# STRATEGY FOR CREATING BIO-COMPOSITES WITH UNIQUE MECHANICAL PROPERTIES

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## 1. Introduction

The dynamic development of technology and civilization requires constant search for new materials with appropriate functional and mechanical properties. Meanwhile, the key problem of material engineering remains the solution to the conflict between high strength and fracture toughness [1]. A need to improve the first property lowers the latter. It is worth looking at how Nature solved this issue. One of the more interesting example are shells of molluscs. On the path of evolution lasting millions of years, these animals have produced material not only of significant strength and fracture toughness, but also light and functional. This result all the more deserves attention because the components used for construction, calcium carbonate (calcite and aragonite) and proteins, are weak. The source of unique mechanical properties lies in a hierarchically complex structure. The most of molluscs, about 90% species, prefer crossed lamellar structure. Usually, it is constructed on three levels. The first order structural unit is a lamella with dimensions of a few millimetres. Inside it, there are parallel stacked laths (2-nd order lamellae). These, in turn, consist of parallel fibres with a thickness of less than 1 micron (3–rd order lamellae). It turns out that the successive first order lamella, adjacent to the consider one, is built analogically, but the fibres are rotated by 90 degrees. In this way, the 0°/90°/0° cross system is obtained. The above described structure is embedded in organic matrix. Thus, the shell is not built in a chaotic manner, but carefully thought out, in accordance with the design of Nature. The question arises what mechanisms to improve mechanical properties are included at the lower scale levels: micro and nanometric one. Despite many works on this subject, a complete answer is still missing [2]. The solution to the formulated problem is important because it can be a biomimetic basis for creation of new materials exhibiting unique mechanical and functional properties. The purpose of the present work is to identify and analyse the mutual orientation (disorientation) of crystallites in calcite layers of shells of two molluscan species *Pinctada margaritifera* and *Pinna nobilis*. The obtained results shed new light on the mechanical response of the shell subjected to an external load.

## 2. Experiment and analysis

The investigation of shell microstructures is performed by means of electron backscatter diffraction (EBSD) method. It turns out that the considered species of molluscs prefer a strictly defined set of disorientations. They are defined by means of an axis around which the rotation by a certain angle generates the crystallite adjacent to the considered one. Among disorientations with high frequencies (Fig. 1 and Fig. 2), there are twins typical for the synthetic calcite ($T_1$, $T_2$, $T_3$) [3], as well as two others of which one ($T'_3$) is new and has not been shown in the literature so far.

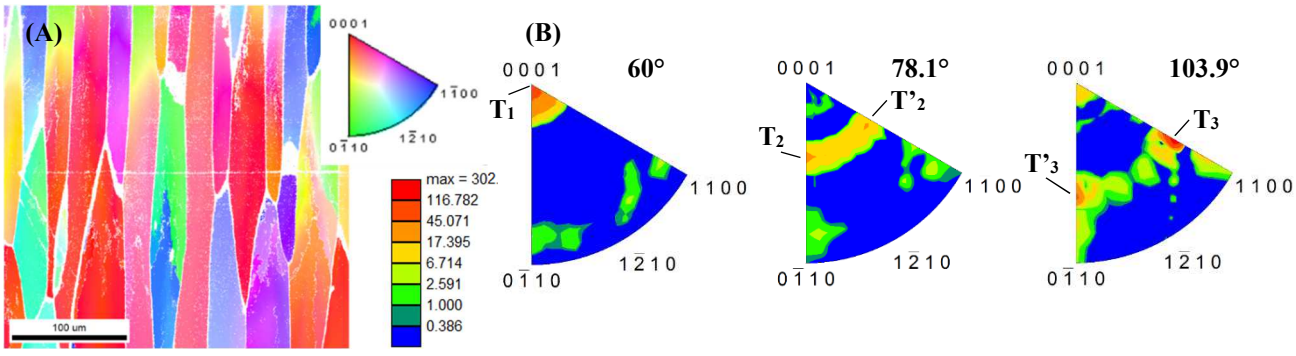


Figure 1 Inverse pole figure (*IPF*) map (A) and axis/angle misorientation distribution function (B) of the *Pinctada margaritifera.*



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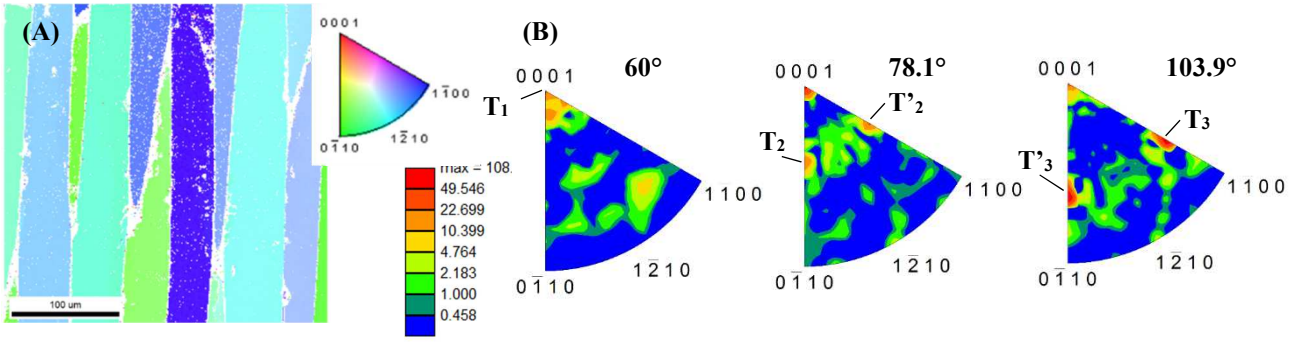


Figure 2 Inverse pole figure (*IPF*) map (A) and axis/angle misorientation distribution function (B) of the *Pinna nobilis*.

To explain the observed regularities, we have examined how the energy of the phase boundary calcite/ calcite changes when one of the crystallites is rotating. The exact determination of this quantity for a large, representative number of disorientations is very difficult and computationally expensive, due to the complex interatomic interactions at the boundary [4]. Therefore, the approximate approach proposed by Gautam and How [5] is used. According to their method, the interfacial energy decreases with the increasing total intensity *I* contained in the overlapping regions diffraction reflections from two phases [6]. Calculations carried out for the calcite / calcite phase boundary show a very interesting distribution of the total overlap intensity *I* (Fig. 3) There are clearly visible energetically favourable disorientations, i.e. those for which the interface energy achieves local minima. It turns out that the distinguished mutual orientations of crystallites are pairs of twins generated by means of two-fold axes related to each other by a mirror plane (1 0 -1 0). As a result, we get two disorientation groups. One of them are twins characteristic of the synthetic calcite, and the latter one are their counterparts with higher interface energy. The identified disorientations are strongly preferred by the studied molluscan species.

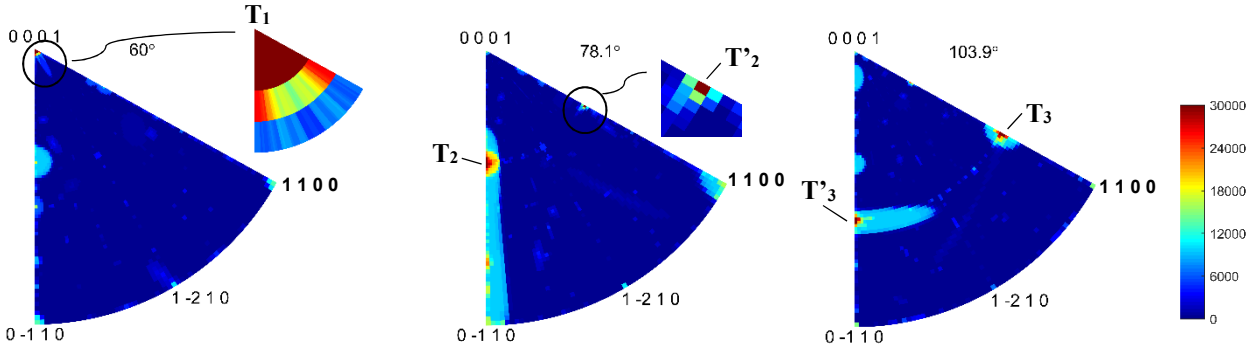


Figure 3 Total overlap intensity as a measure of the interfacial energy

## 3. Conclusions

The bio-composite structure of molluscan shells is highly ordered not only at the macro level, but also micro and nanometric. It has been shown that crystallites of calcite layers are not randomly oriented but in such a way that form low energy boundaries. As a result, there arise twins typical of calcite and their counterparts with slightly higher energies. The formation of this second group of twins is a deliberate effort of Nature. The external load applied to the shell causes crystallite rotation. As a result, the boundaries with higher energies transform into those with lower energies. This process enables dissipation of energy and thus becomes one of the mechanisms that Nature has invented to increase fracture toughness.

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