Biomimetic Designs Inspired by Seashells

Seashells Helping Engineers Design Better Ceramics

Kiran Akella

This article explains some interesting aspects of the mechanical behaviour of seashells. Their unique brick-mortar architecture makes them tougher and stronger than their constituents. Pearly layers in seashells, also known as nacreous layers, have an order of magnitude higher toughness than most ceramics. Replication of these features of seashells in synthetic ceramics can have immediate practical applications; for example, design of lightweight, efficient and cost-effective armour.

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1. Introduction

Seashells are natural ceramics similar to our bones and teeth. Conventionally, ceramics are defined as compounds between metallic and non-metallic elements. The term 'ceramic' comes from the Greek word '*keramikos*', which means burnt stuff. These materials achieve their desired state through a high-temperature heat treatment process called firing. Traditional ceramics such as china, porcelain, bricks, tiles, glasses, etc., are made using clay as the raw material. With advancement in understanding of these materials, the use of ceramics has surpassed traditional applications. Popular modern ceramics such as aluminium oxide, magnesium oxide, silicon carbide, etc., are used in a wide array of application areas such as electronics, automobiles, aerospace and defence. However, applications of ceramics are limited due to their brittle failure characteristics with low energy absorption during failure. Natural ceramics such as bones, teeth, seashells, etc., are different from conventional ceramics. These materials are called ceramics as they are compounds of metallic and non-metallic elements (such as calcium carbonate), but are different since they are not fired like human-made ceramics.

Keywords
Nacreous seashells, layered ceramics, armour design, mechanical properties.

Seashells with nacreous layers have higher toughness than conventional ceramics.

Natural ceramics, especially seashells with pearly layers, also known as nacreous layers, have a distinctly different behaviour from the brittle behaviour of conventional ceramics. They have a layered brick-and-mortar architecture with calcium carbonate platelets as the bricks and protein as the mortar. Behavioural aspects of natural ceramics such as reduced effect of flaws on tensile strength and higher toughness make them desirable for applications such as armour resistant to ballistic impact.

Engineers want to exploit the advantages of ceramics but are struggling to work around its disadvantages. Ceramics are stronger than metals under heavy compressive loads acting in the vicinity of areas subjected to impact. Their much lower density makes them attractive lightweight alternatives to metallic armour. But processing of ceramics requires high temperature and pressure. Hence they are more expensive than metals. Processing limitations also make manufacture of large and thick parts infeasible. Another drawback of ceramics is their brittle behaviour due to which armour suffers heavy degradation on impact. It therefore has lower multiple hits resisting capability than metallic armour.

Armour designers desire ductile ceramics. Attempts were made to achieve this goal by embedding ceramic fibres inside bulk ceramics. Such materials are popularly known as Ceramic Matrix Composites (CMCs). However, CMCs are difficult to process and much more expensive than conventional ceramics. Their application is hence restricted to niche areas such as the nose-cone of a space re-entry vehicle.

To improve the design of armour at reasonable cost, novel designs have to be explored. Studying the microstructure of shells and methods of replication therefore offer a promising opportunity. It opens up a possibility of attaining ductility in ceramics at lower cost. Exploring this possibility might lead us to light, cost-effective and efficient armour.

Seashells have generated sustained interest amongst researchers in the last few decades. Enough data is available on their mechanical properties and the reasons for their superior behaviour as compared to conventional ceramics are also reasonably understood. However an armour design based on this concept is still not available.

In this article, the mechanical behaviour of seashells is presented and their microstructure is explained. Their mechanical behaviour is compared with conventional ceramics. Features of seashell structure that cause its improved behaviour are discussed. Finally, approaches being adopted to replicate its design for developing tough and ductile ceramics are reviewed.

Box 1. Glossary*

Stress is the force divided by the area on which the force acts. Its unit is Pa or Nm^{-2}. ***Strain*** is the proportional change in length. It has no units. ***Strength*** is the stress at which material breaks up. It is also measured in Pa. ***Young's modulus*** is the ratio of stress and strain.

Toughness is the ability of any material to absorb energy per unit volume before rupture. Hence, its units are Jm^{-3}. It is defined as the area under the stress–strain curve of any material. The stress–strain curve is plotted by measuring load versus deformation for a standard specimen. A material is tough if it can bear large deformations (or strains) under heavy loads before failure. Strength and toughness are related. A material is strong when it bears heavy loads before failure. A material is strong and tough when it exhibits large strains under heavy loads before failure.

Brittle failure occurs if a material does not exhibit large strain values before failure. Such a brittle material may be strong but not tough. Since a brittle material fails at low strain values, the failure is sudden. Glass is brittle material but not mild-steel. It has little tendency to deform before fracture. This fracture absorbs relatively little energy, even in materials of high strength.

Ductility is a mechanical property used to describe the extent to which materials can be deformed without fracture. This is also often characterized by the material's ability to be stretched into a wire. A ductile material such as mild-steel or gold can undergo large deformations before failure.

Hardness is the resistance offered by a material to permanent shape change. Commonly, hardness is measured as resistance to scratch or indentation. Hardness is a surface property and not a bulk property.

Percentage elongation is the strain at which rupture of material occurs and is expressed in percentage. Its value is high for ductile materials and very low for brittle materials.

* See Gordon's Book [1].

Shells are formed from secretions of the mantle.

2. Background on Shells

Shells are 'houses' for molluscs and are called exoskeletons. Because of shells, the soft body of a mollusc gets shape and rigidity. In addition, shells perform secondary functions such as: camouflage, aids to dig in mud, anchor, and even help the mollusc have its own farm by allowing in its spines, growth of seaweeds for consumption. Molluscs make shells from calcium that they extract from the environment through food and water. At the time of their birth, molluscs come into the world equipped with their own tiny shells.

The body of a mollusc is made of five main parts (*Figure* 1) namely: (i) foot, a highly muscular organ for locomotion; (ii) head, with eyes and tentacles; (iii) visceral mass, containing digestive excretory, circulatory and genital organs; (iv) mantle, covering the visceral mass; and (v) shell, formed from the secretions of mantle. Two forms of crystallised calcium carbonate are usually observed within the cross-section of shells, commonly known as calcite and aragonite.

Molluscs belong to Phylum Mollusca. There are more than 110,000 species of molluscs within the phylum. Some commonly known molluscs are snails, clams, mussels, squids, octopi, chitons and tusk shells. A majority of molluscs live in marine environments; bivalves and gastropods include some fresh water species and species that live on land such as snails. Of all the classes, bivalves and gastropods are most abundant and include the largest number of species. Most species in these two classes have well-formed shells. Bivalves include clams, oysters, scallops, mussels, etc., and gastropods include abalones, limpets,

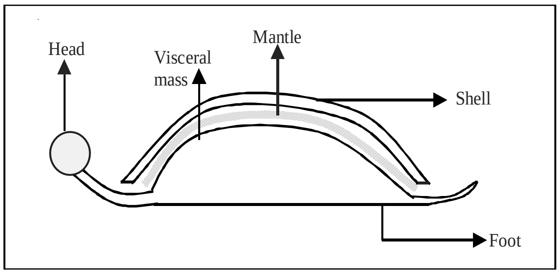


Figure 1. Parts of a generalised mollusc.

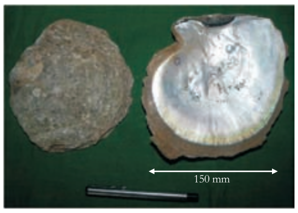


Figure 2 (left). Mussel, a large bivalve with thick nacreous layers purchased from the Kalam Seashell Shop at Rameswaram.

Figure 3 (right). Shells belonging to Trochus family, a gastropod, purchased from the Kalam Seashell Shop at Rameswaram.

conches, etc. Photographs of a bivalve (mussel) and gastropod (trochus) from Kalam seashells shop at Rameswaram is shown in *Figures* 2 and 3. The shining part of the mussel shell shown in *Figure* 2 is the nacreous layer.

3. Microstructure Patterns in Seashells

The microstructure of shell has been studied extensively. Many factors affect it, its environment being one of them. Though there are tens of thousands of mollusc species, microstructural patterns of mollusc shells are few in number and can be listed as: nacreous, prismatic, foliated, cross-lamellar, homogenous and myostracal.

i) *Nacreous microstructure* has brick and mortar type architecture, where 'bricks' are polygonal plate-like structures of $CaCO_3$ (calcium carbonate), and 'mortar' is made of an organic protein matrix. The platelets are about 10 μm in diameter and 0.5 μm thick. A schematic of nacreous microstructure is shown in *Figure* 4.

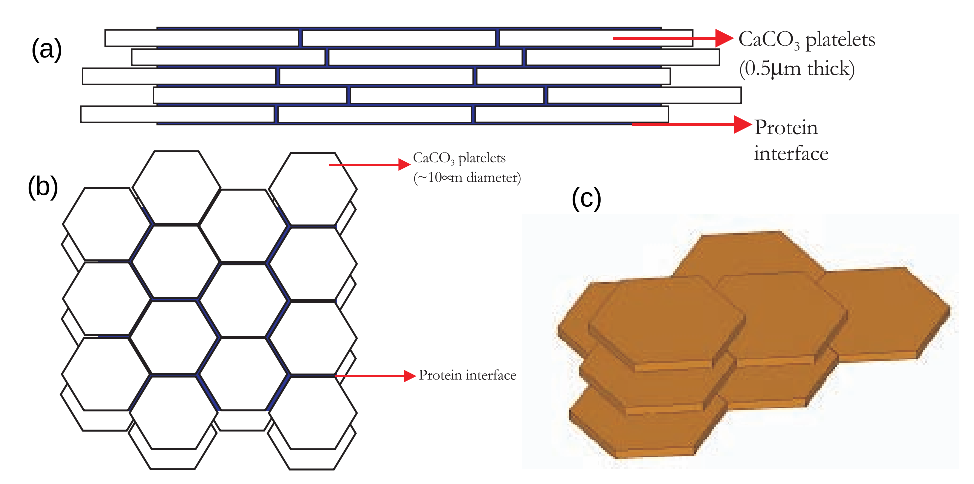


Figure 4. Schematic illustration of the architecture of nacreous microstructure. (a) Schematic illustration of the cross-section; $CaCO_3$ platelets are bricks while protein interface is mortar. (b) Schematic illustration of the polygonal platelets as seen from above. (c) 3D schematic illustration of the architecture.

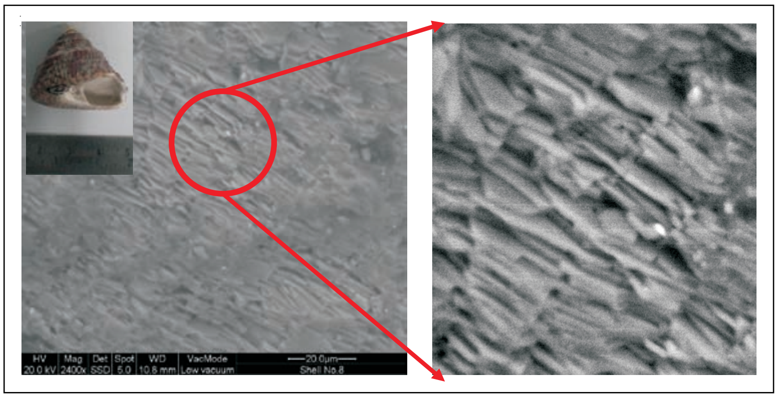


Figure 5. Nacreous microstructure observed in shell belonging to Trochus family.

In *Figure* 5, scanning electron microscope (SEM) picture of a trochus shell with nacreous microstructure photographed at Automotive Research Association of India (ARAI), Pune is shown. The trochus shells have been collected from beaches in western Maharashtra.

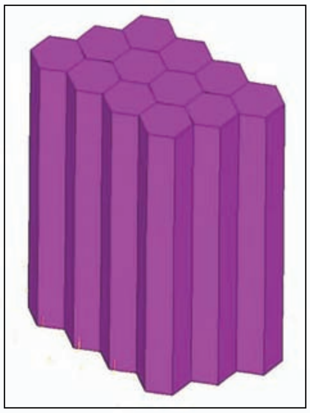


Figure 6. 3D schematic illustration of prismatic microstructure.

ii) *Prismatic microstructure* is made of polygonal prisms and an organic matrix in between. The microstructure is illustrated in *Figure* 6.

iii) *Myostracal microstructure* is similar to prismatic structure, but is made of irregular polygonal prisms.

iv) The cross-section of *foliated microstructure* appears similar to the nacreous structure. However, instead of polygonal platelets, it consists of elongated strips also termed 'laths'.

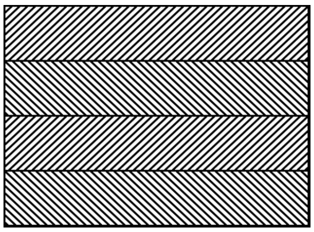
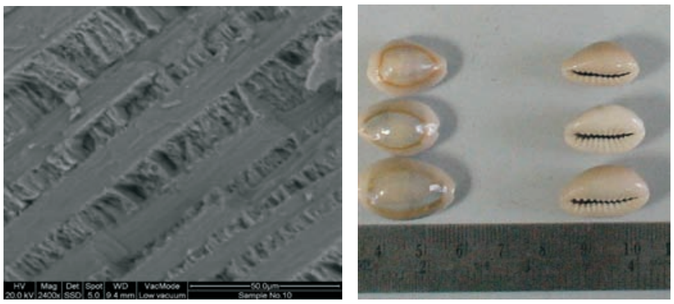


Figure 7. Schematic illustration of the cross-section of cross-lamellar microstructure.

v) *Cross-lamellar microstructure* is composed of elongated strips as in foliated microstructure. However the similarity ends here. The elongated strips are mutually parallel in lamellae or blocks. The elongated strips in the neighbouring lamellae are inclined at high angles as illustrated in *Figure* 7. Interpenetration between lamellae is also sometimes observed. SEM pictures of cross-lamellar microstructure in cowries are shown in *Figure* 8.

vi) *Homogenous microstructure* consists of equidimensional spherical granules, 1–3 μm in diameter as shown in *Figure* 9.



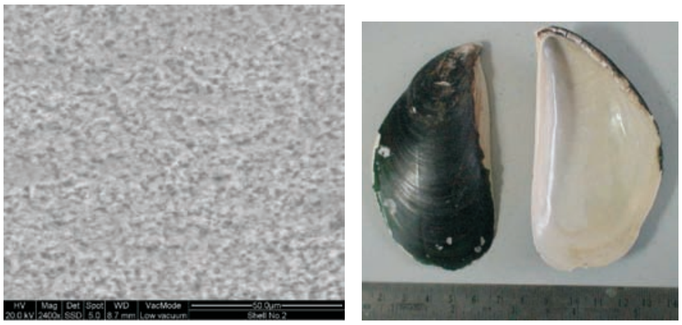


Figure 8 (top). Cross-lamellar microstructure in cowries.
Figure 9 (bottom). Homogeneous microstructure in mussels.

3.1 *Distribution of Microstructural Types*

The type of microstructure in a shell depends on: (a) predecessors from whom the organisms evolved (or phylogeny) and (b) mode of life (environment). As an example of phylogeny, it has been observed that nacreous microstructure is common among groups considered to be primitive and cross-lamellar microstructure is observed among more advanced groups. Nacreous structure was observed to be most resistant to breakage (toughest) and cross-lamellar structure the hardest. As an example of dependency on environment, stronger nacreous structure is found in species subjected to heavy currents, predator attacks and thin-shelled bivalves. Cross-lamellar structure is commonly found in species that burrow and bore where hardness and abrasion resistance is critical.

Shell growth occurs by accretion of its constituents.

The cross-section of the shell is a combination of diverse microstructural units. Shell growth is most often by accretion of the shell constituents in two areas, mantle margin and mantle surface. Mantle surface is in direct contact with the organism and mantle

Some shells can have more than two subdivisions with different microstructural patterns.

margin is exposed to the outer environment. Accretion at mantle margin results in increase of the length and width of the shell while accretion at the mantle surface results in increase of thickness of the shell. In a typical bivalve shown in *Figure* 2, the shining inner layer is due to accretion at the mantle surface and the brown outer layer is due to accretion at the mantle margin. In this shell, brown outer layer has a prismatic microstructure while shining inner layer has nacreous microstructure. In addition to the two subdivisions illustrated here, some shells can have more than two subdivisions with different microstructural patterns.

4. Mechanical Behaviour of Seashells

Different microstructures of seashells have been found to have varying mechanical behaviour under tensile loads, compressive loads, beam bending (flexure), and indentation (hardness). Schematic of the test specimen and loading patterns for tension, compression and flexure are illustrated in *Figure* 10.

• To obtain the *tensile strength*, a tension test is conducted. A specimen is carefully made such that no flaws are introduced while making it. Care is also taken to ensure that the specimen does not fail in the grips of the testing machine since stress is not uniform there. For example, it is made wider at ends. Tensile stress is applied by pulling the specimen (see *Figure* 10a).

• To obtain the *compression strength*, cylindrical specimens are compressed until they break (*Figure* 10b).

• To study the *bending behaviour*, beam specimens are made and tested until failure. The test, also known as 'flexure test', is usually done in 2 configurations: three-point bending (*Figure* 10c) and four-point bending (*Figure* 10d). The bending stresses are highest at the mid-span of the beam and in three-point bending the load is also applied at mid-span. Due to this the failure stress may be influenced by local effects which might lead to incorrect results. Four-point bending is desired when local effects dominate since it eliminates the local effects problem. The

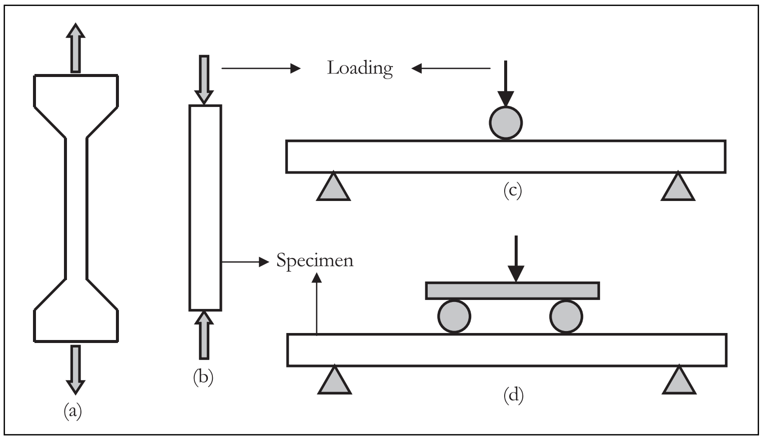


Figure 10. Tests conducted on shell specimen: (a) tension; (b) compression; (c) three-point bending (flexure) and (d) four-point bending (flexure).

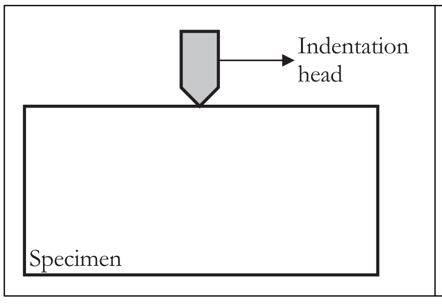
failure stress obtained from flexure test is called the flexural strength of the material.

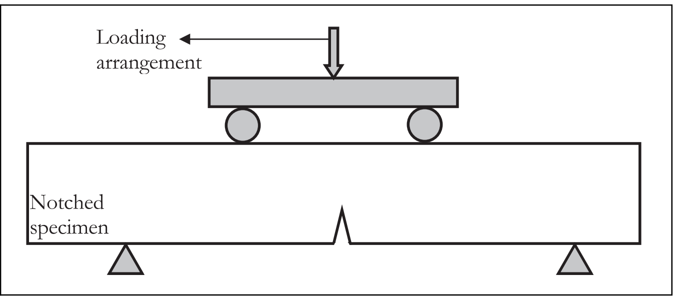
• Indentation test (Vickers hardness test) to study *hardness* has been illustrated in *Figure* 11. A hard tip is chosen and pressed on the specimen. Its surface is carefully prepared to avoid any unnecessary effects due to undulations. The resistance to penetration is measured. Harder the material, greater is its resistance. The test is very useful to quantify a materials resistance to indentation which is an important parameter where hardness is required; for example, resistance to penetration of bullets in armour.

• To measure *toughness*, notched beam test can be conducted. Its schematic is illustrated in *Figure* 12. Specimen preparation and loading is the same as in flexure test except for the notch in the specimen. The failure always occurs at the notch as it acts as a pre-induced crack. The crack propagation behaviour of material

Figure 11 (left). Schematic illustration of Vickers hardness test used to evaluate hardness of a material by measuring resistance to penetration.

Figure 12 (right). Schematic of notched beam test.





Microstructure	Mean tensile strength MPa	Mean compressive strength MPa	Mean flexural strength MPa	Stiffness from flexure tests GPa	Vickers hardness number
Prismatic	60	250	140	30	162
Nacreous	130 (wet) 167 (dry)	380	220	60 (wet) 70 (dry)	168
Cross-lamellar	40	250	100	60	250
Foliated	30	150	100	40	110
Homogenous	30	250	80	60	–

Table 1. Mechanical properties of different seashell microstructures.

can be studied using this test. Area under the load deformation curve obtained by conducting a notched beam test is a measure of toughness and is also known as work to fracture (for more details, see Timoshenko's book [2].

The properties of different microstructures of shells are listed in *Table* 1 (see book by Vincent, 1991 [3]).

From *Table* 1, we observe that nacreous shells have the highest tensile, compressive, flexural strength and stiffness as compared to other microstructures. Cross-lamellar shells have the highest Vickers hardness number. Mechanical properties and fracture of shells with nacreous and cross-lamellar structure have been studied in greater detail due to their superior properties. Shells with nacreous microstructure have been particularly studied as they were found to have the highest toughness.

4.1 *Behaviour of Nacre*

For nacreous shells, the Young's modulus of 70 GPa and tensile strength of 170 MPa was measured by a number of researchers. In comparison, regular advanced ceramics such as alumina and silicon carbide have Young's modulus in the range of 250–350 GPa and tensile strength in the range of 200–350 MPa. Observing these results superficially, one can conclude that the nacre is much weaker than conventional ceramics. We are already far ahead and there is apparently no reason to study shells further.

Nacre has the highest tensile and compressive strength.

But our sense of superiority ends here. If we study the raw materials used, nacre consists of 95% aragonite crystals that have modulus 90 GPa and tensile strength 80 MPa. These values reveal that nacre has higher tensile strength than aragonite, its raw material. Let us compare this with alumina. Alumina, considered as one of the workhorse ceramic materials, is widely used for structural and armour applications. Contrary to the observations of tensile strength in nacre and its raw material, 99.9% alumina with a grain size of 15–45 μm has a flexural strength of 300 MPa whereas single crystal alumina has flexural strength more than 600 MPa (For more details, see ASM *Engineering Materials Handbook* [4]). Thus, nacre has managed to have higher tensile strength than its constituents, whereas engineered ceramics have much lower tensile strength than its raw material. Its unique platelet-by-platelet-assembly manufacturing process and aragonite–protein based brick-and-mortar architecture enables its superior behaviour. Nature uses a weak raw material and makes a strong and tough structure, whereas we use a very strong raw material, subject it to an expensive manufacturing process involving high temperature and pressure and create a much weaker structure. This is a great lesson in effective utilisation of materials that we still have to learn and adapt.

Nacre uses a weak raw material and makes a strong, tough structure.

4.2 *Flaw Dependence*

An interesting aspect of nacre behavior is the ratio of compressive strength to tensile strength. For typical ceramics such as alumina, the compressive strength is 2500 MPa and tensile strength is 200 MPa. The ratio between compressive strength and tensile strength is 12.5. Thus, compressive strength is more than an order of magnitude higher than tensile strength. This is due to the presence of micro-flaws (micro-cracks and pores) that amplify the applied stress. The amplified stress causes rapid expansion of cracks due to the brittle failure of ceramics (see *Box* 1). For compressive stresses, there is no stress amplification due to flaws and cracks do not expand. Flaws are created during fabrication. If we choose a process such that minimum flaws are generated, we achieve higher tensile strength. Such processes

Large difference between tensile and compressive strength means high flaw dependence.

further increase the cost of conventional ceramics. For example, high compressive pressure is applied while manufacturing so that flaws are not created. That brittle ceramics have higher strength in compression than in tension can be easily observed around us. We can never crush and break a glass bead (high compressive strength). We cannot scratch glass (high hardness). However, if we drop a glass slide, it immediately breaks (low tensile strength). Plastic is quite opposite. We can crush it and scratch it easily, but if we drop a plastic piece, it never breaks.

The same tensile and compressive strength is observed in ductile metals such as mild-steel. If the brittle failure of ceramics is altered and made ductile, the tensile strength will increase and be the same as the compressive strength. Such ceramics can be called 'ductile ceramics'. Nacre is a ductile ceramic. Its compressive strength is about 550 MPa and tensile strength is 170 MPa, the ratio is 3. In conventional ceramics, the ratio is more than 10. The tensile strength is high in nacre and closer to its compressive strength due to the reduction in flaw-dependence. This is a major breakthrough that nacre has achieved but engineered ceramics could not. Flaw dependence has been reduced without the expensive manufacturing process required to improve the strength of engineered ceramics. If the flaw-dependence can be reduced in conventional ceramics fabrication process by making them ductile as in nacre without significantly increasing its cost, engineered ceramics may then have much higher tensile strength, say 1000 MPa. It would make ceramics much more attractive to use when compared to metals.

4.3 *Ductile Ceramics*

Nacreous seashells rank amongst the toughest materials known.

Researchers working with structural ceramics are most often trying to make ceramics tougher. Ductile ceramics is their dream. Seashells have elegantly shown the path. The conventional way of making tough ceramics is by incorporating fibres in ceramics. Such materials are popularly known as ceramic–ceramic composites or ceramic–matrix composites. Processing these materials is expensive and time-consuming. Hence, such ceramics find application only in niche areas such as nose cone of an aerospace vehicle. Seashells achieve high toughness without the expensive process.

Large amount of energy is absorbed during fracture in nacre.

It has been observed that work to fracture for nacre varies between 350–1240 J/m^2. These values are an order of magnitude higher than most conventional ceramics such as alumina and silicon carbide where the variation is between 50–100 J/m^2. The work to fracture values of shells is comparable with ductile metals that have a value of about 1000 J/m^2. Even high-strength fibre-reinforced polymer (FRP) composites like carbon-epoxy used for aerospace applications records a value of about 100 J/m^2 only. Thus, seashells rank amongst some of the toughest materials known and inspite of being made with 95% calcium carbonate, which is much weaker than any of the exotic raw materials used in engineered ceramics.

4.4 *Superiority of Nacre*

There are three main aspects in mechanical behaviour of seashells that make them significantly superior to conventional ceramics: (a) they possess a higher strength than their constituents; (b) due to their reduced flaw dependence, they have comparable tensile and compressive strength; (c) they have much higher toughness. It is vital to understand the exact micro-structural features that cause this improved behaviour if replication of these aspects is sought in engineered ceramics. Nacreous seashells have a unique brick-and-mortar architecture consisting of about 95% by weight aragonite and remaining 5% protein matrix (*Figure* 13). This architecture made of stiff aragonite platelets and flexible protein interface causes crack deflection, thereby increasing the energy absorption during fracture. The difference between crack patterns and load-deformation curves

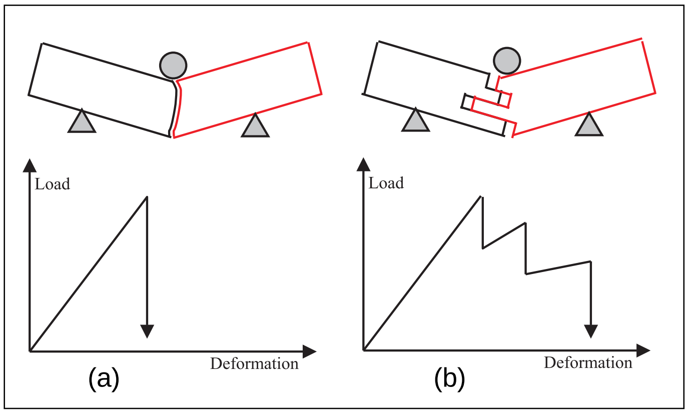


Figure 13. Comparison between failure pattern and load deformation curve of (a) monolithic and (b) nacreous, layered ceramics.

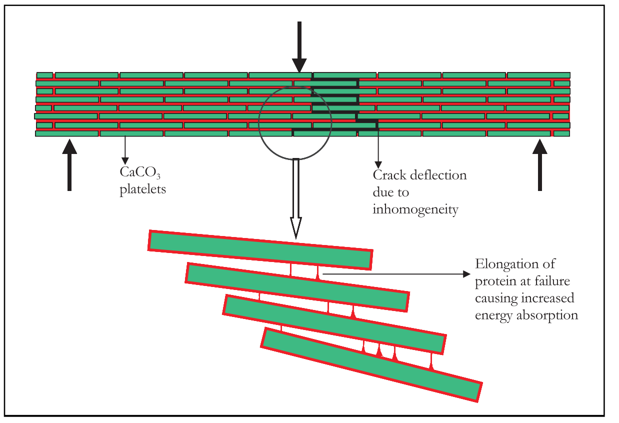


Figure 14. Failure of beams made using nacreous shells.

obtained from 3-point bending tests conducted on monolithic ceramics and nacreous seashells are illustrated in *Figure* 13.

In monolithic ceramics, cracks propagate rapidly through the homogenous material, as they do not encounter the inhomogeneity found in nacre. The protein matrix has very high percentage elongation leading to a large amount of energy absorption in deformation. But the grains in engineered ceramics have weak and brittle grain boundaries, which let cracks pass easily. The bond between protein matrix and aragonite is strong thereby ensuring full utilisation of the elongation of protein matrix. These features of seashell behaviour are illustrated in *Figure* 14. Failure under three-point bending test is used for illustration. All these factors ultimately reduce flaw dependency in shells, the main reason for inferior behaviour of conventional ceramics. Furthermore, there are additional micro-structural features such as non-uniform platelet thickness and nano-undulations in platelets causing mechanical locking and further increasing energy absorption.

5. Biomimetic Approaches to Replicate Nacreous Shells

Efficient armour requires hard, tough and lightweight materials with significant penetration resistance and energy absorbing capabilities. Ceramics are an alternative to metals but costly. Manufacturing complexities and brittle nature of failure further reduce the weight advantage offered by ceramics. If the mechanical behaviour of nacre can be replicated in manmade ceramics,

Biomimetics is the concept of using ideas from Nature.

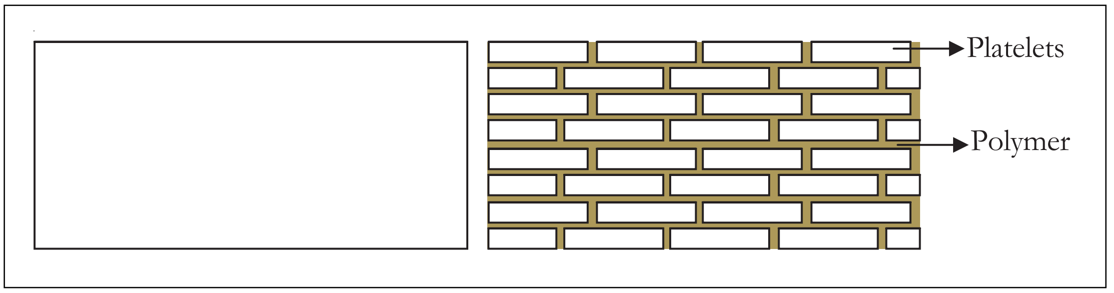


Figure 15. Conventional ceramics are monolithic blocks (left) while nacre (right) is a layered ceramic with brick–mortar architecture.

ceramics would become more attractive. Further, if manufacturing process similar to that used for making nacre by the mollusc can be adopted, sintering and hot pressing may not be required to make tough ceramics, thereby substantially reducing the cost of processing ceramics.

Conventional ceramics are monolithic blocks. To replicate the layered brick-mortar microstructure of nacre, we must make thin layers of ceramics (see *Figure* 15). These ceramic layers must then be bonded with a strong adhesive similar to the protein in nacre. Such adhesives are typically polymers. Proteins are also polymers. A polymer is a large molecule composed of repeating structural units (set of atoms bonded together).

Biomimetics is the concept of using ideas from Nature to develop technologies. Any approach to replicate the microstructure of nacre to improve the toughness of existing ceramics can be called biomimetics. However, the main difficulty to create nacre-like materials is the inability to build thick ceramics of the order of 10 mm with 0.5 μm thick layers as in nacreous microstructure. Achieving a strong bond between the polymer and ceramic layers as in shells is another technical challenge. The organism builds the shell thickness by depositing very small amounts of material. Developing a fabrication process to mimic this stacking is the major bottleneck. An engineering approach would be to use thicker layers that can be easily handled. The gains may not be as remarkable as in seashells but tangible benefits could still be derived. A simple method is given in *Box* 2. The increase in toughness may only be a few times of the monolithic material since the layers are quite thick.

Developing a fabrication process to mimic thin layers in nacre is a major bottleneck.

Box 2. Do-it-yourself Experiment to Understand the Enhanced Toughness of Seashells

One can replicate seashell behaviour with a simple experiment. Glass slides are easily available in any stationery shop. Purchase the microscopic cover glass slides shown in *Figure* A; they are thin enough. Take about 20 such glass slides. Dip them one by one in a beaker containing slow bonding glue. A fast bonding glue will not give enough working time. Choose glue that can be used to stick glass. Epoxy such as Araldite ™ bonds well but it is very thick (viscous). To make it thin, we can heat the beaker or add a solvent such as lacquer thinner, denatured alcohol or acetone. After dipping the glass slide in the thin glue, slowly remove the dipped glass slide and hold it in air till the glue starts becoming a gel. A thin film of glue will form on both sides of the glass slides.

Prepare a stack of 20 such glue-dipped glass slides (*Figure* A). Gently press the stack and keep it pressed until complete gelation of the glue occurs. One has to be careful with two issues here: (a) resistance of glue to flow (viscosity) and (b) the speed of removing the dipped glass slide. If the glue does not flow easily or if the glass slide is removed too quickly from the beaker, proper film formation will not occur and result in a weakly bonded stack. It will not replicate the increased energy absorption of nacreous seashells.

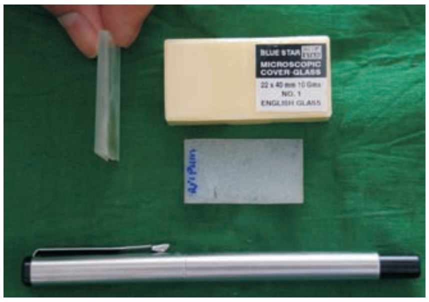
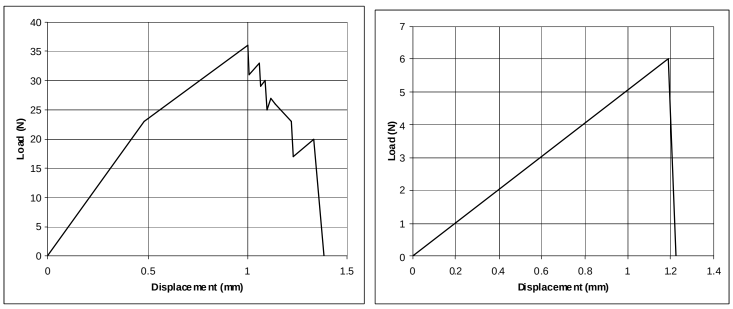


Figure A.

20 glass slides were bonded by a polycarbonate film (total thickness 3.15 mm). 3% by weight solution of polycarbonate in dichloromethane was prepared. Thin films of the polymer were deposited on glass slides by dip coating. Complete removal of the solvent was made sure by heating these slides at 55^0C. Dip coated glass slides with the polymer film on both sides were sandwiched. A total of 20 glass slides were stacked and made to stick together by a step-wise heating to 230^0C in an oven under a load of 200 g. Three-point bend test was conducted on the stack.

The layered glass specimen shows greater area under the curve and therefore higher energy absorption (*Figure* B). This simple experiment demonstrates how seashells absorb greater energy. Increase in number of layers will further increase the energy absorption.

(a)



(b)

Figure B. Load deformation curve for (a) layered specimen versus (b) monolithic glass specimen of same thickness.

Various promising methods are being pursued by researchers to replicate the layered-ceramic microstructure of seashells. Currently, monolithic ceramic parts are made from powder (also known as green form of ceramic) by drying and firing (sintering). To improve their mechanical properties they are sometimes hot-pressed during the manufacturing process. For replication of the layered ceramic structure of nacreous seashells, researchers have modified ceramic fabrication processes using various methods. These methods can be classified into two categories: (1) Sintering thin ceramic plates, subsequently bonding and stacking them; and (2) making a stack with thin ceramics tapes (green tapes) and then sintering the stack.

For replication of the layered ceramic structure of nacreous seashells, researchers have modified ceramic fabrication processes using various methods.

Both methods have their advantages and disadvantages. In the first method, ceramic plates have to be reasonably thick to prevent cracking and warping during fabrication due to shrinkage. They should also be thick enough to avoid cracking during handling actions such as stacking and pressing. In the second method, since stacks are made before sintering, ceramic layers can be made thin. Sintering is done at high temperature after stacking. However, this imposes a severe restriction. The interface material used to bond ceramic layers together is often another ceramic as it should be high temperature resistant. Most polymers having ductile behaviour and high elongation before failure, decompose at the high sintering temperatures required for ceramics. Therefore, not so ductile interfaces like graphite have to be used.

The above restriction does not exist in the first method. Any polymer similar to the behaviour of protein matrix in seashells can be used. In the first method, a wide choice of interface materials with high ductility is available, but it is difficult to make the ceramic layers thin. In the second method, though the ceramic layers can be made thin, the choice of interface materials is severely restricted.

Freeze casting, a recently reported approach, has been developed by researchers in University of California, Berkeley. In this

Biomineralisation is similar to the techniques used by molluscs.

approach, fine ceramic powder is suspended in water. The suspension is then frozen. When this frozen mixture is suddenly heated, the ice melts leaving empty spaces between the ceramic powder creating gaps. These gaps can be used to infiltrate a polymer and recreate the brick-and-mortar microstructure as in nacre. Some researchers have used gel casting with hot-pressing and slip-casting. In these methods, ceramics, in powder or platelet form, are suspended in a polymer using a solvent. The solvent is evaporated leaving a compact ceramic–polymer composite. Pressure can also be applied in this process to improve the compaction. All these methods of replicating nacre can be used to make bulk ceramics with thickness in the range of a few millimeters or centimeters.

Another set of methods are called the bio-mineralisation approaches. A solution is made of organic and inorganic constituents. The organic constituents influence the crystallization of the inorganic phase and well-defined structures as in nacre are formed. This manufacturing technique is similar to that used by the mollusc to create shells. Layer-by-layer assembly is also an approach used to make nacre-like materials. A substrate is immersed in solutions of oppositely charged materials. Thin layers of nanometer dimensions are deposited using this method. In these methods, the orientation of the platelets in the layers is important for achieving improved properties and compaction. For improved orientation of the platelets, the suspension is sometimes centrifuged so that the layers align themselves. In another technique, the layers are spin-coated, i.e., the layers are deposited one-by-one on a spinning substrate. The rate of spin and the viscosity of the ceramic suspension can be controlled to obtain desired layer thickness. Using any of these bio-mineralization or layer-by-layer approaches, researchers have been able to make only thin layers, ranging from a few microns to a maximum thickness of a fraction of a millimeter. Substantial gain in properties has been observed in these methods, but they have still not been scaled up to make specimens of a few millimeters or centimeter thickness.

The methods suitable for bulk ceramics currently do not show the property enhancement as seen in nacre. Bio-mineralization and layer-by-layer approaches show better property enhancement but have difficulties in scaling up and cost-effectiveness. A process completely replicating all the toughening mechanisms in nacre to make products few millimeters in thickness and be cost-effective is therefore still not available. There is a scope for creativity in both the bulk and layer-by-layer type approaches. Therefore, this is currently an area of intense research.

Replication of nacre is currently an area of intense research.

Suggested Reading

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