NATURAL ORGANIC-INORGANIC COMPOSITE SYSTEMS

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Abstract

The aim of this study is the characterization of selected natural composite systems created as organic-inorganic materials. The study is focused on the characterization of the structure and chemical composition of these systems and on the evaluation of basic mechanical parameters of selected samples, too. The detailed description is presented for the structure of sea shells, which are created by interconnected layers of micron crystals and submicron plates of calcium carbonate. These systems were evaluated by scanning electron microscopy, EDX analysis and nanoindentation. The typical structure of nacre is known as a typical arrangement but the arrangement is different for other types of shells. Individual building blocks can also be found with the dimensions complying with the definition of nanostructured materials. The arrangement of the crystal exhibits a recurring motive - crystals are characterized by their shape, mostly pentagons and hexagons, but also their diameter, height and thickness. The difference between the layers as well as their interconnection is characteristic for different kinds of shells. The aim of the structure and the chemical composition study is to obtain all necessary information for constructing similar systems for use in practice.

Key words: natural materials, composite systems, shells, structure, chemical composition.

1. INTRODUCTION

Since time immemorial mankind has observed nature, sought inspiration from it and strove to emulate it. The needs of human beings have also led to inventions whereby people looked to make their life easier and save resources and energy. To this day, a combination of various materials aimed at improving mechanical properties while simultaneously reducing weight is seen as one of the major accomplishments achieved after WW2 is. The development of composite materials has been a major success. However, there has always been the issue of producing them cheaply and in an ecologically-friendly way. An example of a composite material with good mechanical properties that is produced at a minimum cost are certainly shells which protect clams. These shells are composed of variously arranged plates or crystals of various sizes which are joined together by a natural protein-based binder. This composite system provides the exterior of the shell with required strength, rigidity and toughness. Chemically, the crystals are made up from calcium carbonate in the form of aragonite. The organic phase – the natural binder – gives the shell required toughness while the inorganic phase acts as the reinforcing phase of the composite system. Shells vary in size and layer arrangement. The outer layer consists of usually more robust pentagonal or hexagonal crystals whose size varies between several micrometres to several dozen micrometers and are arranged perpendicularly to the inner layer. The inner layer of the shell is composed of calcium carbonate whose pentagonal or hexagonal plates are arranged in layers on top of each other. These plates are hundreds of nanometres thick. This hierarchical structure, organized from the molecular to the microscopic level, ensures that mechanical parameters as well as properties important for the organism are maintained. A significant parameter which should not be overlooked in studying natural structures is the fact that their growth occurs at normal temperatures and pressures and also from elements most commonly found in nature. The millions of years of development have thus resulted in optimized structures created under regular conditions [1, 2].

2. EXPERIMENTAL

2.1. Materials

To study the structure, chemical composition and selected mechanical properties of a common shell the blue mussel (*Mytilus edulis*) was chosen. It is a medium-sized edible marine bivalve mollusc in the family Mytilidae. Blue mussels live in coastal regions in polar as well as temperate waters all around the world, attached to rocks or other solid surfaces. The mussel is smooth, with fine concentric grooves along the line of growth. It is blue, purple or brown and can grow up to 12 centimetres in length. Blue mussels are commonly collected as food from artificially-formed as well as natural areas worldwide. A specimen from our own collections, originating in the Adriatic Sea, was used for evaluation [3].

2.2. Test methods

The basic characterization of the mussel's structure was conducted using a Carl Zeiss Ultra Plus scanning electron microscope. Before microscopic analysis a film of gold 3 nanometres thick was vacuum-deposited on the specimens. The same instrument was used for the EDX analysis of the chemical composition. The nano hardness and the modulus of elasticity were measured on a CSM hardness tester using the Oliver-Pharr method at a maximum test load of 80 mN, a load speed of 160 mN/min, a 15-second load time and a speed of deloading of 160 mN/min, with 32 punctures made using a Berkovich tip at a distance between one and another of 100 μm under standard laboratory conditions.

3. RESULTS AND DISCUSSION

The microscopic and chemical analysis of two samples from the specimen described above – see Figure 1 – showed an overall and detailed arrangement of calcium carbonate plates and crystals – see Figure 2. Figure 2 clearly shows the non-homogenous distribution of individual plates varying in size and mutual arrangement. As a result, it was decided that mechanical parameters will be evaluated only in selected areas of the specimens analysed. Only plates arranged in layers on top of each other which are likely to be similar in terms of their size, shape and composition were chosen for further evaluation. The composition was determined by EDX analysis of both vertical and horizontal planes of plate arrangement – see Figure 4 and Tables 1 and 2. The composition was found to be analogical.

Fig. 1 Blue mussel (*Mytilus edulis*) – Specimens for evaluation.

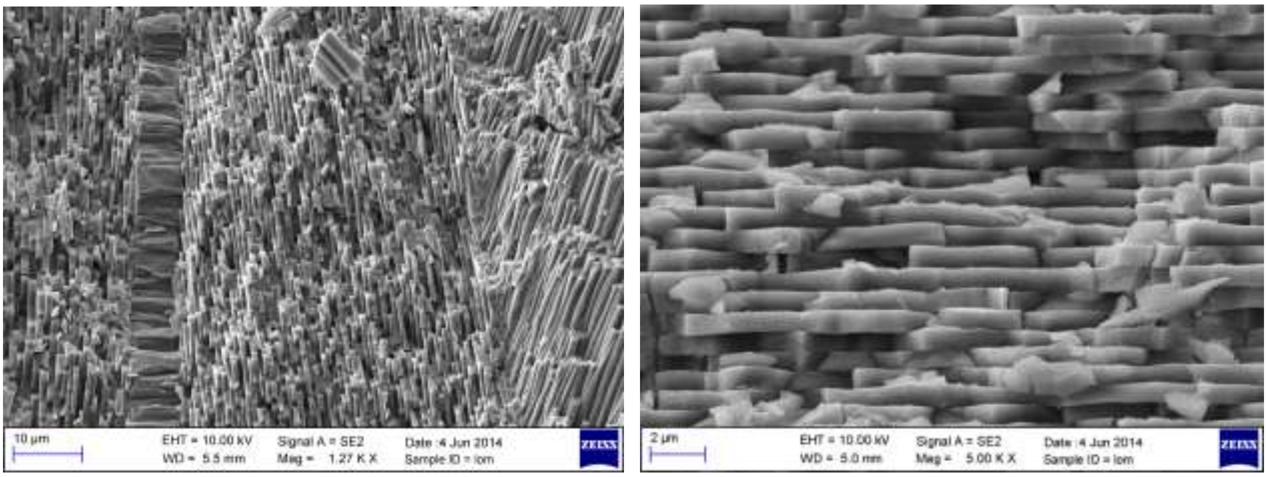


Fig. 2 Plate arrangement – Fracture area and a fracture area detail.

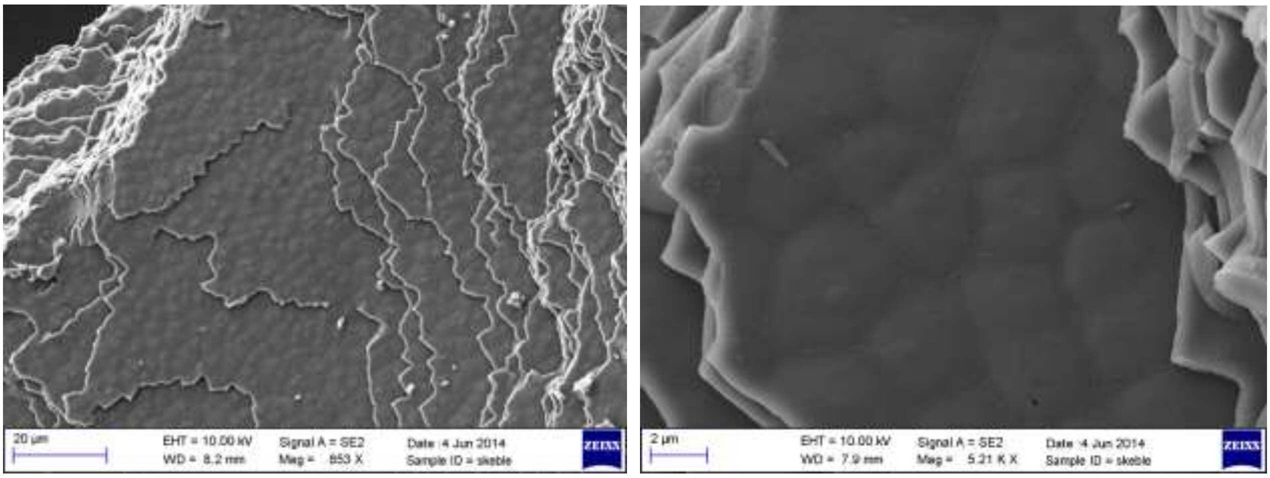


Fig. 3 Overall and detailed view of plate arrangement in nacre-forming layers.

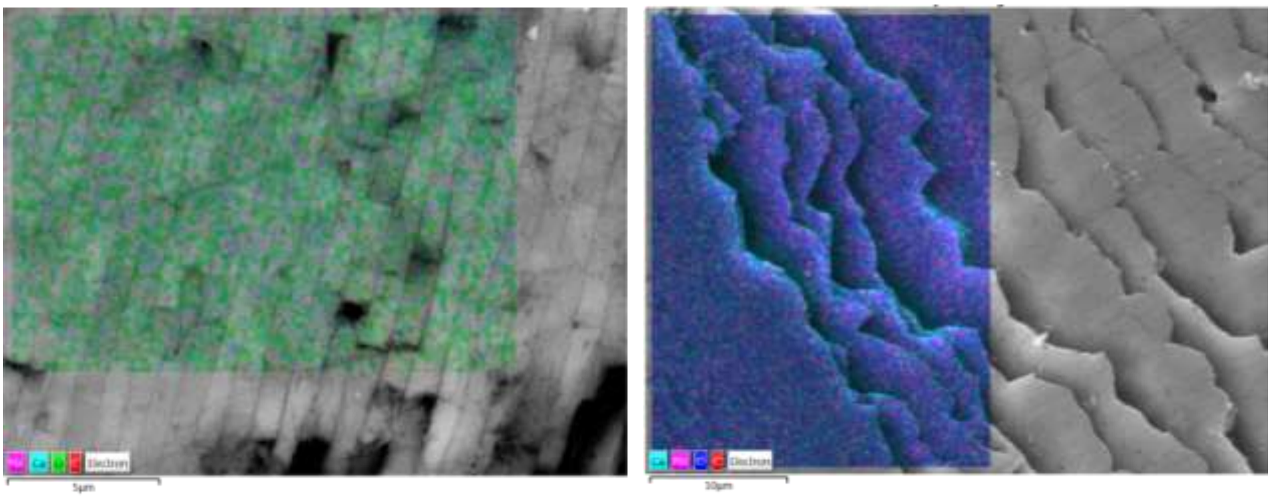
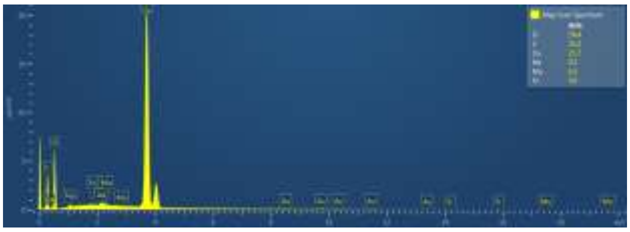


Fig. 4 EDX analysis – Vertical and horizontal arrangement of plates in layers.



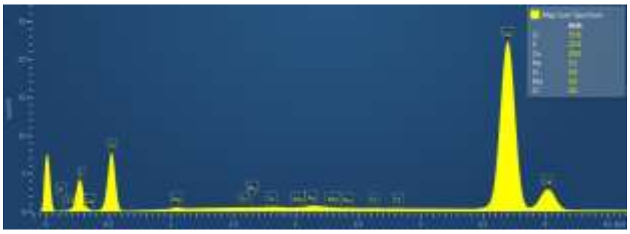


Table 1 Vertical arrangement

el.	O	C	Ca	Na
at %	54.6	23.1	21.8	0.5

Table 2 Horizontal arrangement

el.	O	C	Ca	Na
at %	57	22.5	20	0.3

Figure 3 clearly shows the homogenous distribution of plates, both within a single layer and in layers on top of each other. The plates are between 2 and 5 μm in diameter, around 800 nm thick and their shape is penta- or hexagonal. The image from the nano hardness tester shows a puncture located within a plate's area, not on the edge. Two series of measurements were conducted. The first series used dry samples; the second series used identical samples which had been soaked in sea water for 65 hours. The measurements were processed and their results are shown in Tables 3 and 4.

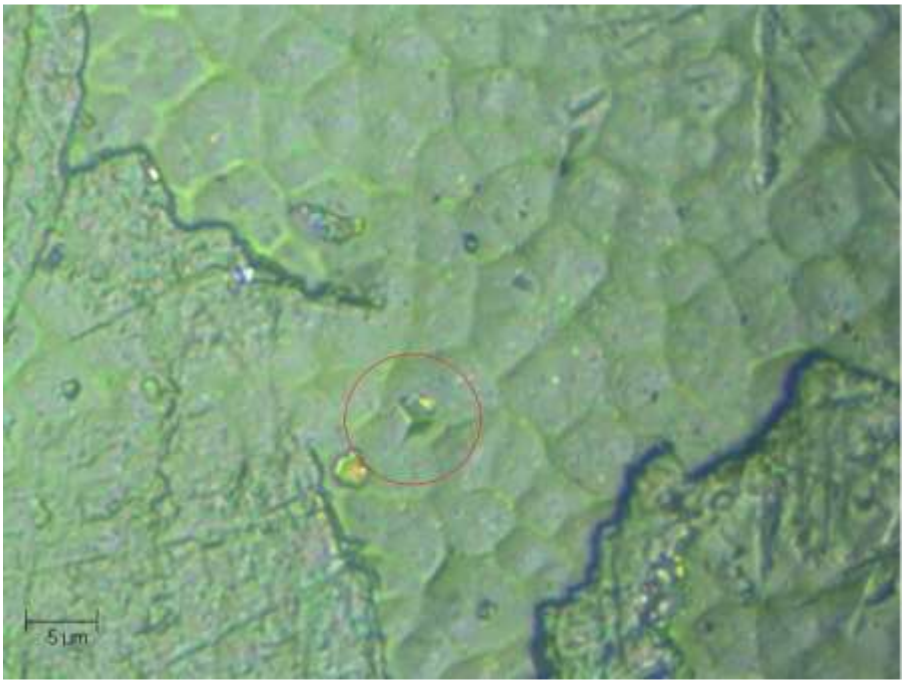


Fig. 5 A visible puncture by a nano hardness tester into the sample evaluated, with the puncture location clearly shown. The sample size is 63 μm × 47 μm.

Table 3 Dry samples

Dry samples	Sample 1	Sample 2
Hardness [HV]	341 ± 15	364 ± 4
EIT [GPa]	59 ± 4	65 ± 1

Table 4 Wet samples

Wet samples	Sample 1	Sample 2
Hardness [HV]	354 ± 10	240 ± 15
EIT [GPa]	44 ± 4	56 ± 1

The evaluation of the mechanical behaviour of selected specimens is based on determining their nano hardness and modulus of elasticity. The hardness and modulus of elasticity were determined for dry and wet samples, each of which was measured 32 times. Tables 3 and 4 show averages from these measurements and standard deviations. Mechanical parameters measured in dry samples are in keeping with studies researching this area. Nacre structure hardness values measured by other authors vary between 290 and 340 HV while the modulus of elasticity ranges from 60 to 100 GPa. The hardness values of wet samples are ambiguous; however, literature references mention an increase in hardness. The modulus of elasticity is slightly reduced, which is in keeping with results referred to in literature. It should be pointed out that the results are compared to those obtained by measuring properties in mussles of different kinds but with the identical composition and arrangement of plates [4, 5, 6, 7].

4. CONLUSION

Based on structural and chemical analyses and the results of measuring selected mechanical parameters it was established that the plates which form the nacre layer in the blue mussel (*Mytilus edulis*) have the following characteristics:

- The plate size varies between 3 and 5 µm and the plates are around 800 nm thick.
- The plates are polygons with n sides, most often pentagons and hexagons, and are arranged in layers.
- The plates are composed of calcium carbonate and held together by a protein-based organic phase.
- The hardness of dry samples varies between 341 and 364 HV, the module of elasticity ranges between 59 and 65 GPa.
- The hardness of wet samples varies between 240 and 354 HV, the module of elasticity ranges between 44 and 56 GPa.
- The influence of wetness is apparent primarily in the modulus of elasticity and is linked to the presence of water which affects the organic – binding – phase, making it softer and ultimately increasing the toughness of the entire composite system.
- Although the nacre layer in the kind of mollusc differs in size and thickness from other kinds, its mechanical parameters are identical.

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