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Research paper

Nacre-like materials using a simple doctor blading technique: Fabrication, testing and modeling

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ABSTRACT

The remarkable mechanical performance of biological materials such as bone, nacre, and spider silk stems from their staggered microstructure in which stiff and strong reinforcements are elongated in the direction of loading, separated by softer interfaces, and shifted relative to each other. This structure results in useful combinations of modulus, strength and toughness and therefore is increasingly mimicked in bio-inspired engineering composites. Here, we report the use of a simple and versatile technique based on doctor-blading to fabricate staggered composites of microscopic alumina tablets with high alignment in a chitosan matrix. Tensile tests on these nacre-like materials show that the modulus and strength of the composite films are enhanced by the incorporation of ceramic tablets, but only up to 15 vol% after which all properties degrade. This phenomenon, also reported in the past for most of nacre-like materials, composed of micro/nano tablets, obtained from different techniques, has been limiting our ability to produce large volumes of high-performance nacre-like materials. Examination of the structure of the films revealed that at lower tablet concentrations the tablets are well-aligned and well dispersed thorough the volume of the film. At 15 vol% and beyond, we observed tablet misalignment and clustering. In order to investigate the impact of these imperfections on material performance we developed large scale finite element models representative of the structure of the composite films. These models show that the mechanical performance significantly degrades with tablet misalignment, and especially at high tablet concentrations. The simulations along with the SEM images therefore quantitatively explain the experimental trends, e.g. the degradation of mechanical properties at high tablet contents.

1. Introduction

Natural materials such as bone (Jager and Fratzl, 2000), nacre (Jackson et al., 1988), tooth enamel (Gao et al., 2003), and spider silk (Buehler et al., 2008) boast unusual and attractive combinations of properties which surpass their engineering counterparts (Ashby et al., 1995; Barthelat, 2007). In particular, these materials combine high strength and high toughness (energy absorption), two properties which are very difficult to achieve simultaneously in engineering materials (Ritchie, 2011). A general strategy which is pervasive across these high-performance materials is the combination of very

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hard and very soft components arranged in complex hierarchical architectures (Meyers et al., 2008; Wise, 1970). A key microstructure across these materials is the staggered arrangement, where stiff and elongated inclusions are aligned with some degree of overlap within a softer matrix (Barthelat, 2007; Barthelat et al., 2007; Currey and Taylor, 1974; Fratzl, 2003; Mirkhalaf et al., 2013). Recent studies revealed that the staggered microstructure is optimum when modulus, strength and toughness are simultaneously desired (Barthelat and Mirkhalaf, 2013; Guo and Gao, 2006). Mollusk species such as Pinctada or Pinna nobilis have nacreous shells with typical staggered microstructures. Sheet nacre from Pinctada is typically composed of ~95 wt% microscopic aragonite tablets which are arranged in a highly regular staggered structure and bonded by ~5 wt% soft polymers which are commonly called "interfaces". The mechanisms of deformation and fracture associated with this microstructure provides interesting combinations of mechanical properties (Barthelat, 2014; Currey, 1977; Jackson et al., 1988; Katti et al., 2001; Wang et al., 2001). In particular, sheet nacre from Pinctada is almost as stiff as aragonite yet it is ~3000 times tougher (Fig. 1a) which is a remarkable level of "toughness amplification" by any standard (Jackson et al., 1988; Rabiei et al., 2010) . Several mechanisms including crack bridging, deflection and process zone contribute to this outstanding toughness amplification (Fig. 1b) (Barthelat and Rabiei, 2011; Ortiz and Boyce, 2008). These remarkable mechanics and properties of natural staggered composites and in particular of sheet nacre from Pinctada has motivated the development and fabrication of a large variety of nacre-like synthetic materials over the past two decades. A wide variety of methods were proposed to fabricate nacre-like structures: sputtering (He et al., 1997), centrifugation and casting (Almqvist et al., 1999), layer by layer assembly (Podsiadlo et al., 2007; Tang et al., 2003), freeze casting of inorganic layers followed by a polymer or a metal filling stage (Deville et al., 2006; Munch et al., 2008), sequential Langmuir–Blodgett film/polymer deposition (Bonderer et al., 2008), vacuum filtration (Yao et al., 2010), sedimentation (Walther et al., 2010), ink-jet printing (Andres and Kotov, 2010), and freeze casting of micro-tablets (Bouville et al., 2014; Hunger et al., 2012) have been utilized to develop bio-inspired staggered composites at micro/nano-scales. In order to have a better control over the morphology of the material, staggered structures have also been fabricated at larger length scales using variety of methods including manual assembly of flat (Clegg et al., 1990; Mayer, 2006) and wavy tablets (Barthelat and Zhu, 2011), rapid prototyping (Espinosa et al., 2009), 3D printing (Dimas et al., 2013), and laser engraving (Mirkhalaf and Barthelat, 2015; Mirkhalaf et al., 2014).

Many of these materials display interesting combinations of mechanical properties (Bonderer et al., 2008; Munch et al., 2008), but the level of toughness amplification and structural organization achieved in these materials is still inferior compared to those of natural nacre. Some of the fabrication methods proposed can also only be used for small volumes of material and cannot scale up to production scales. The most efficient method to make nacre-like materials easily and on large scale remains to this day the "mixing" method, where flat ceramic or mineral platelets are mixed in a solvated polymer, and subsequently aligned using mechanical stress (Almqvist et al., 1999), sedimentation (Walther et al., 2010) or magnetic fields (Erb et al., 2012). A possible limitation of these approaches is that it is difficult to achieve high concentrations of tablets because of the limited packing efficiency. Arrangement and packing of the tablets can be improved using self-assembly (Mirkhalaf et al., 2015), but this careful process is more time consuming and can so far only be performed layer by layer. For all these nacre-like materials, increases of stiffness and strength were reported, but only up to tablet concentrations of 10–20%. This comparably low tablet content results in microstructural characteristics which are far from nacre. However, these materials possess interesting properties rooted in their staggered structure which has been numerically found to be optimum even at low tablet contents when a combination of mechanical properties is desired (Mirkhalaf and Barthelat, 2014). Beyond the 10–20 vol% tablet content threshold, all the mechanical properties of these materials decrease down to levels which may be even lower than the properties of the pure matrix (Bonderer et al., 2008; Das et al., 2013; Podsiadlo et al., 2007). This experimental result, contradicts the prediction of models which suggest that very large concentration of tablets should lead to very high modulus and strength (Jager and Fratzl, 2000). In natural nacre, which serves as model for these bio-inspired composites, the concentration of the mineral tablets is as high as 95 wt%. The fact that synthetic nacres only achieve high properties up to 10–20 vol%

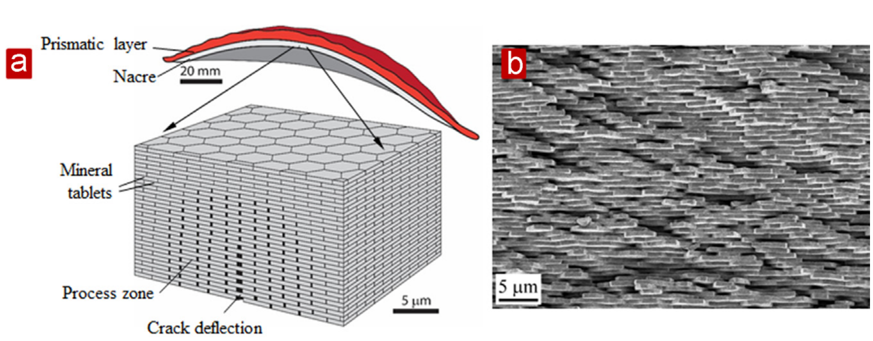

Fig. 1 – (a) Schematic of the microstructure of nacre showing the deformation and toughening mechanisms, (b) SEM image of a fracture surface of a Pinctada nacre showing the staggered arrangement of tablets.