

# Leveraging the High Resolution of Digital Light Processing in the Additive Manufacturing of High-Performance Composites for Biomedical Applications

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This work describes innovative manufacturing technologies that leverage the high resolution of photocuring additive manufacturing techniques such as Digital Light Processing (DLP) for the production of bioinspired ceramic-polymer hybrid materials with enhanced mechanical performance. These high-performance composites find application, among other fields, in bone tissue engineering scaffolds, dental prosthesis and other biomedical implants.

Additive Manufacturing (AM) techniques have been widely used to fabricate porous substrates for biomedical applications. Developing AM scaffolds from materials with bonelike properties that are capable to interact with the tissues and actively induce bone regeneration has permitted overcoming the main issues of currently available procedures for repairing large bone lesions, namely: the limited amount of material and need of secondary surgical sites in the case of autografts, the risk of immunogenic response and disease transmission from donor in the case of allografts, and the fixation problems of current bioinert prostheses. However, pure bioceramic scaffolds are mechanically weak and very brittle, which prevents their widespread use in the repair of bone defects in load-bearing regions of the skeleton. In this work, digital light processing (DLP) is used to obtain composite scaffolds with controlled microstructure, pore architecture and optimal mechanical performance. Concentrated  $\beta$ -tricalcium phosphate (TCP) inks are used to produce porous structures consisting of a tetragonal three-dimensional mesh of interpenetrating hollow tubes that were subsequently impregnated by a polymeric phase to obtain core/shell composite struts. This particular strut architecture offers a promising strategy to optimize the mechanical performance in terms strength, and especially of toughness, of the scaffolds without jeopardizing their bioactivity and osteoregenerative properties.

Ongoing progress towards the additive fabrication of novel ceramic/polymer bioinspired composites with a microstructure mimicking that of the enamel in human teeth are also discussed. Intricate columnar ceramic preforms with intercolumn gaps resembling the convoluted hydroxyapatite-rich rods found in natural enamel can be produced either through direct DLP printing of bioceramic photocurable suspensions or through indirect DLP strategies where a sacrificial negative resin mould is fabricated by DLP. In the latter case, the ceramic preform is produced by casting a highly concentrated ceramic slurry into the mould, which is subsequently eliminated in a heat treatment before sintering the ceramic particles and consolidating the preform. In either case, to obtain the desired bioinspired composites, the ceramic preform is infiltrated by a ductile polymer to mimic the inter-rod sheath in natural enamel. In this way, highly damage-tolerant and wear resistant hybrid biomaterials can be formed. The developed materials will significantly improve the effectiveness and durability of dental restorations over existing commercial alternatives, thus helping to reduce the need for replacement interventions with their associated cost and risk for the patient.

The new bioinspired composites and the novel manufacturing processes described in this work may become essential enabling technologies for the realization of bioinspired high-performance composites, that could not only revolutionize the biomaterials industry, but have a dramatic impact in other industrial applications too.

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