3D printed bone grafts: Toughness enhancement utilizing PCL-based additives

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Introduction

One main goal of bone tissue engineering (BTE) is the replacement of autografts with artificial bone scaffolds as a treatment method for major bone defects. Alternatives to traditional manufacturing methods are needed to meet patient- and defect-specific requirements. One attractive technique for this is digital light processing stereolithography (DLP-SLA). Showing good biocompatibility and low cytotoxicity, vinyl esters (VEs) are promising monomers for BTE applications. Nevertheless, crosslinked VE-thiol networks show very brittle behavior. To overcome this obstacle and decrease brittleness, poly(ε-caprolactone)-derived (PCL) high-molecular weight additives might be utilized.[1] This approach was further investigated, and a library of PCL-based additives was synthesized and tested. In addition, a rigid thiol compound was introduced and compared to a flexible commercially available one.[2]

Methods

Additives and thiols were tested in formulations containing divinyl adipate (DVA) as matrix monomer. Two different toughness enhancing additives (TEAs) containing photopolymerizable end-groups (allyl carbonates) with different molecular weights and two thiols were examined. Their impact on photoreactivity was tested using real time-near infrared photorheology. (Thermo-)Mechanical properties were investigated using dynamic mechanical thermal analysis and tensile testing. As a proof-of-concept, surgical screws were 3D printed with the best-performing formulation. A 3D scan of the printed object was overlayed with the original CAD file to investigate the dimensional accuracy of the printed parts.

Results

Photoreactivity studies showed that upon addition of TEAs, the time until gelation t_{gel} was reduced (minimum t_{gel} was 2.6 s) and an increase in the double bond conversion (DBC) compared to reference formulations without TEA was found. DBCs up to 86 % were observed. Glass transition temperatures were above 37 °C, which is crucial for BTE applications. Tensile testing revealed a substantial increase in mechanical properties: it was possible to triple the materials' tensile toughness. 3D printed parts exhibited low volumetric shrinkage between 100-200 µm and neither cracks nor delamination.

Discussion & Conclusions

The addition of PCL-based TEAs led to an outstanding increase in mechanical properties, especially regarding tensile toughness, without disrupting photoreactivity. Thus, VE-based systems containing TEAs provide an excellent alternative to state-of-the-art (meth)acrylate-based systems.

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References

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