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# Selective laser sintering of hydroxyapatite/poly-ε-caprolactone scaffolds ☆

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ABSTRACT

Selective laser sintering (SLS) enables the fabrication of complex geometries with the intricate and controllable internal architecture required in the field of tissue engineering. In this study hydroxyapatite and poly-ε-caprolactone, considered suitable for hard tissue engineering purposes, were used in a weight ratio of 30:70. The quality of the fabricated parts is influenced by various process parameters. Among them Four parameters, namely laser fill power, outline laser power, scan spacing and part orientation, were identified as important. These parameters were investigated according to a central composite design and a model of the effects of these parameters on the accuracy and mechanical properties of the fabricated parts was developed. The dimensions of the fabricated parts were strongly dependent on the manufacturing direction and scan spacing. Repeatability analysis shows that the fabricated features can be well reproduced. However, there were deviations from the nominal dimensions, with the features being larger than those designed. The compressive modulus and yield strength of the fabricated microstructures with a designed relative density of 0.33 varied between 0.6 and 2.3 and 0.1 and 0.6 MPa, respectively. The mechanical behavior was strongly dependent on the manufacturing direction.



## 1. Introduction

Selective laser sintering (SLS) is an additive manufacturing technology where parts are constructed by the sequential and controlled deposition of powder in a layer by layer fashion. In each layer the powder surface is selectively scanned according to the cross-sectional data of a previously created three-dimensional (3D) computer-aided design model. In the scanned regions particle coalescence is associated with a significant reduction in surface energy, which is the main driving force of sintering [1]. SLS has the potential to fabricate complex geometries with intricate and controllable internal architectures, such as that required for tissue scaffolds. Scaffolds are porous 3D matrices with high surface to volume ratios to which cells can attach and on which they can differentiate.

SLS enables the processing of numerous biocompatible polymers available in the form of powders. Some groups were able to directly fabricate bioceramic bone implants using an experimental SLS system [2,3], however, to process bioceramics a thermoplastic polymer functioning as a binder material is usually required, as the lasers used in typical commercial SLS systems are unable to fuse ceramic particles together. Several biocompatible polymers have been used for SLS fabrication of scaffolds, including polyethylene, polyetheretherketone, polycaprolactone, polylactide glycolide, polyvinyl alcohol and their composites with hydroxyapatite and other bioceramics [4–12]. However, much of this research has only demonstrated the feasibility of fusing powder particles together, and not the fabrication of complex predesigned 3D structures. Studies which did produce complex predesigned 3D structures via SLS were those by Williams et al., Zhou et al. and Partee et al. [13–15]. Williams et al. fabricated cylindrical porous scaffolds with a 3D orthogonal periodic architecture using polycaprolactone with a designed pore size of 1.75 mm. Zhou et al. produced 3D scaffolds with rectangular channels using poly(L-lactide) and poly(L-lactide)/carbonated hydroxyapatite (HA) microspheres. Partee et al. optimized selective laser sintering of polycaprolactone scaffolds using a $2^5$ full factorial design. However, in many other investigations of SLS of biodegradable biomaterials for tissue engineering applications the process was examined using a "one at a time" approach to vary process parameters [2–10]. In fact, the mechanical properties and accuracy of specimens obtained from SLS processing are a result of the interactive influences of the different process parameters. When a combination of several independent variables and their interactions affect the measured responses, response surface methodology (RSM) is an effective tool for investigating the manufacturing process [16]. In this technique a least squares model is fitted to the experimental data which relates the output variables

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to the input parameters. The central composite design (CCD) technique is often used to implement the RSM [17]. Adequacy of a proposed model from this analysis can be checked using analysis of variance (ANOVA) and the response surface plots can be employed to study the system relationships and locate the optimum within the range of investigated variables. In the present work a CCD was used to develop models describing the dependence of accuracy and mechanical properties on process parameters in the three principle building directions.

The main parameters that can be changed in a Sinterstation 2500$^{plus}$ SLS system are part bed temperature, layer thickness, laser power (outline and fill) and scan spacing. Of these parameters part bed temperature and layer thickness were not examined in this study. The processing of PCL is sensitive to temperature but temperature control of the SLS system used is not precise enough to examine its effect within the temperature range suitable for the processing of PCL. The applicable layer thickness is largely dependent on the particle size and as the used particle size was in range of the sintering depth, this parameter was not altered. The effect of laser power and scan spacing on the density and mechanical properties of the parts has been extensively examined by others [10,12,18–22]. It is well established that density and mechanical properties increase with delivered energy density up to a certain level, above which a slight reduction is seen. Part density and mechanical properties are thereby directly related to laser fill power and inversely to scan spacing. It is known that the manufactured samples are not isotropic and that part orientation has a great influence on the mechanical properties [20]. However, the effect of these processing parameters on the accuracy of micro-features has been less explored. Furthermore, the established parameter dependencies have not been validated for different manufacturing directions, nor in the context of the mechanical properties of lattice structures. The work presented in this paper quantitatively relates the accuracy and compressive behavior of lattice structures to the process parameters scan spacing, outline laser power and laser fill power. This analysis was examined for the three main manufacturing directions using CCD to explore higher order and interaction effects.

A powder mixture of polycaprolactone (PCL) with 30 wt.% HA was selected for the current experiments. There are conflicting short-term results reported in the literature about the effect of HA addition to PCL composites in terms of cell attachment, proliferation and differentiation. Some authors have discussed how the presence of HA in PCL scaffolds has little or no effect on biological response [20,23–25]. Others showed that scaffolds with 25 wt.% HA demonstrate improved cell differentiation compared with PCL scaffolds [26]. Additionally, it has been shown that up to 30 wt.% HA addition improves the mechanical properties of samples by increasing their compressive modulus [27,28]. Therefore, PCL with 30 wt.% HA was selected for this study.

## 2. Materials and methods

PCL (Sigma Aldrich Chemical Co.) pellets were cryogenically ground and sieved. The powder had an average particle size of 125 μm, with a particle size distribution of 80% of all particles between 70 and 160 μm, as measured with a Malvern Mastersizer particle size analyzer. PCL is a thermoplastic polyester with a melting point of 60 °C and is favorable for SLS processing as it does not decompose below 300 °C [29]. The HA powder used in this experiment was sold under the brand name Captal 60-1 (Plasma Biotal Ltd.) and had an average particle size of 38 μm. A mixture of the PCL and HA powders containing 30 wt.% HA was produced by physical blending and loaded into the feed chambers of the SLS machine.

Test specimens for mechanical testing and accuracy measurements were cubic lattice structures with a relative density of 0.33, strut size of 0.6 mm and pore size length of 1.2 mm. All specimens were designed using SolidWorks® and were exported into STL file format. Fig. 1 shows the designed geometry and the coordinate system used, where layer deposition is in the *z*-direction. In each build three sets of scaffolds were positioned in such a way that either the scaffold *x*, *y* or *z* axis coincided with the build direction in order to explore issues of anisotropy. A DTM Sinterstation 2500$^{plus}$ with a 25 W power, continuous wave $CO_2$ laser focused to a 410 μm spot was used to fabricate the scaffolds. Laser fill power, outline laser power and scan spacing were varied according to the central composite design described below. Laser power is the power at which the fill scan lines are sintered, scan spacing is the distance between two parallel scan lines and outline laser power is the power applied to the contour line of the features (Fig. 2). All other parameters were kept constant: the laser speeds for the outline and fill scans were 1778 and 5080 mm s$^{-1}$, respectively, part bed temperature was 38 °C and layer thickness was set to 0.15 mm. Excess powder was brushed off the exterior and the internal architecture was cleaned using compressed air.

A central composite design was applied with four design factors, namely laser fill power ($X_1$), outline laser power ($X_2$), scan spacing ($X_3$) and manufacturing direction ($X_4$). This design had a core $2^3$ full factorial design, to which the central and axial points were added. The coded levels and the natural values of these factors set in the statistical experiment are shown in Table 1. Six replicates were run at the central point to allow for repeatability analysis and the whole experiment was performed once in the case of mechanical testing and eight times in the case of accuracy analysis. The upper and lower ranges of the process parameters in Table 1 were selected according to the following criteria. When the highest energy density was delivered to the powder bed, i.e. the highest laser fill power of 11.68 W and the smallest scan spacing of 0.1 mm were applied, the powder was visibly strongly melted by the laser beam. In contrast, applying the lowest laser fill power (8.32 W) and the largest scan spacing (0.2 mm) resulted in weakly sintered, fragile structures. As the speed of the outline scan was significantly lower than that of the fill scan, the outline power in the center point of the design space was set to half of the corresponding laser fill power.

The computations were performed with the aid of Design-Expert® software. The corresponding quadratic models for the response functions (accuracy and mechanical properties) were computed using ANOVA. The *P* value was used as a tool to check the significance of the examined variables. A *P* value of less than 0.05 (i.e. 95% confidence interval) indicates that the examined parameter is significant. Insignificant effects were determined as those having *P* values higher than 0.05 and were excluded from the model. Statistics used to determine whether the constructed

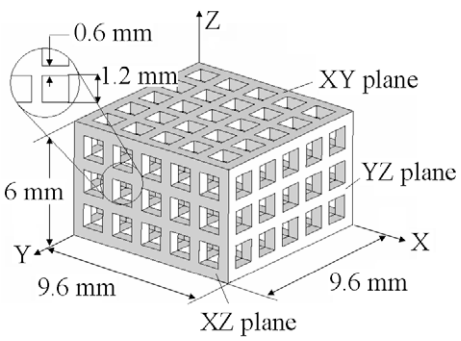


**Fig. 1.** Cubic lattice structure dimensions and the coordinate system used.

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