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Effects of nanostructures on the fracture strength of the interfaces in nacre

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A strengthening mechanism arising from the mineral bridges in the organic matrix layers of nacre (mother of pearl) is presented by studying the structural and mechanical properties of the interfaces in nacre. This mechanism not only increases the average fracture strength of the organic matrix interfaces by about five times, but also effectively arrests the cracks in the organic matrix layers and causes the crack deflection in this biomaterial. The present investigation shows that the main mechanism governing the strength of the organic matrix layers of nacre relies on the mineral bridges rather than the organic matrix. This study provides a guide to the interfacial design of synthetic materials.

The nacre of mollusks, which is considered a natural layered composite containing about 95 vol% interlocking aragonite platelets staggered in successive layers and separated by a 5% organic matrix, has fracture strength and toughness properties that are orders of magnitude higher than those of monolithic aragonite.[1,2] In particular, the microstructure and the performance of the interfaces in nacre, which play a crucial role in this biomaterial service, have become an attractive target for the interfacial design of synthetic materials.[1,3–6] Previous studies deemed the organic matrix layers of nacre (i.e., the interfaces in nacre) to be the structure of biological organic macromolecules composed only of polysaccharide and protein fibers.[1,2,7,8] However, Schaffer *et al*.[9] clearly observed many nanopores in the interlamellar organic matrix sheets of nacre in terms of various microscopic observations, and then pointed out that there might be a number of nanoscale mineral bridges in the organic matrix layers of nacre and gave a statistical distribution. Song *et al*. confirmed the existence of the inorganic nanostructures in the organic matrix layers of nacre and proposed a distribution law of the nanostructures in the organic matrix layers.[10] This is an indication that the mortar layers of nacre should be considered as a composite composed of organic matrix and mineral bridges rather than mere organic matrix, as shown in Fig. 1. These findings have led to further investigations on the mechanical behaviors of the interfaces in nacre.

In terms of the strength, Sarikaya *et al*. indicated that the fracture strength of nacre was related to several factors, including the size and structure of the aragonite platelets and the interfaces between the inorganic and organic components.[1] Smith *et al*. pointed out that the key role to nacre's fracture resistance resided in the polymer adhesive of the organic matrix layers.[11] Evans *et al*.[12] and Wang *et al*.[13] showed that the organic macromolecules of the organic matrix layer of wet nacre produced higher inelastic deformation and provided the interfacial resistance between the platelets. Katti *et al*. studied the effects of the organic component in the interfaces on the mechanical response of nacre by proposing the three dimensional finite element model of nacre, and indicated that the yield stress of the organic phase was very high.[14] Okumura *et al.* presented an analytic solution for a notch crack normal to the layers of nacre and proved that the organic phases effectively reduced the stress concentration near the field of crack tip in nacre.[15] However, the specific role of interfacial and interphasial mechanical relationships at the organic–inorganic interfaces on bulk mechanical behavior of nacre are lacking in literature.[7,14] In the present study, we focus on the interfaces of nacre to investigate the effects of mineral bridges on the fracture strength of the organic matrix layers in nacre.

Samples made of the nacre of *Haliotis iris* shells, which is an abalone shell from New Zealand, were used for testing. The keratin and prismatic layers of the shell were mechanically removed, and the nacre of the shell was washed using distilled water and air-dried at room temperature. Mechanical tests of the nacre specimens were performed by carrying out three-point bending using an Instron 8562 machine, which was operated at a speed of 0.1 mm/min. The depth, width, and length of each of the samples were 0.6, 2.5, and 14 mm, respectively. Note that the span of each of the samples was 10 mm. The narrow slot in each of the samples was introduced by a diamond saw. Microstructural and morphological observations of the testing samples were performed using transmission electron microscopy (TEM; Hitachi H-8100, Japan) at an accelerating voltage of 200 kV. Thin films vertical to the surface of the shell (i.e., the cross sections of nacre) were cut using a diamond saw from tested samples. The samples were then mechanically ground and thin-ion-beam milled, at an angle of 10°, to 50 μm thickness and, finally, perforated under a voltage of 5.5 kV.

To examine the effects of the mineral bridges on the fracture strength of the interfaces in nacre, fracture tests of nacre were carried out by using the three-point bending method, as shown in Fig. 2(a). It has been found that a crack can only propagate in the organic matrix layers or platelet junctions of nacre, as shown in Fig. 2(b). On the cross section of the nacre, it was observed that when a crack was deflected from a platelet junction to an organic matrix layer, the crack traveled in the layer in two opposite directions. The two tips of the crack propagated separately in the organic matrix layer for a distance. The distance of travel of the two crack tips was approximately equal in each of the organic matrix layers, and on the average, one of the two crack tips traveled passed one platelet junction of the above platelet layer. Then the two crack tips were separately arrested by some mineral bridges in different regions in the organic matrix layer [Fig. 2(c)]. With the increase of the applied load, a new crack tip was formed in the platelet junction of the above platelet layer. This crack tip rapidly passed through the junction to the above organic matrix layer. Figure 2(c) shows that when a crack propagated into a region of an organic matrix layer of the nacre, some mineral bridges of the region would prevent the crack from further development in the layer. In particular, on the path of the crack propagation, the organic matrix between successive aragonite platelets was broken, and in the

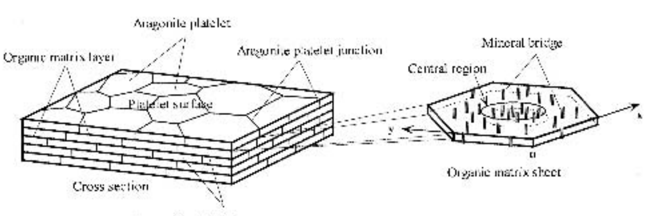

FIG. 1. Schematic illustration showing the "brick and mortar" microstructure of nacre, the mineral bridges in an organic matrix sheet and the coordinate system on the cross section. The thickness of a platelet layer and an organic matrix layer are 500 ± 40 nm and 26 ± 5 nm, respectively. The average width of platelets on the cross section is about 4 μm. The mineral bridges randomly appear in the mortar layers, and their average diameter is 46 ± 8 nm. There is a central region of mineral bridges in the interlamellar organic matrix sheet corresponding to one platelet, in which the number of mineral bridges is about 46% that of the whole platelet while the area of the central region is approximately equal to 1/9 that of the whole platelet.

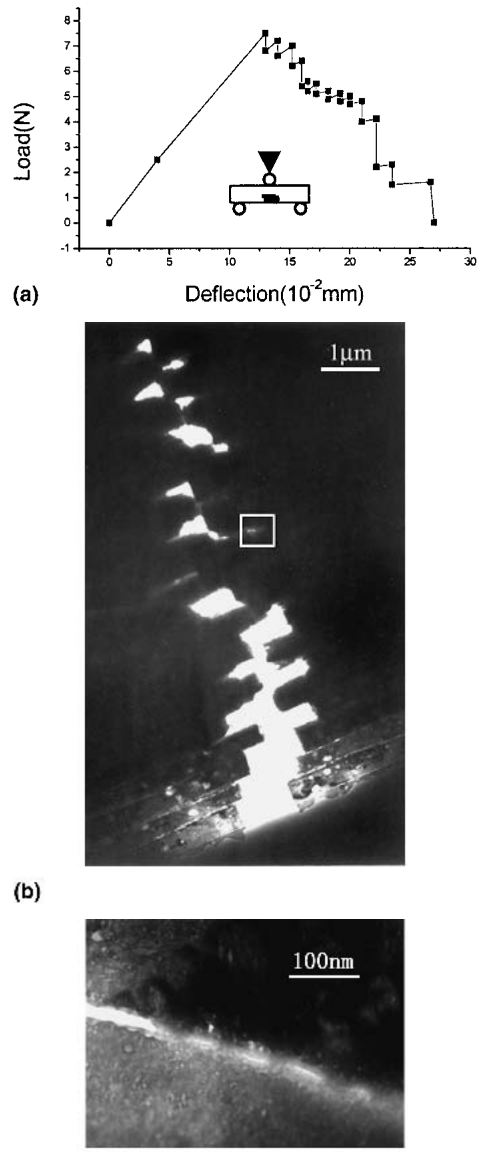

FIG. 2. (a) Three-point bending test curve of nacre. (b) TEM micrograph showing the fracture surface morphology on the cross section of nacre. It indicates that a crack propagates in the organic matrix layers or gaps of nacre. (c) Enlarged view of the boxed area in (b), TEM micrograph showing the mineral bridges that hinder crack propagation in an organic matrix layer.

field near the crack tip, the link between the platelets was just the mineral bridges. Therefore, it is proven that, in the field near the crack tip, the mineral bridges rather than the organic adhesives in the organic matrix layers of nacre play the main role in withstanding the external load. This is an indication that in the interfaces in nacre the following relation is satisfied:

$$\sigma_m \leqslant \sigma_c \leqslant \sigma_f \quad , \tag{1}$$

where σ_m and σ_f are the fracture strength of the organic matrix and the mineral bridges, respectively, and σ_c is the fracture strength of the organic matrix layer (i.e., the composite composed of the organic matrix and the inorganic mineral bridges). Furthermore, the average traveling distance of each crack tip in the organic matrix layers was measured by using image analysis system (Image-Pro Plus 4.5, Media Cybernetics), and statistically determined to be 1.88 ± 0.20 μm. Based on the structure of the organic matrix layers,[9,10] there was an indication that the crack propagation was stopped in the central region of the mineral bridges situated in the organic matrix layers of nacre.

To analyze the effects of the mineral bridges on the fracture strength of the interfaces in nacre, consider an interlamellar organic matrix sheet just corresponding to an aragonite platelet, as shown in Fig. 1. Obviously, due to the existence of the mineral bridges, this sheet possesses anisotropic properties. For convenience, the sheet is approximated as a square with average length, $l_0 = 4$ μm, for its cross section such that l_0^2 is the same as the average area of one platelet.[10] Since total cross-sectional area of the mineral bridges in the sheet is about 2.7 μm^2, which is approximately one-sixth of the area of each platelet, the organic matrix sheet is coarsely treated as a fiber-reinforced composite, which consists of an organic matrix and fibers of the inorganic mineral bridges. Based on the distribution law of the mineral bridges in the organic matrix layers, the volume fraction of the fibers along the side of the sheet is defined as

$$V_f\Big|_{l_1}^{l_2} = \frac{\pi D^2}{4l_0\,(l_2 - l_1)} \int_{l_1}^{l_2}\left(\int_0^{l_0} n(x,y)\mathrm{d}y\right)\mathrm{d}x \quad , \tag{2}$$

where (l_1, l_2) denotes a given region on the side of the sheet in the local x direction satisfying the essential condition, $l_0 \geqslant l_2 - l_1 \geqslant \mathrm{d}x \geqslant D$, in which $D = 46$ nm is the average diameter of the mineral bridges; x and y $(0 \leqslant x,y \leqslant l_0)$ are the local coordinates of the sheet; and $n(x,y) = (N/2\pi\sigma)\exp\{-[(x-\mu)^2 + (y-\mu)^2]/(2\sigma^2)\}$ is the distribution density of the mineral bridges in the sheet, $N \approx 1600$ is the average number of mineral bridges on each platelet, $\mu = 2$ μm and $\sigma = 0.67$ μm are the average value and standard deviation of the distribution, respectively.[10] Obviously, the volume fraction of the organic matrix in the same region is

$$V_m\Big|_{l_1}^{l_2} = 1 - V_f\Big|_{l_1}^{l_2} \quad .$$

From Eq. (2), the average volume fraction of the mineral bridges in the interlamellar organic matrix sheet and in its central region are determined to be

$$V_f\Big|_0^{l_0} = 0.17 \quad ,$$

and

$$V_f\Big|_{\mu-\sigma}^{\mu+\sigma} = 0.35 \quad ,$$

respectively, where $(\mu - \sigma, \mu + \sigma)$ denotes the coordinates of the central region of the sheet on the cross section of the nacre.

In accordance with the composite theory, the average fracture strength of the sheet in the direction of the mineral bridges within the region (l_1, l_2) can be expressed as

$$\sigma_c\Big|_{l_1}^{l_2} = \sigma_m\,(1 + 24\,V_f\Big|_{l_1}^{l_2}) \quad , \tag{3}$$

where the Young's moduli of the organic matrix and the inorganic mineral bridges, $E_m = 4$ GPa and $E_f = 100$ GPa,[7] are used. Note that the Young's modulus of the latter is deemed to be the same as that of aragonite platelet. When the existence of the mineral bridges is not considered in Eq. (3), we have

$$V_f\Big|_{l_1}^{l_2} = 0 \quad .$$

This equation is, thus, reduced to

$$\sigma_c\Big|_{l_1}^{l_2} = \sigma_m \quad ,$$

which is the traditional fracture strength of the organic matrix interfaces in nacre. In contrast, when the existence of the mineral bridges is considered, the average fracture strength of the interfaces is determined to be

$$\sigma_c\Big|_0^{l_0} = 5\sigma_m \quad ,$$

for the whole sheet, in particular,

$$\sigma_c \Big|_{\mu-\sigma}^{\mu+\sigma} = 9.4\sigma_m \quad ,$$

for the central region of the sheet. These results indicate that the mineral bridges significantly increase the fracture strength of the interfaces in nacre in the direction of the mineral bridges.

These results illustrate that when a crack is propagating toward the central region, on the one hand, the fracture strength of the organic matrix layer is rapidly enhanced with the increase of the density of the mineral bridges. On the other hand, there are no inorganic mineral bridges in the platelet junctions of nacre. The fracture strength of the platelet junctions is less than that of the central region in organic matrix layers. When the applied load is increased, the crack has to form a new tip at a platelet junction of the neighboring platelet layer. Therefore, the crack is arrested in the central region of this organic matrix layer, and then passes through the platelet junction to the next organic matrix layer. There is a clear indication that the mineral bridges cause deflection of the crack. Figure 3 shows the fracture strength encountered in an organic matrix layer on one platelet with the average length l_0 on the cross section of nacre.

As far as the whole nacre is concerned, its fracture strength is governed by some mechanisms acting in concert.[1,8] However, each of the strengthening mechanisms

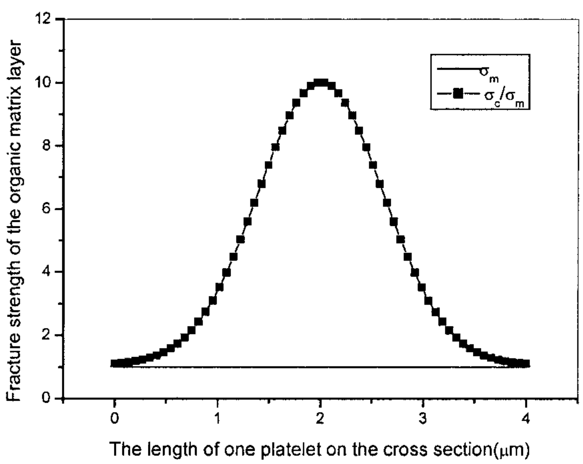

FIG. 3. Plots showing the fracture strength in the organic matrix layer on one aragonite platelet on the cross section of nacre. The horizontal line and the curve stand for the fracture strength of the organic matrix layer without and with mineral bridges, respectively.

is intimately associated with the interfaces of the nacre, of course, with the mineral bridges in the organic matrix layers.

The above study shows a nanostructural mechanism for enhancing the fracture strength of the interfaces in nacre. This novel mechanism derives from the mineral bridges in the organic matrix layers of nacre. It is not only able to control crack propagation in nacre, but also increase the mechanical performances of the interfaces in the natural layered materials. Therefore, this type of nanostructure in the interfaces should be given sufficient attention in the future interfacial design of synthetic materials.

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