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Mechanical properties of crossed-lamellar structures in biological shells: A review

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ABSTRACT

The self-fabrication of materials in nature offers an alternate and powerful solution towards the grand challenge of designing advanced structural materials, where strength and toughness are always mutually exclusive. Crossed-lamellar structures are the most common microstructures in mollusks that are composed of aragonites and a small amount of organic materials. Such a distinctive composite structure has a fracture toughness being much higher than that of pure carbonate mineral. These structures exhibiting complex hierarchical micro-architectures that span several sub-level lamellae from microscale down to nanoscale, can be grouped into two types, i.e., platelet-like and fiber-like crossed-lamellar structures based on the shapes of basic building blocks. It has been demonstrated that these structures have a great potential to strengthen themselves during deformation. The observed underlying toughening mechanisms include microcracking, channel cracking, interlocking, uncracked-ligament bridging, aragonite fiber bridging, crack deflection and zig-zag, etc., which play vital roles in enhancing the fracture resistance of shells with the crossed-lamellar structures. The exploration and utilization of these important toughening mechanisms have attracted keen interests of materials scientists since they pave the way for the development of bio-inspired advanced composite materials for load-bearing structural applications. This article is aimed to review the characteristics of hierarchical structures and the mechanical properties of two kinds of crossed-lamellar structures, and further summarize the latest advances and biomimetic applications based on the unique crossed-lamellar structures.

1. Introduction

In nature, living things tend to evolve unique biological structures or special biological functions to survive and adapt to the surrounding environment (Fratzl and Weinkamer, 2007; Chen and Pugno, 2013; Barthelat et al., 2016; Meng et al., 2016). Nature mother is fully ahead of engineers in making use of well-architectured materials with unique mechanical properties (Barthelat, 2015). Ever since human beings have existed, designing structural materials by imitating things in nature has been an extremely important means to pursue more reliable and convenient life. However, according to the published reports, the first work about the study of biological systems as structures can only be traced back to the early parts of the twentieth century (Thompson, 1968). After about one century of studies, this fascinating research field has gained rich achievements, which are in a great need for systematizing. Recently, Naleway et al. (2015) proposed a new system of eight structural design elements, including fibrous, helical, gradient, layered, tubular, cellular, suture, and overlapping, which are the most common ones amongst a wide variety of animal taxa. For each structural element, there are various micro-morphologies or -arrangements, which also need further systematizing. For example, molluscs, being the second largest group in the animal kingdom (Vermeij, 1993), present a layered structure that can be categorized into seven kinds of generally accepted structures, i.e., columnar and sheet nacres, prismatic, crossed-lamellar, foliated, homogeneous, and complex crossed-lamellar structures (Bøggild, 1930; Taylor and Layman, 1972; Carter, 1990). A mollusc shell usually exhibits single or several kinds of microstructures that cooperate to provide a complex array of multi-functional properties. Nature has evolved a huge variety of hierarchical structures over billions of years. Although some simple analytical and numerical models have been put forwarded, drawing from the inspiration of extraordinary natural structures, to illustrate the basic mechan-

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ical design principles of biocomposites, (Gao, 2006), it is still at a premature infant stage for the studies about the role of hierarchy on the mechanical behavior of biological materials.

It is well known that biological shells are actually a type of two-phase composite materials consisting of calcium carbonate $CaCO_3$ (over 90%) and protein matrix (Currey, 1999; Harper, 2000; Marin et al., 2007). The inorganic phase is usually brittle and the organic phase very soft. Ji and Gao (2004a, 2004b) modeled the fracture process in an organic-inorganic hybrid with a hard phase interspersed among a soft phase, and they found that the organic layer can effectively enhance the toughness of biocomposites through crack shielding and impact protection. Thus, despite being highly mineralized, shells exhibit superb structural robustness. In the past few decades, biological shells have attracted considerable attention (Currey and Taylor, 1974; Jackson et al., 1988; Kamat et al., 2000; Li, 2007; Meyers et al., 2008a; Li and Ortiz, 2014), focusing especially on nacre (Jackson et al., 1990; Menig et al., 2000; Li et al., 2004; Lin and Meyers, 2005; Meyers et al., 2008b; Huang and Li, 2013; Jiao et al., 2016a), and crossed-lamellar structure (Currey and Kohn, 1976; Wilmot et al., 1992; Kuhn-Spearing et al., 1996; Liang et al., 2008; Ji et al., 2015a).

Meyers et al. (2008a) reported the hierarchical structures in nacre of Abalone consisting of a layered structure of hard aragonite tiles glued by organic matrix interlayers (only ~5 wt.%), as shown in Fig. 1a. The nacre of Abalone is exceptionally strong, and its fracture toughness is beyond that of the single crystals of the pure mineral by 3000 times (Jackson et al., 1988). The outstanding mechanical performance of nacre could be understood via different mechanical models for sliding between tiles as follows: (1) the inter-tile layers formed by nanoasperities providing the major source of shear resistance, (2) organic layers acting as viscoelastic glue, and (3) mineral bridges enhancing crack propagation resistance (Lin, 2008). This is the major reason why mimicking the nacre structural features has become a fascinating and thriving area in recent years (Munch et al., 2008; Mirkhalaf et al., 2014; Shao and Keten, 2015; Naglieri et al., 2015; Valashani and Barthelat, 2015; Djumas et al., 2016). For example, Bouville et al. (2014) fabricated a nacre-like bulk hybrid ceramic-based Al_2O_3/PMMA composite, and observed that the composite had a superb combination of high strength (470 MPa), high toughness (22 $MPam^{1/2}$), and high stiffness (290 GPa). The hierarchical structures, mechanical properties, and toughening mechanisms in nacre and nacre-like bio-inspired materials have been documented in several review articles that emphasized different aspects of the subject (Sun and Bhushan, 2012; Corni et al., 2012; Nudelman, 2015; Kakisawa and Sumitomo, 2011; Bhushan, 2016).

The other structure in shells of special interest is the crossed-lamellar structure, which is hierarchically constructed, and can be further divided into several sub-order lamellae, as schematized in Fig. 1b taking *Strombus gigas* shell for example (Menig et al., 2001; Meyers et al., 2008a). Compared with the arrangement of nacre (two-dimensional structure with in-plane isotropy), crossed-lamellar structure presents an obvious anisotropic feature in a three dimensional view. The unique hierarchical architecture of crossed-lamellar structure

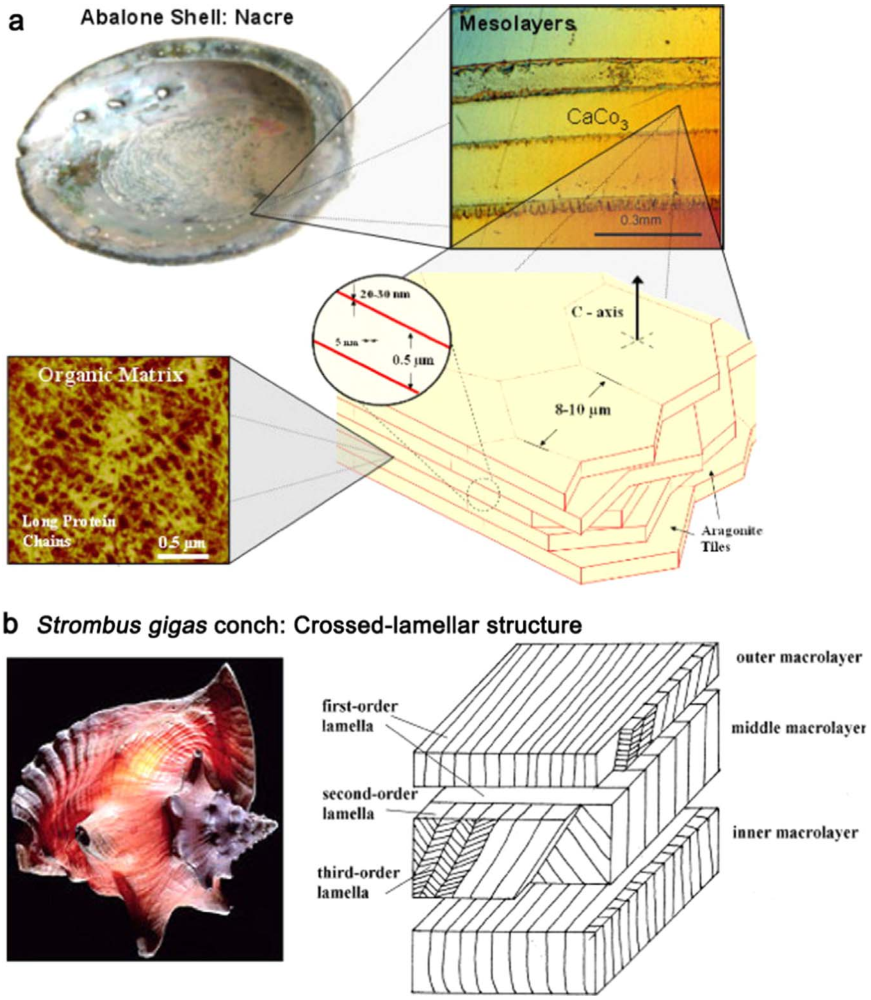

Fig. 1. (a) Hierarchy of abalone structure. Clockwise from top left: entire shell; mesostructure with mesolayers; microstructure with aragonite tiles; nanostructure showing organic interlayer comprising 5 wt.% of overall shell. (b) Conch shell. Left: overall view; Right: schematic drawing of the crossed-lamellar structure. Each macroscopic layer is composed of 1st-, 2nd- and 3rd-order lamellae. (a) and (b) Adapted from Meyers et al., 2008a.