

FLAW TOLERANT BULK AND SURFACE NANOSTRUCTURES OF BIOLOGICAL SYSTEMS

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ABSTRACT

Bone-like biological materials have achieved superior mechanical properties through hierarchical composite structures of mineral and protein. Gecko and many insects have evolved hierarchical surface structures to achieve superior adhesion capabilities. We show that the nanometer scale plays a key role in allowing these biological systems to achieve such properties, and suggest that the principle of flaw tolerance may have had an overarching influence on the evolution of the bulk nanostructure of bone-like materials and the surface nanostructure of gecko-like animal species. We demonstrate that the nanoscale sizes allow the mineral nanoparticles in bone to achieve optimum fracture strength and the spatula nanoprotusions in Gecko to achieve optimum adhesion strength. Strength optimization is achieved by restricting the relevant dimension to nanometer scale so that crack-like flaws do not propagate to break the desired structural link. Continuum and atomistic modeling have been conducted to verify this concept.

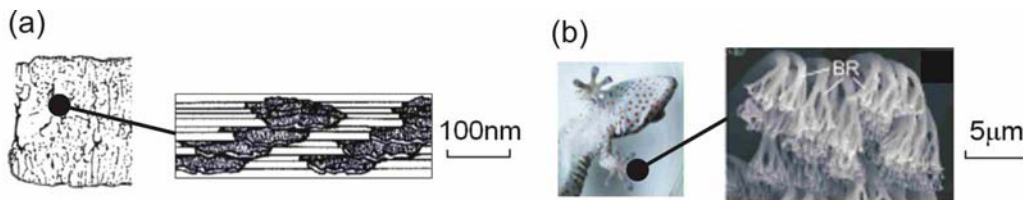


Fig. 1: Nanostructure of bones (a) and the toe of geckos (b) that consists of a terminal nanostructure called spatula of about 200-500 nm in diameter.

1. INTRODUCTION

New challenges in materials science in the 21st century will include the development of multi-functional and hierarchical materials systems. Nanotechnology promises to enable mankind to design materials using a bottom-up approach, that is, to construct multi-functional and hierarchical material systems by tailor-designing structures from atomic scale and up. However, there is almost no theoretical basis on how to design a hierarchical material system to achieve a particular set of functions. One strategy is to look among solutions in nature for hints on advanced materials design.

Biological materials, such as bone [1] exhibit many levels of hierarchical structures from macroscopic to microscopic length scales. The smallest building blocks in such materials are generally on the nanometer length scale. For instance, the nanostructure of bone (Fig. 1 (a)) consists of mineral crystal platelets with thickness around a few nanometers embedded in a collagen matrix [1, 2].

Interesting nanostructures of biological systems for superior mechanical properties are not just limited to bone-like nanocomposites. Gecko and many insects have evolved elaborate hierarchical surface structures in their foot hair to achieve extraordinary adhesion capabilities. These animals possess ability to adhere to vertical surfaces and ceilings. A gecko is found to have hundreds of thousands of keratinous hairs or setae on its foot; each seta is 30~130 μm long and contains hundreds of protruding nanoscale structures called spatula (Fig. 1 (b)). Here we focus on

the following questions. Why is nanoscale is so important to biological systems? What are the basic mechanisms and principles behind biological nanostructures?

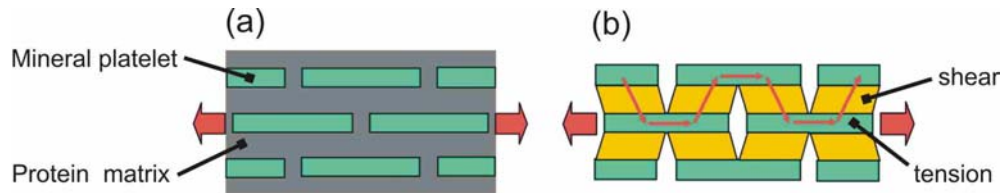


Fig. 2: A simple tension-shear chain model of biocomposites. (a) Schematic of staggered mineral crystals embedded in a soft (protein) matrix. (b) Tension-shear chain model showing the path of load transfer in the mineral-protein composites.

2. THE PROTEIN-MINERAL BULK NANOSTRUCTURE OF BONE-LIKE BIOCOMPOSITES

Experimental observations (e.g. [1, 3] and further references in [4]) have shown that, at the most elementary structure level, biological materials exhibit a generic structure consisting of staggered mineral platelets embedded in a soft matrix (Fig. 2 (a)). Under an applied tensile stress, the path of load transfer in the mineral-protein biocomposites can be represented by a tension-shear chain model [4] where the mineral platelets carry tensile load and the protein transfers load between mineral crystals via shear (Fig. 2 (b)). In this tension-shear chain model, the mineral-protein composite is simplified to a one-dimensional chain consisting of tensile springs (mineral) interlinked by shear springs (protein). The integrity of the composite chain structure is hinged upon the strength of mineral platelets since breaking of the platelets would destroy the critical structural links in the composite, leading to disintegration of the protein-mineral network. The strength of mineral platelets plays a crucial role in the fracture energy of the composite. In order to achieve high fracture energy, the mineral platelets must be able to sustain large tensile stress without fracture.

How to optimize the strength of the mineral platelets? The Griffith theory of fracture [5] and common engineering experiences have shown that the strength of brittle solids is determined by pre-existing flaws. It was pointed out that the nanometer scale is the key to optimizing mineral strength [4]. At the simplest level, this can be understood from the following consideration. A perfect, defect-free mineral particle should be able to sustain mechanical stress near the theoretical strength σ_{th} of the material. However, we assume that the particle contains crack-like flaws. For example, protein molecules trapped within the mineral crystals during the biomineralization process are mechanically equivalent to embedded microcracks. Consider a crack in a thin strip (mineral particle) as shown in the inlay of Fig. 2 (a). With $E^* = E/(1 - \nu^2)$, Poisson's ratio ν and E as Young's modulus, the strength of the material can be calculated to be

$$\sigma_f = \sqrt{4\gamma E^* / h}$$

for a mineral platelet width h and fracture surface energy γ . According to

this expression, the strength of the material approaches infinity when h goes to zero. This is physically impossible, since the largest stress material can sustain is σ_{th} . This suggests that there exists a transition between crack propagation governed by the Griffith criterion and uniform rupture of atomic bonds at theoretical strength at a critical length scale [4]

$$h_{cr} = \frac{4\gamma E^*}{\sigma_{th}^2}. \quad (30)$$

Taking a rough estimate $\gamma=1 \text{ J/m}^2$, $E_m = 100 \text{ GPa}$, and $\sigma_{th} = E_m / 30$, we find h_{cr} to be around 30 nm for a half-cracked platelet [4]. The nanometer scale not only allows the strength of mineral particles to be optimized near theoretical strength but also renders these particles insensitive to crack-like defects (flaw tolerance).

This concept has so far been discussed only within the framework of continuum mechanics. Here we conduct atomistic simulations to confirm the flaw tolerance concept (details see [6]). Figure 3 (a) plots the critical failure stress normalized by the theoretical strength, indicating a smooth transition between crack propagation governed by the Griffith condition for thick layers

($\sqrt{h_{cr}/h} < 1$) to uniform rupture at theoretical strength for thin layers ($\sqrt{h_{cr}/h} > 1$). This result is fully consistent with previous analysis [4]. Figure 3 (b) plots the distribution of normal stress ahead of the crack. As the strip width is decreased, stress concentration at crack tip disappears and the stress distribution becomes uniform near the crack tip, and thus the solid has become insensitive to flaws.

Further analysis of the protein-mineral bulk nanostructure of bone-like biocomposites focuses on the stiffness (discussion of the interplay of the soft protein matrix and the stiff mineral platelet material, and the impact of the aspect ratio of mineral platelet) and the fracture energy (including a discussion on sacrificial Ca^{++} bonds) can be found in [6].

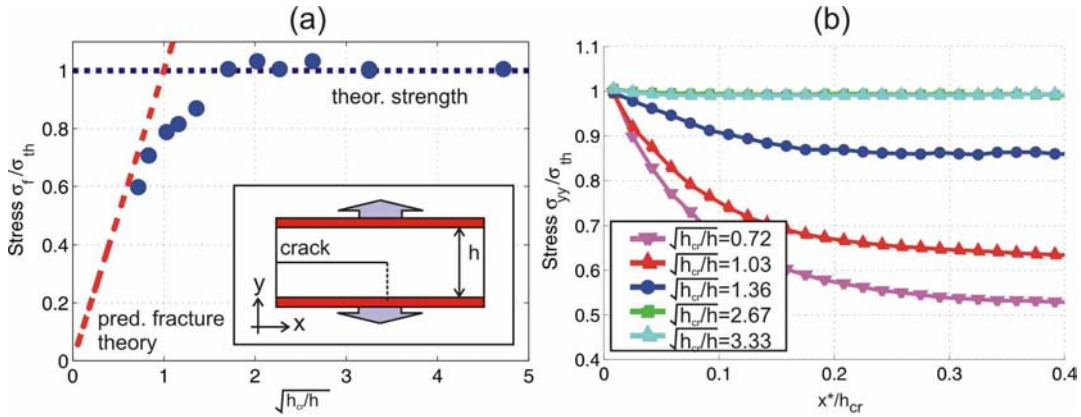


Fig. 3: (a) Fracture strength as a function of layer width h , and (b) stress distribution ahead of the crack for different layer widths h .

3. FLAW TOLERANT SURFACE NANOSTRUCTURE OF GECKO FOR ADHESION

The concept of nanoscale flaw tolerance can be discussed in a more general context to include the surface nanostructure of gecko. Among the hairy biological attachment systems, the density of surface hairs (setae) increases with the body weight of animal, and gecko has the highest density among all animal species that have been studied [7].

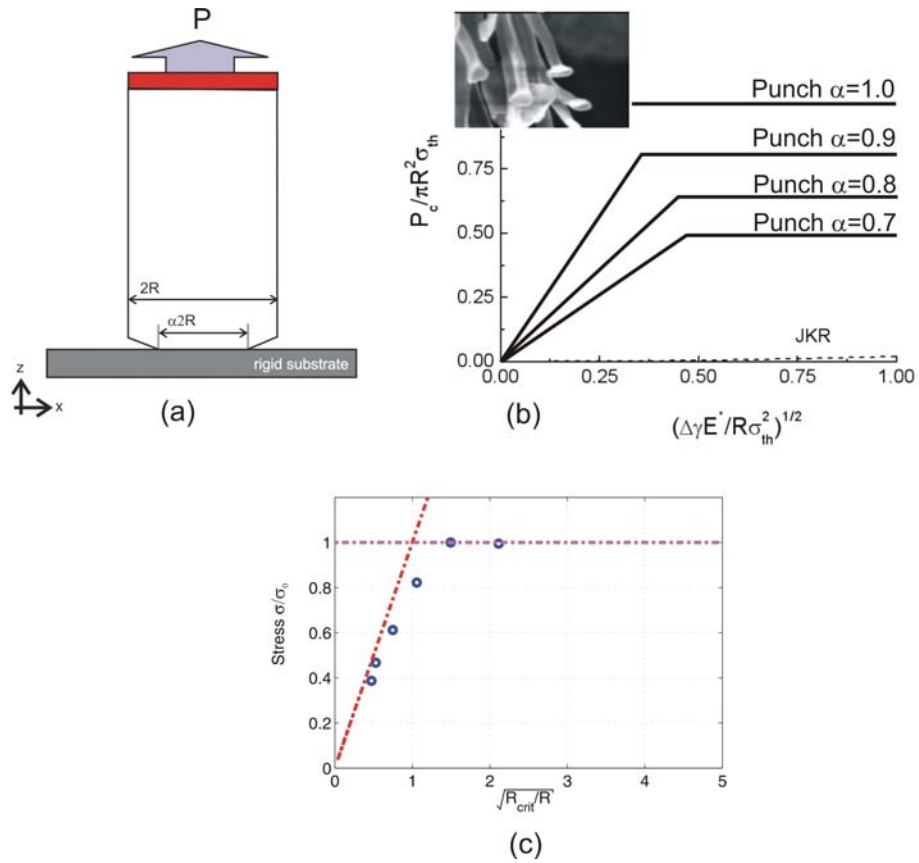


Fig. 4: (a) Geometry of the model for the spatula. (b) Adhesive strength as a function of the radius. At the critical radius, the adhesive strength is independent of flaws and is at its theoretical limit. (c) Atomistic simulation results (details will be explained in a forthcoming publication). These results suggest that the flaw-tolerance concept also holds at the atomic scale.

The most terminal (smallest) structure of gecko's attachment mechanism is called spatula (Fig. 1 (b)) which is about 200-500 nanometers in diameter. Why is the spatula size in the nanometer range? To understand this, we have modeled the spatula as an elastic flat-ended cylindrical hair in adhesive contact with a rigid substrate [8]. The radius of the cylinder is R . To test the ability of the flat cylinder to adhere in the presence of adhesive flaws, imperfect contact between the spatula and substrate is assumed such that the radius of the actual contact area is $a = \alpha R$, and $0 < \alpha < 1$, as shown in Fig. 4 (a); the outer rim $\alpha R < r < R$ represents flaws or regions of poor adhesion. The adhesive strength of such an adhesive joint can be calculated by treating the contact problem as a circumferentially cracked cylinder, in which case the stress field near the edge of the contact area has a square-root singularity with stress intensity factor [9]. Similarly as in the previous section, this leads to a critical length scale, the spatula radius, when adhesion becomes insensitive to flaws. The critical radius is given by

$$R_{cr} = \beta^2 \frac{\Delta\gamma E^*}{\sigma_{th}^2} \quad (24)$$

where $\beta = \sqrt{2/(\pi\alpha F_1^2(\alpha))}$, F is a function that varies slowly between 0.4 and 0.5 for $0 \leq \alpha \leq 0.8$ (for details, see [9]), and $\Delta\gamma$ is the surface energy. The theoretical strength of the interface is given by σ_{th} . Figure 4 (b) plots the apparent adhesive strength for $\alpha = 0.7, 0.8$ and 0.9 , together with the case of flawless contact ($\alpha = 1$). The corresponding result of a hemispherical tip based on the JKR model is plotted as a dashed line for comparison (in plotting the JKR curve, we have taken E^*/σ_{th} to be 75) [10]. The flat-ended spatula achieves the maximum adhesion strength much more quickly than the hemispherical configuration.

The parameters for the van der Waals interaction and the Young's modulus of spatula (keratin) are $\sigma_{th} = 20 \text{ MPa}$, $\Delta\gamma = 0.01 \text{ J/m}^2$, $\Delta\gamma/\sigma_{th} \cong 0.5 \text{ nm}$ and $E^* = 2 \text{ GPa}$. This gives the critical size for adhesive strength saturation as $R_{cr} \cong 225 \text{ nm}$ which matches the radius of gecko's spatula that is typically around 100-250 nm: The analysis suggests that the nanometer size of the spatula structure of gecko may have been evolved to achieve optimization of adhesive strength in tolerance of possible contact flaws. Further analysis on this problem with a focus on the adhesion strength of spatula arrays is given in [6].

Finally, Figure 4(c) shows atomistic simulation results (details will be explained in a forthcoming publication). The simulation results strongly suggest that the flaw-tolerance concept also holds at the atomic scale. Our analysis of the stress distribution suggests that it becomes homogeneous, as the radius approaches the critical length scale.

4. SUMMARY

This paper aimed to provide a unified treatment of flaw tolerant nanostructures of biological systems. At a nanometer critical length determined by fracture energy, Young's modulus and theoretical strength, the mineral crystals in biocomposites become insensitive to pre-existing crack-like flaws and the strength of mineral can be maintained near the theoretical strength of the material despite of defects. Following the same principle, the nanometer size of spatula, the most terminal adhesive structure of gecko, achieves maximum adhesion strength and become tolerant of potential contact flaws. This concept was exemplified for the strength of mineral crystals using a joint atomistic-continuum investigation.

It is interesting to note that the protein-mineral structure of biocomposites is consistent with the ancient Chinese philosophy that combination of "Ying" and "Yang", things of complementary nature or properties, results in perfection and harmony in nature. In biological materials, the mineral platelets act as the "yang" phase (stiff, hard, brittle, non-dissipative, non-yielding), and in contrast, the protein acts as the "ying" phase (soft, gentle, ductile). The nanometer scale plays the key role in the property optimization of mineral-protein structure (further discussion see [6]).

5. REFERENCES

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