

The influence of internal length scales on mechanical properties in natural nanocomposites: A comparative study on inner layers of seashells

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Abstract

Natural materials exhibit outstanding properties compared to their single constituents because of their hierarchical alignment. Therefore, they can be used as a guide to enhance the properties of artificial nanocomposite materials, which eventually could excel compared to their biological counterparts. In this study, seashells of five species with different microstructures were compared by correlating the sizes and aspect ratios of the building blocks to their mechanical behavior. The analyzed nacreous seashells were *Trochus maculatus*, *Haliotis rufescens* and *Pteria penguin*; the non-nacreous seashells were *Meretrix lusoria* and *Pecten maximus*. The results were used to determine the optimal values for the shape, size and volume fraction of the structural elements with regards to hardness, Young's modulus and fracture toughness. Surprisingly, the aspect ratio of the mineral phase in all seashells investigated was found to be close to the optimal value for strength as predicted by theory.

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1. Introduction

Most living organisms need structural tissues to survive: bones, shells, teeth, beaks or corals are only a few examples. Such structures often consist of micro- and nanocomposite materials where organic and inorganic components are organized in sub-structures optimized by evolution to withstand environmental stresses associated with their biological function. Although the technology of composite materials has succeeded in creating highly specialized, high performance materials, it is still far from being able to replicate the complexity and elegance of most biological composites. A prerequisite for producing such biomimetic materials with properties close or even superior to biological composites is to understand the influence of the geometry of structural elements, such as size and aspect ratio, on

the overall mechanical properties. Therefore a systematic comparative investigation on biological model systems is needed to understand this correlation.

Although biological composites have various shapes, they derive their remarkable properties by the same concept: combination of organic and inorganic components and their well-defined arrangement in preferred orientations over several length scales. The hard inorganic phase composed of, e.g., calcium carbonate, calcium phosphate or amorphous silica [1] is surrounded by the relatively soft organic matrix, typically consisting of organic macromolecules such as keratin, collagen or chitin [1,2]. While the hard phase provides stiffness and mechanical stability to the system, the function of the matrix is to maintain the geometry of the structure and to distribute mechanical stress among the hard constituents. At the same time, the matrix provides high fracture toughness and improves fatigue resistance, both typically poor in hard materials.

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The shape and the arrangement of the constituents is a crucial factor contributing to the excellent mechanical properties of the biological composites, e.g., high stiffness and strength on the one hand and facilitated energy dissipation in the case of fracture on the other. Menig et al. [3], in a study on the quasi-static and dynamic mechanical response of *Haliotis rufescens* shells, found crack deflection, plastic microbuckling under compressive loading and viscoelastic deformation of the organic matrix to be the most important mechanisms contributing to the unique mechanical properties. The proteins of the matrix have a large deformation potential by domain unfolding and interface slipping [4–6]. Furthermore, toughening mechanisms due to nanoscale asperities on the platelet surfaces of the mineral phase are reported [7,8].

The most prominent arrangements of organic and inorganic constituents found in seashells are nacreous and cross-lamellar. The best investigated structure (brick-and-mortar structure) is the nacre of *H. rufescens* (also referred to as red abalone) consisting of polygonal aragonite platelets (~95 wt%) stacked in layers and embedded in the matrix (~5 wt%) [3,9–11]. *H. rufescens* grows by sequential deposition of aragonite and organic layers perpendicular to the platelet diameter [10]. The growth is guided and controlled by the organic matrix [10,12]. The cross-lamellar structure (e.g., inner layer of *Pecten maximus*) is built up by aragonite needles (third-order lamellae), which are arranged in bundles to form second-order lamellae. Parallel bundles are combined to form a first-order lamella with a plate-like shape [13]. In neighboring first-order lamellae, the bundles of second-order lamellae are rotated 60–90° against each other [13].

So far, most of the studies on mechanical properties have focused on single species. In this work, five seashell species, three with a nacreous structure and two non-nacreous, were systematically investigated to relate microstructure (platelet size, platelet aspect ratio and matrix fraction) to mechanical properties (such as hardness, Young's modulus and fracture toughness).

2. Materials and methods

The seashells analyzed in this work are *Trochus maculatus*, *H. rufescens*, *Pteria penguin*, *P. maximus*, and *Meretrix lusoria*. *H. rufescens* seashells were purchased from Oceanzone (Germany), all other seashells from Conchology Inc. (Philippines). They were stored in a dry state, in air and at room temperature.

The top layers of the examined seashells were cut away and the inner layers were sectioned into parallelepipedal samples using a wire saw. For X-ray diffraction (XRD) experiments, these samples were used without further preparation. For thermogravimetric analysis (TGA), the samples (4 mg to 6 mg) were grinded in a mortar. For scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman measurements, the specimens were mechanically cleaved by means of compression

applied perpendicularly to the macrolayers of the seashell [14]. Cross-sectional specimens for SEM images were produced by bending of the samples perpendicularly to the macrolayers until cracking. For microindentation experiments, samples were embedded in polymer resin (Demotec 15 plus) and ground with abrasive paper (P600). For nanoindentation experiments, the specimens of *T. maculatus*, *H. rufescens*, and *P. penguin* were cleaved as described above, whereas the specimens of *M. lusoria* and *P. maximus* were polished. The samples of *M. lusoria* were additionally put into 9 M LiBr solution [15] for 1 h and rinsed afterwards with distilled water to remove a distracting layer of the organic matrix on the surface.

Microhardness was measured with a microindenter (Micro-Duromat 4000, Reichert-Jung, Austria) using a Vickers tip (MD 4000V, Reichert, Austria). The maximum load was 0.5 N and the loading rate 0.1 N s⁻¹. The indent diameter was measured with an optical microscope. For *T. maculatus*, *P. maximus*, and *M. lusoria*, two shells per species were measured. 40 measurements were placed on each shell. For *H. rufescens*, four shells were examined and 20 measurements were placed on each shell. Four samples of one *P. penguin* shell were examined. 20 measurements were placed on each sample.

Nanoindentation measurements were performed using a TriboIndenter (Hysitron Inc., USA) with a Berkovich tip (opening angle 142.3°) in load-control mode. Before placing the indents, the sample surfaces were scanned (20 μm × 20 μm) with the indenter tip to find the optimum indent positions. A partial-unloading function consisting of 10 loading and unloading segments with increasing peak load (maximum load 2000 μN) was used. The loading and unloading rates were 300 and -200 μN s⁻¹. At each peak load, a hold time of 1 s was added. A total of 25–30 indents were applied on one sample of each shell species.

The unloading segments of the curves were analyzed by the Oliver–Pharr method [16]. For the calculation of the Young's modulus of the specimen E_{sp} , the following equation was used [16]:

$$\frac{1}{E_r} = \frac{1 - \nu_{sp}^2}{E_{sp}} + \frac{1 - \nu_i^2}{E_i} \quad (1)$$

where E_r is the reduced modulus resulting directly from indentation experiments, E_i and ν_i are the Young's modulus and the Poisson's ratio of the diamond indenter tip (1141 GPa and 0.07) and ν_{sp} is the Poisson's ratio of the specimen (here defined to be 0.3 as valid for most materials).

Only indentation curves with equal initial slope were used for further analysis to exclude the effects of unexpected surface features (e.g., surface roughness, inclined surface or remains of the organic matrix). As an example, the dotted grey curve of *P. maximus* (indent 3) in Fig. 6a was not selected because the starting slope was considered anomalous when compared to a proper curve (solid grey), while both curves of *H. rufescens* (black) were incorporated in the analysis.

| ID | Title | Pages |
|------|--|-------|
| 1742 | The influence of internal length scales on mechanical properties in natural nanocomposites: A comparative study on inner layers of seashells | 13 |

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