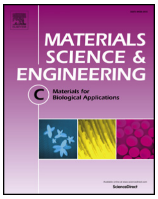
Materials Science & Engineering C 91 (2018) 78–93

Contents lists available at ScienceDirect

Materials Science & Engineering C

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



Multiscale structure of nacre biomaterial: Thermomechanical behavior and wear processes

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ARTICLE INFO

Keywords:
Nacre
Organic matrix
Multiscale analysis
Frictional dissipated power

ABSTRACT

Sheet nacre is a hybrid biocomposite with a multiscale structure, including nanograins of $CaCO_3$ (97% wt% – 40 nm in size) and two organic matrices: (i) the *interlamellar* mainly composed of β-chitin and proteins, and (ii) the *intracrystalline* composed by silk-fibroin-like proteins. This material is currently contemplated for the manufacture of small prostheses (e.g., rachis and dorsal vertebra prostheses) which are subjected to micro-slip or fretting motion. In this work, the tribological behavior of nacre is studied by varying the frictional dissipated power from few nW to several hundred mW, in order to assess the various responses of the different nacre's components, independently. Results reveal various dissipative mechanisms vs. dissipated frictional power: organic thin film lubrication, tablet's elastoplastic deformations, stick-slip phenomenon and/or multiscale wear processes, including various thermo-mechanical processes (i.e., mineral phase transformation, organics melting and friction-induced nanoshocks process on a large range). All these mechanisms are controlled by the multiscale and anisotropy of its structure – and especially by its both matrices and respective orientation vs. the sliding direction.

1. Introduction

Sheet nacre (the pearly internal layer of molluscan shells) is a biocomposite displaying an organomineral *multiscale* structure [1–6]. It exhibits high strength and toughness though it is primarily composed of a hard and very brittle ceramic – so-called aragonite (97%wt.) [7,8]. The well-known nacre's superior mechanical properties lie in its hierarchical structure (Fig. 1) meaning that particular structures exist at distinct length scales. Thus, Dutta et al. [9] first reported the importance of length scales in maximizing both load-transfer capability and resistance to crack initiation in composites both under static and impact rates of loading.

At the first hierarchical level (Fig. 1a), sheet nacre is usually described as a layered *brick* & *mortar* architecture [3,7]: *bricks* correspond to aragonite tablets (1–5 μm long and 500 nm thick) while the *mortar* appears as an *interlamellar* organic matrix made of highly cross-linked protein of polysaccharide and β-chitin (30 nm thick) [2]. Although this organic matrix constitutes a few percent of the total weight of the shell (< 3%wt.) it has a significant influence on the overall mechanical properties of nacre, as demonstrated by many authors from years (e.g., [2,10–13]). Indeed, *interlamellar* layers of polymers act as energy absorbers which limit the propagation of cracks and finally avoid the formation of critical failure within the biocomposite [13].

However, recent works [4–6,14] demonstrated a second hierarchical level which takes place within the tablet (Fig. 1b). The latter is indeed not purely mineral but is itself an organomineral composite – Fig. 1c and d – constituted by aragonite biocrystals (40 nm in size, Fig. 1e) drowned within a 4 nm thick *intracrystalline* organic matrix – constituted by silk-like proteins – organized as a tridimensional structure forming the micro-sized flat tablets (thickness about 500 nm, Fig. 1b) [15]. Hence, these tablets are further able to dissipate energy by elastic-plastic deformation leading to an overall increase in fracture toughness [14,16].

Because its hierarchical structure is a great source of inspiration in the design of new kinds of composites, sheet nacre has been largely studied from decades by researchers and engineers [13,17–20]. In particular, this material is currently being studied in two main research fields: (i) the creation of new organic/inorganic bio-inspired hybrid

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https://doi.org/10.1016/j.msec.2018.05.029
Received 21 August 2017; Received in revised form 26 March 2018; Accepted 7 May 2018

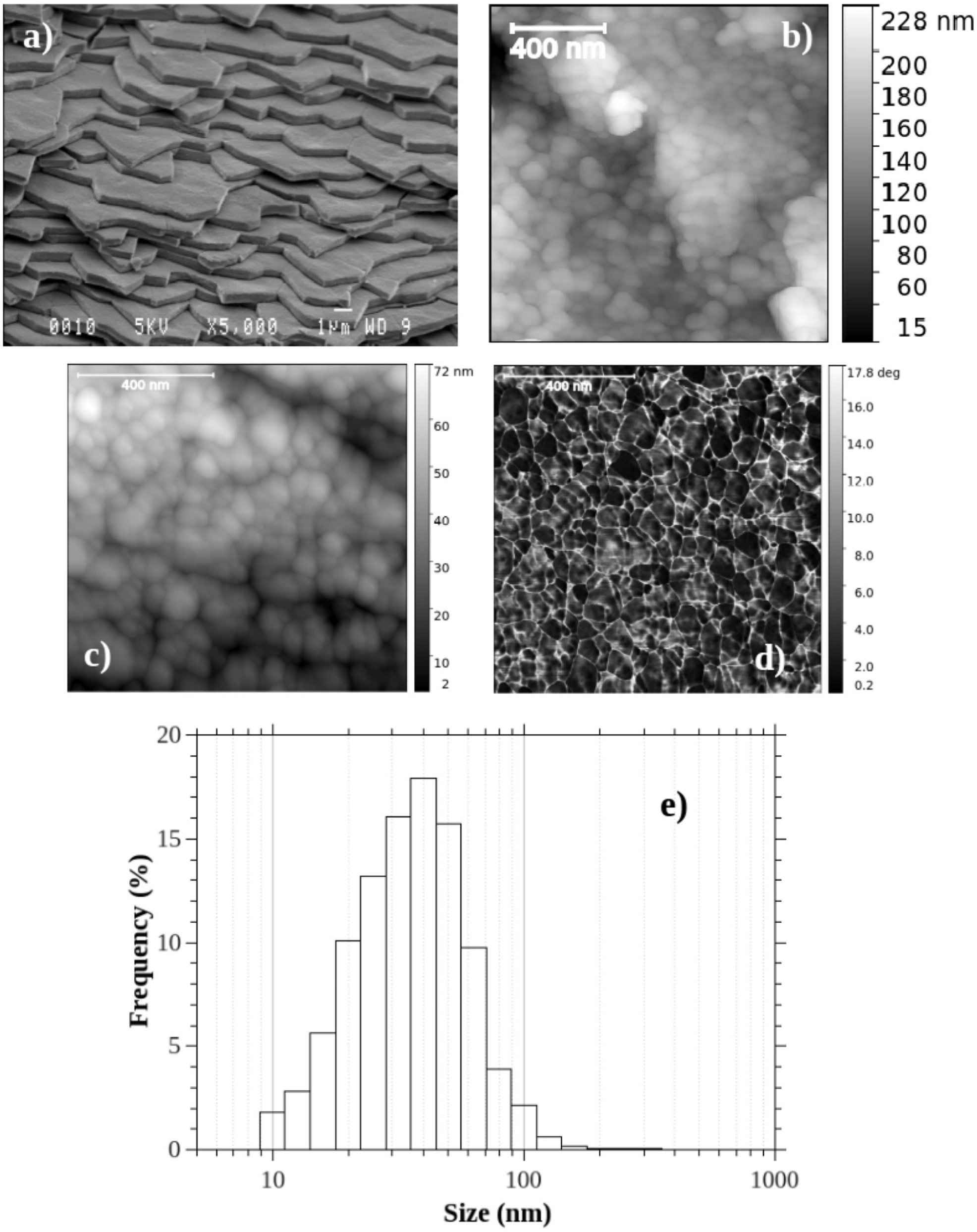

Fig. 1. Multiscale structure of nacre a) the brick & mortar architecture; b) enlargement on the edge of a brick revealing biocrystals; typical AFM views of the polished top surface of an aragonite platelet observed in tapping-mode: (c) height map; and (d) phase contrast map. These maps reveal the nanosized biocrystals of $CaCO_3$ surrounded by the intracrystalline organic matrix; e) distribution in size of the biocrystals constituting tablets after image analysis on AFM maps.

materials [13,17–19] and (ii) the design of small prostheses [20–23]. In this framework, classical approaches consist to strive to produce synthetic composites that display desired mechanical properties by mimicking the nacre structures at different scales [18]. On the one hand, investigations conducted by Dutta et al. [13] provided guidelines for designing light-weight and tough adhesively bonded structures and staggered architecture composites. On the other hand, Zhu et al. [19] created a nacre-like material at the microscale which is composed of PMMA tablets layered as a columnar arrangement where interactions between layers are only controlled by the tribological aspects at the interfaces [24]. At a lower scale, Tang et al. [20] created an interesting organic/inorganic nanolayered structure of polyelectrolytes and clays. Because this nanolayered material exhibits tensile strength and Young's modulus very close to the bone ones, it seems to be a good candidate for creating medical implants.

Another way followed by researchers is to looking at the possibility of using nacre for reconstructing human bodies [21–23]. Owing to its natural biocompatibility with human, nacre became an obvious candidate as a possible alternative to existing implant materials [8,23]. Indeed, current implants display a lot of drawbacks which are mainly connected to tribological behavior such as unsatisfactory life time or wear particles-induced inflammatory reactions, for instance. Thus, Atlan et al. [21] first tested nacre as a bone implant and showed that nacre implant triggers and encourages osteogenic – or bone forming – activity [22].

Taking into account the natural biocompatibility of nacre with bone as well as its tremendous durability connected to its great mechanical properties, this materials could definitely be considered as a potential substitute for defective bone [21–23] by direct implant or by creating some new organic/inorganic bio-inspired hybrid materials [20]. However, these challenging applications clearly need some knowledge about the frictional and wear behavior of this material [25–31].