Novel materials for high-resolution three-dimensional printing using surface-selective laser sintering

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Abstract. A new approach for high-resolution three-dimensional printing using selective laser sintering is proposed. Novel ultrafine powder is synthesized and modified to face the requirements of the laser sintering process. The effect of the powder particle size and shape on the characteristics of the sintered structures is studied.

1. Introduction

Selective laser sintering is one of the most studied and established additive manufacturing (AM) technique based on the fusing of powdered material using laser radiation. This process involves fabrication of a three-dimensional (3D) object within a powder bed, which gradually indexes down as each layer is selectively fused according to a computer-aided design (CAD) model [1].

The only criteria when selecting the polymer material for SLS process is expected to be a powder form. However, the suitable material should also possess certain thermal properties and have absorption bands at the wavelength of the laser used. To overcome these limitations a modification of the conventional SLS – surface selective laser sintering (SSLS) – was proposed [2]. SSLS is based on layer-by-layer sintering of various polymer particles by heating absorbing nanoparticles (carbon or gold nanoparticles) or substances (water, various dyes) uniformly distributed over their surface. That makes fabrication of three-dimensional structures from any polymer particles possible using absorbing agent as a “glue”.

Being a powder bed fusion technique, surface selective laser sintering allows to produce 3D objects of any shape and predetermined complex geometry as there is no need in the support structures during the build. The spatial resolution of the formed structures directly depends on the physical properties of the particles (e.g., particle size, size distribution and shape) as well as the laser radiation parameters (e.g., laser power, laser beam diameter and scan speed) [3].

Nowadays, the most widely used polymers in SLS technology are semi-crystalline thermoplastics, typically polyamides (PAs; nylon) 12 and 11 [4], - more than 95% of the total AM consumption. With the particle size from 40 to 80 µm and, thereby, spatial resolution of 200 µm PA12 meets the requirements of industrial applications. For the purpose of improvement of the spatial resolution of 3D structures significant research is conducted to produce new polymers available for laser sintering process as well as to modify current laser systems.
In this study, a unique combination of two promising approaches is proposed. On the one hand, the use of fundamentally new polymer powders for SLS consisting of micron sized spherical particles with practically monodisperse size distribution. On the other hand, the use of the earlier developed strategy of surface selective laser sintering to achieve a higher spatial resolution of three-dimensional objects formed.

2. Materials and methods

2.1. Materials
Commercially available polyamide (PA12, EOS, Germany) was used as a reference material. Poly(methyl methacrylate) (PMMA) particles were synthesized by the dispersion polymerization in supercritical carbon dioxide (scCO2) as described in [5].

2.2. Experimental setup
Experiments in the formation of the layers and their further laser sintering were carried out on a specially developed setup shown in Fig. 1. The system consisted of a module for layer-by-layer application of ultrafine powders (Fig. 1 “1”) and the module of the scanning focused laser beam (Fig. 1 “2-5”).

Figure 1. Experimental setup for SLS of polymeric powders:
1 – layer formation module;
2 – laser source with a wavelength of 405 nm;
3 – lens;
4 – galvanic scanner with f-theta objective;
5 – PC.

Basic building block of the layer formation module was made of stainless steel and contained two cylindrical chambers with pistons. Every piston was 30 mm in diameter equipped with an individual step drive providing maximum movement of 30 mm with a minimum pitch of 15 μm. The transfer of a new powder layer was carried out by a specialized device equipped with a removable polished hollow shaft (8 mm in diameter) which had a rotative levelling surface for the formation of a uniform and dense powder layer.

The main components of the scanning laser beam module included 405 nm diode laser (Fig. 1 “2”), model MDL-III-405 (Changchun New Industries Optoelectronics Tech. Co., Ltd, P.R. China), with the radiation power range from 10 to 90 mW and commercially available mirror galvanic scanner (Fig. 1 “4”) (LSCan XY, Ateko, Russia) operating in a wide range of wavelengths (from UV to near IR). The laser beam was focused on the surface of the powder with the system of lens (Fig. 1 “3”) and f-theta SL-
266-100-160 objective (Ronar-Smith, Singapore) into a spot with a diameter of about 20 μm (at a level of \(1/e^2\)).

The movement of the pistons as well as the scanning laser beam was controlled with the developed in IPT RAS software installed on a personal computer (Fig. 1 “5”).

2.3. Unsintered powder removal

One of the important and crucial stages of 3D printing of polymer structures by the SSLS method was the final procedure of removing powder particles that were not exposed to laser radiation. In the case of PMMA (the characteristic width of the sintered tracks is less than 100 μm) attempts to simply extract these particles with compressed air (as it is usually done for polyamide) led to the destruction of the resulting structures due to their insufficient mechanical strength.

In order to remove unsintered PMMA particles a method of washing out by processing the formed structures in an ultrasonic bath with a 0.25% aqueous solution of magnesium laureth sulfate (Industria Chimica Panzeri Srl, Italy) was proposed. After that, the samples were washed with distilled water and dried in air at a temperature of 20°C for 24 hours for further analysis.

2.4. Structural analyses

The initial powders as well as the structure of the resulting samples were examined without further processing with a Phenom ProX Scanning Electron Microscope (Phenom, The Netherlands).

3. Results and discussion

The appearance of the polymeric powder used in laser sintering process is presented in Fig. 2.

![Microphotographs of the raw powdered materials: A – polyamide 12, B – poly(methyl methacrylate).](image)

PA12 had a characteristic particle size of 60 - 80 μm whereas the PMMA particles were produced from dispersion polymerization in supercritical carbon dioxide at ca. 3 μm particles. Because of the small size of the PMMA particles static forces predominate and the relatively large specific surface causes particle coagulation and formation of polymer agglomerates with a characteristic size of 20 μm.

To eliminate surface electrostatic effects in ultrafine polymer powder that could affect powder deposition levelling device and pistons of the developed layer formation module were electrically isolated from the rest of the experimental system and were able to be grounded or a constant potential was able to be applied to them in the range of ± 48 V. The resulting thicknesses of the powder layers were 150 μm and 40 μm for PA12 and PMMA, respectively, equivalent to two to three times the
recommended average particle size. This ensures that most particles receive direct contact from the laser rather than relying on particle-to-particle conduction.

For high-resolution laser sintering process the 405 nm diode laser was used as it had a high quality monochromatic laser beam with the characteristic diameter of 20 µm. The fact that both PA12 and PMMA were virtually transparent to the wavelength used requires addition of an absorbent material. To do this we added a small amount of a disperse red dye to provide an absorption band at 405 nm and to carry out the SSLS process. The optimal laser parameters were laser power of 80 mW and scanning speed of 5 and 10 mm/s for PA12 and PMMA, respectively.

Typical structures obtained by the SSLS method from commercial PA12 and ultrafine PMMA powders under the action of continuous laser radiation at a wavelength of 405 nm are presented in Fig.3.

![Figure 3. Formed using surface selective laser sintering method structures from: A – polyamide 12, B – poly(methyl methacrylate).](image)

Typical experimental width of the sintered tracks was 200-300 µm for PA12 powder and 80-90 µm – for PMMA powder which showed the significant improvement of the spatial resolution of the formed structures when using novel poly(methyl methacrylate) microparticles in comparison with commercially available polyamides.

4. Conclusion
Experimental system for forming homogeneous thin layers of ultrafine PMMA powders and their further laser sintering has been developed. Based on the used laser radiation source with the wavelength of 405 nm the optimization of powders optical characteristics has been conducted using a red dye as radiation absorbing agent for the surface selective laser sintering.

Thus, unique powder materials were developed for using in the process of three-dimensional printing based on surface selective laser sintering. There was a significant (almost threefold) increase in spatial resolution of formed polymer structures in comparison with traditional materials used.

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