Quantitative evaluation of toughening mechanisms in abalone nacre

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Tensile and fracture tests for dried nacre were carried out. Dried nacre fractured in a brittle fashion, but its toughness was 10 times greater than that of natural CaCO₃. A simple model in which plates interlock was proposed based on the observations of fracture behavior and the fractured surface. The contribution of interlocking to toughness was estimated; it was confirmed that the interlocking of the plates is the main factor in the toughening of dried nacre.

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Key-words : Nacre, Fracture behavior, Toughness

Abalone nacre is known as a well-organized inorganic/organic composite with a laminar structure in which polygonal aragonite (orthorhombic CaCO₃)-rich plates with a thickness of several hundred nanometers and a width of several micrometers are stacked precisely, like bricks. The interfaces between the plates are filled with an organic matrix whose volume fraction is only about 5%.1) The plates are arranged in columns as illustrated in Fig. 1, with well-defined core and overlap regions, designated as “columnar nacre”.2) Nacre has a good balance of strength and toughness despite its ceramic-based composition. Nacre’s fracture mechanism is quite complicated, with hierarchical and multi-step behaviors: crack deflection at the interface, interlocking and bridging by the plates, pulling out of the plates and bridging by organic matrix. These mechanisms operate on the order of submicrons, which is two to three orders smaller than in the conventional artificial composites. Gao et al. suggests that the size of the aragonite plate in nacre is selected to ensure optimum fracture strength and maximum tolerance of flaws.

Nacre’s mechanical properties change under hydrated conditions because the gel-like protein is susceptible to changes in moisture content.2)3)13) Specifically, a hydrated nacre has a good mechanical response of “work hardening” behavior, similar to that of metals, with an elongation of 1% and a high work of fracture (WOF) of over 1 kJ/m². This can be attributed to the multiple pullouts of the plates; the continuous pullout at the joints of the plates causes apparent large elongation, and the apparent deformation helps form a “damage zone”, which results in the relaxation of stress concentration at the crack tip.

The behavior of dried nacre is more brittle, although the yield stress and the strength are higher than in the case of hydrated nacre; it deforms elastically almost up to a maximum load followed by an abrupt fracture with little plastic deformation. That is why less attention has been paid to dried nacre. However, it still has a much higher critical stress intensity factor, KIC, of over 2 MPa·m¹/² than that of monolithic aragonite, 0.25 MPa·m¹/². Higher yield stress and strength with high reliability are of great value in machine design. The underlying mechanism in dried nacre may provide a simpler and more practical composite design principle than the complex multi-stage mechanisms of hydrated nacre, which might be difficult to reproduce using current technologies. This study focuses on the fracture behavior and toughening mechanism of dried nacre and evaluates its characteristics quantitatively by a simple fracture model.

Columnar nacre from the shell of Haliotis gigantea was cut into dog-bone-type tensile test specimens with a gauge length of 2 mm and a cross section of 1 × 1 mm. The loading direction was set to the plate plane. Single edge notched (SEN) specimens of 6 × 2 × 1 mm (gauge length, L × width, W × thickness, B) were also prepared for tensile fracture testing. A notch of ∼1 mm was introduced in the direction across the plates by a diamond saw; the curvature of the notch tip was ∼25 μm. The specimens were dried on a heating plate at 313 K for 72 h, and then either a tensile test or a tensile SEN fracture test was performed in air at room temperature with a crosshead speed of 0.05 mm/min. Elongation of the specimen during the test was measured using a machine vision...
From the linear response up to the fracture stress, it is assumed that the plates were interlocked with each other during the loading and that the joints became unlocked at a moment near the fracture stress. The fracturing of the dried nacre under tension was thus determined by the interlocking strength at the joints of the plates, rather than by the strength of the plates themselves. Considering that there cannot be a defect larger than the plate thickness in the direction through the thickness, the lower limit of the strength of the plate can be roughly estimated by $K_{\text{IC}} = (\pi t)^{1/2}$, where $K_{\text{IC}}$ is the critical stress intensity factor of monolithic aragonite and $t$ is the plate thickness. The estimated plate strength is 199 MPa with $t = 500 \text{ nm}$ and $K_{\text{IC}} = 0.25 \text{ MPa} \cdot \text{m}^{1/2}$, so it is reasonable that the plates were not fractured. The joints were well designed so that the advantage of plate strengthening by the thinning effect could be obtained; the joints were unlocked just before the plates fractured, typically at 80% of the plate strength. The strong interlocking of the dried nacre plates provides high strength, comparable to that of monolithic aragonite (100–180 MPa$^{2,13}$) despite the large material interface.

The origins of the interlocking are elucidated in several reports: surface waviness of the plates$^{2,13}$, nano-asperities on the plates$^{6,15}$, organic bridging between the plates$^{10–12,16}$ and mineral bridging between the plates$^{8,10}$. It is believed that mechanical locking by surface waviness primarily provides sliding resistance during the continuous pull-out of the plates, thus inducing “work-hardening” behavior in hydrated nacre. This hypothesis suggests that, in dried nacre, the organic matrix stiffened by dehydration prohibits the lateral expansion [x direction shown in Fig. 2(a)] and thus strengthens the interlocking. It is also possible that the dehydrated organic phase increases shear bonding strength, acting as hardened glue at the interface. The nano-asperities and mineral bridging can contribute initial interlocking of the plates before the pull-out starts, especially at the interfaces that drying delubricates. The combination of these factors is thought to form a strong interlocking of plates in dried nacre.

The load-displacement curve [see Fig. 2(c)] of the SEN fracture test also showed a linear increase of the load with the displacement and the following abrupt fracture. The apparent critical stress intensity factor, $K_{\text{IC}}$, was calculated from the maximum load to be $2.2 \pm 0.2 \text{ MPa} \cdot \text{m}^{1/2}$. A plain strain state in front of the notch tip can be ensured by $B(\sigma_y/K_{\text{IC}})^2 > 2.5$, where $\sigma_y$ is the yield stress. Although the exact value of $\sigma_y$ is unknown it is reasonable to assume that $\sigma_y$ is almost the same as the maximum stress just before the fracture in the tensile test because the stress-strain relationship is linear up to the point of catastrophic failure. $B(\sigma_y/K_{\text{IC}})^2$ is 3.7 with $\sigma_y$ of 141 MPa, satisfying the conditions for the plain strain state. The fracture surface after the test shows the fracturing at the plate joints as was observed in the tensile test. The substantial fracturing of dried nacre did not occur through crack propagation straight through the plates, as is the case in monolithic ceramics, but rather by the unlocking of the plate joints, although the macroscopic fracture behavior is apparently brittle. The damage zone size in front of the notch tip when the fracture occurs at the maximum load, $r_p$, can be estimated by,

$$r_p \approx \frac{1}{6\pi} \left( \frac{K_{\text{IC}}}{\sigma_y} \right)^2$$

(1)

in the plane strain state. The size of damage zone in hydrated nacre is reported to spread over 1 mm ahead of notch tip, and can be seen as a color-changed area in macroscopic observation. In the zone multiple pullout by ~400 nm occurs resulting in large energy dissipating of 750 N/m$^2$. The dried nacre, however, shows no
In conventional ceramics composites, micro-fractures in a composite accumulate by microcracking, crack deflection, bridging by a reinforcement, and so on. For this purpose, a complex microstructure, in which the phase interface is easily debonded, is designed. To increase the strength and stiffness of ceramics materials, defects must be eliminated and the microstructure must be made uniform. The strength and Young’s modulus of such composites are significantly low compared with the intrinsic properties of ceramics, e.g., most composites have a strength of several hundred MPa and a Young’s modulus of several tens to a hundred GPa, whereas ceramics reinforcements used in such composites have a strength of several GPa and a Young’s modulus of several hundred GPa. However, nacre increases toughness without sacrificing either strength or stiffness: an extremely high volume fraction of aligned aragonite phase, a submicron-thin plate, and a well-controlled interlocking of the plates combine to form conflicting mechanical properties.

The toughening mechanism of dried nacre is quite simple but has not been applied to composites. Most laminar structures are over 10 micrometers thick and formed of continuous (not segmented) plates; the primary toughening mechanism is crack deflection. It is known that a fine reinforcement has high strength, e.g., a ceramics whisker, but no composites have a structure in which such a reinforcement is aligned and densely packed to the degree that nacre does (95 vol.%) The results of this study will contribute to the design of new composites.

Fig. 3. (Color online) Schematic illustration representing the stress field in front of the notch tip and the effect of interlocking expressed as a closure stress field.

color changed area in front of notch suggesting the absence of accumulative pullout. The size of damage zone estimated by Eq. (1) in dried nacre is 13 μm in which 20–30 layers of the plates are included. We assume that the plates within the damage zone are involved in toughening in front of the notch tip by their interlocking. The effect of interlocking is expressed as a closure stress field in front of the notch tip, $\sigma_{\text{lock}}$, and its contribution to toughness, $\Delta K_{\text{lock}}$, is given by,

$$\Delta K_{\text{lock}} = 2 \int_{a}^{a + \tau} G(x, a + \tau, w)\sigma_{\text{lock}}(x)dx$$  \hspace{1cm} (2)$$

Where $G(x, a, W)$ is a weight function for a single edge notch in a specimen and $x$ is the position in the notch (see Fig. 3). In the plane strain state, the closure stress in the damage zone can be elevated to $\sqrt{3}\sigma_y$ due to the constraint in the $z$ direction. The upper limit of $\Delta K_{\text{lock}}$ is obtained when we ignore any relaxation of the constraint in the damage zone and make $\sigma_{\text{lock}}$ constant, $\sqrt{3}\sigma_y$ through the damage zone. The calculated maximum $\Delta K_{\text{lock}}$ is 2.8 MPa·m$^{1/2}$ with $\sigma_{\text{lock}} = \sqrt{3}\sigma_y$; the value is an order of magnitude larger than that of monolithic aragonite and is on the same order of the toughness of dried nacre measured in the fracture test. The estimation suggests that the main toughening mechanism of dried nacre is the interlocking of the plates at the notch tip.

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