

# A bionic material for shells and its mechanics research

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## Abstract

Shell is one of composite natural organic and inorganic hybrid hierarchical biological composite materials. The distinct "bricks-mortar" structure in a hierarchical fashion which results in its special mechanical properties. In this work, the principle of mechanical properties of nacre layer, the bionic materials of three layers of shells, the methods of producing bionic materials will be discussed. The inspiration of the bionic materials was explored recently, additionally some opinions and ideas are put forward.

## Keywords

Hierarchical structure; nacre; strength and toughness.

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## 1. Introduction

Bionic materials are the man-made materials which were produced according to the operation of living system and the structure of natural biomaterials. Natural biological materials such as bamboo, wood, bones, shells, have a very good comprehensive performance through the fine combination of complex structures although the composition is simple, people have received great inspiration from the natural biological research. Nowadays, with the development of technology, composite materials are more and more widely used, and the performance requirements are also increasingly high. Among the many natural biomaterials, the shell pearl layer has received wide attention due to its unique structure, extremely high strength and good toughness, and has become a model structure for the preparation of lightweight and high strength super toughness layered composites. A series of bionic high-strength and super-toughness layered composites have been prepared in material science, mechanical and civil engineering, and aerospace fields.

## 2. The hierarchical structure of shells

Shell is mainly composed of three layers: the outermost layer is the cuticle layer, is a hard protein, with good wear resistance and water resistance; the middle is the prismatic shell, it occupies most of the shell, composed of angular column calcite, cuticle and prismatic layer can only be secreted by the back edge of the coat film; the inner layer is a nacre, also composed of angular column calcite, it is formed by the whole surface of the coat film secretion, thickened, shiny and has strong toughness. Although the shapes of the each shell are different with various colors, the chemical components are similar.  $\text{CaCO}_3$  takes up 95 % of the whole shells protein-polysaccharides occupy the remaining 5%. In the study of the shell surface morphology and Marine biological adhesion, foreign scholars have done a lot of work. Andrew Scardino<sup>[1]</sup> and other researchers studied the attachment of marine deorganisms of purple mussels and pearl shellfish, getting the conclusion that the shell surface microstructure and its anti-pollution properties are correlated. Jilin University conducted several experiments and <sup>[2]</sup> reached the following conclusion that under a certain load, the friction factor decreases rapidly with the increase of the sliding speed, providing a basis for the shell cuticle layer to have a certain wear resistance. The "bricks-mortar" structure of nacre is formed by the

accumulation of organic horizons and mineral layers and can be observed at an appropriate magnification.

### 3. The nacre of shells and its toughening mechanism

The nacre is made of aragonites. The horizontal growth of the text stone slab connects the adjacent crystals to each other to form a text stone layer. The text stone layer connects from an organic matrix about 30nm thick to form the pearl layer. Most stone tablets are five and hexagonal, but also rhomboid, round and irregular polygons. Observation of individual tablets by atomic force microscopy revealed that they were composed of nanocrystalline of pebble-like polygons. It is such a highly complex and exquisite multi-scale, multi-stage assembly structure that makes the shell show good mechanical properties. According to the different stacking way of the aragonite in nacre, there are two kinds of structure, one is cohimanar-stack structure and another one is brick-mortar structure<sup>[3]</sup>. The former mainly exists in the bivalves, the latter is in the gastropods. The former newborn crystals are deposited at the edge of the steps and connected to the microlayer structure through the lateral extension; the latter newborn crystals are formed at the top of the stack and then grow laterally in contact with the adjacent stack, which form the microlayer of the nacre. On the vertical section, the axis of the aragonites of the brick-mortar structure is not arranged regularly, while the upper and lower microlayer slabs in the stacked structure are arranged regularly along the growth direction of the layer, with only a small offset of 20 and 30nm. In addition, through the atomic force microscopy (AFM) observation, we found that the two aragonites also have micro difference, manifested in concave shape of the aragonites, with many concentric rectangular rings on the surface. Although cohimanar-stack structure is also concave, it is more flat without rectangular rings on its surface. It confirms that the brick-mortar structure and cohimanar-stack structure are different whether at a micro level or macro level. There are differences that show the particularity of its biological mineralization mechanism. Extensive work was done to explore the toughening mechanism of the nacre. The toughening effect of the frequent crack deflection and classical stone sheet extraction on the nacre has been confirmed, but the simple "brick-mud" structural model does not fully explain the energy consumption measured by the experiment. The frequent crack deflection and rock extraction on the nacre have been confirmed, but the simple "brick-mortar" structure model does not fully explain the energy consumption. The discussion of different scales shows that plastic deformation of inorganic organic matter and good adhesion with inorganic layer is common in the shell nacre layer. The nanoscale organic matter bridging model proposed by Smith is used to explain the microscopic slip deformation observed in the strong binding interface and tensile tests of biomolecular and inorganic phases. However, the model contributes little to explain the reinforcement of the binding interface. The inorganic surface microprotrusion interlock model [4,5] and [6] and the nanocrystalline deformation and offset model [7] explain the reinforcement effect. In addition, the waveform surface model [8] complements the reinforcement effect of lateral expansion between macrolayers. This is the result of various mechanisms that are inseparable from the composition and special structure of the nacre. There are four specific reasons to discuss why the "brick-mortar" structure can lead to a strong toughness of the shells. First, deflection of cracks can increase the extension pathway thus increase the absorption of fracture work, and the extension of the crack from one favorable direction to the unfavorable direction can cause a significant increase in the extended resistance and thus the external force rises, resulting in an improvement in the toughness of the shells. Second, the bridging of the organic matter means the organic matter between aragonite layers sticks the two layers and prevent them from separating easily, so the stress strength factor at the crack tip is reduced and the crack expansion resistance is enhanced. In addition, there is a strong interface between organic matter and aragonite layers, so the friction between two layers increases and the shells are tougher. Third, aragonite blocks also called fibers, the breaking of the shells means the fibers will be pull out, so the frictional force and adhesive strength can resist the extension of the cracks and the energy needed to break rises thus shells are harder to break. Fourth, the existence of mineral bridges and nanopores

and the randomness of their location strengthens the deflection effect of the cracks, due to the resistance force between the cracks.

#### 4. Preparation and research of shell bionic materials

People seek the design method and inspiration of bionic materials from the research of shell special structure, and determine the performance parameters, summarize the rules, and reveal the composition mechanism and operation mechanism of shells through exploring the relationship between their structure and function. On this basis, using bionic design methods and concepts to realize the development of layered composite materials which is tough and lightweight.

##### 4.1 Anti-pollution ability of the surface of the shells

According to the characteristic parameters of shell surface, researchers in Wuhan University of Technology[9] prepared an experimental model for imitating the microstructure of the shell surface by sandpaper grinding, precision machining and biological replication molding, which was used in pollution-prevention of ships. This bionic materials of the surface of shells can prevent biological attachment. It also has some advantage, for example it is more environmental-friendly than chemical reagent and more efficient than manual cleaning.

##### 4.2 abrasive resistance of corneum

Jilin University [10] confirmed that the cuticle has good abrasive resistance, but current research for bionic coatings of shell cuticle are not enough. The bionic coating of the shell cuticle has good water resistance and certain abrasive resistance. At present, many biodegradable materials such as whole starch plastic are green, but has poor water resistance, which is easy to decompose in water, limiting its scope of use, if the surface is coated with a layer of bionic materials for the corneum, the properties of its green products remains and the water resistance is greatly improved .

##### 4.3 the brick-mortar structure of nacre

The alternating arrangement of aragonite crystals and organic matrix is the key to its high toughness. According to this principle, material scientists started the development of bionic materials for nacre. Belcher and other scientists observed the structural and morphology for mother of pearl during different feeding periods, researching the feasibility of using the "Christmas tree" model to describe the mechanism of formation of mother of pearl. Clegg[11] coated the SiC sheet with graphite colloid, deposited and sintering, and made a composite laminate material with a graphite layer of thickness 3~25 pm and SiC layer of thickness 150 pm, which greatly improved the rupture toughness and the rupture power by about 100 times.

Zhang Yongli [12] prepared SiC / Al laminate composite by thermal compression craft, and its fracture toughness was 2 ~ 5 times higher than inorganic SiC, which showed that its toughness was significantly improved compared with inorganic raw materials. Huang Yong and other researchers [13] used rolling film or delay forming process, successfully prepared Si<sub>3</sub>N<sub>4</sub>/BN layer structure characteristics. By optimizing the structural design and geometric parameters of the material, excellent mechanical properties can be obtained: fracture toughness in 20~28 MPa m<sup>1/2</sup>, fracture work is higher than 4000 J/m<sup>2</sup>, and the bending strength can be maintained at 500~700 MPa, unique structure characteristics of layer ceramic materials determine its unique fracture behavior. SaridayaM[14] made nacre ceramic toughening composite with Al as soft layer and B<sub>4</sub>C as crystal phase layer , whose fracture toughness increases by 30%. Al<sub>2</sub>O<sub>3</sub> / epoxy resin and Al<sub>2</sub>O<sub>3</sub> / aramid fiber-reinforced epoxy laminated pearl-layer material prepared by Mukherjee et al. were improved by 25% compared to Al<sub>2</sub>O<sub>3</sub> / arlon fiber-reinforced epoxy compared with single-phase Al<sub>2</sub>O<sub>3</sub>.

Due to the high toughness of nacre, its bionic materials is used to produce the military weapons like tanks, and also used to reduce the brittleness of ceramics.

## 5. Preparation of bionic materials

Material bionic design can be divided into three parts: structural bionic, functional bionic and system bionic. At present, the design of bionic structural materials mainly includes the selection optimization of structure components, geometric parameters and interface properties. People seek the design method and inspiration of bionic materials from the research of the special structure of the nacre. They explore the relationship between its structure and function, determining the performance parameters, summarize the rules, and revealing the composition mechanism and operation mechanism. On this basis, go deep into bionic, the use of bionic design methods and concepts to achieve the new development of high-strength super-toughness layered composite materials. There are three method to produce bionic materials: bottom-up self-assembly approach layer-by-layer methodology, directional freezing. The bottom-up self-assembly method means some small structural units (such as atoms, molecules, nanoparticles, etc.) constitute relatively large and complex structural systems (at the nanoscale). It is prevalent in the construction of multi-level fine structure. In this way, the orientation of crystal growth is controlled by the organic phase as a template. The inorganic crystals nucleate in supersaturated solution and grow [11] by consuming amorphous phases. People imitate the processing process in organisms from single molecule to nanoscale, micron scale and macroscale. Layers layer self-assembly is a simple and multifunctional surface modification method developed in the 1990s. LBL initially prepared a polyelectrolyte self-assembled multilayer film using alternating deposition in a negatively charged polyelectrolyte solution. Later, layer assembly of interaction based on hydrogen bond , step by step chemical reaction , molecular recognition , charge transfer [12], coordination bond , and surface gel gel process [13] was also developed and the method was widely used in the preparation of multifunctional thin film materials with nanostructures .In recent years, the construction of nacre by assembly. Directional freezing is a physical process used for casting complex shaped castings that has been used in the preparation of porous ceramic materials since the 1960s . The structural parameters such as overall porosity, aperture and pore shape prepared by this method can be controlled by adjusting the process conditions. Deville [14] learned from the formation of natural sea ice and used its principle to disperse ceramic particles in water to construct fine imitation shell structures. This simple process composite has complex layered structure, porous bracket surface and mineral bridge are connected between the layers, extremely similar to the microstructure of the inorganic components of the nacre . Electrophoretic deposition refers to the process in which colloidal particles in colloidal solution discharge to the electrode surface under the action of external electric field, it is a bionic material preparation process which is capable of constructing nanoscale and nano-scale microstructure. Electrophoretic decomposition is popular for its simple process,short time consuming,low cost and good operation control. However, the properties of the nacre is quite complex, the current, voltage, dispersion medium, and the pH,additive type, deposition temperature and matrix surface state. Therefore, there are many problems in practical application to be systematically study.

## 6. Conclusion

According to the previous research results, compared with biomaterials, the structural design is not fine enough for the bionic materials of shells, and the materials can not reach the perfect structure of the nacre, but it has a great contribution to the improvement of some mechanical properties of the objects. Therefore, it is necessary to make a more detailed study on the characteristics of shells, find the combination point of model and bionic material design in practical application, expand the ideas of material and structural design, prepare better bionic materials, and promote the rapid development of biomaterology.

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