On flaw tolerance of nacre: a theoretical study

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As a natural composite, nacre has an elegant staggered ‘brick-and-mortar’ microstructure consisting of mineral platelets glued by organic macromolecules, which endows the material with superior mechanical properties to achieve its biological functions. In this paper, a microstructure-based crack-bridging model is employed to investigate how the strength of nacre is affected by pre-existing structural defects. Our analysis demonstrates that owing to its special microstructure and the toughening effect of platelets, nacre has a superior flaw-tolerance feature. The maximal crack size that does not evidently reduce the tensile strength of nacre is up to tens of micrometres, about three orders higher than that of pure aragonite. Through dimensional analysis, a non-dimensional parameter is proposed to quantify the flaw-tolerance ability of nacreous materials in a wide range of structural parameters. This study provides us some inspirations for optimal design of advanced biomimetic composites.

1. Introduction

Through millions of years of evolution by natural selection, biological materials have obtained superior mechanical and physical properties to fulfil their biological functions [1–6]. It has also been recognized that most biological materials (e.g. animal bones, mollusc shells, spider webs, silkworm cocoons and the hairy attachment pads of geckos, spiders and beetles) generally retain and tolerate, rather than simply exclude, structural flaws, such as voids, micro-cracks, impurities and geometrical imperfections. These materials could even undergo occurring–healing–reoccurring cycles of such structural flaws [2–6]. The outstanding mechanical properties and flaw-tolerance ability of these natural composites are attributed to not only their chemical compositions but also their hierarchical structures at micro- and nanoscales. Studying how nature tackles flaws without severely compromising survivability and mechanical properties can reveal the laws of design of biological materials and provide inspirations for biomimetic design, optimization and fabrication of artificial materials. In recent years, therefore, considerable effort has been directed toward investigating the composition–structure–property–function relations in biological materials. Though the stiffening, strengthening and toughening mechanisms of some representative biological material, such as bones, teeth, woods, silks, seashells and collagenous tissues have attracted much attention [1,3,7–18], the strategies selected by natural composites to deal with structural flaws still remain elusive [6,19–22].

Owing to its outstanding mechanical performances, nacre (or the mother-of-pearl)—the pearly inner layer and protective armour of many mollusc shells—has received extensive interest [23–30]. Nacre consists of about 95 vol% inorganic aragonite platelets and about 5 vol% protein-rich organic phase, arranged into a staggered ‘brick-and-mortar’ architecture [23,26]. The superior mechanical properties of nacre result mainly from its highly ordered and hierarchical structure. Previous experimental and theoretical studies have focused on the stiffness, strength and fracture toughness of nacre with intact microstructure [7]. However, both the nacre itself and its building blocks often have structural flaws of different sizes, caused by imperfect growth, environmental impacts or other reasons [4,27]. Somewhat surprisingly, these defects do not endanger the survival of mollusc shells or severely compromise the mechanical properties necessary for their...
biological functions. In recognition of the susceptibility of aragonite platelets to small flaws, Gao et al. [6,19–21] proposed the flaw-tolerance concept of platelets at the nanoscale to ensure the integrity of platelets under high stresses. They demonstrated that the flaw-tolerance feature is of great significance for the remarkable mechanical properties of biological materials. To date, nevertheless, it is still unclear how the flaw-tolerance feature of platelets is upscaled to create superior mechanical properties of nacre with pre-existing defects.

The synthesis of artificial nacreous materials has emerged as a potential way to manufacture biomimetic ceramic composites with high toughness. Some novel materials with improved strength and toughness have been successfully produced by mimicking the ‘brick-and-mortar’ microstructure of nacre [31–37]. Some synthetic techniques inspired from biological materials have also been proposed to design novel materials [24,38,40]. For these techniques, both the mechanical properties and their flaw-tolerance ability are of great concern because of the ubiquitous presence of flaws [41]. Therefore, a good understanding of the relationship between the flaw-tolerance property and the hierarchical microstructure of nacre is essential for design of biomimetic materials.

Among all stiffening and strengthening mechanisms, the crack-bridging effect of platelets plays a crucial role in the mechanical behavior of nacre [7,24]. As the fibre-induced crack bridging in fibre-reinforced composites [41], the crack-bridging mechanism of platelets in nacre makes the most significant contribution to its high fracture toughness. Besides, the contributions of some other mechanisms (e.g. mineral bridges across organic layers, nanoasperities and wavy patterns on the platelet surfaces) partly come from their involvement in the crack-bridging mechanism of platelets [24,27,40]. To date, however, there is a lack of investigations on the flaw-tolerance property of nacre and its dependence on microstructures. In previous fracture mechanics studies of fibre-reinforced composites, a continuous cohesive zone model has always been adopted. However, the discrete nature of the crack bridging of platelets demands the application of a discontinuous crack-bridging model to correlate the fracture property with microstructural parameters. In this paper, therefore, we will investigate the influence of pre-existing crack-like flaws on the strength of nacreous materials. The attention is focused on how the discontinuous platelet bridging underlies the superior strength of flawed nacre. Only crack-like flaws are considered in this work because they have the most significant degrading effect on the material strength.

This paper is outlined as follows. In §2, the discontinuous platelet-bridging model proposed by Shao et al. [40] is modified to calculate the strength of nacre containing an embedded crack-like flaw. In §3, we analyse and discuss the flaw-tolerance property of nacre. A systematic parametric study is conducted as well to explore the quantitative relation between the strength and flaw tolerance. In §4, we present a dimensional analysis and derive an empirical dimensionless parameter to correlate the strength with microstructural parameters of nacre.

2. Discontinuous crack-bridging model

2.1. Model of platelet bridging

In this section, a microstructure-based fracture mechanics model recently proposed by the authors [40] is modified to predict the strength of nacreous materials with crack-like flaws. Consider a nacre with a ‘brick-and-mortar’ microstructure consisting of stiff platelets (mineral phase) and soft interlayers (organic macromolecular phase), as shown in figure 1a. Assume that the vertical joint is in the centre of the subsequent brick. This microstructure closely resembles the nacreous layer of bivalve molluscs, while the nacre from abalone has a slight offset between columns of platelets. The present theoretical model can be easily extended to the latter type of microstructure by simply modifying such geometric parameters as the pull-out length. For the sake of simplicity, the nacre is assumed to have a pre-existing embedded crack-like flaw perpendicular to the longitudinal direction of platelets. The flaw length, denoted as 2c, is much larger than the thickness of a platelet (figure 1a).

A virtual configuration where no platelet has been pulled out from the crack faces is defined as the reference state. Refer to a Cartesian coordinate system (O – xy), where the origin O is located at the centre of the crack, the x- and y-axes are parallel and perpendicular to the crack plane, respectively. In the remote field, a uniform tensile stress σ is applied along the y-direction (figure 1a). Such a mode-I crack problem is of particular interest, and many experiments measuring the strength and fracture toughness of nacre concern this symmetric crack configuration. The plane-strain conditions in the x–y plane are assumed because the average diameter of platelets is much larger than their thickness. Because of the symmetry, we consider only the left half of the model, as illustrated in figure 1c.

For such a crack problem in a microstructured material, one should first define the critical state of crack propagation. Experimental observations [11,27] showed that under an externally applied load, microvoids are first nucleated in the originally intact organic phase ahead of the initial crack tip, i.e. point C in figure 1a. The formation of a microvoid in the front of the crack tip indicates the pull-out of a platelet and the formation of a bridge between the two crack faces. The further increase in the applied load will cause distributed damage or a cloud of dispersed microvoids around the crack tip. In this study, however, our attention will be focused on the crack-bridging effect of platelets, the most important mechanism that endows the material with the merit of flaw tolerance [41]. Usually, the damage zone is far from being fully developed when a nacreous material approaches its theoretical strength, as is demonstrated in §3. The shielding effect of microvoids on the crack-tip stress field and its contribution to material strength can be estimated by a combination of the fracture mechanics method presented here and a damage mechanics model accounting for distributed microvoids, but is omitted in this work for simplicity. In addition, nonlinear fracture mechanics methods based on such concepts as the J-integral can be used to address the toughening effects of crack diversion, the frictional effects from platelet sliding, the viscoelasticity and plasticity of the organic constituent, and other nonlinear mechanisms [42]. In this work, we use the concept of stress intensity factor (SIF) to investigate the crack-bridging effect of platelets. Though relatively simple, this approach can reveal the prominent features of the crack-bridging mechanism of platelets in nacre, as we show below.

In the discontinuous crack-bridging model, the right and left ends of the crack-bridging zone, i.e. C and C' in figure 1c, are referred to the physical or real crack tip and the fictitious crack tip, respectively. According to the scenario elaborated above, the definition of the critical state of crack propagation
In consistency with many previous studies on the fracture behaviour of structurally toughened composites [43–45], we use the SIF as the parameter to judge the occurrence of crack propagation. The SIF at the crack tip \( C' \) caused by the remotely applied tensile stress \( s_1 \) is expressed as \[ K_1 = s_1 \sqrt{\frac{24}{\pi a}} \] where \( a = c + \lambda_{br} \) is the half-length of the fictitious crack with a cohesive zone, and \( \lambda_{br} \) is the length of each crack-bridging zone. In the reference configuration with \( s_1 = 0 \), no platelet has been pulled out, and therefore \( \lambda_{br} = 0 \). When the external load reaches a threshold, a microvoid will form in the thin organic layer just ahead of the crack tip \( C \), causing the pull-out of the first platelet (figure 1c). The corresponding SIF \( K_1^0 \) induced by the corresponding remote stress is referred to the intrinsic toughness of nacre without any toughening effect of the crack-bridging mechanism, \( K_{IC}^0 \), that is \[ K_1^0 = K_{IC}^0. \] With the increase in the applied stress, more and more platelets will be pulled out from the two crack surfaces, leading to the extension of the crack-bridging zone (figure 1c). For simplicity, we treat the material outside the bridging zone as a homogeneous, isotropic and linear elastic medium (figure 1b), and its effective Young’s modulus \( E \) is approximated by the elastic modulus in the in-plane direction of nacre. The effect of anisotropy on the mode-I SIF in figure 2 can be considered by using the method described by Tada et al. [47] but is neglected in this paper. Thus, a two-dimensional crack-bridging model considering the microstructural feature of nacre is established, as shown in figure 2a. As the crack-bridging forces induced by the platelets in the cohesive zone are transferred to the matrix via the organic interfaces and the platelet thickness is much larger than the organic layer thickness, it is appropriate to assume a series of discrete concentrated forces, as shown in figure 2b.

When the remote stress increases to another threshold value, the crack will enter into a stage of steady-state propagation, during which the crack propagates but the crack-bridging zone keeps a constant length. During the propagation of the platelet-bridged crack, the following critical condition of SIFs should be satisfied \[ K_1^0 + K_1^{br} = K_{IC}^0. \]
Two-dimensional crack-bridging model of nacre with an embedded flaw. (a) Crack-bridging model of platelets in nacre subjected to uniaxial tension in the far field. (b) Discrete concentrated forces induced by the crack-bridging platelets in the cohesive zone. Here, 1, 2, . . . , N are the sequence numbers of the concentrated forces, and \( \lambda_{b,i} \) is the crack-bridging zone length, \( \nu(i) \) is the crack surface displacement, \( f(v(\xi)) \) is the bridging force at the \( i \)-th interface, \( d \) is the thickness of a platelet, \( d_{int} \) is the thickness of each organic layer and \( s = d + d_{int} \). (Online version in colour.)

Here, \( K_{b,i}^{br} \) denotes the reduction of SIF caused by the bridging forces and is calculated by [48, 49]

\[
K_{b,i}^{br} = -\frac{1}{\sqrt{\pi s}} \int_{-a}^{a} \sigma_{b,i}(\xi) \left( \frac{\sqrt{a - \xi}}{a + \xi} + \frac{\sqrt{a + \xi}}{\sqrt{a - \xi}} \right) d\xi. \tag{2.4}
\]

where \( \sigma_{b,i}(\xi) \) is the bridging traction. The length of the crack-bridging zone is expressed as

\[
\lambda_{b,i} = N(d + d_{int}), \tag{2.5}
\]

where \( d \) and \( d_{int} \) are the thicknesses of a platelet and an organic layer, respectively, and \( N \) is the number of the discrete bridging forces or twice the platelet number in the crack-bridging zone. As aforementioned, the crack-bridging traction is treated as a series of concentrated forces \( f(\xi) \) (figure 2b). Here, \( \xi \) denote the locations where these forces act and are given by

\[
\xi_i = \begin{cases} (i - N)d + (i - N + 1)d_{int} - c, & \text{when } i \text{ is odd} \\ (i - N)(d + d_{int}) - c, & \text{when } i \text{ is even}. \end{cases} \tag{2.6}
\]

Herein and in the sequel, the index \( i \) takes the integers from 1 to \( N \). The bridging force \( f(\xi) \) is determined by

\[
f(\xi_i) = \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right]. \tag{2.7}
\]

where \( l \) is the length of a platelet. \( v(\xi) \) is the crack opening displacement at the position \( x = \xi \) and equal to the pull-out length of the platelet therein. \( \tau(\xi) \) is the average shear stress on the interface between the bridging platelet and the matrix. As the cohesive law of interfaces, \( \tau(\xi) \) is assumed as a function of the relative sliding displacement between two neighbouring platelets, \( v(\xi) \), that is,

\[
\tau(\xi_i) = \tau(v(\xi_i)). \tag{2.8}
\]

Its expression is given in §2.2.

Thus, the bridging traction acting on the two crack faces in the crack-bridging zone can be expressed as

\[
\sigma_{b,i}(\xi) = \sum_{i=1}^{N} f(\xi) \cdot \delta(\xi - \xi_i), \tag{2.9}
\]

where \( \delta(\xi - \xi_i) \) the Dirac’s delta function centred at \( \xi = \xi_i \), takes the value of 1.0 m\(^{-1}\) at \( \xi = \xi_i \) and 0 m\(^{-1}\) otherwise.

From equations (2.4)–(2.9), the SIF induced by the discontinuous crack-bridging platelets is recast as

\[
K_{b,i}^{br} = -\frac{1}{\sqrt{\pi s}} \sum_{i=1}^{N} \left[ \int_{a}^{b} \tau(\xi) \left[ \frac{1}{2} - v(\xi_i) \right] \left( \frac{\sqrt{a - \xi}}{a + \xi} + \frac{\sqrt{a + \xi}}{\sqrt{a - \xi}} \right) d\xi \right]. \tag{2.10}
\]

The theoretical model described above allows us to predict the tensile strength of nacre with crack-like flaws and to quantify the contributions of microstructural parameters, as is shown below.

### 2.2. Interfacial cohesive law

In the crack-bridging model, one needs to determine the force in each platelet in the cohesive zone as a function of its pull-out length or the crack-opening displacement. As the direct determination of the cohesive force–displacement relation is difficult, we here assume that the shear stress \( \tau(\xi) \) at the platelet–matrix interface and the relative sliding displacement \( v(\xi) \) have a nonlinear, trapezoid-like cohesive relation [40], as shown in figure 3. Then, one has

\[
\tau(v) = \begin{cases} v \frac{\tau_{max}}{\delta_1} & 0 \leq v \leq \delta_1 \\ \frac{\tau_{max}}{\delta_2} \delta_1 \leq v \leq \delta_2, \\ \frac{\delta_2 - v}{\delta_2 - \delta_1} \tau_{max} & \delta_2 \leq v \leq \delta_3, \end{cases} \tag{2.11}
\]

where \( \delta_1, \delta_2 \) and \( \delta_3 \) are material constants and \( \tau_{max} \) is the interfacial strength. In equation (2.11), \( \delta_1 \) denotes the critical displacement where the linear stage ends, \( \delta_2 \) is the critical displacement where the interfacial shear stress starts declining and \( \delta_3 \) stands for the ultimate pull-out length of a platelet. We let \( \delta_1^{c} \equiv \delta_3 – \delta_2 \) denote the dimensionless value of \( \delta_3 \). The energy dissipated by per unit area of an interface during the pull-out process is determined by the area of the trapezoid in figure 3 and expressed as

\[
S = \int_{0}^{\delta_1^{c}} \tau_0 d\xi = \frac{1}{2} \tau_{max}(\delta_3 - \delta_2 - \delta_1). \tag{2.12}
\]

### 2.3. Calculation of crack-opening displacement

To determine the crack-bridging forces of individual platelets at positions \( \xi_i \) one needs to calculate the corresponding crack-opening displacements, \( v(\xi) \). For a finite crack embedded in an infinite body subjected to the far-field SIF \( K_{1}^{\infty} \) and the bridging traction \( \sigma_{b,i}(\xi) \), the opening displacement is expressed as [46]

\[
v(x) = \frac{2K_{1}^{\infty}}{E\sqrt{\pi a}} \sqrt{a^2 - x^2} - \frac{2}{\pi E \text{P.V.}} \int_{-a}^{a} \sigma_{b,i}(\xi) \ln \left[ \frac{a^2 - \xi^2 + \sqrt{a^2 - x^2}^2}{a^2 - \xi^2 - \sqrt{a^2 - x^2}^2} \right] d\xi. \tag{2.13}
\]
Figure 3. Nonlinear interfacial cohesive law correlating the interfacial shear stress $\tau$ with the sliding displacement $v$ for the crack-bridging platelets. $S$ denotes the total energy dissipation per unit area of the interface and is calculated by the area underneath the trapezoidal curve.

where $P.V.$ presents the Cauchy principal value of the integral. From equations (2.4)–(2.10) and (2.13), the crack-opening displacement induced by the discontinuous crack-bridging zone can be calculated by

$$v(x) = \frac{2K^\infty}{E\sqrt{m}} \sqrt{a^2 - x^2}$$

$$- \frac{2}{\pi E P.V.} \sum_{n=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \ln \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right) \right\}.$$

$$v(\xi) = \frac{2\sqrt{a^2 - \xi_i^2}}{E \sqrt{m}} K_0^0$$

$$+ \frac{2\sqrt{a^2 - \xi_i^2}}{mE} \sum_{n=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \ln \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right) \right\}$$

$$- \frac{2}{\pi E P.V.} \sum_{n=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \ln \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right) \right\}.$$

Then letting $x = \xi$ in equation (2.15), we obtain a system of $N$ discretized equations for the crack-opening displacements in the crack-bridging zone

$$v(\xi) = \frac{2\sqrt{a^2 - \xi_i^2}}{E \sqrt{m}} K_0^0$$

$$+ \frac{2\sqrt{a^2 - \xi_i^2}}{mE} \sum_{n=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \ln \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right) \right\}$$

$$- \frac{2}{\pi E P.V.} \sum_{n=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \ln \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right) \right\}.$$

with $i = 1, 2, \ldots, N$. Obviously, the function $v(\xi)$ monotonically increases with respect to $\xi$, and $0 < v(\xi) \leq \delta_C$ should be satisfied by each bridging platelet. The crack-opening displacements in the bridging zone can be solved via a numerical iteration method. We gradually increase the number $N$ of crack-bridging platelets and use each value of $N$ to solve for a corresponding set of $v(\xi_i)$ through iteration. The entire calculation will be terminated when $N$ is large enough so that $v(\xi_i) \geq \delta_C$, which indicates the saturation of the bridging zone and the achievement of steady crack propagation. Thereafter, substituting the obtained crack-opening displacements at $\xi_i$ into the cohesive law in equation (2.11) leads to the values of the tensile forces of the platelets in the crack-bridging zone.

To ensure the conditions for the appropriate application of the concept of SIF, the initial crack-like flaw size should be much larger (e.g. 50 times) than the platelet thickness. In addition, a constraint condition is required to guarantee the integrity of platelets before they are fully pulled out. In other words, a platelet subjected to a high stress may rupture and then lose its ability to transfer the bridging force between the two crack faces. All broken platelets should be excluded from the bridging zone in order to prevent the overestimation of the stiffening effect. Because of the brittle feature of the platelets, we use the maximal tensile stress criterion: a platelet will break when its stress $\sigma$ reaches the ultimate strength of aragonite, $\sigma_{\text{max\_aragonite}}$. Thus in the bridging zone, there should be $\sigma < \sigma_{\text{max\_aragonite}}$, which can be rewritten as

$$2 \sum_{i=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \right\} < d\sigma_{\text{max\_aragonite}}.$$

2.4. Calculation of material strength

The calculation method described above enables us to determine the crack-opening displacements and the platelet forces in the cohesive zone, and thereby one can establish the relation between the crack-bridging zone length $\lambda_\nu$ and the remote stress in the stage of crack propagation. From equations (2.1), (2.3), (2.10) and (2.11), one obtains

$$\sigma^\infty = \frac{K_0^0}{\sqrt{m}}$$

$$= \frac{1}{m} \sum_{i=1}^{N} \left\{ \tau(\xi_i) \left[ \frac{1}{2} - v(\xi_i) \right] \right\} \left( \frac{\sqrt{a^2 - \xi_i^2} + \sqrt{a^2 - x^2}}{\sqrt{a^2 - \xi_i^2} - \sqrt{a^2 - x^2}} \right)$$

When the crack-bridging zone extends to a certain length, the stress $\sigma^\infty$ will reach its maximal value, $\sigma_{\text{ultimate}}$, which is regarded as the strength of the nacreous material with a crack-like flaw of length $c$. Equations (2.11), (2.16) and (2.18) constitute a complete set of equations for analysing the variation of the critical stress with the extension of the crack-bridging zone.
Table 1. Parameters and their values adopted in the calculations.

<table>
<thead>
<tr>
<th>parameters</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>length of platelet, (l)</td>
<td>(5 , \mu\text{m} ) [50]</td>
</tr>
<tr>
<td>thickness of platelet, (d)</td>
<td>(400 , \text{nm} ) [27,50]</td>
</tr>
<tr>
<td>thickness of organic layer, (d_{\text{org}})</td>
<td>(30 , \text{nm} ) [11]</td>
</tr>
<tr>
<td>toughness without bridging, (K_c)</td>
<td>(1 , \text{MPa m}^{1/2} ) [40]</td>
</tr>
<tr>
<td>nacre stiffness, (E)</td>
<td>(60 , \text{GPa} ) [24,27]</td>
</tr>
<tr>
<td>shear strength of interface, (\tau_{\text{max}})</td>
<td>(30 , \text{MPa} ) [26,51]</td>
</tr>
<tr>
<td>characteristic shear displacement, (\delta_1)</td>
<td>(5 , \text{nm} ) [25,26]</td>
</tr>
<tr>
<td>characteristic shear displacement, (\delta_2)</td>
<td>(300 , \text{nm} ) [25,26]</td>
</tr>
<tr>
<td>normalized characteristic displacement</td>
<td>(0.44 ) [40]</td>
</tr>
<tr>
<td>corresponding to pull-out of platelets, (\delta_{\text{eff}})</td>
<td>(s_{\text{th}})</td>
</tr>
<tr>
<td>strength of platelet, (\sigma_{\text{th}})</td>
<td>(5 , \text{GPa} ) [52,53]</td>
</tr>
</tbody>
</table>

As aforementioned, the application of the SIF concept requires that the crack length is much larger than the platelet thickness. For a shorter crack, the above method will overestimate the material strength. Therefore, we introduce another ceiling stress, which the strength value should not surmount. For the ideal microstructure of nacre considered in this paper, this ceiling stress is taken as the theoretical strength of nacre, \(\sigma_{\text{th}}\). Following previous theoretical analysis [24,38], \(\sigma_{\text{th}}\) is expressed as

\[
\sigma_{\text{th}} = \frac{l}{2(d + d_{\text{int}})} \tau_{\text{max}}. \tag{2.19}
\]

It is emphasized that equation (2.19) holds only when the interfacial failure occurs before the tensile failure of individual platelets. When \(\sigma_{\text{th}}\) reaches \(\sigma_{\text{th}}\), the tensile stress within an individual platelet is estimated as \(\sigma_{\text{th}}(1 + d_{\text{int}}/d)\), which is of order of \(10^2 \, \text{MPa} \), significantly lower than the platelet’s strength \(\sigma_{\text{max}}\), which is in the order of 1 GPa (table 1). Therefore, interfacial failure governs the theoretical strength of nacre and equation (2.19) will be used in our model. In all, the material strength is determined by

\[
\sigma_{\text{ultimate}} = \min \left\{ \max_{\lambda_{\text{br}}} \sigma_{\text{max}}(\lambda_{\text{br}}), \sigma_{\text{th}} \right\}. \tag{2.20}
\]

It is worth mentioning that besides the crack-bridging mechanism of platelets, the above fracture mechanics model can account for the influences of some other factors, such as nonlinear properties of the organic phase, the overall Young’s modulus of nacre, the formation of distributed voids in the vicinity of the crack tip and crack diversion. The effects of interfacial properties and Young’s modulus are discussed in §3.2. Such mechanisms of distributed damage can be indirectly taken into account by considering their effects on the geometric and material parameters in this model but detailed discussions are omitted here.

### 3. Flaw tolerance of nacre

#### 3.1. Effect of flaw size

By using the fracture mechanics model described in §2, we first analyse the strength–flaw size relation of natural nacre in this section. The values of the parameters in the model are taken according to relevant experimental results, as listed in table 1. It is mentioned that the nacres of different mollusc species (e.g. bivalve and abalone) have some differences in microstructures and mechanical properties. Here, only some representative values of geometric and materials parameters are taken for illustration. The exact values of these parameters do not interfere with the main conclusions, as demonstrated below.

For different values of the crack length \(c\), the curves of the applied tensile stress \(\sigma_{\text{th}}\) with respect to the crack-bridging zone length \(\lambda_{\text{br}}\) are obtained from equation (2.18), as shown in figure 4. Obviously, \(\sigma_{\text{th}}\) decreases with the increase in the flaw size. When the nacre has a longer crack (e.g. \(c = 100 \, \mu\text{m}\)), the \(\sigma_{\text{th}}\)-curve is always lower than the ceiling stress \(\sigma_{\text{th}}\). In this case, the tensile strength of nacre is sensitive to the crack length and equal to the peak value of the \(\sigma_{\text{th}}\)-curve, that is, \(\sigma_{\text{th}} = \max(\sigma_{\text{th}}(\lambda_{\text{br}}))\).

\[\text{cut-off by ceiling stress}\]

![Figure 4. Variation of the critical tensile stress \(\sigma_{\text{th}}\) with respect to the crack-bridging zone length \(\lambda_{\text{br}}\). \(\sigma_{\text{th}}\) is calculated from equation (2.18). \(\sigma_{\text{th}}\) denotes the theoretical strength given by equation (2.19) and is a ceiling stress of \(\sigma_{\text{th}}\), as given in equation (2.20). (Online version in colour.)](http://rsif.royalsocietypublishing.org/)

Based on the above results, we illustrate the dependence of the tensile strength of a nacreous material on the flaw size in figure 5. With the decrease in the flaw size, an obvious transition from the flaw-sensitive stage to the flaw-tolerant stage is observed. The critical flaw size between the two stages, denoted as \(c_{\text{crit}}\), is regarded as a quantitative measurement of the flaw tolerance of nacreous materials. Using the parameters in table 1, our calculations predict that for most natural nacres, \(c_{\text{crit}}\) has a value of about 40 \(\mu\text{m}\). Indeed, recent experimental observations [27] showed that some embedded crack-like flaws of about 20 \(\mu\text{m}\) in length do exist in natural nacres of, for instance, abalone. Our theoretical analysis demonstrates that the presence of these pre-existing flaws do not significantly lower the material strength and survivability.

A quantitative comparison between the flaw-tolerance properties of nacre and pure aragonite will be more instructive for understanding the significant role played by the
‘brick-and-mortar’ structure in nacre. According to the Griffith criterion, which can well predict the strengths of brittle materials, the critical crack length of pure aragonite phase reads [46]

\[ c_{\text{crit}}^{\text{aragonite}} = \frac{1}{\pi} \left( \frac{K_{\text{IC}}^{\text{aragonite}}}{\sigma_{\text{max}}^{\text{aragonite}}} \right)^2, \] (3.1)

where \( K_{\text{IC}}^{\text{aragonite}} \) and \( \sigma_{\text{max}}^{\text{aragonite}} \) are the fracture toughness and tensile strength of pure aragonite, respectively. Their values are about 0.25 MPa m\(^{1/2}\) (in the order of 1 MPa m\(^{1/2}\)) and 5 GPa, respectively [52–54]. Equation (3.1) renders a very small flaw tolerance of natural nacre, but if they are overly thin or overly long, the flaw-tolerance feature will be greatly compromised.

As can be seen from figure 6d, increasing the effective Young’s modulus \( E \) of the matrix can yield a synergetic enhancement of the strength and flaw tolerance of the composite. Natural nacres have high stiffness \( E \) as a result of the staggered ‘brick-and-mortar’ structure consisting of very thin mineral platelets glued by the organic phase into a staggered pattern [38]. Our calculations show that in order to achieve a high effective elastic modulus, the aspect ratio of platelets, \( l/d \), should be larger than a value of about 1000, which also benefits the improvement of the tensile strength and flaw-tolerance property of the composite. This result helps us to design artificial nacreous materials with comprehensive mechanical properties.

In addition, we examine the influences of the plastic pull-out length \( \delta_2 \) and the ultimate pull-out length \( \delta_{\text{eff}}^{\text{IC}} \) in the cohesive law in equation (2.11) on the strength and flaw tolerance of the material. Figure 6f shows that only a slight increase in the strength and flaw-tolerance parameters can be found with increasing \( \delta_2 \) and \( \delta_{\text{eff}}^{\text{IC}} \). Our analysis reveals that the interface strength \( \tau_{\text{max}} \) and energy dissipation \( S \) in the cohesive constitutive relation of the organic phase play a significant role in the mechanical behaviour of nacre. In actual materials, higher values of \( \delta_2 \) and \( \delta_{\text{eff}}^{\text{IC}} \) usually correspond to a higher S. Therefore, it is usually beneficial for the enhancement of the mechanical properties of nacreous materials to produce the interface layers with relatively large values of \( \delta_2 \) and \( \delta_{\text{eff}}^{\text{IC}} \), which can be achieved by, for instance, employing polymeric glues capable of multi-stage unfolding and extension mechanisms [54] and maintaining proper water content in the organic phase.

**4. A universal relation for strength of nacre-containing microcracks**

To further correlate the strength of nacre with its microstructural parameters, we conduct a dimensional analysis in this section. A universal relation for the strength of nacre is provided and it will be demonstrated by a large number of numerical examples.

In this fracture mechanics model, the normalized stress of a nacreous material with a crack-like defect is a function of the following parameters:

\[ \frac{\sigma_{\text{ultimate}}}{\sigma_{\text{th}}} = f(c, d, d_{\text{lat}}, l, E, \tau_{\text{max}}, \delta_1, \delta_2, \delta_{\text{eff}}, K_{\text{IC}}^{\text{aragonite}}). \] (4.1)

For the problem under study, the contribution of energy dissipation in the elastic stage (figure 3) of the pull-out process of a platelet is much smaller than that in the plastic or plateau stage. Keeping this in mind, the parameter \( \delta_1 \) is obliterated from equation (4.1). Then, one has

\[ \frac{\sigma_{\text{ultimate}}}{\sigma_{\text{th}}} = f(c, d, d_{\text{lat}}, l, E, \tau_{\text{max}}, \delta_2, \delta_{\text{eff}}^{\text{IC}}, K_{\text{IC}}^{\text{aragonite}}). \] (4.2)
Among all parameters in this equation, there are only two independent dimensions, which may be taken as \( c \) and \( \tau_{\text{max}} \). Applying the Pi theorem in dimensional analysis to equation (4.3) gives

\[
\frac{\sigma_{\text{ultimate}}}{\sigma_{\text{th}}} = \Pi \left( \frac{d}{c} \cdot \frac{d_{\text{int}}}{c} \cdot \frac{l}{\tau_{\text{max}}} \cdot \frac{E}{c} \cdot \frac{\delta_{\text{eff}}}{c} \cdot \frac{K^0_{\text{IC}}}{\tau_{\text{max}} \sqrt{c}} \right). \tag{4.3}
\]

Further, we introduce two characteristic length parameters with clear physical meaning to simplify equation (4.3). One is the total thickness of a mineral platelet and an organic layer, denoted as

\[
D = d + d_{\text{int}}, \tag{4.4}
\]

and the other is [41]

\[
\Delta = \frac{\delta_{\text{q}} E}{\tau_{\text{max}}}, \tag{4.5}
\]

which stands for the effective bridging effect of platelets.

Here, \( \delta_{\text{q}} \) is the maximal pull-out length of a crack-bridging platelet and is empirically expressed as

\[
\delta_{\text{q}} = a \cdot \delta_2 + \beta \cdot \delta_c = a \cdot \delta_2 + \beta \cdot \delta_{\text{eff}} l, \tag{4.6}
\]

where the coefficients \( a \) and \( \beta \) are two constants reflecting the contributions of the plastic plateau and the softening stage in the cohesive law in figure 3, respectively.

With the two characteristic lengths \( D \) and \( \delta_{\text{q}} \), equation (4.3) can be simplified into the following function form involving only four variables:

\[
\frac{\sigma_{\text{ultimate}}}{\sigma_{\text{th}}} = \Pi \left( \frac{c}{D} \cdot \frac{d}{\Delta} \cdot \frac{1}{\tau_{\text{max}}} \cdot \frac{c}{\tau_{\text{max}} \sqrt{c}} \cdot \frac{K^0_{\text{IC}}}{\Delta} \right), \tag{4.7}
\]

For the ideal ‘brick-and-mortar’ microstructure shown in figure 1, we have considered \( K^0_{\text{IC}} \) as a constant. For simplicity,
we obliterate the last term in the parenthesis in equation (4.7) and this treatment will be demonstrated by our numerical results. Among the first three terms in equation (4.7), we first test the ability of the combinatorial parameter $c/\Delta$ on unifying the effects of stiffness and interfacial properties on material strength. As shown in figure 7, the strength curves generated under different combinations of stiffness and interfacial properties collapse onto a master curve as a function of the parameter $c/\Delta$, indicating the robustness of this parameter in describing material strength in a unified manner. However, it cannot describe the size effect of platelets. To find a better combinatorial parameter that can describe all those effects of stiffness, interfacial properties and platelet sizes, the preceding three terms in equation (4.7) is further combined into a single reduced parameter, $c l/ (D\Delta)$, which will build a master curve describing the flaw sensitive-tolerant transition of nacre strength. Thus, equation (4.7) reduces to

$$\frac{\sigma_{\text{ultimate}}}{\sigma_{\text{th}}} = \Pi \left( \frac{c l}{D\Delta} \right).$$

To validate this relation, a large number of numerical examples are calculated by using the crack-bridging model in §2 in a broad range of microstructural and mechanical parameters. The results are shown in figure 8. It is found that despite the simplifications we have made in the derivation of equation (4.8), it fits all numerical results with quite high accuracy. Therefore, our dimensional analysis has well captured the prominent principles and physical mechanisms underlying the macroscopic response of nacreous materials to microstructural flaws, and equation (4.8) can indeed provide a master curve to predict the strength of this kind of material. Because of its simplicity, the relation in equation (4.8) can be easily applied for both natural and artificial materials.

To gain better understanding of the master curve in figure 8, the physical meaning of the parameter $c l/ (D\Delta)$ is explained as follows. It can be decomposed into two multiplicative parts, $c/ D$ and $\Delta/l$. The former is the flaw size normalized by the characteristic structural thickness, and the latter stands for the effective pull-out length of crack-bridging platelets with respect to the overall platelet length. The material will undergo the flaw sensitive–tolerant transition when the above two effects (i.e. $c/ D$ and $\Delta/l$) are comparable. This has also been demonstrated by our numerical examples in figure 8, as the material’s strength approaches the theoretical strength (i.e. reaches the critical flaw-tolerant state) around $(c/ D)/(\Delta/l) = 0.3 \sim 1$.

5. Conclusion

Natural composites, such as nacre and bone, always have some structural flaws, which, however, generally uncomprise the mechanical properties and overall survivability of the materials. As a primary mechanism against failure in nacre, platelet bridging can greatly improve not only the strength and fracture toughness but also the ability to tolerate microsized flaws. In this paper, we have presented a micro-structure-based fracture mechanics model to investigate the tolerance ability of nacre to crack-like flaws. By introducing two characteristic length scales, we have obtained a dimensionless parameter $c l/ (D\Delta)$ to predict the strength of nacreous materials with crack-like flaws.

Our analysis shows that owing to the crack-bridging effect of platelets, nacre shows a superior property of flaw tolerance. A crack-like flaw of up to 40 $\mu$m in size would have little degradation to the material strength and this critical flaw size is three orders higher than that a pure aragonite can bear. This finding reveals the significant role that the elegant ‘brick-and-mortar’ microstructure plays in the flaw-tolerance property of nacreous materials. This also inspires the design of advanced artificial nanocomposites with improved flaw-tolerant ability. For example, both the thickness and length of platelets should be in an optimal range in order to achieve a superior flaw-tolerance property.

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