

# Summary

The aim of this thesis was the elaboration of dense, porous and multi-layer hydroxyapatite (HA) ceramics to be used in biomedical applications. The production was made through two advanced methods: gelcasting and robocasting techniques, both based on the colloidal ceramic processing suitable for the production of high-performance complex geometries. Two different batches of a commercial type HA were used in production. The preliminary characterisations showed that both batches were calcium deficient HA with different Ca/P ratios, but similar particles size distribution. The dispersion process of HA powders was carried out through dry and wet ball-milling (DBM and WBM) processes, providing powders with different particle size distributions which were used in the production processes.

The optimisation of the sintering process of the powders was accomplished by conducting dilatometry tests on the samples made from DBM and WBM powders. The effect of the heating rate and the initial particle size on the sinterability and the grain growth were investigated and on the ground of these results, the sintering process was optimised. An abnormal grain refinement during the sintering process was observed for the samples made from the powder with the lower Ca/P ratio leading to a bimodal grain size distribution of the final material. Further analyses showed that the grain refinement resulting from the HA to tetracalcium phosphate (TTCP) phase transformation which took place at 1300 °C.

The gelcasting of the porous and the dense samples were conducted using agar as an environmentally friendly non-toxic gelling agent. Dense samples with densities up to 97 %TD were obtained using WBM powders. These high densities led to the high mechanical performance of the dense samples. The foaming method was used for the development of macroporosity in the porous samples. Highly porous structures in the porosity range of 63% to 87% characterised by spherical interconnected pores were obtained. The effect of different constituents of the ceramic slurry on the porosity and pore sizes of the porous samples were investigated. The mechanical properties of dense and porous samples were studied by conducting uniaxial compression tests. Moreover, functionally graded multifunctional scaffolds, mimicking the natural bone structure, were developed using the optimised dense and porous gelcasting techniques in which the dense part

had the load-bearing function and the porous layer fulfilled the biological requirements.

Dense, porous and functionally graded multilayer samples were also produced by robocasting technique. Different ink formulations were needed for successful production of each part. The samples were characterised by fully dense struts comparable to gelcast samples and the successive layers were well squeezed together. Optimisation of the paste formulation led to the production of multilayer structures with pore sizes more than 1.3 mm which is not achievable with other methods. The crack formation and propagation leading to the fracture of the porous robocast samples were studied using an environmental SEM (ESEM) equipped with the in-situ compressive device. The mechanical properties of the dense and porous robocast samples were found lower than the samples made by the gelcasting technique.

*In vitro* bioactivity tests were performed on the produced samples to investigate their bone formation ability. All the tested samples were found to be covered by an apatite layer confirming their osteoconductivity. However, the samples made from the powder with lower Ca/P ratio formed a thicker bioactive layer.

Polymer-ceramic composite layers were added to the multilayer robocast samples to add antibacterial functionality to the samples. Incorporation of a small amount of Ag<sup>+</sup> ions in the composite materials was found as a powerful tool to prevent post-surgery infection after implantation of the orthopaedic implants.