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Fracture strength of biomimetic composites: scaling views on nacre

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Abstract

Nacre, layered structure on the nanoscale, found inside certain seashells, shows remarkable strength due to the tiny amount of soft glues between hard sheets. In this paper, we develop an anisotropic elastic theory and fracture mechanics for the laminar structure at the level of scaling laws to reproduce the essence of the previous results in a much simpler way.

1. Introduction

Strong materials found in Nature sometimes take advantage of remarkable composite structures (tooth, timber etc); this might be one of the key factors that have propelled the science and industry of biomimetic composite materials [1]. Among them, nacre and related structures made by stacking soft and hard sheets have received considerable attention [2]. In a series of papers [3–6], we have studied such soft–hard laminar structures on nanoscales to present one possible scaling view.

The structure and notation are illustrated in figure 1. A typical thickness d_s of the soft layer made from a protein, *conchiolin*, is dozens of nanometres, which is much smaller than the micrometric thickness d_h of the hard layer composed of *aragonite*. The elastic modulus E_s of the soft layer is also much smaller than E_h for the hard layer. We define two small quantities

$$\varepsilon_d = d_s/d_h, \qquad \varepsilon_0 = E_s/E_h. \tag{1}$$

An interesting property of nacre is that ε defined by

$$\varepsilon \equiv \varepsilon_0/\varepsilon_d \tag{2}$$

is very small. We will work in the limit of $\varepsilon_0, \varepsilon_d, \varepsilon \ll 1$, and also in the continuum limit where relevant length scales are much larger than the layer spacing d:

$$d = d_s + d_h. \tag{3}$$

We emphasize here that under these conditions our theory is applicable to a general layered structure other than nacre. Physically, ε_d *has to be small to make a relatively rigid material*

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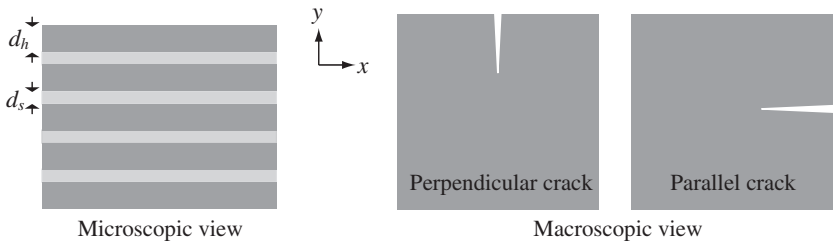

Figure 1. Nacre-type structure of materials: hard layers (of elastic modulus E_h) of typical thickness d_h are glued together by soft layers (of elastic modulus E_s) of typical thickness d_s. The cracks in the y–z plane and the x–z plane are called perpendicular and parallel fractures, respectively (the z-axis is perpendicular to this page).

(as a whole), while ε (*and thus* ε_0) *has to be small to reduce the stress concentration around the tip to enhance the toughness*; these conditions seem to have indeed been selected in nacre.

We have studied both perpendicular and parallel fractures (see figure 1) within the linear elastic fracture mechanics (LEFM [7]) under the plane strain condition (the sample is thick in the z direction) [3–5]. In this paper we derive the essence of our previous results in a much simpler way though only at the level of scaling laws.

2. Anisotropic elastic energy for the layered structure

We introduce the strain field defined on a scale larger than d (while E_s and E_h are defined for each layer): $e_{ij} = (\partial_i u_j + \partial_j u_i)/2$ for deformation fields u_i where $(x_1, x_2, x_3) \equiv (x, y, z)$. Pulled in the y direction (where the only non-zero component of the stress tensor is σ_{yy}), only the soft part (see figure 1) stretches in the limit $E_\mathrm{s} \ll E_\mathrm{h}$: $\sigma_{yy} \simeq E_\mathrm{s}(d/d_\mathrm{s})e_{yy} \equiv E_0 e_{yy}$ ($E_0 = \varepsilon E_\mathrm{h}$); due to the low thickness of the soft layers, the original soft modulus E_s is replaced by a larger modulus E_0. In contrast, for pulling in the x direction only the hard part responds: $\sigma_{xx} \simeq E_\mathrm{h}(d/d_\mathrm{h})e_{xx} \simeq E_\mathrm{h} e_{xx}$. As for shear forces, we have to distinguish the effects of σ_{xy} (stress in the x direction) and σ_{yx} (in the y direction) because of the anisotropy of the system. For σ_{xy}, only the soft part is elongated: $\sigma_{xy} \simeq E_\mathrm{s}(d/d_\mathrm{s})e_{xy} = E_0 e_{xy}$. On the other hand, for σ_{yx}, the hard sheets will respond. However, on scales larger than d (which is required for the continuum theory), it is the bending energy that is more appropriate than the usual shear energy: for a typical deformation in the y direction, δu, over a typical distance along the x direction, X, the two energies per one hard sheet (per unit length in the z direction) scale like $E_\mathrm{h}(\delta u/X)^2 X d$ and $E_\mathrm{h} d^3 (\delta u/X^2)^2 X$ (the bending modulus of the single sheet scales like $E_\mathrm{h} d^3$ [8]), respectively, and, thus, shear always needs larger energy than bending when $X \gg d$; this implies that the bending is always preferred as the mode of deformation. In this way, we can understand (ignoring numerical coefficients) the elastic energy (per unit volume) proposed in [5]:

$$f = E_\mathrm{h} e_{xx}^2 + E_0 e_{yy}^2 + E_0 e_{xy}^2 + E_0 e_{xx} e_{yy} + K_\mathrm{B}(\partial^2 u_y/\partial x^2)^2 \tag{4}$$

where

$$K_\mathrm{B} = E_\mathrm{h} d^2 \equiv E_0 l^2, \tag{5}$$

with

$$l = d/\varepsilon^{1/2}. \tag{6}$$

Here, l is much longer than the layer period d. The bending term becomes important also in certain liquid crystals [9]. However, there is a significant difference from the present situation:

in liquid crystals, l is replaced by a much smaller length of the order of atomic scales, which results in a strain distribution quite different from that of nacre (see below).

3. Scaling structure of the elastic energy

An important difference from the conventional isotropic elastic theory is that, in an anisotropic system such as nacre, there exist two distinct length scales X and Y. In contrast, in isotropic systems at equilibrium when the elastic body is perturbed over a range of R in the x direction, the deformation relaxes out at the same distance R also in the y direction; this is because the deformation field of an isotropic system satisfies an elliptic differential equation *with a unique length scale*, i.e., the Laplace equation (under the plain strain condition), while the deformation in nacre does not satisfy the Laplace equation. Note here that, in the context of a fracture problem of an semi-infinite plate, X corresponds to the length of the parallel fracture while Y corresponds to that of the perpendicular fracture.

Thus, a local energy (per unit volume) of nacre is dimensionally expressed as

$$f \simeq E_{\mathrm{h}} \left(\frac{u_x}{X}\right)^2 + E_0 \left(\frac{u_y}{Y}\right)^2 + E_0 \left(\frac{u_x}{Y} + \frac{u_y}{X}\right)^2 + E_0 \frac{u_x}{X}\frac{u_y}{Y} + K_{\mathrm{B}} \left(\frac{u_y}{X^2}\right)^2 . \tag{7}$$

At equilibrium (statics), f is locally minimized for both variables u_x and u_y; we have two *linear* equations for u_x and u_y. Seeking the relevant solution by requiring $(u_x, u_y) \neq (0, 0)$, via the determinant of a 2×2 matrix, we have an equation for X and Y. This equation has two solutions specifying a relation between X and Y: one corresponds to perpendicular fractures while the other corresponds to parallel fractures. We should note a limitation of this type of dimensional expression: relative signs (or phases of complex numbers) can sometimes be specified only from physical consideration.

3.1. Parallel fractures

The solution for parallel fractures gives a relation, $X^2 \simeq Y^2(1 + l^2/X^2)$, which implies two regimes for this problem: $X \gg l$ and $X \ll l$.

For large fractures ($X \gg l$), we have an isotropic relation,

$$X \simeq Y. \tag{8}$$

On the other hand, with an aid of a relation $\partial f/\partial u_x = 0$ together with equation (8), we obtain an anisotropic deformation field,

$$u_x \simeq \varepsilon u_y; \tag{9}$$

we find $u_x \ll u_y$, which is appropriate for parallel fractures. Using equations (8) and (9), we can estimate the magnitude of each term in equation (7). Keeping terms only at the leading order in ε, we arrive at

$$f \simeq E_0(u/R)^2 \tag{10}$$

where we denote scales of X ($\simeq Y$) and u_y as R and u, respectively. This corresponds to a more precise form $f \simeq E_0(\partial u_y/\partial y)^2 + E_0(\partial u_y/\partial x)^2$ shown in [4].

For small fractures ($X \ll l$), we have instead

$$X^2 \simeq Yl, \tag{11}$$

which implies $X \gg Y$. The deformation field satisfies $u_x \simeq l\varepsilon u_y/X$. Here, we note an important condition for a continuum theory, $X, Y > d$. This condition, together with equation (6), results in $\varepsilon l^2/X^2, \varepsilon l^2/Y^2 < 1$, which implies $\varepsilon l/X, \varepsilon l/Y < \varepsilon^{1/2} \ll 1$ (note

also that this does not necessarily imply $l < X, Y$; e.g. $X > \varepsilon^{1/2} l$ satisfies both $l > X$ and $\varepsilon l/X < 1$). Thus, we again find $u_x \ll u_y$. In this way, we arrive at

$$f \simeq E_0(u/Y)^2 \simeq K_{\mathrm{B}}(u/X^2)^2 \tag{12}$$

which corresponds to $f \simeq E_0(\partial u_y/\partial y)^2 + K_{\mathrm{B}}(\partial^2 u_y/\partial x^2)^2$ shown in [5].

3.2. Perpendicular fractures

The solution for perpendicular fractures gives the anisotropic relations, $Y \simeq \varepsilon^{1/2} X, u_y \simeq \varepsilon^{1/2} u_x$ for which $u_x \gg u_y$. These relations lead to an energy

$$f \simeq E_{\mathrm{h}}(u/X)^2 \simeq E_0(u/Y)^2. \tag{13}$$

Here, u denotes not u_y but u_x. This energy corresponds to $f \simeq E_{\mathrm{h}}(\partial u_x/\partial x)^2 + E_0(\partial u_x/\partial y)^2$ shown in [4].

4. Scaling views on fracture mechanics

We consider a fracture in nacre-type materials. We will develop below scaling arguments in order to reproduce our previous results but only dimensionally. Similar arguments in a different context were presented in [9].

4.1. Parallel fractures

For *large cracks* ($X \gg l$), as discussed above, there is only one length scale characterizing the strain distribution ($X \simeq Y \equiv R$) and, thus, the potential energy per unit crack front length (in the z direction) is dimensionally given by

$$F \simeq E_0(u/R)^2 R^2 - \sigma u R + 2G_{\parallel} R \tag{14}$$

where the first two terms describe the elastic potential energy and the last term an energy loss due to creation of new surfaces in this system: $G_{\parallel}$ is the fracture energy (energy required to create a unit area). We minimize this energy with respect to u to find a Hooke's law

$$\sigma \simeq E_0 u/R \tag{15}$$

which leads to an optimized energy value,

$$F_m \simeq -\sigma^2 R^2/E_0 + 2G_{\parallel} R, \tag{16}$$

which is quadratic in R; the maximum is given at $R = R^*$:

$$\sigma \simeq (G_{\parallel} E_0/R^*)^{1/2}. \tag{17}$$

When $R < R^*$, F_m decreases with decrease in R; a fracture with the size smaller than R^* tends to close to lower the energy. In contrast, when $R > R^*$, F_m decreases with increase in R; a fracture with size larger than R^* tends to expand. Thus, equation (17) corresponds to a critical failure stress. From equations (15) and (17), we have

$$u \simeq (G_{\parallel} R^*/E_0)^{1/2}. \tag{18}$$

Equations (17) and (18) give scaling structures for the stress and deformation fields obtained more precisely in [4]: the stress scales like $R^{-1/2}$ and the deformation is parabolic ($\sim R^{1/2}$) as in the conventional LEFM[1]. They also give a scaling relation

$$\sigma u \simeq G_{\parallel}, \tag{19}$$

[1] Equation (17) implies a failure stress $\sigma_a \simeq (G_{\parallel} E_0/a)^{1/2}$ for the crack size a. On the other hand, the stress singularity near the tip ($R < a$) can be expressed as $\sigma(R) \simeq \sigma_\infty (R/a)^n$ because $\sigma(R)$ should go back to the remote stress σ_∞ when $R \simeq a$. The exponent n can be determined by requiring that $\sigma(R)$ be independent of a near the tip; at the critical point of failure we can set $\sigma_\infty \simeq \sigma_a \sim a^{-1/2}$, which leads to $n = -1/2$, or $\sigma(R) \simeq \sigma_\infty (a/R)^{1/2} \sim R^{-1/2}$. Similar arguments lead to $u \sim R^{1/2}$.

which gives that the product σu (at the critical state where $R \simeq R^*$) gives the fracture energy. The estimation of $G_\parallel$ under viscoelastic effects of the thin layers is discussed in [6].

In conventional LEFM, the stress intensity factor K scales as $(\mathcal{G}E_0)^{1/2}$ where $\mathcal{G}$ is *the energy release rate* and *its critical value* is the fracture energy ($G_\parallel$). Equation (17) suggests that K scales not as $(\mathcal{G}E_0)^{1/2}$ but as its critical value $(G_\parallel E_0)^{1/2}$; this is logical because in equations (17)–(19) we are always at the critical point of failure ($R \simeq R^*$).

For *small cracks* ($X \ll l$), the strain distribution is anisotropic: $X \gg Y$. This is quite different from certain cases for liquid crystals [9], for which, instead, $Y \gg X$. The potential of our system is given by

$$F \simeq K_{\mathrm{B}}(u/X^2)^2XY - \sigma uX + 2G_\parallel X. \tag{20}$$

We minimize this energy with respect to u to find a Hooke's law $\sigma \simeq E_0 u/Y$, which corresponds to $\sigma_{yy} \simeq E_0 \partial u_y/\partial y$. Note here that the dominant component of the stress field tensor is σ_{yy} (e.g. $\sigma_{xy} \simeq E_0 \partial u_y/\partial x \simeq E_0(u/X) \ll \sigma_{yy}$ due to equation (11)). The energy optimized for u is here given by $F_m \simeq -\sigma^2 X^3 l/K_{\mathrm{B}} + 2G_\parallel X$. This takes its maximum value at $X \simeq X^* \simeq \sqrt{Y^* l}$, where

$$\sigma \simeq \left(\frac{K_{\mathrm{B}}G_\parallel}{l}\right)^{1/2}\frac{1}{X^*} \simeq \left(\frac{G_\parallel E_0}{Y^*}\right)^{1/2}, \qquad u \simeq \left(\frac{lG_\parallel}{K_{\mathrm{B}}}\right)^{1/2} X^* \simeq \left(\frac{G_\parallel Y^*}{E_0}\right)^{1/2}. \tag{21}$$

Equation (21) gives scaling structures for the stress and deformation fields (predicting the non-parabolic, lenticular crack tip shape) as well as a scaling relation $\sigma u \simeq G_\parallel$. We emphasize here that the stress thus obtained (which is proportional to strain) is indeed anisotropic: $\sigma \sim 1/X \sim (Yl)^{-1/2}$. The stress and deformation fields obtained in [5] are also consistent with these scaling structures; we can check that, dimensionally, $\sigma(x, y)$ and $u(x, y)$ derived in [5] do indeed reduce to equation (21) by setting $x^2 \simeq yl$ (because we are always in the regime specified by equation (11) at the scaling level).

4.2. Perpendicular fractures

The strain distribution is anisotropic ($X \gg Y$) and, thus, the potential is given by

$$F \simeq E_{\mathrm{h}}(u/X)^2XY - \sigma uY + 2G_\perp Y, \tag{22}$$

where $G_\perp$ is the fracture energy. We minimize this energy with respect to u to find a Hooke's law $\sigma \simeq E_{\mathrm{h}}u/X$, which corresponds to $\sigma_{xx} \simeq E_{\mathrm{h}}\partial u_x/\partial x$ (the dominant stress tensor component in this case is σ_{xx}). The energy optimized for u is here given by $F_m \simeq -\sigma^2 Y^2/(\varepsilon^{1/2}E_{\mathrm{h}}) + 2G_\perp Y$, which is maximum at $Y \simeq Y^* \simeq \varepsilon^{1/2}X^*$, where

$$\sigma \simeq \varepsilon^{1/4}\left(\frac{G_\perp E_{\mathrm{h}}}{Y^*}\right)^{1/2}, \qquad u \simeq \varepsilon^{-1/4}\left(\frac{G_\perp}{E_{\mathrm{h}}}Y^*\right)^{1/2}. \tag{23}$$

Scaling structures for the stress and deformation fields in equations (23) are in accord with results in [4].

5. Fracture strength: matching of different scale views

We have proposed a novel way of estimating the fracture strength by matching two stress expressions obtained on different scales [3, 10]. For example, in the case of perpendicular fracture, on scales larger than d we have the continuum theory discussed above; equation (23) gives that the stress concentration is impaired by a factor $\varepsilon^{1/4}$; the tip stress scales as $\sigma(r) \simeq \varepsilon^{1/4}\sigma_\infty(a/r)^{1/2}$ with a and σ_∞ being the crack length and the remote stress, respectively (see footnote 1). On scales smaller than d (but larger than a_{h} with a_{h} being a typical defect size

in aragonite) we can consider another continuum theory *inside the aragonite sheet*; the failure stress in the smaller scale should be the conventional brittle failure stress: $\sigma_0 \simeq (E_h \gamma_h / a_h)^{1/2}$ (γ_h is the fracture energy of the homogeneous aragonite). The former larger scale expression should turn over to the latter smaller scale one on the scale d at the critical point of failure: $\sigma(r = d) \simeq \sigma_0$ where σ_∞ should be interpreted as the failure stress of the composite σ_F. From this we obtain $\sigma_F = \varepsilon^{-1/4}(d/a)^{1/2}\sigma_0$. On the other hand, the fracture strength of the non-layered pure aragonite with the same crack of the size a is $\sigma_F^{(0)} = (E_h \gamma_h / a)^{1/2}$ in the LEFM. Thus, we have $\sigma_F = \varepsilon^{-1/4}(d/a_h)^{1/2}\sigma_F^{(0)}$. Since the layer period d is much larger than the cavity size a_h, this enhancement factor $\varepsilon^{-1/4}(d/a_h)^{1/2}$ is larger than one and the order turns out to be comparable with the experimental results. Other cases of parallel cracks are discussed in further detail, including viscoelastic effects, in [6].

In conclusion, we have shown that our previous results can be essentially reproduced resorting only to scaling arguments, clarifying in what situation the bending becomes important (see above equation (4)).

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