USPOREDBA MIKROSTRUKTURE LJUŠTURE OGRCA I PRILJEPKA
COMPARISON OF MICROSTRUCTURE OF THE ADRIATIC MONODONTA AND THE MEDITERRANEAN LIMPET

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Sažetak

Rad prikazuje usporedbenu analizu mikrostrukture dviju jadranskih školjaka, koje obje pripadaju u skupinu morskih puževa. Iako su te školjke iz razreda puževa (lat. Gastropoda) u koljenu mekušaca, one imaju znatno različitu mikrostrukturu. Detailna mikrostrukturna analiza pokazala je da je struktura ljuštura ogrca uglavnom sastavljena od sedefa. S druge strane, ljuštura priljepka građena je od poprečno lamelarne strukture gotovo po cijelom poprečnom presjeku. Prosječne izmjerene debljine aragonitnih pločica su 0,454 μm, odnosno 0,360 μm kod ogrca, odnosno priljepka.

Ključne riječi: prirodni materijali, ogrc, priljepak, mikrostruktura

Abstract

The paper presents and compares the results of microstructural analysis of two different Adriatic Sea shells, both belonging to the species of sea snails, namely the Adriatic Monodonta and the Mediterranean limpet. Although both seashells are coastal marine gastropod molluscs, they do have a very distinctive microstructure. The detailed microscopic analysis has shown that the Monodonta consists mainly of nacre. On the other hand, the limpet’s shell showed a crossed-lamellar microstructure, which extends through almost the whole cross section of the shell. Average measured aragonite layers thicknesses are 0.454 and 0.360 μm in Monodonta and limpet shell, respectively.

Keywords: natural materials, Monodonta, limpet, microstructure
INTRODUCTION

Biological systems are self-assembled organized structures, all with a wonderfully detailed, economic and well-adjusted microstructure. The different structures have been developed in nature through billions of years. The study of the structure of natural materials is currently a very attractive scientific discipline. The development of the so-called biomimetic materials is based on the inspiration from nature, where the principles copied from the nature are used in developing novel materials and composites.

Biological organisms produce composites that are organized in terms of composition and structure, containing both inorganic and organic components in complex structures. They are hierarchically organized at the nano, micro, and meso levels. [1]

One of the most studied seashells is abalone (lat. Haliotis rufescens), which belongs to the species of marine snails of the genus Haliotis. The abalone shell is made up from layers of thin CaCO₃ plates. The size of the plates is about 500 nm [2] and the crystal form of CaCO₃ is called aragonite. The plates are joined by a much thinner organic component layer.

The mechanical response of the abalone shell is correlated with its microstructure and damage mechanisms. The mechanical response is found to vary significantly from specimen to specimen and requires the application of Weibull statistics in order to be quantitatively evaluated. In quasi-static and dynamic compression and three-point bending tests the abalone shell showed orientation dependence of strength. The compressive strength when loaded perpendicular to the shell surface is approximately 50% higher than parallel to the shell surface. The compressive strength of abalone is 1.5–3 times the tensile strength. This differs significantly from the technical ceramics where the compressive strength is usually an order-of-magnitude greater than the tensile strength. Crack deflection, delocalization of damage, plastic microbuckling (kinking), and viscoplastic deformation of the organic layers are the most important mechanisms contributing to the unique mechanical properties of this shell. [3]

The Vickers micro-hardness of different sea shells has been studied as a function of the indentation load. The Adriatic Sea seashells abalone (lat. Haliotis tuberculata), smooth clam (lat. Callista chione), and warty venus (lat. Venus verrucosa) were analysed, and the results showed that the measured micro-hardness does depend on the load, which indicates the influence of the indentation size effect. The best correlation between measured values and proposed models has been achieved by using the modified proportional specimen resistance model. [4, 5]

A recent study of the organic inter-lamellar layers, mesolayers and mineral nanobridges in abalone nacre has estimated the tensile strength of the organic interlayer at 2 MPa. The tensile strengths of the abalone nacre parallel to the tablet layer is 100–150 MPa, while perpendicular to the tablet layer is 3–5 MPa. Thus, the resistance of the organic nanolayer and mesolayer contribute little to the overall strength. Their primary purpose is to subdivide the aragonite matrix and thereby control the crack propagation path. [6]

Figure 1 shows the four basic types of sea shells microstructure (Web-1). These are:
1. Fibrous Prismatic
2. Nacre
3. Simple prismatic
4. Crossed lamellae

Nacre is also called the mother-of-pearl, because its crystalline structure is similar to the smooth surface and has similar visual effect as those observed in natural pearls. Different seashells have different microstructure of the inner and outer layer depending on the seashell’s size, natural habitat, mollusc class etc. A very interesting example is the noble pen shell or fan mussel (lat. Pinna nobilis), which on the inner layer of the narrow part has a nacreous structure composed of aragonite platelets surrounded with an organic phase, and on the outer layer a polygonal prismatic structure with a high length/thickness ratio of the column crystals. [7]

Figure 1: Four basic types of microstructure of sea shells (Web-1)

MATERIALS AND METHODS

The presented research shows the results of microstructural analysis of two resembling types of sea shells: the Adriatic Monodonta (lat. Monodonta turbinata) and the Mediterranean limpet (lat. Patella caerulea).

The Monodonta and the limpet both belong to the species of sea snails, which are coastal marine gastropod molluscs. Since these seashells belong to the group of sea-snails, they live in shallow sea and are able to move.
Monodonta turbinata is widespread in the upper layers of the littoral zone of the Adriatic Sea. The sea snail shell is solidly built and is spirally twisted from the top to the outside of the spiral. It grows up to 4 cm, and its weight is up to 15 g. The average weight of the animal is 5 g. It inhabits the whole Adriatic Sea on the rocky sea shore. Figure 2 represents Monodontas as viewed from different angles (Web-2).

The abundance of this species testifies to its adaptation to different environmental conditions. Due to periodical change of water and air, sharp temperature drops, surf impact, and water desalination because of precipitation, the environmental conditions are complicated and variable. According to observations, Monodonta turbinata easily survives in these conditions, enduring long drying, very high temperatures, desalination, and water pollution. In the tidal zone, the massive shell is one of the most important adaptations. It protects the body from wave crashes and water loss and prevents superheating of body in summer and freezing in winter [8].

The Monodonta was compared to the microstructure of the common Mediterranean limpet (lat. Patella vulgate). Figure 3 presents the inside and the outside surface of the Mediterranean limpet or Patella (Web-3). The limpet grows up to a length of 70 mm, and has a weight up to 50 g. The average specimen is about 50 mm in diameter. It lives in shallow wasters attached to the rocky sea shore.

Limpets also experience harsh environmental conditions in their natural habitat, including temperature fluctuations, high pressures, variable pH, low and variable oxygen concentrations, normally toxic levels of sulfides and heavy metals, and various mechanical predatory attacks. Nanoindentation was used to locally determine the mechanical properties of the limpet's aragonite-based shell and was found the indentation stiffness of 70 GPa, and indentation hardness values of 2 GPa [9].
The structures of Monodonta and the limpet were analysed using the scanning electronic microscope TESCAN VEGA TS5136LS with EDS. The specimens that are to be analysed using this type of device should have at least some electrical conductivity, which inorganic components of the dried seashells do not have. Therefore, the specimens had to be coated with an electrically conductive media. A thin layer of the palladium-gold alloy was applied using the sputter coating method, which is a physical vapour deposition (PVD) method of depositing thin films by sputtering. Sputtering ejects the atoms from the solid material due to bombardment of the material by energetic particles. [10]

The investigated surfaces were obtained by cracking the seashells manually. Figure 4 shows the actual investigated Monodonta and the location where the shell was cracked and analysed. It was observed that the shell of Monodonta was quite brittle and it was not difficult to obtain a uniform cross section.
On the other hand, the much thinner limpet shell was much more difficult to crack. Figure 5 shows the macro view of the limpet with the analysed location indicated.

**Figure 5: The analysed part of the Mediterranean limpet**

### RESULTS

After a detailed microscopic analysis it was found that the Monodonta consists mainly of nacre, around 90% by volume. Monodonta showed the structure of thin uniform aragonite plates. Figure 6 shows the fine arrangement of the platelets in the inner surface using a magnification of 9050 times.

**Figure 6: Inner surface of the Monodonta**
The remaining part of the Monodonta sea snail shell belongs to the outer thin layer, which is dotted on the macroscopic scale. This part of the sea shell has the crossed lamellae type of microstructure, as can be seen on Figure 7.

Figure 7: Outer surface of the Monodonta

Figure 8 shows the thickness measurement data of the aragonite platelets in Monodonta, with the applied magnification level of 28140 times.

Figure 8: Measurement of the aragonite platelet thickness in Monodonta
The study of the microstructure of the limpet has shown that the limpet shell possesses a crossed-lamellar microstructure, with all the lamellae oriented under the same angles. Furthermore, it was interesting to notice that this microstructure extends through the whole cross section of the shell. Figure 9 shows the microstructure on the very inner edge (bottom low part of the image), using a large magnification (2520 x).

Figure 9: The microstructure of the inner surface of the Mediterranean limpet

Figure 10 presents the microstructure of the Mediterranean limpet as seen on the outer surface (945 x).

Figure 10: The microstructure of the analysed Mediterranean limpet (945 x)
It is easy to conclude that the structure of the limpet is crossed-lamellar throughout the shell cross section. Since the limpet's shell is not spiral as in a typical snail, nor it is of bivalve seashell type, it is really quite peculiar. Figure 11 shows the thickness measurement data of the aragonite platelets in limpet, with the applied magnification level of 8060 times.

![Image](image_url)

Figure 11: Measurement of the aragonite platelet thickness in limpet

The aragonite platelets thickness measurements for the Monodonta and the limpet are summarized in Table 1. The mean, standard deviation and the standard error of the mean after adjusting for a small sample size are also given in the table.

<table>
<thead>
<tr>
<th>Measured thickness, um</th>
<th>Aragonite layers in:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monodonta</td>
</tr>
<tr>
<td>0.4496</td>
<td>0.4467</td>
</tr>
<tr>
<td>0.4572</td>
<td>0.3953</td>
</tr>
<tr>
<td>0.4407</td>
<td>0.3289</td>
</tr>
<tr>
<td>0.4782</td>
<td>0.3467</td>
</tr>
<tr>
<td>0.4440</td>
<td>0.3467</td>
</tr>
<tr>
<td>Mean</td>
<td>0.45394</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.014934</td>
</tr>
<tr>
<td>Standard error of the mean</td>
<td>0.0066787</td>
</tr>
</tbody>
</table>

The measured values of aragonite crystal thicknesses are comparable to the typical literature values of ~0.5 um of thickness [11]. Figure 12 presents a diagram with the average measured thickness of Monodonta and limpet in um, with the added standard error bars of plus/minus one standard deviation.
CONCLUSION

Adriatic Monodonta and the Mediterranean limpet both belong to the species of sea snails.

Monodonta’s microstructure consists mainly of nacreous structure, with layers of parallel thin aragonite platelets. Considering the smooth and small radii of the Monodonta’s shell it seems reasonable to construct such a spiral structure using only flat parallel building elements. This spiral structure can be compared to the man-made spiral structures such as for example the entirely self-supporting stair cases, which are made without any central pillar for the stability.

The limpet, although being also a sea-snail, is characterised by a completely different microstructure, i.e. cross-lamellar. As seen on the macroscopic level, the limpet is purely conical. It can be concluded that the best way to achieve such a macroscopic architecture in nature is to align many levels of lamellae in crossed directions. This way the building elements act as they are supporting one another.

The thicknesses of the layers also differ significantly, with the limpet having much tinier platelets. The presumed reason for this phenomenon is the greater hardness of the limpet compared to the Monodonta, which will be investigated in the further research.

REFERENCES


Web sites: