XXI International Congress of Theoretical and Applied Mechanics
Warsaw, Poland, August 15-21, 2004

NANOSCALE MECHANICS OF BIOLOGICAL MATERIALS

Huajian Gao

Max-Planck Institute for Metals Research, D-70569 Stuttgart

Biological materials, such as shell, bone and tooth 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. Understanding the mechanisms by which nature design strong and tough composites with weak materials can give us a guideline for the synthesis of man made novel materials. Previous researches showed that although they have various hierarchical structures, the biological materials have similar elementary building blocks. X-ray scattering (SAXS), Transmission Electron Microscopy (TEM) and high voltage electron microscopy (HVEM) have shown that many biomaterials share a generic nanostructure consisting of staggered nanoscale mineral crystals with very large aspect ratios embedded in a soft protein matrix. Why is nanoscale so important to nature materials? What are the roles of protein in the strength and toughness of biological materials? Why do the mineral crystals have a large aspect ratio? In this lecture, we will discuss these questions from several aspects, such as mechanics of protein, the fracture strength of mineral crystal at nanoscale, stability of the nanostructure and the interface strength between mineral and protein, etc.

Protein arrests the crack and dissipates fracture energy

Protein plays a crucial role in the strength and toughness of biological materials due to its intrinsic mechanical properties. We have developed a fracture model of biocomposites based on a Virtual-Internal-Bond (VIB) approach. With this model we have simulated the fracture behaviors of biocomposites. The results show that the protein layer is very effective in eliminating stress concentration near crack-like flaws, thereby arresting the crack. We also observed microcrack nucleation at the tensile zone between the mineral platelets, while not destroying the integrity of the structure, can dissipate fracture energy and delocalize damage in the material. In addition, protein has strong viscoelastic properties that can help biomaterials dissipate fracture energy under dynamic loading. A composite model evaluating the viscoelastic properties of biocomposites is developed to describe the effect of protein on the viscoelastic properties of composites. By this composite model, we demonstrate that bone and dentin with larger volume concentration of protein exhibits better viscoelastic properties than sea shells.

Fracture strength of nanometer sized mineral crystals

We find that there exists a critical length scale for the maximum strength of mineral crystals. This critical length scale is estimated as

$$h^* = \alpha^2 \frac{E\gamma}{\sigma_{th}^2}$$

where E and γ are Young's modulus and surface energy, and σ_{th} is the theoretical strength of mineral. The parameter α is approximately equal to $\sqrt{\pi}$ for a thumbnail-crack spreading over half the thickness of a mineral crystal. When the size of the mineral crystal is less than this critical length scale, the fracture strength of the cracked crystal is identical to that of a perfect crystal. 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. In order to model failure mechanisms in nanocrystals, we have used the VIB method which incorporates an atomic cohesive force law into the 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.

Stability of nanocrystals

The fact that the mineral nanocrystals in biomaterials exhibit very large aspect ratios raises the issue of structural buckling under compressive loading. We show that the key to this question is the generic nanostructure of biomaterials in which the mineral nanocrystals are stabilized by the surrounding protein matrix. This is especially interesting in view of the three-orders of magnitude difference in elastic modulus between protein and mineral. A unique feature of the biological nanostructure is that, at large aspect ratios of mineral crystals, the buckling strength approaches a constant lower threshold value independent of the crystal geometry. The existence of a buckling strength independent of the detailed geometrical parameters of mineral is critically important from the point of view of structure robustness as the composite behavior of biomaterials or biomimicking materials should not depend sensitively on small variations in crystal size and shape. The large aspect ratios play a key role in the stability of mineral crystals by which relatively weak support from protein layer is accumulated and amplified to be significant. This is analogous to the stability of DNA double helix in which relatively weak hydrogen bonds can make the double helical structure quite stable under the help of its long chain.

Interface strength

The interface between mineral and protein plays a critical role in the viability of biocomposites. The interface properties can be extremely crucial as the force transfer between inclusions and matrix hinges upon a robust interfacial bonding along their interface. For nanocomposites, the interface properties can dominate overall material properties. A simple

fracture model is developed to study the composite fracture strength in the presence of interface failure, where we find that the large aspect ratio again plays an important role in amplifying the interfacial strength. Molecular dynamic simulation is performed to study binding between protein and mineral under various loading conditions.

Biological Attachment Systems

Geckos have evolved elaborate adhesive structures which allow them to move along vertical walls and ceilings against their body weight. There is strong evidence that the adhesion of Gecko is due to van der Waals interaction between a contacting surface and hundreds of thousands of keratinous hairs or setae on Gecko's foot; each seta is 30-130 μm long and contains hundreds of 200-500nm projections or spatula. While contact mechanics suggests that the refinement of structure size results in greater adhesive strength, some important questions remain unsolved: What is the significance of nanometer length scale for adhesion? What is the optimum adhesive strength of a structure? How can a structure optimized for attachment simultaneously allow easy detachment, as reversible adhesion is crucial for animal's movement? We show that the nanometer range of the spatula size of Gecko may have evolved to optimize the adhesive strength and maximum tolerance of imperfect adhesion (for robustness). Our analysis also indicates that the asymmetrical structure of Gecko's seta structure may been designed to simultaneously allow robust attachment and easy detachment.

Reference:

[1] H. Gao, B. Ji, I.L. Jaeger, E. Arzt and P. Fratzl, "Materials Become Insensitive to Flaws at Nanoscale: Lessons from Nature," 2003, *Proceedings of the National Academy of Sciences of USA*, Vol. **100**, pp. 5597–5600.