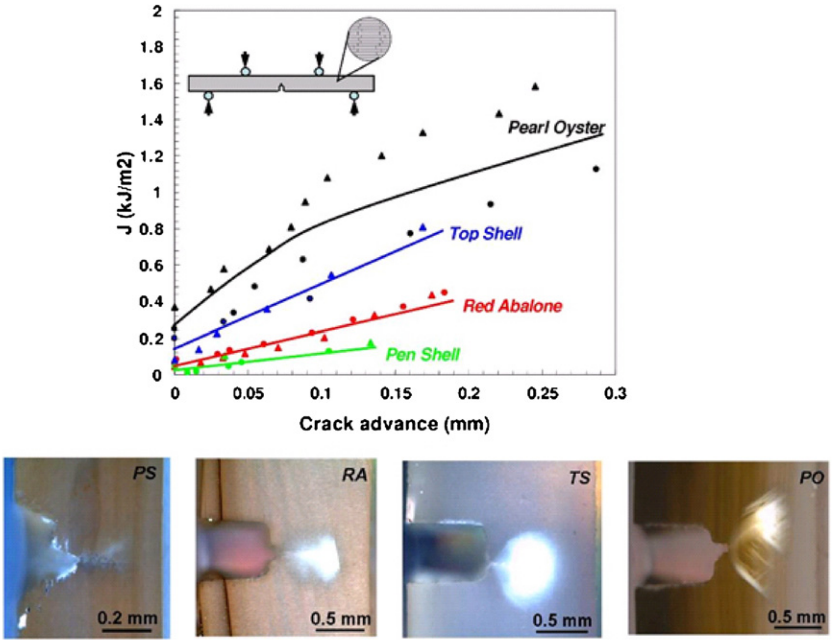


Figure 5. Fracture resistance curves for four nacres, and optical images obtained *in situ* (in order of increasing toughness).

species: two bivalves with sheet nacres (pearl oyster and pen shell) and two gastropod shells with columnar nacres (top shell and red abalone). Resistance to cracking was measured in the direction normal to the tablets. Nonlinear fracture mechanics and the *J*-integral were used as measures of toughness. Figure 5 shows that for all nacres the toughness increases as the crack advances. This important feature is a trademark of tough material, and indicates that the material can slow down or even arrest crack propagation. All nacres are not equal in this regard: pearl oyster is clearly the toughest, while pen shell is the weakest. The fact that the size of the process zone (white region) correlates well with toughness confirms that process zone toughening is prominent in nacre. Advancing a crack will therefore consume a large amount of energy dissipated in the process zone.

The deformation and fracture mechanisms in nacre are now understood enough to abstract key structures and mechanisms which can be implemented in artificial nacres (step 2 in the three biomimetic steps described in the introduction).

6. Biomimetic nacres

The remarkable combination of stiffness and toughness on nacre has motivated the development of a variety of 'artificial nacres' fabricated using a wide range of materials and techniques. These materials share some common characteristics: they consist of stiff and hard microscopic inclusions with high aspect ratio held together by softer, more ductile materials. The list of materials inspired from nacre is long and only three recent contributions are discussed here.

The 'nanostructured artificial nacre' developed by Tang *et al* was fabricated using layer-by-layer deposition techniques, leading to alternated nanoscale layers of clay platelets and polyelectrolytes [10]. Up to 200 layers were fabricated to form 5 μm thick films. Under tension the clay layers slide on one another while electrostatic interactions maintain cohesion over long sliding distances, achieving large overall strains. Another interesting example is the alumina/chitosan polymer developed by Bonderer *et al* [11]. In this case the construction was based on colloidal assembly, and the aspect ratio of the alumina inclusion was carefully designed to promote tablet sliding over tablet fracture. The resulting material, while still having low ceramic content, showed a lot of the characteristics of nacre in terms of structure and mechanics. The third example is the alumina/PMMA brick and mortar composite developed by Munch *et al* [12]. In that work microscopic ceramic 'bricks' were formed from alumina powder using ice platelets as a template. After sintering and infiltration by PMMA, this material is currently the closest to natural nacre in terms of composition and structure, and it shows impressive deformation and toughness characteristics and toughening mechanisms similar to nacre (although the improvement of toughness still does not match that of natural nacre). These three examples illustrate innovative fabrication techniques that were developed for the purpose of mimicking the complex structure of nacre, and how the structure of some of these synthetic materials can come very close to the natural model.

These materials, while impressive achievements, still suffer from limitations from their fabrication techniques which cannot properly duplicate the key features of nacre with sufficient accuracy. As a result, none of them can truly duplicate the collective tablet sliding mechanism, and none of them can approach the degree of improvement that nacre boasts over its mineral constituent. These examples therefore also illustrate the significant obstacles involved in fabricating ceramic composites mimicking nacre.

An alternate approach to this problem is to 'relax' the requirements on small length scale, and to work at millimeter

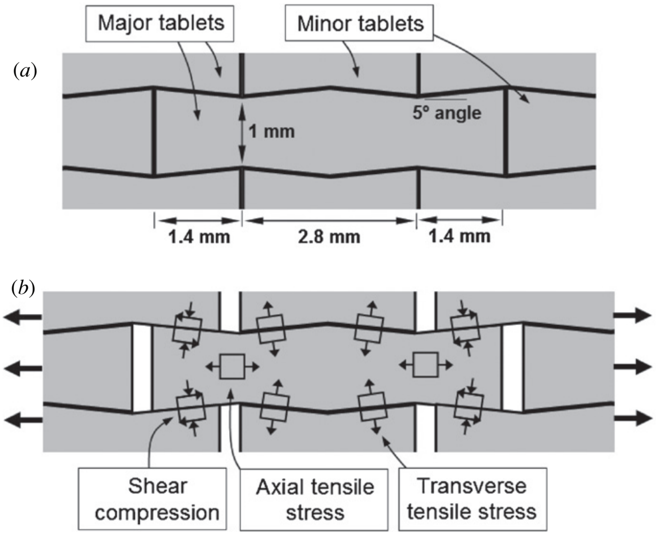


Figure 6. (*a*) Artificial nacre geometry with dimensions; (*b*) main stresses involved when the material is loaded in tension

scales instead of microscopic scales. Fabrication techniques at larger scales offer more control on the structure of the material, which ultimately can lead to successful duplication of key structures and mechanisms. For example Espinosa *et al* [25] fabricated a nacre-like composite with 1 mm thick tablets using rapid prototyping techniques. The waviness of the tablet, so important to tablet sliding and strain hardening in nacre, was explicitly incorporated in the form of dovetails at the end of the tablets. This composite showed tablet sliding with some amount of locking, but the hardening behavior of nacre could not be successfully duplicated.

Following the same philosophy of working at larger scales, we milled PMMA plates using CNC machining techniques. PMMA was chosen for its ease of machining and its brittleness compared to other polymers (the objective being to make a quasi ductile material out of brittle tablets). The dimensions and arrangement of the tablets are shown in figure 6(*a*). Two types of tablets were machined: long 'major tablets' and shorter 'minor tablets'. The stacking of these two types of tablets filled a two-dimensional space and generated overlap regions between the tablets. Tablet waviness was introduced by machining 5° angled features at the top and bottom surfaces of the tablets. The angle, tablets aspect ratio and overlap length were chosen to promote tablet sliding and progressive hardening [26]. The mechanics of progressive locking is shown in figure 6(*b*).

As the tablets are pulled the major tablets carry the axial tensile stress. The interfaces in the overlap region fail first, but still transmit shear stresses. In addition the dovetail geometry generates compressive stresses across the interface in the overlap region, progressively increasing the resistance to sliding. This transverse compression is balanced by transverse tensile stresses in other regions (the core regions). Another way to look at this mechanism is to realize that the dovetail, when pulled out, will tend to spread the upper and lower layers apart, generating tension in the mating part of the dovetail. These tensile stresses in the transverse direction are magnified by stress concentrations at the corners of the minor tablets. They can therefore become significant and lead to tablet delamination, which immediately shuts off the locking mechanism and precipitates overall failure. In this work none of the different glues tried in assembling the tablets was strong enough to resist delamination in the core region. In natural nacre the glue is perhaps superior to synthetic glues available [20], but it is also possible that the core regions are reinforced by mineral bridges [21]. A similar strategy was adopted for this artificial nacre: no glue was actually used, and the tablets were assembled manually and maintained in place by transverse brass fasteners, acting as reinforcement for the core regions. Preloading of the fastener-induced transverse compression in the material, which in effect offsets the tensile stress generated by the dovetail mechanism and prevented delamination. The resulting material was a 7 × 7 tablet, two-dimensional composite made of closely packed angled tablets (figure 7(*a*)), duplicating the key features identified in natural columnar nacre (but at a larger length scale).

This material was tested in tension using a miniature loading stage (E. Fullam, NY), and the key mechanisms of nacre were duplicated for the first time: all the tablets slid on one another, and progressive locking generated by the dovetail was sufficient to spread this deformation mechanism to the entire sample (figure 7). The stress–strain curves showed significant hardening in the sliding stage, in some cases accompanied with noisy signals attributed to stick–slip events typical of dry friction (figure 8). During tablet pullout the contact area also decreased, reducing the amount of load transfer. The maximum stress corresponds to the point where the hardening was not sufficient to offset the loss of contact area. At this point softening started and a localization appeared. All the additional deformations concentrated in the localization band, up to complete failure at almost 10% overall strain. Interestingly, the hardening rate and strength of the composite increased as the fasteners were tightened. This was explained by the transverse compression generated by the fasteners in the overlap regions, resulting in higher frictional force and higher resistance to sliding. This material therefore possesses a 'tunable' tensile strength that can be adjusted by the level of tightening of the fasteners. This 'artificial nacre' demonstrates how key structures and mechanisms of natural nacre can be successfully duplicated in a synthetic composite. Here the stacking pattern and waviness of the tablets nacre were duplicated. The transverse fasteners acted as reinforcement in the core regions, similar to the mineral bridges in nacre. Dry friction replaced the organic materials of natural nacre to transmit shear stresses from tablet to tablet. The resulting biomimetic structure in effect turned a brittle material (PMMA fails at a strain of 1–2%) into a ductile material that fails at almost 10% strain. The low strength of the composite currently limits its possible engineering applications, but replacing the PMMA tablets by ceramics and optimizing the microstructural parameters will certainly lead to novel materials with unique combinations of stiffness, hardness and toughness.

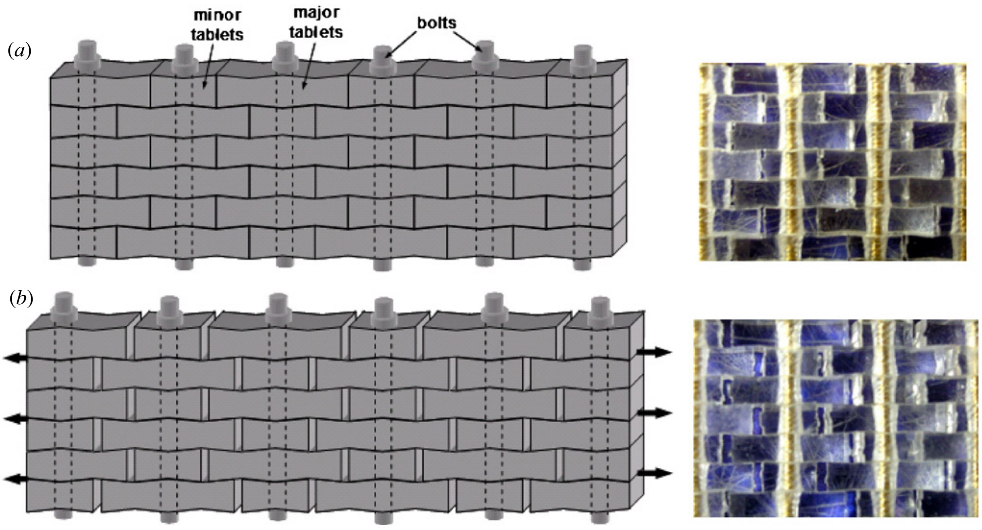


Figure 7. (*a*) Schematic and optical image of the assembled artificial nacre. The brass bolts are visible though the clear PMMA tablets. (*b*) In tension the tablets progressively lock and slide on one another in the entire specimen.

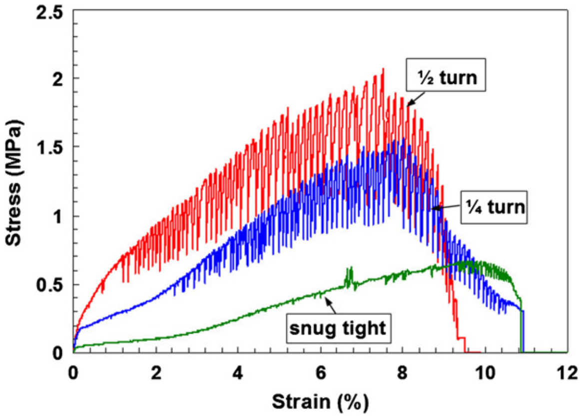


Figure 8. Tensile stress strain curves for artificial nacre for different levels of bolt tightening.

7. Conclusions

Nacre is a complex natural material which was finely tuned over evolution to achieve specific mechanisms and high toughness, and duplicating these mechanisms in artificial materials can open new pathways toward tougher engineering ceramics. In terms of biomimetics, every feature of natural nacre does not need to and should not be replicated. It is therefore critical to identify key structures and mechanisms in this material. In nacre, collective tablet sliding and strain hardening were demonstrated to be critical to toughness. The key structural features for this mechanism are stiff tablets with a high aspect ratio arranged in a staggered fashion so they can overlap, with a tightly packed arrangement to form a dense material. The interface should be weak enough to fail before the tablets fracture, and should generate hardening so tablet sliding can spread. Currently there is no technology that enables the implementation of these features at the microscale. This work however demonstrates that these key features can be successfully replicated in a millimeter size composite, which, for the first time, could duplicate the collective tablet sliding mechanism of nacre. This 'artificial nacre' is of course in some aspects different from natural nacre. However biomimetics is not copying, and this material provides an example of how a successful biomimetic design only incorporates a few key structures and mechanisms abstracted from a natural model. Finally, while the low strength of this material currently limits its use in actual structural applications, optimization of materials and structure is expected to lead to new high-performance materials with unique combinations of structural properties.

Acknowledgments

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