ELASTIC PROPERTIES OF NACRE ARAGONITE TABLETS

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ABSTRACT

Nacre has recently attracted the attention of the research community. This biocomposite has exceptional strength and toughness with respect the materials it is made of. The design of nano and micro composite inspired from nacre requires a deep understanding of nacre microstructure and mechanical properties. In this work, the elastic properties of aragonite tablets in nacre were determined using nanoindentation on cleaved specimens from a Red Abalone seashell. Aragonite has a significant elastic anisotropy, and has a strong texture in nacre tablets. Low penetration depths (<50 nm) were employed to avoid the effect of the interfaces. The results were strongly disturbed by the surface roughness of the specimens. Standard analysis methods failed to give consistent results. Instead, a Hertzian contact analytical solution was fitted onto the experimental curves when roughness effects were accounted for. The results demonstrate that the presence of intracrystalline proteins in the tablets do not significantly deviate their elastic properties from those based on single crystal aragonite elasticity. The methodology presented here can be used for other similar cases such as thin films on substrate.

INTRODUCTION

Nacre is a hard biological tissue found in the inner layer of some seashells such as Oyster or Abalone. It is a composite material mainly composed of an aragonite phase (95% vol.) arranged in microscopic tablets, bonded together by a biopolymer mortar (Fig. 1). Aragonite is a very poor ceramic, but by the addition of a small amount of the organic phase and a well-designed microstructure nacre achieves strength and toughness that are 20 to 30 times higher than monolithic aragonite [1]. When stretched along the tablets, nacre can accommodate significant deformations as the tablets slide on one another. Its remarkable design and the multiscale mechanisms responsible for its behavior have attracted much attention in the past few years. Experimental investigations included mechanical tests at the macroscale, using tensile [2,3], three-point bending [3,4], four-point bending configurations [4] and microindentation [5]. Efforts in modeling were also made [3,5,6,7,8]. It is striking, however, that almost no attempt was made to directly probe the mechanical properties of single tablets. As a result various moduli were used to describe the elasticity of the tablets: *100 GPa* [3], *70 GPa* [6] or *50 GPa* [8]. Recently Katti et al. [7] performed indentation on individual tablets, but by using standard load-deflection analysis method [9] only a single isotropic elastic modulus (*99.5 GPa*) could be measured, while it is known that the aragonite crystal has a significant anisotropy. In order to model the behavior of nacre with accuracy, a proper description of the mechanical behavior of the aragonite tablets is needed. In the present work, nanoindentation techniques were used to probe the elastic properties of aragonite tablets. Because of the reduced thickness of the tablet (*400 nm*), low depths were employed. For this reason, together with a significant roughness and elastic anisotropy, conventional data reduction techniques were inappropriate and an alternate approach was used.

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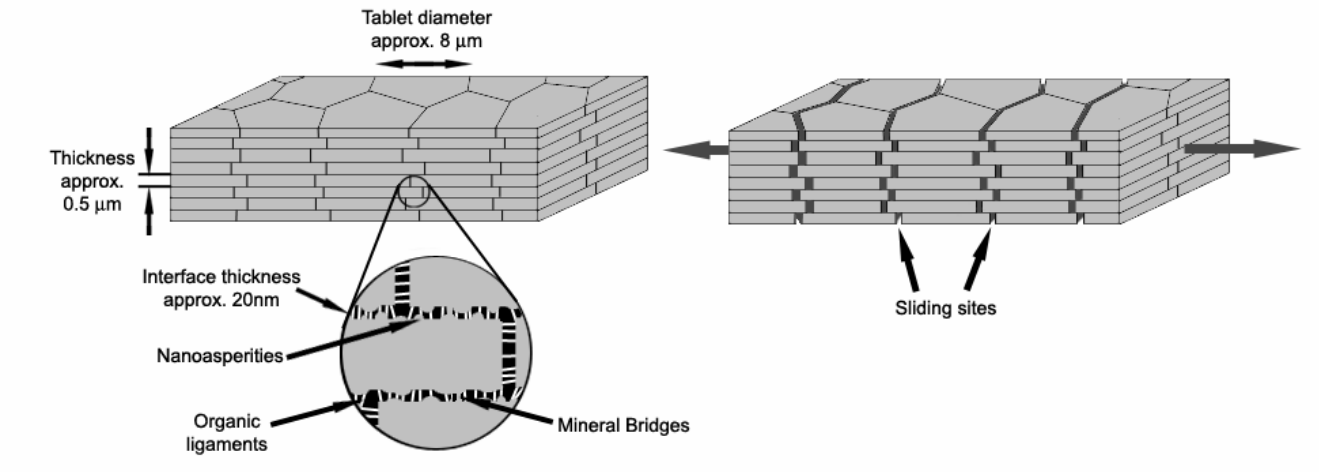

Figure 1: Schematic of the microstructure of nacre from Red Abalone and a deformation mode of interest: nacre can accommodate large deformations as tablets slide along one another.

ARAGONITE TABLETS IN NACRE

Aragonite is an orthorombic form of calcium carbonate ($CaCO_3$). Its structure is composed of densely packed layers of calcium ions and carbonate groups perpendicular to the c axis. During biomineralization, the crystal growth has a preferred orientation, so that the c [001] axes of the grains are invariably aligned with the normal to the surface of the tablets [1]. Each tablet is composed of several grains, and the a and b directions are random in the plane of the tablets, although twinning type relations between grains were observed [1]. The aragonite crystal has orthotropic elastic properties and its stiffness coefficients are well established [10]:

$E_1 = 144\ GPa$	$\nu_{12} = 0.44$	$G_{12} = 47.2\ GPa$
$E_2 = 76\ GPa$	$\nu_{13} = -0.06$	$G_{13} = 25.6\ GPa$
$E_3 = 82\ GPa$	$\nu_{23} = 0.18$	$G_{23} = 41.3\ GPa$

For the purpose of developing models for the behavior of nacre, it is useful to consider the elastic response of the tablets at the macroscopic scale. The in-plane elasticity of the tablets is resulting from contributions of the a and b axes of the crystal. Assuming that the orientation of a and b follows a uniform distribution in the plane of the tablets, these two directions equally contribute to the in-plane properties. On the other hand, the out-of plane elastic behavior is directly controlled by the elasticity along the c axis of the crystal. By applying different loading configurations to this system (in-plane and out-of-plane uniaxial stress, in-plane and out-of-plane shear stress) and setting the polycrystalline material with random in-plane direction equivalent to a transversely isotropic solid, the five equivalent transversely isotropic elastic constant were derived:

$$E_z = E_3$$

$$\nu_{zp} = \frac{E_3}{2}\left(\frac{\nu_{13}}{E_1} + \frac{\nu_{23}}{E_2}\right)$$

$$E_p = 4\left(\frac{1}{E_1}(1 - 2\nu_{12} - \nu_{13}) + \frac{1}{E_2}(1 - \nu_{23}) + \frac{1}{G_{12}} + \frac{2\nu_{zp}}{E_z}\right)^{-1}$$

$$\nu_p = \frac{E_p}{2G_{12}} - 1$$

$$G_{zp} = \frac{G_{31} + G_{32}}{2}$$

Which yielded the values:

$$E_z = 82\ GPa,\ E_p = 107\ GPa,\ \nu_p = 0.25,\ \nu_{zp} = 0.08,\ G_{zp} = 33.45\ GPa$$

These values reflect the elastic properties of aragonite tablets free of inclusions. However it is also known that the biomineralization process leaves residues of organic material within the aragonite crystal [11]. Whether or no these intracrystalline organic molecules affect the elastic behavior of the aragonite tablets needs to be assessed.

EXPERIMENTAL PROCEDURE

Red abalone *(Haliotis rufescens)* shells from California were purchased from a seashell store. Cubes of nacre of about 3 mm in size were harvested from the inside layer. Using a sharp razor blade, the specimens were cleaved along the direction of the tablets. The freshly cleaved faces were then thermally etched in order to burn the organic material away. Preliminary Atomic Force Microscopy on the surface revealed nanoasperities of amplitude of about 35 nm in height on the surface of the tablets. Nanoindentations were performed on flat areas of the cleaved surface using a diamond Berkovich tip with a Nanoindenter XP system (MTS Systems Corporation, Eden Prairie, MN). The system has resolutions of 0.02 nm and 50 nN for displacement and load, respectively. Instrumented indentations were performed at depths of 25, 50, 100 and 250 nm. The loading sequence used was the following: penetration of the indent down to the specified depth at constant velocity (1 nm/s), load held constant for 10 seconds, and unloading (1 nm/s).

ANALYSIS

A now well accepted analysis technique for the determination of modulus and hardness from instrumented nanoindentation was proposed by Oliver and Pharr [9]. Using the indentation depth and a shape function characterizing the geometry of the indenter, the modulus of the material is computed from the initial unloading stiffness. The method has proven robust and accurate for a variety of materials, but requires the accurate determination of the indentation depth. Fig. 2 shows the load-displacement curves obtained on nacre tablets, for depths in the 40 nm range. Such low depths were employed to alleviate the effect of the softer tablets interface located at about 400 nm below the surface [12]. At these low depths the roughness (about 35 nm) strongly interferes with the determination of the actual penetration depth so the conventional analysis method did not give consistent results. In addition, the preliminary results for the elasticity of the tablets showed significant anisotropy, which is not taken in account in the conventional data reduction methods.

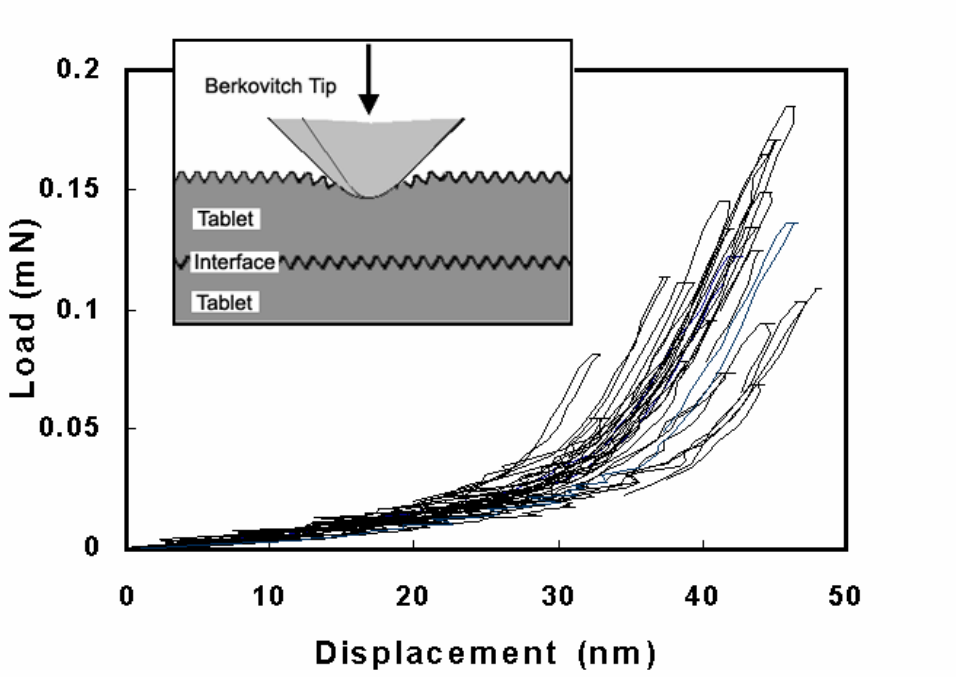

Figure 2: Load-Displacement curves for 25 indents on aragonite tablets. Different local roughnesses explain the inconsistency of the curves.

Another type of approach had therefore to be used in this work. Careful inspection of the load-deflection curves reveals that they can be decomposed into 4 stages. Stage I is dominated by the plastic deformation of the asperities. AFM images such as the one shown on Fig. 3 suggest that 3-4 asperities are engaged at this stage. The end of this stage comes when the asperities are close to be completely flattened, at a displacement of about the measured heights of the asperities (35 ± 10nm). In stage II, the response is dominated by the elastic loading of the bulk material. This is characterized by a significant increase in stiffness. During stage III the load is held constant and a small amount of creep is observed. Stage IV is the unloading of the

bulk of the crystal. The unloading does not show any residual deformations in the bulk of the tablets, which indicates that they were loaded elastically. No significant indent was left on the surface and the only indication of the loading is the flattened roughness (Fig. 3). The variation in asperity heights is responsible for the disparity of the load-displacement curves of Fig. 2, and a proper horizontal shift of the curves could remove roughness stochasticity, as shown in Fig. 4. The curves then agreed very well and could be used for further analysis.

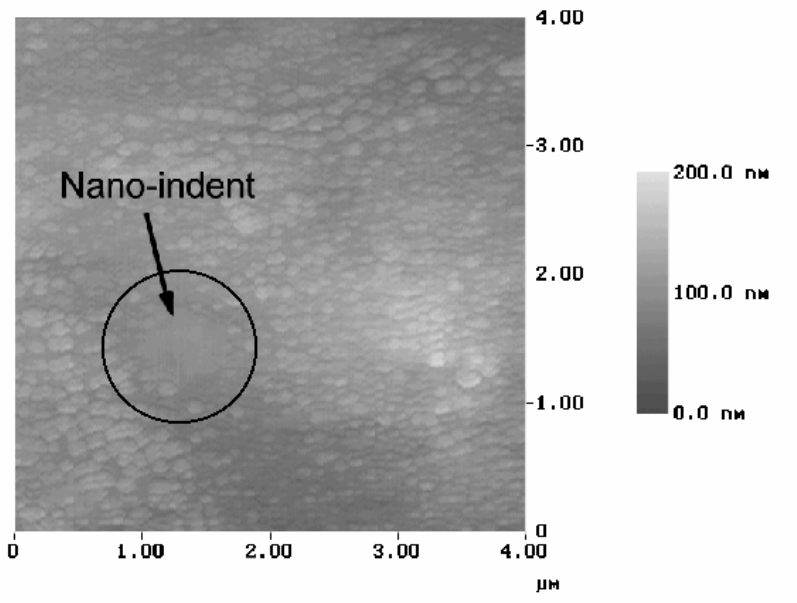

Figure 3: Atomic Force Micrograph of a microscopic size indent on a aragonite tablet. The indent can be identified from a circular region of flattened asperities

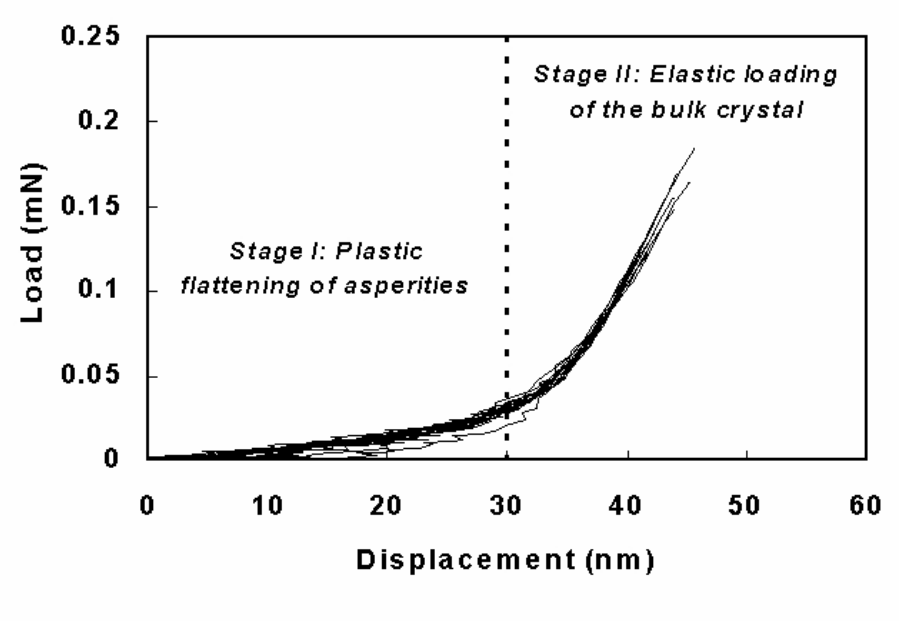

Figure 4: Load-deflection curve after horizontal shifting (only the loading stages are shown).

The elastic loading of the bulk of the tablets was be used to determine the elastic properties of aragonite in nacre. This identification was done through an elastic contact model between the indenter and the tablets. The model requires the exact geometry of the Berkovich tip indenter, and AFM images such as the one shown on Fig. 5a revealed that the tip roundness cannot be neglected for the low depths considered here. Further analyses yielded the exact radius of the tip, which was found to be 400 nm. Under this axisymmetric loading, the contributions of the crystallographic orientations a and b were lumped into a single in-plane contribution. The tablets were then assumed to be transversely isotropic, with elastic constants equal to those presented above. An analytical solution for the elastic contact between a deformable sphere and a transversely isotropic half-plane was given by Hanson [13] and used in this work. The sphere was set to have a radius of 400nm with the elastic

constants of diamond (E= 1140 GPa, ν= 0.07). As a basis for the tablets, the five transversely elastic constants derived above for aragonite were used in the model. The most relevant approach for this case was to assume that the presence of intracrystalline molecules within the tablets would affect their elastic properties altogether. Fig.5b shows the results for the Hanson model using the elastic constants found above (E_z = *82 GPa,* E_p = *107 GPa,* ν_p = *0.25,* ν_{zp} = *0.08,* G_{zp} = *33.45 GPa*) as well as results using the same constants scaled by a factor of 1.1 (stiffer) and 0.9 (softer). The original values, derived from aragonite single crystal elasticity, were found to provide the best fit for the experimental curves.
The intracrystalline proteins remaining from the biomineralization of the aragonite tablets therefore do not have a significant effect on the elastic properties of single crystal aragonite.

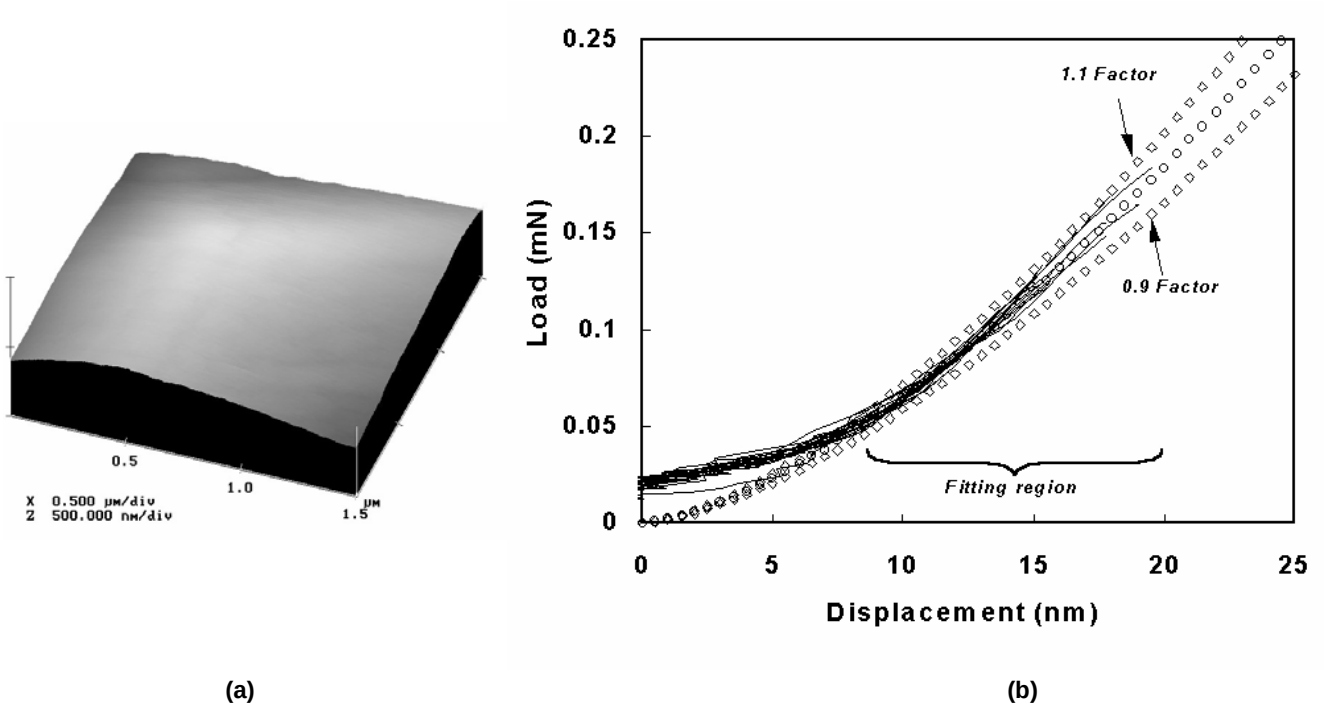

Figure 5: (a): Atomic Force Micrograph of the tip used in the experiments. For very low depths, the tip can be assumed to be a sphere. (b): Experimental load-displacement curves and Hanson model, using the aragonite 5 elastic constants scaled by a factor of 1.1 and 0.9. The model using the original values lies in between and provide the best fit to the experimental data.

CONCLUSIONS

Nacre from seashell has remarkable mechanical properties, which needs to be investigated in depth through experiments and models. The knowledge of the elastic properties of the aragonite tablets is essential for an accurate description of its behavior. To investigated them Nanoindentation at low depth was used, and severe limitations (roughness of the surface, underlying interface, crystal anisotropy) made conventional instrumented indentation data reduction inaccurate. A different approach was used instead, where an analytical elastic contact solution was fitted onto the experimental curves. The results showed that the intracrystalline molecules remaining from the biomineralization of the tablets do not deviate their elasticity significantly from single crystal aragonite. The in-plane elastic constant of the tablets is higher than the values used in the past to model nacre, which makes nacre even more intricate to study: With a composite modulus of 40 to 50 GPa, this means that the modulus of the interface should be below 1 GPa. Other interesting results are the out-of-plane elastic properties, which might have an important effect on the sliding of tablets, through transverse compression build-up created by the nanoasperities climbing each other [6]. The transverse behavior is controlled by a lower modulus (82 GPa versus 107 GPa for the in-plane modulus), and the out-of-plane Poisson's effect created by the tension along the tablets is minimal (ν_{zp} = *0.08*).
This experimental and analysis method can be used for wider ranges of problem, when the depth of penetration has to be reduced and when the roughness is significant. Transversely isotropic materials such as ultrananocrystalline diamond films deposited on silicon substrate could be investigated using the same approach.

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