Acta Biomaterialia 6 (2010) 4081–4089

Contents lists available at ScienceDirect

Acta Biomaterialia

journal homepage: www.elsevier.com/locate/actabiomat

Failure mode transition in nacre and bone-like materials

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ARTICLE INFO

Article history:
Received 18 December 2009
Received in revised form 26 March 2010
Accepted 14 April 2010
Available online 18 April 2010

Keywords:
Biological materials
Fracture
Nacre
Bone
Micromechanics

ABSTRACT

Mineralized biological materials such as nacre or bone achieve remarkable combinations of stiffness and toughness by way of staggered arrangements of stiff components (nanoscale or microscale fibers or tablets) bonded by softer materials. Under applied stress these components slide on one another, generating inelastic deformations and toughness on the macroscale. This mechanism is prominent in nacre, a remarkable material which is now serving as a model for biomimetic materials. In order to better identify which type of nacre should serve as a biomimetic model, the toughness of nacre from four different mollusk species was determined in this study. Nacre from the pearl oyster was found to be toughest, and for the first time remarkable deformation and fracture patterns were observed using in situ optical and atomic force microscopy. Under stress, stair-like deformation bands deformed at an angle to the loading direction, forming a dense, tree-like network. This marks a clear difference from the now well-documented "columnar" failure mode, in which deformation bands are perpendicular to the loading direction. Analytical and numerical models reveal the conditions for the transition between the columnar and stair failure modes, namely large or random overlap between inclusions and local shear stress generated by inhomogeneities in the material. "Stair" failure promotes spreading of non-linear deformation and energy dissipation, which translates into a greater toughness overall. A similar mechanism may also occur in bone, which has a microstructure which is in many ways similar to sheet nacre.

1. Introduction

Structural biological materials like seashells or mineralized skeletons are composed of relatively weak, small scale structural components, but assembled in intricate ways that lead to remarkable combinations of stiffness and toughness. In some cases the degree of "amplification" of mechanical performance from the base components is unmatched by any synthetic material [1,2]. A well-known example of this performance is nacre from mollusk shells, which is made of microscopic mineral tablets closely stacked to form a three-dimensional brick wall structure (Table 1). The mineral represents 95 vol.% of the material, the remaining 5 vol.% being organic materials located mostly at the interfaces between tablets [3]. Nacre is therefore a highly mineralized and stiff material, yet it is 3000 times tougher than the brittle mineral it is made of [1]. There is, therefore, a great interest in understanding the mechanisms behind this remarkable performance, in order to duplicate them in artificial, biomimetic materials [2]. In fact, biomimetic materials inspired by nacre have already started to emerge [4,5]. The staggered arrangement of the tablets in nacre dictates a specific mechanism, where applied tensile loads are transferred through tensile stress in the mineral tablets and shear stress at the softer interfaces between tablets. With sufficient applied load the tablets "slide" on one another, this "sliding" being mediated by thin layers of softer organic materials capable of accumulating large deformations while dissipating energy [6]. Resistance to shearing at the interface is provided by the organic material [6,7], by nanoasperities [8] and by mineral bridges [9]. The tablets also show some waviness, which impedes tablet sliding and generates strain hardening [10], delaying localization and propagating the sliding mechanism over large volumes (Table 1). These mechanisms are now well documented for the case of columnar nacre [10] (columnar nacre from red abalone is perhaps the most studied nacre). In columnar nacre the tablets are arranged in columns (Table 1), with well-defined core and overlap regions [10]. In this quasi-periodic structure sliding only occurs in the overlap regions, generating deformation bands perpendicular to the loading direction [8,10]. Cracks eventually also follow the overlap regions [11].

In contrast, sheet nacre has a more random staggered arrangement, with no well-defined overlap and core regions (Table 1). While tablet sliding has been observed in sheet nacre [3,8,12], its exact deformation and cracking patterns are unclear. In terms of macroscopic properties, previous studies showed that sheet nacre from the pearl oyster *Pinctada margaritifera* is slightly stiffer and stronger than columnar nacres [3,8], but this is not true for all sheet nacres [3]. It is also not clear which of the two types of nacre

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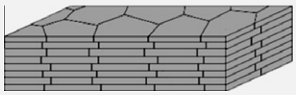
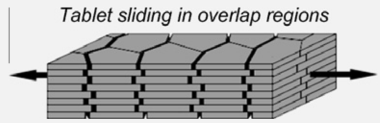
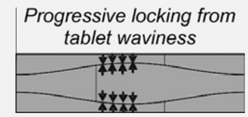
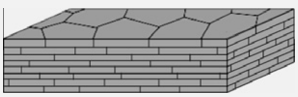
1742-7061/$ - see front matter
doi:10.1016/j.actbio.2010.04.008

Table 1
Tablet arrangements for columnar and sheet nacres with known deformation and hardening mechanisms.

Microstructure	Deformation mechanism	Hardening mechanism
Columnar 		
Sheet 	Tablet sliding, but deformation pattern unclear	Not known

tends to be toughest. This is a lack in the context of biomimetic materials, because fabrication procedures have now been refined to a degree allowing unprecedented control over the microstructure [4,13]. Identifying the best natural nacre to serve as a "biomimetic model material" has therefore become increasingly important.

Nacre is part of a wider category of mineralized tissues with a "staggered arrangement" of stiff inclusions aligned along the direction of loading and bonded by softer organic materials. Bone, for example, also follows this "universal" microstructural design over multiple length scales [14]. In particular, the sliding of mineralized collagen fibrils along one another on the microscale was demonstrated to provide the large inelastic strains observed on the macroscale [15]. There are several analogies between nacre and bone, but the experimental study of the failure of bone at small length scales is considerably more difficult than that of nacre, because of the helicoid lamellar structure of the osteons [18]. In terms of modeling, small two-dimensional representative volume elements are typically used [16,17] so as to capture the load transfer from shear at the interface to tension in the inclusions. These models provide analytical solutions for modulus and strength and useful insights into micromechanical design and structural optimization. This type of model, however, relies on the assumption that the structure and displacement are periodic. In consequence, the models predict that the separation of the inclusions forms a uniform network of deformation bands perpendicular to the loading direction. In reality it may not be the case because mineralized fibrils follow a random overlap, so that the failure of bone on those length scales may follow the "stair" pattern described here.

In this article a comparative study of the fracture toughness of four selected nacres is first presented. Significant differences in toughness are reported and, in addition, a new "stair" type of failure mode was observed in sheet nacre. In the second section a simple analytical model demonstrates how the transition between "stair" and "columnar" failure modes is controlled by a combination of microstructure and local shear stress. This finding is finally confirmed by larger scale numerical simulations presented in the last section. The implications on biomimetics and on our understanding of how natural composites with staggered arrangements deform and fail is finally discussed.

2. The fracture of sheet and columnar nacres

The nacres tested in this study consist of two columnar nacres and two sheet nacres. Besides different tablet arrangements, the tablets themselves showed a range of thicknesses and aspect ratios (Table 2). Top shell showed the thickest tablets, followed by pearl oyster, red abalone and pen shell. The tablet aspect ratio was highest in pen shell, followed by red abalone, top shell and pearl oyster, which displayed the tablets with the smallest aspect ratio. These differences in mean thicknesses and aspect ratios between each of the four species were highly statistically significant ($P < 0.001$ from an independent sample t-test with $n = 250$).

Table 2
Characteristics of the nacres tested in this study (thickness and aspect ratio given as means ± standard deviation).

Species	Nacre type	Tablet thickness (μm)	Tablet aspect ratio
Top shell (TS) *Trochus niloticus*	Columnar	0.74 ± 0.08	10.80 ± 3.47
Red abalone (RA) *Haliotis rufescens*	Columnar	0.45 ± 0.06	12.49 ± 7.97
Pearl oyster (PO) *Pinctada margaritifera*	Sheet	0.50 ± 0.11	8.91 ± 4.68
Pen shell (PS) *Pinna nobilis*	Sheet	0.43 ± 0.10	14.37 ± 9.04

2.1. Specimen preparation

Specimens were prepared by first harvesting a 20 × 50 mm plate from the shells using a diamond saw. The surfaces of the plate were then ground and finished using a milling machine in order to obtain flat and parallel faces. The plate was then cut into slices using a high precision diamond saw. At this point a pre-notch was made using a diamond saw. One side of the specimen was then polished and the notch was deepened and sharpened with a fresh razor blade. The specimens were oriented so cracking would occur across the layers (Fig. 1). Typical specimen dimensions were 20 mm long, ~0.1–1 mm thick and ~0.2–2 mm wide. Moreover, in order to comply with the ASTM requirement [18], the notch length was maintained within ~0.45–0.55 of the width. Samples were kept hydrated throughout all the steps of preparation, storage and experiment.

2.2. Experimental procedure

The fracture tests were performed using a four point bending fixture mounted on a miniature loading stage (Ernest F. Fullam Inc., Latham, NY). Four point bending was preferred over three point bending because it generates a more uniform bending moment, enabling potential deflection of the crack away from the initial crack line. The loading stage and sample were first placed under an optical microscope (BX-51M, Olympus, Markham, Canada) equipped with a CCD camera (RETIGA 2000R, Qimaging, Surrey, Canada) and the specimens were loaded at a rate of $0.002\ \mathrm{mm\ s^{-1}}$ up to failure.