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Mechanical behavior of mother-of-pearl and pearl with flat and spherical laminations

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ABSTRACT

Laminated structure reduces the common inverse relationship of strength and toughness in many biological materials. Here the mechanical behavior of pearl and nacre with spherical and flat laminations was investigated and compared with the geological aragonite counterpart. The biological ceramics demonstrate higher strength, better reliability, and improved damage resistance owing to their laminated arrangement. Kinking and delamination occur in pearl to resist damage in addition to the crack-tip shielding mechanisms as in nacre, such as crack deflection, bridging, and platelet pull-out. The fracture mechanisms were interpreted in terms of the stress state using finite element simulation. This study may help clarify the compressive mechanics of laminated sphere between platens and advance the understanding on the mechanical behavior of biological and bio-inspired laminated materials.

1. Introduction

Synthetic ceramics have long been widely used in high-stress and high-temperature operating conditions, owing to their properties of high strength, high stiffness, good wear-resistance and high thermal stability [1–3]. Nonetheless, ceramics fail catastrophically without plasticity because of their less flexible covalent and ionic bonds [1,2]; such brittleness restricts the engineering applications of ceramics [3]. In comparison, natural biological ceramics synthesized by living organisms balance strength and toughness better than synthetic materials because of their hierarchical structures formed through self-assembly [4–7]. For instance, the laminated structure in natural ceramics features parallel stacking of building blocks layer-by-layer, as seen in the inner-layer shells of many mollusks, such as pearl oyster and abalone [8]. Crack deflection and bridging can be introduced by the laminated structure, contributing to improved fracture toughness [9,10]. Such structure has also been widely mimicked in a series of bio-inspired materials [11,12]. The mechanical properties of laminated materials depend strongly on their detailed structural characteristics, *e.g.*, the orientation and thickness of constituent platelets [13,14]. For example, the compressive strength is approximately 2.3 times higher in the direction normal to the nacre layer (540 MPa) compared to the parallel direction (235 MPa) in abalone shell [14]. Understanding the structure-mechanical property relations serves as the basis for the bio-inspired design of high-performance laminated ceramics.

As a unique laminated arrangement, the spherical laminations are common in natural materials and components, ranging from asteroids to plant seeds, and in synthetic nanoparticles [15–17]. Remarkable mechanical properties can be generated in materials with spherically laminated structure or made from their precursors [18–20]. The spherically laminated carbon nanospheres exhibit superelastic deformation behavior and good structural stability that no phase transformation occurs under high pressure [18]. Unprecedented hardness and thermal stability are achieved in diamond with nano-twinned structure fabricated from the precursors of spherically laminated carbon nanoparticles [20]. However, the structure-mechanical property relations as well as the deformation and fracture mechanisms of these spherically laminated materials have rarely been explored. Besides, the compression of spheres between flat platens, as a fundamental mechanics problem, is of significance in a range of fields, such as the transportation of iron ore pellets and the production of lightweight building materials [21,22].

Pearl that is produced by living mollusks is a biological ceramic having the same component of mainly aragonite as its mother – nacre [23–25]. Aragonite and calcite are two common mineral forms of calcium carbonate in mollusk shells with the former generally existing in nacreous layer [26,27]. The building blocks are arranged in spherically laminated architecture in pearl [23,24], which is distinct from the nacre's flat laminations. In this work, the structures and mechanical properties of nacre and pearl were investigated and compared to geological aragonite. The deformation and fracture mechanisms were clarified and correlated to their distinct structures.

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2. Materials and methods

Air-dried shells in length of about 17 cm and width of approximately 13 cm of *Sinanodonta woodiana* (Bivalvia: Unionidae) freshwater mussels and their produced pearls in diameters of 5–10 mm were obtained from a freshwater farm in Zhuji City, Zhejiang Province, China. Geological aragonite mined in Morocco was bought from a local craft shop. The external dark brown layers of as-received shells have been removed by mechanical grinding. The longitudinal and transverse directions of shell were defined to be parallel and vertical to the growth line (Fig. 1a).

For structural characterization, shells and pearls were sectioned along different directions and equatorial plane using an STX-202A water-cooled low-speed diamond saw (Shenyang Kejing, China). The sections were sequentially ground using SiC abrasive papers of grades of 1200 and 2000, carefully polished using diamond polishing paste with grit size of 0.5 μm, etched in 2 wt.% ethylenediamine tetraacetic acid (EDTA) for 1–2.5 min, and then washed with distilled water immediately and dried in air. The samples were sputter-coated with thin gold film using a 208HR sputter coater (Cressington, UK) at an electric current of 20 mA for 240 s and observed by field emission scanning electron microscopy (SEM) using an LEO Supra 55 instrument (Carl Zeiss, Germany) at an accelerating voltage of 10 kV. The fine structure was characterized by a field emission transmission electron microscopy (TEM) on a Tecnai G2F20 system (FEI, USA) at an accelerating voltage of 200 kV. For preparing the TEM specimens, thin sections were cut from nacre and pearl along different directions, manually ground using 2000-grade SiC abrasive papers to a thickness of approximately 70 μm, and then glued onto copper grids. The samples were ion-milled at an accelerating voltage of 5 kV and electric current of 2 mA with an inclination angle of 10° for 5 h and subsequently at 5° for 30 min using an EM RES101 ion beam milling system (Leica, Germany). These specimens were sputter-coated with thin carbon film in thickness of about 25 Å using a Model 681 high resolution ion beam coater (Gatan, USA) before observation.

Vickers hardness testing was performed on the polished longitudinal and transverse sections of nacre and the equatorial plane of pearl with one diagonal of indenter parallel to the laminates using an AMH43 microhardness tester (LECO, USA). The indentation load and dwelling time were 200 gf and 13 s. Geological aragonite was also tested for comparison.

Rectangular specimens in dimensions of $2 \times 2 \times 4$ mm^3 were excised from nacre using low-speed diamond saw. Uniaxial compression testing was conducted at a constant strain rate of 10^{-4} s^{-1} at room temperature using an Instron 8871 machine (Instron, USA). The loading direction was perpendicular to the aragonite laminates. Geological aragonite specimens of the same sizes were prepared and compressed along the [001] crystallographic orientation. Spherical pearls in diameters of approximately 6 mm were compressed between two flat platens made of high-strength steel at a displacement rate of 0.036 mm/min. A special fixture was used to avoid the rolling of pearls on the platen. At least 11 samples were tested for each material to ensure a good reliability.

The samples were sputter-coated with gold film and examined by SEM after indentation and compression. The compression of one pearl was stopped prior to the final fracture to reveal the deformation mechanisms. The unloaded sample was sputter-coated with gold and observed by SEM. Subsequently, this pearl was embedded in epoxy resin, sectioned along its meridian plane, sputter-coated with gold, and then examined by SEM to characterize the internal morphology.

The deformation behavior of an ideal elastic-plastic sphere compressed between two stiff platens was computed by finite element simulation in both spherical and Cartesian coordinates. For the finite element analysis, the diameter of sphere and the applied compressive displacement were set as 6 mm and 161 μm, which were consistent with the actual tests. The strength and Young's modulus of the material were set as 793 MPa and 19.7 GPa based on the experimental results. The Poisson's ratio was chosen as 0.3 according to Ref. [28,29].

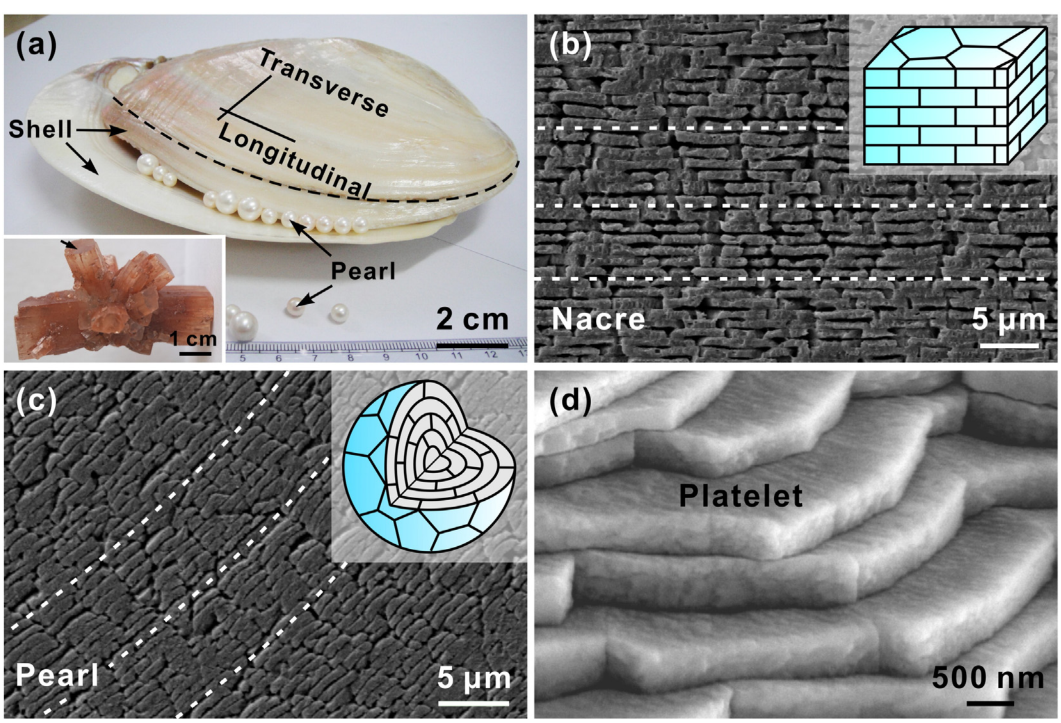

Fig. 1. (a) Macroscopic appearance of *Sinanodonta woodiana* shells, pearls and geological aragonite. The dashed curve indicates the growth line of shell. The arrow in the inset indicates the (001) crystallographic plane of aragonite. (b, c) SEM micrographs of the cross sections of nacre and pearl etched in 2 wt.% EDTA for 2.5 min and 1 min. Their structures are schematically illustrated in the insets. The dotted lines denote the orientations of laminates. (d) Magnified morphology of the aragonite platelets in pearl.