

Current advances and issues of calcium phosphates 3D-printing. A focus on the Digital Light Processing technique

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Calcium phosphates are classified as bioceramics and widely used in clinical bone repair, due to their excellent biocompatibility, bioactivity, and ability to promote the differentiation and proliferation of stem cells. To mimic the architecture of cancellous bone, calcium phosphates are typically shaped as porous scaffolds, with specific characteristics regarding porosity level, pore and interpore channel sizes to supply proper cell attachment and vascularization.

In this frame, additive manufacturing technologies, such as robocasting and vat-photopolymerization techniques (precisely, Stereolithography and Digital Light Processing - DLP), have demonstrated a superior ability compared to traditional technologies in fabricating scaffolds with customized architecture and internal geometry, and many structures have already been biologically validated by in-vitro and in-vivo tests. On the contrary, only a few studies have been dedicated to the fabrication of 3D dense parts and to their mechanical characterization, meaning that a deep comprehension of the reliability of the 3D printing technologies for these bioceramics is still lacking.

This work discusses our recent developments on dense and porous calcium phosphate structures, fabricated by two 3D printing techniques: DLP and robocasting. Although these two technologies are significantly different, both require the study and optimization of some key parameters: the preparation of the ink (in particular the optimization of the solid loading and of the rheological behavior), the set-up of the printing parameters, the post-processing and sintering conditions.

In this work, a special attention is paid to the DLP technology, with the aim of disclosing the role of hydroxyapatite median particle size (MPS), curing depth-to-layer thickness ratio (CD/LT), and debinding process on the printing/debinding flaws and flexural strength of the sintered parts.

Specifically, a commercial hydroxyapatite was milled for different times, obtaining powders with an MPS ranging from \cong 0.3 to 3.0 μ m. As-sintered bars showed regular shape and without apparent delamination between layers. However, after thermal debinding, delamination and vertical cracks formed, whose number and extension decreased with increasing MPS. The strategies to minimize such flaws are presented in this work: the optimized bars achieved a flexural strength of >100 MPa, which is among the highest values for dense HA fabricated by lithography-based techniques.