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Research Paper

The weak interfaces within tough natural composites: Experiments on three types of nacre

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ABSTRACT

Mineralization is a typical strategy used in natural materials to achieve high stiffness and hardness for structural functions such as skeletal support, protection or predation. High mineral content generally leads to brittleness, yet natural materials such as bone, mollusk shells or glass sponge achieve relatively high toughness considering the weakness of their constituents through intricate microstructures. In particular, nanometers thick organic interfaces organized in micro-architectures play a key role in providing toughness by various processes including crack deflection, crack bridging or energy dissipation. While these interfaces are critical in these materials, their composition, structure and mechanics is often poorly understood. In this work we focus on nacre, one of the most impressive hard biological materials in terms of toughness. We performed interfacial fracture tests on chevron notched nacre samples from three different species: red abalone, top shell and pearl oyster. We found that the intrinsic toughness of the interfaces is indeed found to be extremely low, in the order of the toughness of the mineral inclusions themselves. Such low toughness is required for the cracks to follow the interfaces, and to deflect and circumvent the mineral tablets. This result highlights the efficacy of toughening mechanisms in natural materials, turning low-toughness inclusions and interfaces into high-performance composites. We found that top shell nacre displayed the highest interfacial toughness, because of higher surface roughness and a more resilient organic material, and also through extrinsic toughening mechanisms including crack deflection, crack bridging and process zone. In the context of biomimetics, the main implication of this finding is that the interface in nacre-like composite does not need to be tough; the extensibility or ductility of the interfaces may be more important than their strength and toughness to produce toughness at the macroscale.

1. Introduction

A large number of materials in nature are mineralized in order to properly fulfill their functions. For example bone, seashells or teeth contain large amounts of minerals (varying from about 30 to 70 vol% in bone to 95% in seashells) which are required for high stiffness and hardness. In the most extreme cases where hardness is critical, tissue can contain up to 99 vol% mineral (tooth enamel, and sea urchin spines). The structure and mechanics of these hard biological tissues have been of great interest to material scientists over the past two decades because of their remarkable mechanical performance (Wang and Gupta, 2011; Launey et al., 2010; Imbeni et al., 2005, Espinosa et al., 2009; Barthelat et al., 2007a).

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Despite high contents of brittle minerals, these materials exhibit outstanding strength and toughness originating from the way these ingredients are combined into intricate architectures (Barthelat et al., 2007a; Launey et al., 2010). The mineral phase itself comes in the form of micro- or nano-size layers, rods, grains or platelets bonded by soft organic materials (proteins and in some cases, polysaccharides). The mineral provides stiffness but it is brittle and linear elastic, so that it is the interfaces which provide energy dissipation (nacre, bone (Fratzl et al., 2004; Fratzl, 2007; Dastjerdi et al., 2012; Fantner et al., 2006, Smith et al., 1999a; Hansma, 2005)), control crack deflection (glass sponge spicules (Sarikaya et al., 2001; Mayer and Sarikaya, 2002), conch shell (Kuhn-Spearing et al., 1996)), or guide cracks towards regions of the material where they become trapped (as in tooth enamel (Imbeni et al., 2005)). Despite the central role of these interfaces in high performance natural materials, too often little is known on their composition, structure and properties. Nacre is one of these materials controlled by interface mechanics. Nacre is the iridescent layer found inside the shell of many mollusk species, and it has attracted a great deal of attention for biomimetic purposes owing to its high performance and robust, albeit relatively simple structure (Barthelat, 2007; Barthelat and Zhu, 2011; Deville et al., 2006; Munch et al., 2008). Nacre is composed of about 95 vol% brittle aragonite (one of the crystalline forms of calcium carbonate), and of about 5% organic material (a compound of proteins and polysaccharides) (Sarikaya and Aksay, 1995). The microstructure of nacre resembles a brick-wall, where 0.2–0.9 μm thick aragonite tablets are cemented together by means of thin 30 nm organic layers serving as "mortar" (Fig. 1) (Currey, 1977). The staggered arrangement of the tablets in nacre is a remarkable design feature which provides the structure with outstanding combination of stiffness, strength and toughness (Jäger and Fratzl, 2000; Rabiei et al., 2010; Gao, 2006; Jackson et al., 1988).

Under tension, the tensile stress in tablets is transferred to the neighboring platelets through the soft interfaces enclosing the tablet (Jäger and Fratzl, 2000; Kotha et al., 2001). Since the tablets in nacre are essentially brittle and linear elastic, the toughness and energy absorption capability of the structure stems from mechanisms working at the interface (Fratzl et al., 2004) including inelastic shear deformation of the organic phase (Smith et al., 1999b), interlocking of nano-asperities (Wang et al., 2001) and microscale waviness (Barthelat et al., 2007a), and fracture of mineral bridges (Song and Bai, 2003). Several models have so far been proposed for the structure of the organic polymers (Schäffer et al., 1997; Blank et al., 2003; Weiner et al., 1984), but the most widely accepted model consists of three layers where a stiff core of fibrous chitin is sandwiched between two proteinic sheets (Schäffer et al., 1997). The organic materials are strongly bonded onto the mineral tablets, and in fact they extend into the mineral tablets in the form of a fine network organized around mineral nanograins (Blank et al., 2003; Rousseau et al., 2005). Single-molecule force spectroscopy on freshly cleaved interfaces using atomic force microscopy (AFM) showed how the organic layer dissipates energy through unfolding of macromolecules and rupture of sacrificial bonds, a process which is reversible and repeatable (Smith et al., 1999a). The properties of the organic layers were also recently investigated by Meyers et al. (2009) who used nanoindentation techniques to deflect thin organic membranes. Their findings suggest that while the organic phase at the interface is essential to the growth of the shell by means of subdividing the mineral phase into thin platelets, it may not have a significant role in providing mechanical strength (Meyers et al., 2008). A more recent AFM study has shown that biopolymers connecting two adjacent aragonite tablets in nacre exhibit strain hardening in tension, which can translate into higher strength and toughness for nacre (Xu and Li, 2011). Bezares et al. (2010) have also recently investigated the constitutive properties of organic matrix from red abalone nacre by using tensile and time dependent relaxation tests on demineralized samples. They demonstrate that the organic framework essentially follows a viscoelastic behavior mainly governed by the chitin core of the matrix. The properties of the matrix were also evaluated by indirect means. For example, the shear strength of the organic interface was evaluated from simple shear tests on whole nacre samples (25 MPa (Barthelat et al., 2007a)), while the maximum elongation was evaluated from imaging (600 nm (Barthelat et al., 2007a)). Combining this data led to the cohesive law of the interface, which represents the traction across the interface as function of opening and/or sliding. In turn, the area under the cohesive law can be used to evaluate toughness, which gives a value of about 10 J/m^2 (Barthelat et al., 2007a). This value is surprisingly low, and contrasts with a common perception of the nacreous proteins as a tough adhesives. For comparison, the estimated toughness of nacreous interfaces is only five times higher than a typical office tape on glass (2 J/m^2, measured from peel tests (Dastjerdi et al., 2012)). With these

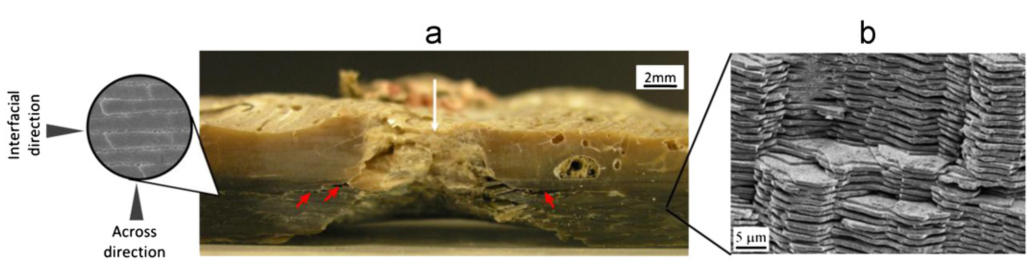

Fig. 1 – (a) Cross section of a punctured red abalone shell (Yourdkhani et al., 2011). Red and white arrows in the picture indicate the cracks deflected through the interface of the tablets and the puncture direction, respectively and (b) SEM micrograph showing the brick and mortar microstructure of nacre. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)