Quantifying the role of mineral bridges on the fracture resistance of nacre-like composites

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Abstract

The nacreous layer of mollusk shells holds design concepts that can effectively enhance the fracture resistance of lightweight brittle materials. Mineral bridges are known to increase the fracture resistance of nacre-inspired materials, but their role has been difficult to quantify. The challenge has been to isolate and control mineral bridge connectivity in a model composite with microstructures on the same scale as the biological material. In this study, we fabricate these tunable nacre-like composites from highly aligned alumina platelets, interconnected by titania mineral bridges and infiltrated with epoxy matrix phase, and experimentally quantify the influence of mineral bridge density on the fracture properties. Mineral bridge density from image analysis of composite cross sections was correlated with the fracture behavior in mechanical tests and a quantitative model was developed using the insight that shear lag describes the stress transfer through the mineral phase. This model quantitatively describes the relationship between the fracture strength of the composite, platelet strength, and mineral bridge density, which provides powerful guidelines for the design of lightweight brittle materials with enhanced fracture resistance. We illustrate this potential by fabricating nacre-like bulk composites with unparalleled fracture strength, 20% stronger than the previously reported materials.

1. Introduction

Stiffness, strength, and fracture toughness are an antagonistic combination of materials properties that are difficult to achieve in man-made composite materials. In contrast, biological composites, like nacre, access this combination of properties by employing hierarchical structures and complex chemical and physical interactions across multiple length scales[1-4]. In bioinspired composites research, work has been conducted toward identifying the underlying design principles of these biological materials for translation to future engineering composites[5-7]. However, the structural complexity of these multi-scale biological composites makes it often times difficult to identify and quantify the individual structure-property relationships. Biological materials vary depending on species, region of sampling and season, and variation of even a single parameter can alter the balance of physical interactions across the hierarchical structure, resulting in compounded effects on the mechanical behavior.

A biological material whose structure and properties have been extensively studied is the nacreous layer of the mother of pearl[7-10]. Interest in this biological material stems from its ability to combine high strength, stiffness and toughness using intrinsically weak mineral building blocks.[9, 10] Nacre consists of mineral platelets arranged in brick and mortar structure at very high mineral content. The platelets are separated by a thin biopolymer layer and interconnected to one another through mineral bridges. The interaction of mineral content, aspect ratio and interconnectivity between the platelets all play a role in the stiffness, strength and toughness of the biological composite. Notably, the strongest nacre-inspired composites all have mineral bridge interconnectivity [11-13].

Despite the insights obtained so far, only a few quantitative descriptions for how mineral bridges contribute to the mechanics of the nacre structure have been reported. Proposed analytical models have yet to be validated experimentally in nacre-like materials with tunable mineral bridges at the length scales and properties comparable to the biological system. Working at the same length is critical when studying brittle materials that are scale sensitive[7]. This requirement is not fulfilled by current 3D printing technologies, which produce brick and mortar designs with platelets about 10-100 times larger than the biological material. Further, biological nacre has a very high ratio between the stiffness of the platelets, Ep, and the stiffness of the matrix, Em: Ep/Em is on the order of 109. In comparison, typical 3D printed multi-material polymers have an Ep/Em ratio on the order of 104. Thus, these polymer models likely over-emphasize the role of the matrix contributing towards the strength of the composite, especially when extrapolating to composites with high mineral content[18],[14]. In this context, building simplified nacre-inspired composites with structural features and constituent mechanical properties comparable to those found in the biological material should allow for a more systematic study of the structure-property relationships underlying the effect of mineral bridges on the mechanics of nacre.

Nacre-like composites featuring a brick-and-mortar structure and mineral interconnectivity at length scales and modulus ratio comparable to those of the biological counterpart were recently developed using a vacuum-assisted magnetic alignment process (VAMA).[12] In this approach, a rotating magnetic field is used to align magnetized alumina microplatelets suspended in a liquid, while vacuum consolidates the aligned material on a filter; akin to a paper making process. This process results in bulk-scale green bodies of highly aligned platelets. Pressure assisted sintering is then used to consolidate the green bodies into nacre-like scaffolds, which can be infiltrated with monomers to generate brick-and-mortar architectures after polymerization. Mineral bridges can be created between the bricks if alumina platelets with a titania coating are used during the VAMA process. Bridges of controllable size are formed upon dewetting of the titania from the alumina surface during sintering. Mineral interconnectivity is controlled by adjusting the processing temperature.[12] Analysis of the mechanical properties of brick-and-mortar architectures produced via this approach led to important insights into the role of interconnectivity on the strength of nacre-like composites. However, the simultaneous variation of the platelet content and the fraction of mineral bridges did not allow for a quantitative description of the isolated effect of mineral bridges on the composite properties.

Here, we quantify the effect of mineral bridges alone on the mechanical response of nacre-like composites featuring length scales and stiffness ratio comparable to those found in the biological material. To this end, nacre-like composites with fixed mineral density (volume fraction) and tunable density of mineral bridges were prepared. This was accomplished by mapping the design space of the sintering process to identify the sets of temperatures and pressures that lead to composites with fixed mineral volume fraction but variable mineral bridge densities. Composites with tunable mineral bridge densities are then investigated by image analysis and flexural bending tests to obtain structure-property relationships for these model nacre-like materials. Using the experimental data, we develop a shear-lag model that quantitatively describes the relationship between mineral connectivity and composite strength, elastic modulus and toughness. Moreover, we observe that residual stresses introduced during scaffold fabrication strongly affect the ultimate strength that is achievable with these composites. Despite these residual stresses, we present nacre-like composites with optimum mineral bridging and small platelet sizes that exhibit the highest strength reported for brick-and-mortar structures while also maintaining non-catastrophic failure.

2. Materials and Methods

Building on a previously established technique [12], we produced 20g/48 mm green body scaffolds by magnetically aligning titania coated alumina micro-platelets in aqueous suspension and consolidation them by vacuum filtration. Sintering under pressure consolidated the scaffolds into brick and mortar microstructures intercconnected by nanoscale “mineral briges”, Fig. 1, resembling the microstructure of biological nacre. Systematic variation of temperature and pressure enabled the identification of isodense scaffolds with variable mineral bridge contact strength. Scaffolds were then infiltrated with commcial epoxy (Sikadur 300) to form polymer matrix composites. These composites were microscructurally characterized by scanning electron microscopy and image analysis, which was then correlated with mechanical properties in three point bending.

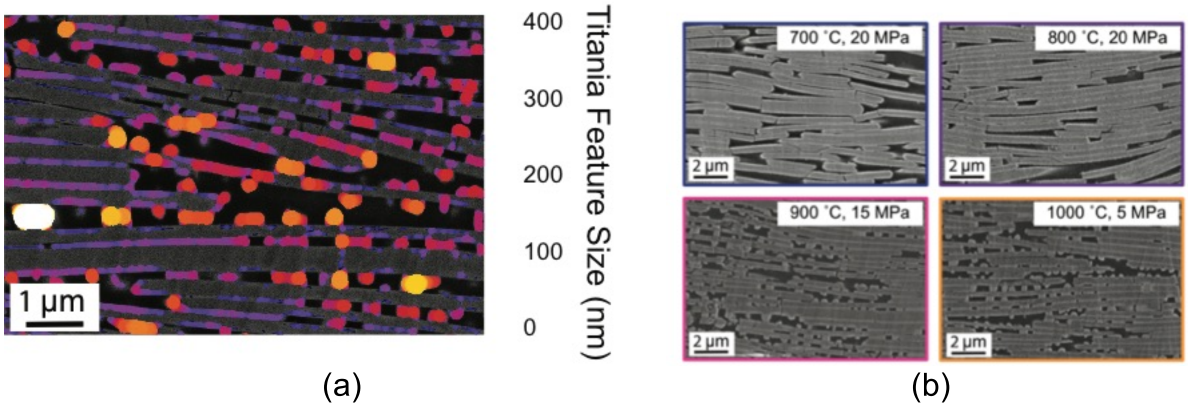

Fig 1. Shows (a) an SEM image of the microstructure in the synthetic nacre like composites with an overlay of the local titania bridge feature size, where brightness of the feature correlates with the size of the mineral bridge. By tuning the temperature and pressure processing parameters, we are able to tune the interconnectivity of mineral bridges to provide a model system for interface studies.

3. Results and Discussion

On the basis of experimental observations, the fracture strength of samples is set by assuming platelet pull-out as the main failure mode. Using a rule of mixture approach, the shear lag model predicts the composite strength to vary as follows:

$$\sigma_c = \alpha V_p \sigma_p + (1 - V_p)\sigma_m$$ (Equation 1)[7]

where α is a stress transfer efficiency term, Vp is the volume fraction of platelets, and σp and σm are the platelet strength and matrix strength, respectively. The stress transfer term α depends on the fracture behavior of the composite. For composites failing in pullout mode containing square platelets in a plastic matrix[20] the stress transfer efficiency term has been previously derived as

$$\alpha = \frac{\tau S}{\sigma_p},$$ (Equation 2)

which results in the simplified relationship:

$$\sigma_c = \tau S V_p + (1 - V_p)\sigma_m, \qquad \text{(Equation 3)}$$

where S is the aspect ratio of the platelet and τ is shear strength of the matrix or of the platelet-matrix interface.

This model can be simplified then by futher with a few assumptions. First, the contribution of the polymer tensile strength to the composite strength, $(1-V_p)\sigma_m$, is assumed to be negligible, since elastic modulus of the platelets (Ep ~300 GPa) is 2 orders of magnitude higher than that of the polymer matrix (Em ~3 GPa).

$$\sigma_c \sim \gamma\ \tau_{mb} S V_p \qquad \text{(Equation 4).}$$

The above scaling argument should be valid when the fracture process occurs predominantly through a platelet pull-out mechanism, however there is an upper limit when the mode fracture of these composites is no longer dominated by pull-out but instead by platelet fracture. The strength of composites failing under such mechanism can also be predicted using a shear lag model and is given by :

$$\sigma_{\text{c, max}} \approx \frac{1}{2}\sigma_p V_p \qquad \text{(Equation 5)}$$

However, SEM imaging of composite cross-sections observes that sintering under pressure leads to extensive bending of the alumina platelets). Since the platelets are flat in the green scaffold, these deformations must result from the application of external pressure during sintering. The bending stresses introduced during sintering can reduce the effective strength of the platelets by allowing fracture to initiate at lower stresses on the tensile face of the platelet. This in turn should reduce the maximum composite strength. One can estimate the effect of the residual bending stress, λ, on the composite strength by substituting an effective platelet strength, $\sigma_{p,eff} = \sigma_p - \lambda$ into Equation 5:

$$\sigma_{c,\max} = \frac{1}{2}(\sigma_p - \lambda)V_p, \qquad \text{(Equation 6).}$$

Given the limitations represented in eqantion 5 and equation 6, one possible way to improve the achievable fracture strength is to increase their effective strength of the platelets by selecting smaller platelets. Although smaller platelets are also subjected to residual stresses after hot pressing, Griffith's law predicts higher fracture strength for smaller reinforcement sizes. This should eventually increase the load bearing capacity of the nacre-like architecture by extending the maximum strength limit imposed by the platelet fracture mode (equation 5).

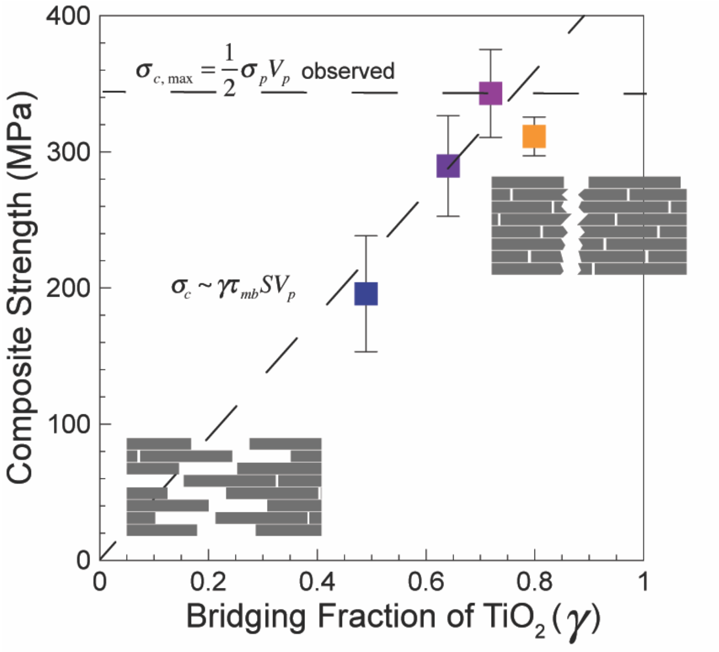

Fig. 2. Mechanical behavior of nacre-like composites with varying mineral bridge fraction. Strength increases with mineral bridging fraction up to 0.8 and decreases thereafter. Schamtics illustrate the transition in failure mode as the mineral bridge fraction is increased.

4. Conclusions

Mechanical measurements on model nacre-like composites show that mineral bridges increase the fracture strength of brick-and-mortar architectures by enhancing stress transfer throughout the stiff inorganic phase. The fracture strength of such nacre-like composites was found to increase linearly with the density of mineral bridges between platelets until the stress level carried by the inorganic phase reaches the strength of individual platelets; this relationship can be quantitatively described with a simple shear lag model. In addition to the mechanical strength, the fracture toughness of the composites also shows a linear dependence on the density of mineral bridges. This shows that mineral bridges can enhance the fracture strength of nacre-like composites while still promoting the onset of toughening mechanisms typical of brick-and-mortar architectures. As a result, antagonistic properties such as fracture strength, elastic modulus and toughness can be simultaneously obtained.

For the manufacturing process used in this study, we observe the fracture strength of the composite to be limited by residual stresses introduced into the material during pressing at high temperatures. Our shear lag model properly captures this effect by considering that the residual stresses reduce the effective strength of the platelets. To compensate for this undesired effect, we show that composites with higher fracture strength can be made using thinner, stronger platelets. Thinner platelets increase the strength of the composite as expected from Griffith's law. This new nacre-like composites exhibit the highest yet reported combination of specific stiffness and strength. Besides the remarkable fracture resistance achieved, our work on nacre-like composites demonstrates the potential of bio-inspired synthetic architectures in providing a tunable model system to investigate the underlying design principles of more complex hierarchical biological materials.

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