

# 3D printing of biodegradable poly(L-lactide)/hydroxyapatite composite by composite extrusion modeling

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*Abstract: The usage of biodegradable polymers as implant material instead of metal is of growing interest because no second surgery is needed and the healing time is shortened. Combining biodegradable polymers with hydroxyapatite particles leads to implants with osteoconductive properties and improved mechanical strength. Using 3D printing it is possible to generate highly structured and complex or even individualized implants based on a patient data set. This work details a preliminary study on the 3D printing of a commercially available biodegradable poly(L-lactide)/hydroxyapatite composite using the novel composite extrusion modeling (CEM) process. Optimized printing parameters have been investigated and first 3D printed specimens have been analyzed regarding their density and microstructure. Furthermore, first benchmark parts show the potential of manufacturing implants by CEM 3D printing using this composite material.*

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## I. Introduction

3D printing of biodegradable composites is of high interest for many medical applications such as the manufacturing of patient specific implants. Furthermore, local production is possible using 3D printing that can lead to a reduction of the operation time [1]. Printing techniques for biodegradable composites are presented by Puppi et al. [2]. Most melt extrusion additive manufacturing (ME-AM) techniques such as the frequently used fused filament fabrication (FFF) require composite feedstocks in the form of filaments with defined diameter and sufficient mechanical stability. In contrast, the novel composite extrusion modeling (CEM) can process conventional injection molding feedstocks in the form of pellets or granules since this process is based on a miniaturized screw extruder [3]. This is very advantageous compared to FFF since a very broad range of plastic but also composite materials from the field of injection molding can be directly used.

However, 3D printed parts often do not feature the same density or quality compared to conventional manufactured or rather injection molding parts due to the layer-wise printing process. Therefore, optimization of the printing parameters is necessary for achieving the best part quality as well as the desired density and finally mechanical stability.

This work aims to process a commercially available biodegradable poly(L-lactide)/hydroxyapatite composite using CEM 3D printing. This feedstock is intended for injection molding. In order to process this feedstock in a CEM 3D printer, appropriate printing parameters have to be investigated. Then, first 3D printed specimens are analyzed regarding their density and microstructure.

Furthermore, first benchmark parts are printed to demonstrate the potential of manufacturing implants by CEM 3D printing using this composite material.

## II. Material and methods

A commercial injection molding feedstock RESOMER® Composite L 210 S + 25% HA provided by Evonik Industries AG, Darmstadt, Germany is used as a feedstock for 3D printing. This composite material consists of poly(L-lactide) with 25% hydroxyapatite. Before printing, the feedstock is dried at 80°C for 4 hours in a furnace and cooled down in a desiccator.

3D printing is conducted using the CEM printer ExAM 255 by AIM3D GmbH, Rostock, Germany. The nozzle temperature is 215°C and the printing speed is 50 mm/s.

In order to find the optimized extrusion multiplier (EM), a specific cylinder (EM-tower) with 20 mm diameter and 25 mm height consisting of 2 outlines and 0% infill is printed at which the EM is varied step by step after a specific number of printed layers. Cubes with 10 mm edge length are printed with 100% infill using the optimized EM for density measurement. The density of the raw material and the printed cubic parts are measured according to DIN EN ISO 1183-1 with a pycnometer using ethanol (99.8%) to prevent hydrolytic degradation of the material. Finally, initial porous structures, an osteosynthesis plate and further benchmarks are printed in order to demonstrate the capability of the printing process.

The microstructure analysis of the surface of printed cubes is performed with Field Emission Scanning Electron Microscope (FE-SEM) Supra 25 (Carl Zeiss AG, Jena,

Germany) to investigate the printing quality and HA particle distribution.

### III. Results and discussion

The EM-tower was successfully printed, subsequently cut vertically and used to identify optimized EM (see Figure 1). By optical inspection, regions of under and over extrusion were identified and the optimized EM was found to be 1.5.

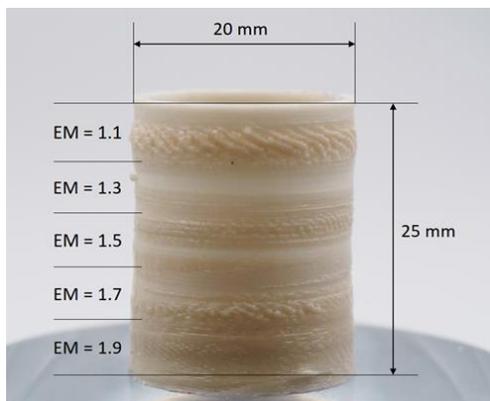


Figure 1: 3D printed EM tower for the detection of the optimized EM.

The density of the printed cubes (see Figure 2 (a)) was  $1.45 \pm 0.014 \text{ g/cm}^3$  whereas the granules feature a density of  $1.49 \pm 0.092 \text{ g/cm}^3$  which means that the printed parts achieve approximately 93% of the density of the raw material. This is probably due to voids inside the infill structure of the cube caused by minor fluctuations in the material extrusion rate.

The osteosynthesis plate with three holes directly after 3D printing is depicted in Figure 2 (b). The part shows a high geometric accuracy and surface quality. The lines in the middle hole are due to an oozing of the extruder and had to be removed in the postprocessing step. Furthermore, various benchmark parts featuring porous structures as well as fine details could be printed successfully (see Figure 2 (c) and (d)). These results indicate that it is possible to print scaffolds for bone replacement with a defined pore size to achieve high osteoconductivity [4].

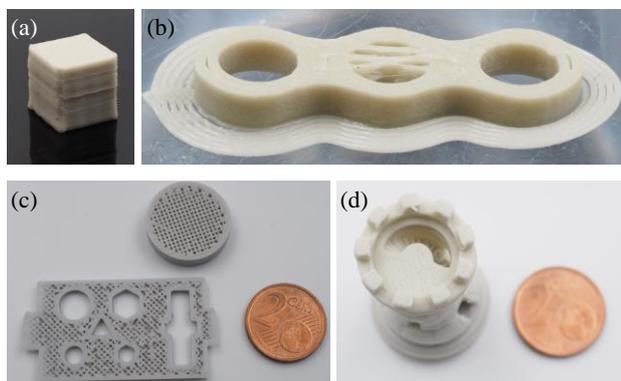


Figure 2: (a) Printed cube for density measurement; (b) Osteosynthesis plate with (23x7.5x2.5) mm in size; (c) Porous structures with 50% infill; (d) Benchmark part chess tower featuring fine internal details

FE-SEM images of the side surface of a density cube are shown in Figure 3. The single layer caused by the layer-

wise printing process can clearly be recognized. Furthermore, hydroxyapatite particles of a size of approximately  $1 \mu\text{m}$  can be seen on the surface of the single struts. The particles are distributed nearly homogeneously on the surface.

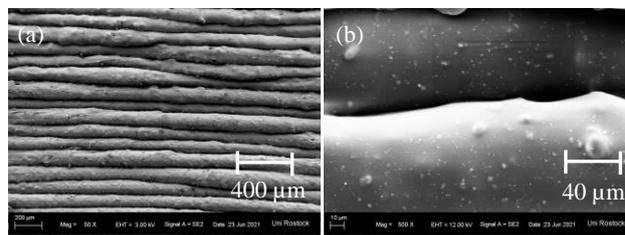


Figure 3: FE-SEM images of the side surface of the printed density cube; (a) the single printed layers as well as minor fluctuations in the material extrusion rate can be recognized; (b) equally distributed small hydroxyapatite particles can be found on the surface.

### IV. Conclusions

This preliminary study successfully demonstrated the 3D printing of a commercial medical biodegradable injection molding feedstock using the novel CEM 3D printing technique. The benchmark parts featuring fine details could be printed in good quality. However, the density of the parts is significantly lower than the density of the raw material which presumably leads to worse mechanical properties compared to parts processed via injection molding.

Therefore, further investigations have to be performed. More printing parameters such as temperature, printing speed and layer height must be investigated systematically in order to further improve the density and printing quality. To ensure the preservation of the material properties of the biodegradable composite such as its molecular weight, the inherent viscosity of the material has to be analyzed before and after 3D printing [5].

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#### AUTHOR'S STATEMENT

Conflict of interest: Authors state no conflict of interest. Informed consent: Informed consent has been obtained from all individuals included in this study.

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