FLAW TOLERANT NANOSTRUCTURES OF BIOLOGICAL MATERIALS

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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 nanoprotrusions 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.

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, to this date, 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.
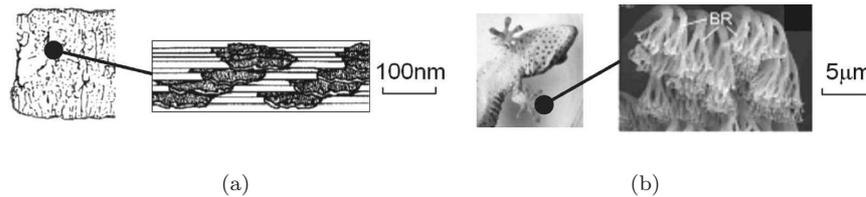
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(a)   (b)

Figure 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.

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. 1a) 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 the nanocomposite structure of bone. 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 $30 \sim 130\mu$m long and contains hundreds of protruding nanoscale structures called spatula (Fig. 1b). We attempt to address the following questions. Why is nanoscale is so important to biological systems? What are the basic mechanisms and principles behind biological nanostructures?

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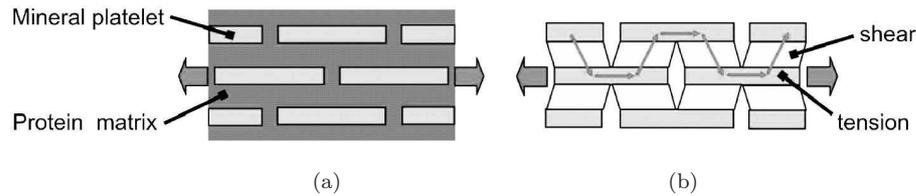
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Figure 2. A simple tension-shear chain model of biocomposites. (a) Schematic of staggered mineral crystals embedded in a soft (protein) matrix. (b) Tension-shear chain model showing the path of load transfer in the mineral-protein composites.

tical 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. Considering all potentially existing cracks in a thin strip, the largest crack, and hence the most dangerous one, will be a crack about half the strip width. The key idea of flaw tolerance [4,6] is that cracks confined in a small structure do not propagate until the material around the crack uniformly reaches the theoretical strength. This can also be demonstrated with the crack configuration shown in Fig. 3. In this configuration, the strength of the material can be calculated from the Griffith theory as $\sigma_f = \sqrt{4\gamma E^*/h}$ for a mineral platelet width h and fracture surface energy γ, where $E^* = E/\left(1 - \nu^2\right)$, E being the Young's modulus and ν the Poisson ratio. According to this expression, the strength of the material approaches infinity when h goes to zero. This is physically impossible since the largest stress a material can sustain is limited by an upper bound (theoretical strength) 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]

$$h_{cr} = \frac{4\gamma E^*}{\sigma_{th}^2}.\tag{1}$$

Taking a rough estimate $\gamma = 1\,\text{J/m}^2$, $E_m = 100\,\text{GPa}$, and $\sigma_{th} = E_m/30$, we found h_{cr} to be around $30\,\text{nm}$ 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 also been studied by atomistic simulations (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 the continuum mechanics 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 on 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 fracture energy (including a discussion on sacrificial Ca^{++} bonds) can be found in [6]. The interested reader is referred to references [4,6-9] for further details of our group on this topic.
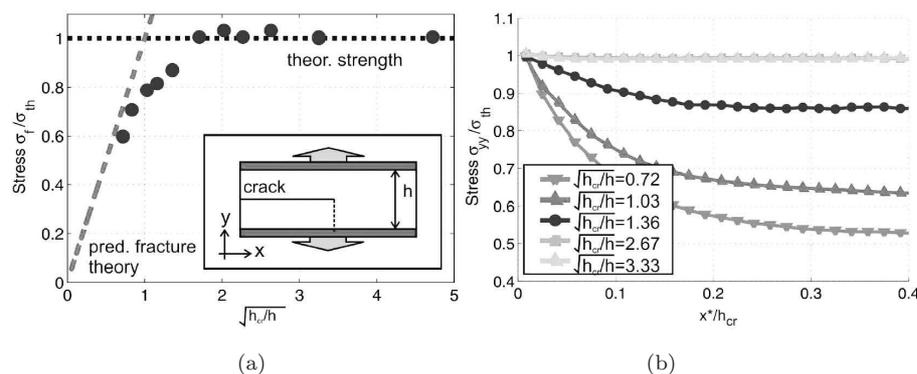

(a)   (b)

Figure 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 [10].

The most terminal (smallest) structure of gecko's attachment mechanism is called spatula (Fig. 1b) 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 [11]. 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 [12]. Somewhat similar to the case of nanoscale mineral platelets in bone, a critical length scale for the spatula radius exists when adhesion becomes insensitive to crack-like flaws. The critical radius is
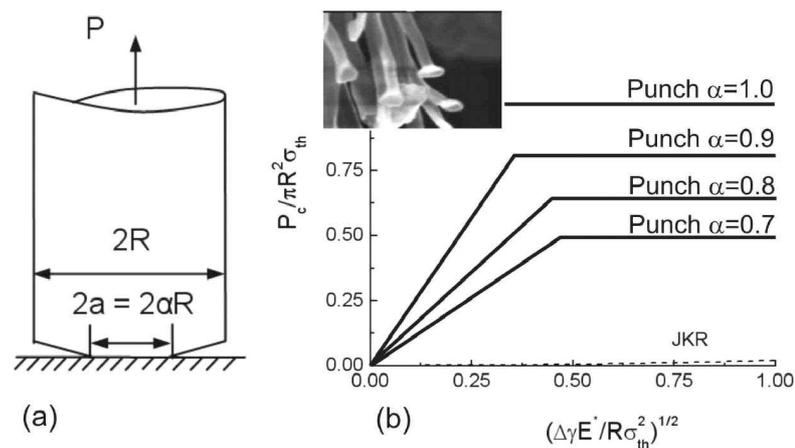

Figure 4.   (a) Geometry of the model for the spatula. (b) Adhesive strength as a function of the radius. At the critical radius, the adhesive strength is independent of flaws and is at its theoretical limit.

given by

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

where $\beta = \sqrt{2/\left(\pi\alpha F_1^2(\alpha)\right)}$, F is a function that varies slowly between 0.4 and 0.5 for $0 \leqslant \alpha \leqslant 0.8$ (for details see [11]), and $\Delta\gamma$ is the surface energy. The theoretical strength of van der Waals interaction across the interface is denoted by σ_{th}. Figure 4(b) plots the apparent adhesive strength for α=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) [12]. The flat-ended spatula achieves the maximum adhesion strength much more quickly than the hemispherical configuration. Further numerical studies based on the Tvergaard–Hutchinson model [13] of adhesion, as shown in Fig. 5, confirmed that the adhesion stress indeed becomes uniform as the size of the contact area is reduced to below the critical length.
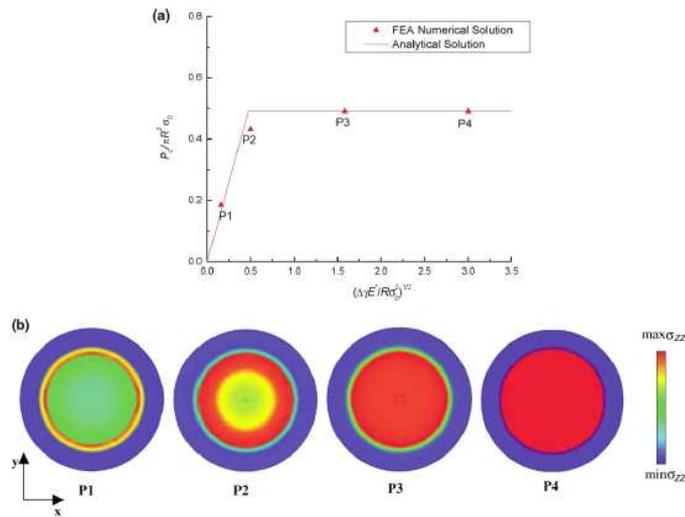

Figure 5.   Numerical results of the Tvergaard–Hutchinson model for the adhesion of a flat-ended cylinder partially adhering to a rigid substrate. The real contact area is assumed to be 50% of the total area of the punch (a=0.7). (a) The normalized pull-off force shows saturation at a critical size, in good agreement with the simple analysis from Griffith criterion. (b) The traction distribution within the contact area becomes more uniform as the size is reduced. Below the critical size, the traction becomes uniform and equal to the theoretical strength of van der Waals interaction. An arbitrary scale has been used here to plot the traction distribution. (Figure adopted from Ref. [11].)

The parameters for the van der Waals interaction and the Young's modulus of spatula (keratin) are $\sigma_{th} = 20\,\text{MPa}$, $\Delta\gamma = 0.01\,\text{J}$, $\Delta\gamma/\sigma_{th} \cong 0.5\,\text{nm}$ 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]. Recently, Gao and Yao [14] have shown that, for contact between any two elastic materials, it is possible to design an optimal shape of the local contact surface to achieve theoretical pull-off force. However, such design tends to be unreliable at the macroscopic scale because the pull-off force is sensitive to small shape variations in the contact surface. A robust design of shape-insensitive optimal adhesion becomes possible when the diameter of the contact area is reduced to length scales on the order of 100 nm. In general, optimal adhesion could be achieved by a combination of size reduction and shape optimization. The smaller the size, the less important the shape. At large contact sizes, optimal adhesion could still be achieved if the shape can be manufactured to a sufficiently high precision. The robust design of optimal adhesion at nanoscale provides further support for the flaw tolerant theory of nanoscale contact in biological adhesion structures.

4.   Summary

This paper aimed to provide a unified treatment of flaw tolerant nanostructures of biological materials. At a nanometer critical length determined by fracture energy, Young's modulus and theoretical strength, the mineral crystals in biological materials such as bone 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 has been studied via continuum and atomistic modeling.

Interestingly, the protein-mineral structure of bone appears to conform to the ancient Chinese philosophy that combination of "Yin" 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 "yin" phase (soft, gentile, ductile). The nanometer scale plays the key role in the property optimization of mineral-protein structure.

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