NANOSCALE MECHANICAL PROPERTIES IN BONE AND DENTIN

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Bone and dentin are organic-inorganic hybrid composites of protein and mineral with superior strength, hardness and fracture toughness. It is quite a marvel that nature produces such tough materials out of protein constituents as soft as human skin and mineral constituents as brittle as a classroom chalk. What are the mechanisms in it? Previous researches [1-8] showed that bone and dentin as well as other biomaterials have complicated hierarchical structures. For instance, bone has up to 7 hierarchical level of organization from microstructure of mineral crystals and collagen molecules to the macrostructure of cancellous and cortical bone. Dentin is also a calcified tissue somewhat similar to bone, where the collagen-rich organic matrix reinforced by calcium phosphate mineral particles. It is very interesting that, the basic building mineral crystal is in nanoscale, e.g. scanning small-angle x-ray scattering tests showed [4, 5], the thickness of mineral crystals are normally several nanometers in bone and dentin. Why nanoscale is so important for nature? What the roles of protein as the organic phase are, in the strength and toughness of bone and dentin, and how to model the relation of mineral crystals and collagen molecules in their microstructure? In this paper, we will answer these questions from three aspects: the fracture strength of mineral crystal at nanoscale; the mechanics of protein in fracture of biocomposites; the viscoelastic properties of bone and dentin because of protein.

FRACTURE STRENGTH OF MINERAL CRYSTALS AT NANOSCALE

In this work, we proved that the fracture strength of a "cracked" mineral crystal could be calculated from the Griffith criterion of fracture mechanics as

$$s_{\text{frac}} = a\, E\Psi, \qquad \Psi = \sqrt{\frac{g}{Eh}} \tag{1}$$

where E and γ are Young's modulus and surface energy of mineral crystal, respectively, and h is the thickness of the crystal. The parameter a depends on the crack geometry and is approximately equal to $\sqrt{p}$ for the half-cracked crystal (with surface crack length equals thickness of crystal). We found that there exists a critical length scale

$$h^* \approx a^2 \frac{gE}{s_{th}^2} \tag{2}$$

below which the fracture strength of a cracked crystal is identical to that of a perfect crystal, where s_{th} is the theoretical strength. Taking a rough estimate γ=1J/m^2, E= 100 GPa, and s_{th}=E/30, we estimate h^* to be around 30 nm. This length scale indicates that the nanometer size of mineral platelets in biomaterials may be the result of fracture strength optimization. When the mineral size exceeds this length scale, the fracture strength is sensitive to structural size and the material is sensitive to crack-like flaws and fails by stress concentration at crack tips. As the mineral size drops below this length scale, the strength of a perfect mineral crystal is maintained despite of defects. We assume that the nanometer size of the mineral crystals is selected to ensure optimum fracture strength and maximum tolerance of flaws (for robustness). In addition, fracture of solids involves breaking of atomic bonds, which is inherently a nonlinear process. In order to model failure mechanisms in nano crystals, we have developed a Virtual Internal Bond (VIB) [9, 10] method which incorporates an atomic cohesive force law into constitutive model of materials. Our simulation shows that the stress field becomes more and more uniform as the thickness of the platelet decreases and eventually reaches the theoretical strength at the critical length scale as the crystal is loaded close to the failure limit.

PROTEIN ARRESTING THE CRACK

Protein plays a crucial role to the high strength and toughness due to its intrinsic mechanical properties. A fracture model of biocomposites was developed via a Virtual-Internal-Bond approach. With this fracture model we simulated the fracture behaviors of biocomposites. The results showed that the protein layer was very effective to eliminate the stress concentration ahead of the crack tip and arrest the

crack. We also observed that the microcracks nucleated at the tensile zone between the mineral platelets, which can dissipate the fracture energy and delocalize the damage of the materials. This observation was proved by the experiments [11]. In addition, our analysis proved that through the design of the nature, i.e. the large aspect ratio and the staggered alignment of the mineral crystals, bone and dentin could save their high stiffness and strength from soft protein. Protein is not "weak" in biocomposites any more, as its strength is amplified by the large aspect ratio of the mineral crystals.

VISCOELASTIC PROPERTIES WITH PROTEIN

The volume fraction of protein in bone and dentin are more than 50% [5], which are much higher than that of sea shells which is only about 0.1%-5% [12, 13]. According to Darwinism, this should have its reason of natural evolution to "increase the individual's ability to compete, survive, and reproduce". The bone and dentin experience more dynamic load in the life of animal, but sea shells experience mainly static force or low frequency dynamic force under the sea, although the sea shells may also experience the impact by the surf sometimes. This question is supposed to be answered by studying the viscoelastic properties of biocomposites. Protein has strong viscoelastic properties that can help bone and dentin dissipate the fracture energy under the dynamic load. The fact of the shapes of the relaxation curves being similar for bone and the demineralized bone demonstrates the main contribution of protein to the viscoelastic properties of bone [14, 15]. A composite model to evaluate the viscoelastic properties of biocomposites was developed to describe the effect of protein on the viscoelastic properties of bone and dentin, and the main parameters are studied. By this composite model, we demonstrated that bone and dentin having larger volume concentration of protein displays better viscoelastic properties than the sea shells with less protein. The enhance parameter λ of viscoelastic properties of biocomposites is influenced by the aspect ratio of mineral crystals and the volume fraction of protein. Since high aspect ratio of mineral crystals can offset the viscoelastic properties of biocomposites, system with the larger aspect ratio of mineral inclusions should have much larger volume fracture of protein to get a reasonable improve of the viscoelastic properties.

This study throws the light on our understanding the concept of nature designing the hard and tough materials with brittle and soft hybrid materials. Soft and viscoelastic protein wrapping the nano sized mineral crystals makes bone and dentin strong and tough. On the other hand, protein also has potential to bring problems to the stiffness and strength of biomaterials due to its weak and soft properties. Nature subtly solved this problem by using the high aspect ratio of hard mineral crystals to save the strength and hardness of biocomposites. This design concept is very valuable to the synthesis of man made organic-inorganic hybrid materials with super mechanical properties in the future.

Keywords: Bone and dentin, Nanoscale, fracture strength, viscoelastic

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