BIOMIMETIC CONVERSION OF RED SEA CORALLINE STRUCTURES FOR IMPLANT PURPOSES

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INTRODUCTION

Hydroxyapatite (HAp) was first derived from coral in 1974 by Roy and Linnehan [1] and has been used as a bone graft substitute in non-load bearing orthopaedic surgery for nearly 20 years. After grafting it is desirable for bone ingrowth to occur as quickly as possible as the strength of the region, which has been implanted, is dependent on a good mechanical bond forming between the implant and the surrounding regions in the body. The rate at which ingrowth occurs is dependent on various factors, including pore size and interconnectivity of the implanted material [2]. It is therefore necessary to develop a precise knowledge of the factors, which influence the microstructure and the pore size in the converted hydroxyapatite structure. A new species, which was found and cloned under field and laboratory conditions, was used in the present study in the production of sol-gel coated coralline hydroxyapatite.

EXPERIMENTAL

The coral of species Millepora dichotom, was obtained from the Red Sea, Israel. It was cleaned, heat treated and then converted to hydroxyapatite via a hydrothermal method with a temperature of 250°C and pressure 3.9 MPa. The coralline hydroxyapatite was then dip-coated via a new alkoxide sol-gel method.

The coral was analysed before and after heat treatment, after hydrothermal conversion and after sol-gel coating. The characterization techniques employed were X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, differential thermal analysis (DTA-TGA), Environmental scanning electron microscopy (ESEM) and inductively coupled plasma – mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

The XRD pattern after conversion and coating showed a major phase of hydroxyapatite (JCPDS 9-0432). A minor phase of β -tricalcium phosphate was also observed. The XRD pattern demonstrated high crystallinity and an absence of any CaO or CaCO₃ peaks, confirming completion of the reaction.

The IR spectra of the coralline hydroxyapatite exhibited peaks at 1051, 962, 603, 571, 474 cm⁻¹ corresponding to P-O bond. Absorption bands at 3571 and 3178 are due to the O-H bond. A peak at 2345 was due to the CO_2 in the air. Two peaks at 1458 and 879 cm⁻¹ correspond to $CO_3^{2^-}$. This is evidence that carbonate ions have been substituted into the lattice in place of some OH⁻ ions.

The Raman spectra of the coralline hydroxyapatite showed a single peak at 958cm⁻¹, corresponding to symmetric stretching of the phosphate group.

Thermal analysis of the coralline hydroxyapatite displayed a weight loss of 4.39%. However, an endotherm was observed at 699°C, indicating a minor presence of carbonated impurities.

Analysis by ESEM revealed no significant changes in morphology of the coral once converted to hydroxyapatite and coated. The pore size was found to be approximately $25-75\mu m$, which is significantly smaller than corals of the Porites species [3]. This indicates that this hydrocoral species may be of higher mechanical strength due to lower porosity.

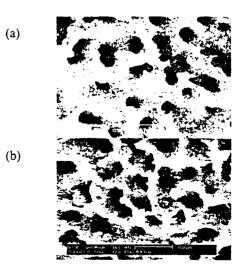


Figure 1: Comparison of Red Sea hydrocoral (a) in original state and (b) after hydrothermal conversion.

ESEM images of the cross-section of the hydrocoral reveal a vein-like structure (Figures 1 and 2). This offers a material with a high similarity to the structure of natural bone.

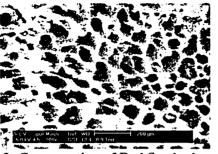


Figure 2: Cross-section of Red Sea hydrocoral.

Upon high magnification, the coral and coralline hydroxyapatite were shown to contain nanopores and mesopores. Once coated, the nanopores and mesopores were no longer visible (Figure 3). By concealing these pores, an increase in strength of the material can be expected.



Figure 3: Coated coralline hydroxyapatite at high magnification.

CONCLUSION

Millepora dichotom from the Red Sea, Israel was successfully converted to monophasic hydroxyapatite. FTIR, XRD and ESEM confirm pure hydroxyapatite, however, with a minor presence of carbonated impurities. Pore sizes were observed to be around $25-75\mu m$, which are much smaller than the converted Goniopora species. It is expected that this coral will have higher mechanical properties than the currently available other corals.

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