Research of Helicoidal Layup of Clam Shell

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Molluscan shell is a kind of natural composite with excellent fracture strength and fracture toughness, which can be attributed to its unique microstructures. Scanning electron microscope (SEM) observation shows that Clam shell is a bio-ceramic composite consisting of aragonite and organic materials. These aragonite and organic materials distribute in the shell in the form of layers parallel with the surface of the shell. The observation also shows that the aragonite layers contain numerous thin and long aragonite strips, which are dozens of nanometers in diameter and can be regarded as aragonite fibers. These aragonite fibers align in the layers with different orientations. A kind of particular helicoidal layup of these aragonite fibers is found. The maximal pull-out force of the helicoidal layup of the aragonite fibers is analyzed, which accounts for the high fracture toughness of the shell. A comparative experiment for the maximal pull-out forces of both the helicoidal and the 0° layups is conducted, which shows that the maximal pull-out force of the helicoidal layup is markedly larger than that of the conventional 0° layup.

Key Words: Clam Shell, Microstructure, Helicoidal Layup, Pull-Out Force, Fracture Toughness

1. Introduction

Molluscan shell is a kind of bio-ceramic composite. The composite is composed of 95–99% crystalline calcite or aragonite (form of calcium carbonate (CaCO₃)) and protein film with the weight fraction from 0.1% to 5%(1), serving as binder. Although the composite contains over 95% CaCO₃ in the form of aragonite, the fracture work it can bear can be up to 3 000 times that of pure aragonite(1). Such high fracture toughness should be attributed to its exquisite microstructure, for example, the arrangement of the aragonite and organic matrix. The investigation to the microstructure may reveal the toughening mechanisms of the shell, which may provide guidelines for people to develop high performance synthetic ceramic composites(2).

Generally, a molluscan shell can be divided into three primary sections: periostracum, prismatic layer and nacreous layer. Periostracum is the outer layer, consisting mainly of conchiolins. The prismatic layer is the middle layer, consisting mainly of orientated calcitic crystals. The nacreous layer is the inner layer, consisting mainly of orientated aragonite crystals(3),(4). The inorganic aragonite or calcitic crystals act as ‘sheets’ or ‘bricks’ and the organic protein acts as ‘mortar’. The combinatorial microstructure of the inorganic ‘sheets’ (or ‘bricks’) and the organic ‘mortar’ endows the shell with excellent mechanical properties(5). In this paper, SEM observation on the microstructures of a Clam shell shows that the shell consists of laminated aragonite and organic materials. It also shows that each aragonite layer consists of many sheets of aragonite, and each aragonite sheet is composed of aragonite strips. The aragonite sheets or strips in different aragonite plies distribute in different directions, which compose different layups. A kind of particular helicoidal layup is found. The microstructural models of both the helicoidal and 0° layups are suggested and the maximal pull-out forces of the two kinds of layups are analyzed and compared with each other. It shows that the maximal pull-out force of the helicoidal layup is markedly larger than that of the 0° layup. Meanwhile, the maximal pull-out forces of both helicoidal layup and 0° layup are investigated with specially designed experiments, which gives identical conclusions.

2. SEM Observation of the Microstructure of Clam Shell

The molluscan shell used in this study is the shell of a Clam (Fig. 1). The samples for SEM observation are prepared by the following approaches: taking the shell from...
the mollusc, immersing it in liquid nitrogen for about two minutes, followed by breaking it down transversely with a small hammer. The samples are then placed in a metal tray using viscid fabric. An about 12 nm thick gold-palladium coating is made with a sputter coater. These samples are then observed using an Amray KYKY-1000B SEM under the voltage of about 15 kV and with magnification ranging from 20 to 11 000.

SEM observation shows that the molluscan shell is a bio-ceramic composite consisting of aragonite and collagen. Although there are various microstructures and micro-frameworks in the shell, the microstructure of laminated aragonite sheets consisting of numerous aragonite strips is the most characteristic of the shell. Figures 2 through 4 show that the main microstructural characteristics of the shell at different scales. It can be seen in Fig. 2 that the aragonite layers are piled up one by one and felted by the organic matrix, look like a laminated composite. A common characteristic is that all the aragonite layers are thin and parallel with the surface of the shell (Fig. 2). The other characteristic is that the each aragonite layer consists of numerous aragonite sheets (Fig. 3). These aragonite sheets are perpendicular to the layers where they are located. More careful observation shows that these aragonite sheets also consist of numerous aragonite strips that can be regarded as the finer microstructure of the shell (Figs. 3 and 4). These aragonite strips have a long and thin shape and its diameter is about several dozens of nanometers. These aragonite strips can be regarded as aragonite fibers, which have different orientations in different aragonite layers (Figs. 2–4), a kind of typical helicoidal layup of the aragonite fibers is observed (Figs. 2 and 3).

3. Analysis of Helicoidal Layup of Aragonite Fibers

SEM observation shows that the all aragonite plies in the Clam shell are parallel to the surface of the shell and consist of many thin aragonite fibers. Such layered microstructure may make the orientation of the aragonite fibers be coincided with that of the maximal principal stresses in the shell when the shell subjects external load. It can also be imagined that the fibers in the shell may be pulled out from the matrix when fractures occur to the shell, and the maximal pull-out force of the fibers is closely related to the fracture toughness of the shell, i.e., the capability of the resisting fracture of the shell\(^{[6]}\). The larger the maximal pull-out force is, the more the fracture toughness of the shell increases. The SEM observation also shows that there is a kind of helicoidal layup of the aragonite fibers in the shell. The helicoidal layup can effectively improve the fracture toughness of the shell compared to that of 0° layup, which can be proved with the simple models of the helicoidal and 0° layups by compar-
Fig. 5  The model of aslant fiber

Fig. 6  The model of helicoidal layup

Fig. 7  The model of 0° layup

Atively analyzing the maximal pull-out forces of the two kinds of layups.

Assuming an aragonite fiber is embedded in an organic matrix and a pull-out force is applied to its end. The length and the radius of the fiber are $l$ and $r$, respectively. Suppose the interfacial shear stress between the fiber and the matrix is uniform, and increases continuously with the increase of the applied force, and the maximum applied force is reached when the interfacial shear stress reaches the interfacial shear strength, $\tau_s$. The maximal pull-out force of the fiber whose orientation is along the orientation of the pull-out force can be given as

$$(P_{\text{max}}) = 2\pi rl \tau_s,$$  

(1)

Furthermore, if the fiber is aslant embedded in the matrix (with a aslant angle $\phi$) and a pull-out force is applied on its end (Fig. 5), the pull-out force of the aslant fiber can be described with the model for a string passing over a tiny frictional pulley and the maximal pull-out force of the aslant fiber is determined with(7):

$$(P_{\text{max}})_\phi = 2\pi rl \tau_s \exp(\phi f),$$  

(2)

where $f$ is a snubbing friction coefficient between the fiber and the matrix.

Figure 6 shows a simple model of the helicoidal layup. In the model, the thickness of the aragonite layers is neglected because it is very thin. The model can reflect the main structural characteristic of the layup and make the analysis easy, but it may not be reliable if the thickness of the aragonite layer cannot be neglected.

The model consists of five aragonite fibers embedded in organic matrix. The five fibers have identical length $l$ and radius $r$, and the pull-out force is applied to the end of these fibers (Fig. 6). Following the previous assumption, the interfacial shear stress between these fibers and the matrix is uniform and increases continuously with the increase of the applied force, and the maximum applied force is achieved when the interfacial shear stress reaches the interfacial shear strength, $\tau_s$. It is known from Fig. 6 that each fiber in the helicoidal layup can be regarded as an aslant fiber embedded in the matrix with different aslant angles, making contribution to the resistance against the pullout of the helicoidal layup. The total pull-out force of the helicoidal layup is the summation of the contributions from all the fibers in the layup. Because the helicoidal layup is laterally symmetry, the maximal pull-out force of the helicoidal layup can be obtained as

$$(P_{\text{max}})_{\text{hel}} = 2\pi rl \tau_s \left(1 + 2 \sum_{i=1}^{n} \exp(i\phi f) \right), \quad (i\phi \leq 90^\circ),$$

(3.a)

$$n = (m - 1)/2,$$  

(3.b)

where $m$ is the number of the fibers in the layup and $\phi$ is the helicoidal angle of the layup. For comparison, the maximal pull-out force of 0° layup (see Fig. 7), consisting of the fibers with the same perimeters, length and number as that of the helicoidal layup, and embedded in same matrix as the helicoidal layup, was also analyzed. Letting the helicoidal angle $\phi$ (Eq. (3)) equal zero, the maximal pull-out force of the 0° layup can be obtained as

$$(P_{\text{max}})_0 = m(P_{\text{max}})_{\phi=0} = 2\pi mrl \tau_s,$$  

(4)

Suppose the helicoidal angle of the helicoidal layup is 10°, the snubbing friction coefficient is 0.5, the interfacial shear strength is 2.0 MPa, the radius and length of the fibers is 1 mm and 100 mm, respectively. One can obtain the relationship between the maximal pull-out force and the number of the fibers for the helicoidal and 0° layups. Figure 8 shows the variation of the maximal pull-out forces of the
helicoidal and 0° layups against the number of the fibers, respectively. It can be seen from Fig. 8 that the maximal pull-out force of the helicoidal layup is distinctly larger than that of the 0° layup. It can also be seen that the more the fibers, the larger the differences of the maximal pull-out forces between the helicoidal and 0° layups. Assuming the radius and length of the fibers is 2.5 mm and 40 mm, the helicoidal angle of the helicoidal layup is 20°, the interfacial shear strength is 4.0 MPa, the fiber number is 3, neglecting the crack of the matrix, the maximal pull-out forces of the 0° and the helicoidal layups are 14.7 and 19.5 kN, respectively. However, if the fiber number is 5, the maximal pull-out forces of the 0° and the helicoidal layups are 28.3 and 34.6 kN respectively. Defining a ratio of the maximal pull-out force of the helicoidal layup to that of 0° layup as

\[
\tilde{P} = \frac{(P_{\text{Hel}})_{\text{max}}}{(P_{0\ell})_{\text{max}}}, \qquad (5)
\]

one obtains

\[
\tilde{P} = \left(1 + 2\sum_{i=0}^{n} \exp(i\phi f)\right) m, \quad (i\phi \leq 90°) \quad (6)
\]

Equation (6) shows the ratio \(\tilde{P}\) of the maximal pull-out forces of the helicoidal layup to that of 0° layup. The larger the ratio \(\tilde{P}\) is, the more the maximal pull-out force of the helicoidal layup would increase compared with that of the 0° layup. Figure 9 shows the variation of the ratio of the maximal pull-out forces \(\tilde{P}\) against the number of fibers \(m\), from which it can be seen that the larger the number of fibers, the more the maximal pull-out force of the helicoidal layup increases compared with the 0° layup.

4. Experimental Verification

The advantage of the helicoidal layup in enhancing the fracture toughness of the shell was experimentally investigated. Firstly, a set of specimens of the helicoidal layups with different number of fibers (3, 5 and 7) was fabricated by embedding steel-threads (serving as fibers) in epoxy resin matrix according to the structure of the helicoidal layup (Fig. 6). The diameter and the length of these fibers are 2 mm and 40 mm, respectively, and the helicoidal angle is 20°. For comparison, the specimens of 0° layup with same fiber numbers as corresponding helicoidal layups were also fabricated. One end of the fibers remains outside the specimens for applying the pull-out forces. The tests were performed on an Instron 1342 Material Testing System. The load was applied to the ends of these fibers with a special clamp. The experimental results are plotted in Fig. 9. It shows that the more the fibers are, the more the maximal pull-out force of the helicoidal layup will increase compared with that of corresponding 0° layup. In Fig. 9 the predicted values are slightly different with the experiment results, which can be attributed to the error of the adopted parameters, for example, the strength of the interfacial shear, and the experimental condition that is different from the ideal one used in analysis. Although it was observed in the experiment that the larger the number of fibers is, the more the maximal pull-out force will increase compared with that of the 0° layup, such increase is limited by the strength of the matrix at excessive fibers due to matrix cracking. It is suggested that the effective and rational application of the helicoidal layup should be based on more theoretical and experimental investigation, and detailed analysis on the properties of fibers, matrix as well as the interfacial property of fiber/matrix.

5. Conclusions

The SEM observation of Clam shell reveals that the shell is a bio-ceramic composite consisting of laminated aragonite and organic matrix. The aragonite layers in the organic matrix are parallel to the surface of the shell and of very thin thickness. Each aragonite layer consists of numerous aragonite sheets and each aragonite sheets are composed of numerous thin aragonite fibers. These aragonite fibers distribute in the matrix with different orientations, and a kind of helicoidal layup of the aragonite fibers is found. The effect of the layup on the fracture toughness of the shell is investigated both theoretically and experi-
mentally by comparing the maximal pull-out forces of the composite with the helicoidal layup with that with the 0° layup. It shows that the maximal pull-out force of the former is distinctly larger than that of the latter. The larger the number of fibers is, the more the maximal pull-out force will increase compared with that of the 0° layup. The reasonable agreement between the experimental and analyzed results demonstrates both the advantages of the microstructure of the composite and the validity of the model suggested for the microstructure of the helicoidal layup.

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