

INTERACTION OF LASER RADIATION WITH MATTER. LASER PLASMA

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Surface-selective laser sintering of thermolabile polymer particles using water as heating sensitizer

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Abstract. **We report the implementation of a novel scheme for surface-selective laser sintering (SSLS) of polymer particles, based on using water as a sensitizer of laser heating and sintering of particles as well as laser radiation at a wavelength of 1.94 μm, corresponding to the strong absorption band of water. A method of sintering powders of poly(lactide-co-glycolide), a hydrophobic bioresorbable polymer, after modifying its surface with an aqueous solution of hyaluronic acid is developed. The sintering thresholds for wetted polymer are by 3–4 times lower than those for sintering in air. The presence of water restricts the temperature of the heated polymer, preventing its thermal destruction. Polymer matrices with a developed porous structure are obtained. The proposed SSLS method can be applied to produce bioresorbable polymer matrices for tissue engineering.**

Keywords: *surface-selective laser sintering, three-dimensional polymer structures, water, wettability.*

1. Introduction

The selective laser sintering (SLS) [1, 2] is rather efficient in producing three-dimensional structures with prescribed topology within the frameworks of a rapidly progressing branch of modern science and industry knows as 'additive technologies' [3]. The SLS method is based on sintering material particles by their laser heating and melting. The controlled motion of the laser beam allows layer-by-layer construction of an article with the topology prescribed by a computer model using fine-dispersed powder materials, e.g., metals, ceramics, polymers and different composites.

One of the promising applications of the SLS method is the creation of three-dimensional biocompatible structures for various biomedical applications, in particular, in implantology and tissue engineering [4–6]. The method of surface-selective laser sintering (SSLS), developed by us [7, 8], is a version of the SLS aimed at producing biodegrading polymer carrier matrices, necessary for tissue engineering. It is based on sintering polymer particles with the size 50–200 μm by near-IR laser radiation (for which polymers are practically transparent) at the expense of the absorption of radiation by nanoparticles of a sensitizer (carbon or gold), added to the polymer powder in a small amount (mass concentration not greater than 0.1%). In this case, the sensitized heating occurs only in the near-surface zone of the polymer particles, where the absorber (sensitizer) particles are located, and the particles become integrated (sintered).

If the choice of laser irradiation parameters is correct, then the most part of the polymer particle is not heated, thus allowing layer-by-layer synthesis of three-dimensional polymer matrices without essential thermal degradation of the polymer and bioactive compounds, included in it [9]. The SSLS method proposed by us allowed, in particular, the formation of the polylactide carrier matrix aimed at replacing the bone defect. The stem cells were introduced into the matrix, and then the obtained tissue-engineered structure was implanted into the hipbone of a rat (at the position of artificially created bone defect), which in four weeks led to the complete replacement of the matrix with an inherent bone tissue due to regeneration processes [10].

With all advantages of the developed SSLS method, it still requires the use of nanoparticles to sensitize the absorption, and these particles are foreign for the organism. In the present paper, we propose and study a new version of the SSLS method, in which the heating is sensitized by liquid water, strongly absorbing radiation of a thulium fibre laser at a wavelength of 1.94 μm. This laser has recently entered the number of practical laser sources of the near-infrared range, particularly promising for applications in the field of laser medicine [11–13]. With this laser, the possibility of using water for efficient sensitizing of the polymer heating in the SSLS method is due to the presence of a strong absorption band of water near 1.94 μm with the absorption coefficient ~130 cm^{-1} [14].

2. Materials and methods

As a source material for sintering and creation of matrix structures, we used powders of poly(lactide-co-glycolide) (a copolymer of lactic and glycolic acids) (Purasorb PDLG 7502, Purac). To obtain particles of required dispersity (from 50 to 100 μm) the initial PDLG 7502 granules were powdered in a rotor mill and sequentially sifted through the sieves with the mesh size 100 and 50 μm. Initially, poly(lactide-co-glycolide) is hydrophobic and so that to provide its wetting it was hydrophilised by a 1% solution of a low-molecular (M_w = 55 kDa) hyaluronic acid (HA) and dried in air. The layer of the PDLG 7502 powder treated in this way was deposited on a silica substrate, where it was wetted with deionized water

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using an aerograph (BD 180K, Fenghua Bida Machinery Manufacture Co., China). The source of radiation for the SSLS was a fibre laser (LS 1.9, IRE Polus) with a radiation power $W \leqslant 5$ W at a wavelength of 1.94 μm. The silica optical fibre had a diameter 0.6 mm and a numerical aperture 0.22. The optical fibre exit terminated with a focusing sphere having a diameter 1.3 mm.

The filaments sintered from polymer particles (corresponding to the tracks of the laser beam on the surface of the polymer powder) were produced both on the dry and on the wetted powder using different powers of laser radiation. The radiation beam diameter at a distance 1 mm from the edge of the focusing sphere amounted to 0.35 ± 0.05 mm, and the scanning velocity of the laser beam was equal to 1 mm s^{-1}. The obtained structures were studied by optical and scanning electron microscopy using a LEO 1450 microscope (Carl Zeiss).

3. Results and discussion

3.1. Absorption of laser radiation

To determine the absorption coefficient of the polymer used we fabricated a poly(lactide-co-glycolide) PDLG 7502 film with a thickness of 1 mm. The spectrum of its absorption, measured using an Impact 410 IR Fourier spectrometer (Nicolet, USA), is presented in Fig. 1.

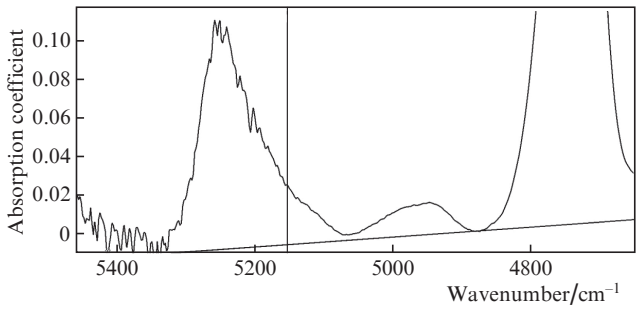

Figure 1. IR absorption spectrum of the PDLG 7502 film. The position of the wavenumber 5155 cm^{-1}, corresponding to $\lambda = 1.94$ μm, is shown by a vertical line. The sloped straight line is the baseline.

The absorption coefficient $k_{1.94}$ measured at a wavelength 1.94 μm amounted to 0.25 ± 0.1 cm^{-1}. By the direct measurement of the transmission coefficient for laser radiation [using a power meter (Coherent, USA) in the same sample of the film], we obtained a close value of the absorption coefficient $k_{1.94} = 0.3 \pm 0.05$ cm^{-1}. Thus, at $\lambda = 1.94$ μm the absorption of radiation by water is nearly by 400 times greater than the absorption by the polymer. In a wetted powder, the presence of water at the surface and between polymer particles almost completely determines the total absorption of laser radiation and, via the heat transfer, provides the sensitized heating of the polymer powder particles. In a dry powder, radiation is absorbed inside polymer particles and heats them. Since the radiation absorption in the polymer at $\lambda = 1.94$ μm is relatively small, the attenuation of the radiation intensity with increasing propagation depth occurs mainly due to the scattering of radiation by powder particles.

3.2. Measurement of the wetting angle

Polylactides and poly(lactide-co-glycolide)s are widely used as biocompatible bioresorbable polymers [15], but their hydrophobic behaviour hampers the primary cell adhesion and complicates the cell growth, at least at the initial stage of the interaction with tissues or cultural media. The modification of these polymers by processing in the solutions of polysaccharides or water-soluble protein biopolymers allows an increase in the surface hydrophilisation degree [16, 17]. To increase the water receptivity, we treated the initial powder of the polymer with a 1% aqueous solution of HA. The microscopic photography images of the source PDLG 7502 powder and the powder processed with the HA solution are presented in Fig. 2. After the treatment, the surface of the particles becomes smoother. Besides that, the polydispersity of the particles increases at the expense of the sedimentation of HA onto the sample surface from the solution in the course of drying.

The degree of wetting was determined by means of a sessile drop technique, i.e., by measuring optically the contact angle on the surface of the sample [18, 19]. Figure 3 presents photographs of drops on the surface of the intact polymer powder and the one treated with the HA solution. The shape of the drop on the intact polymer (Fig. 3a) was almost time-independent. The measured contact angle amounted to 100° ± 8°. On the contrary, the drop on the treated surface completely soaked into the polymer material during the time ~10 s (Figs 3b, c). Thus, a thin layer of HA appearing at the

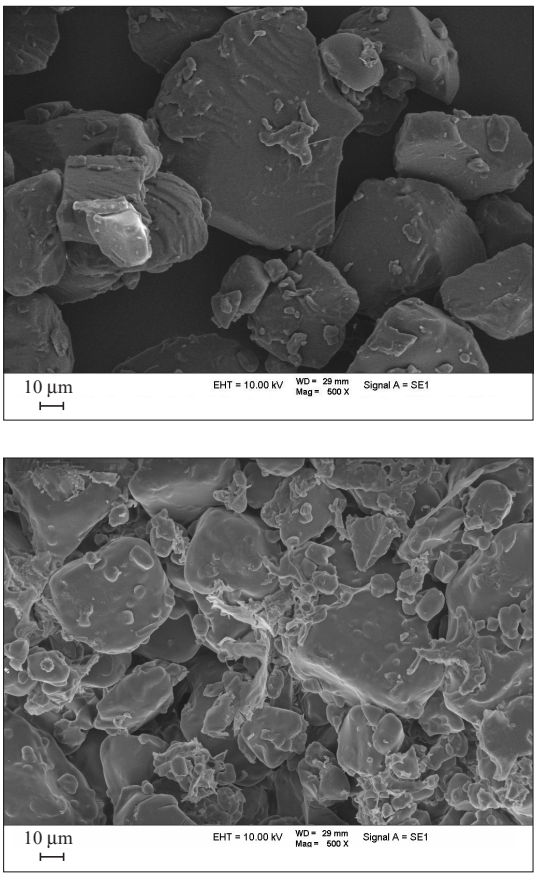

Figure 2. Microphotographs of the source powder of (a) the polymer and (b) the powder treated with the HA solution.

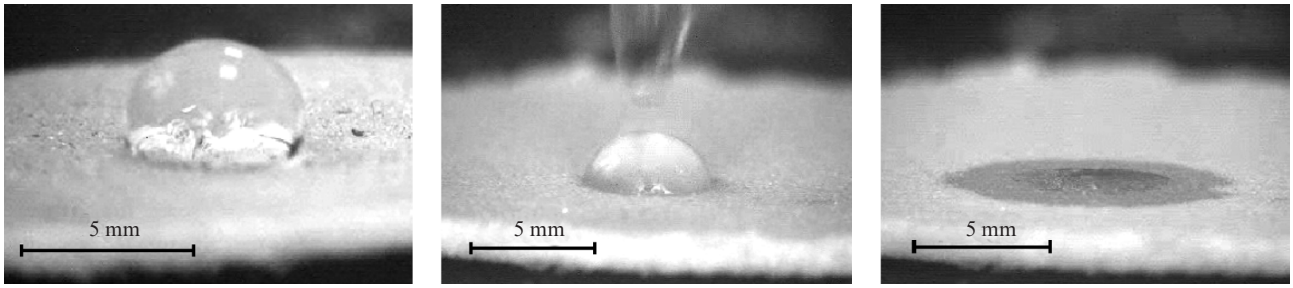

Figure 3. Photographs of water drops (a) on the surface of the intact polymer powder and (b–c) on the powder surface after the treatment of its particles with the HA solution: (b) the moment of drop application and (c) the drop after 10 s.

surface of poly(lactide-co-glycolide) essentially enhanced its hydrophilic behaviour.

3.3. Determination of the sintering threshold

In the course of sintering, the surface of the powder was separated by 1 mm from the edge of the optical waveguide lens. The radiation beam diameter at the surface was equal to 0.35 mm. We defined the threshold of laser sintering as a minimal power of laser radiation W_{thr}, at which the integration of polymer particles occurred, and the polymer filament produced along the laser beam track could be extracted from the surrounding powder without any mechanical destruction. Without the wetting procedure (at the expense of absorption by the polymer itself) the powder sintering threshold amounted to 0.15 W, and after the powder wetting it was 0.05 W.

3.4. Structure of sintered filaments

Figure 4 shows microphotographs of sintered poly(lactide-co-glycolide) filaments, produced along the laser beam tracks on the water-wetted powder surface for different laser powers W, and Figs 5 and 6 show the microphotographs of fragments of these filaments and their cross sections. Similar microphotographs of the polymer filaments and their cross sections are presented in Figs 7 and 8 for the samples obtained by dry powder sintering.

There are essential differences between the structures of the polymer filaments, sintered in dry and wetted powders.

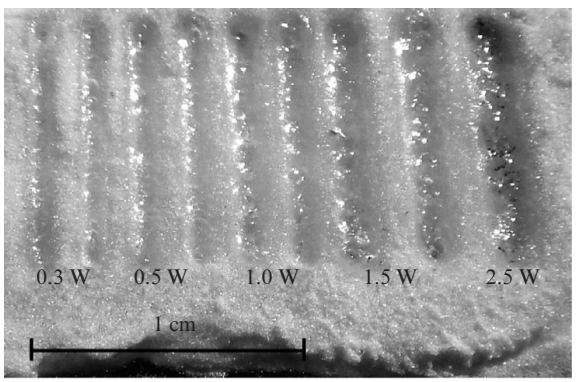

Figure 4. Photograph of polymer filaments sintered in a water-wetted powder at different laser radiation powers. The powder layer thickness is 1 mm.

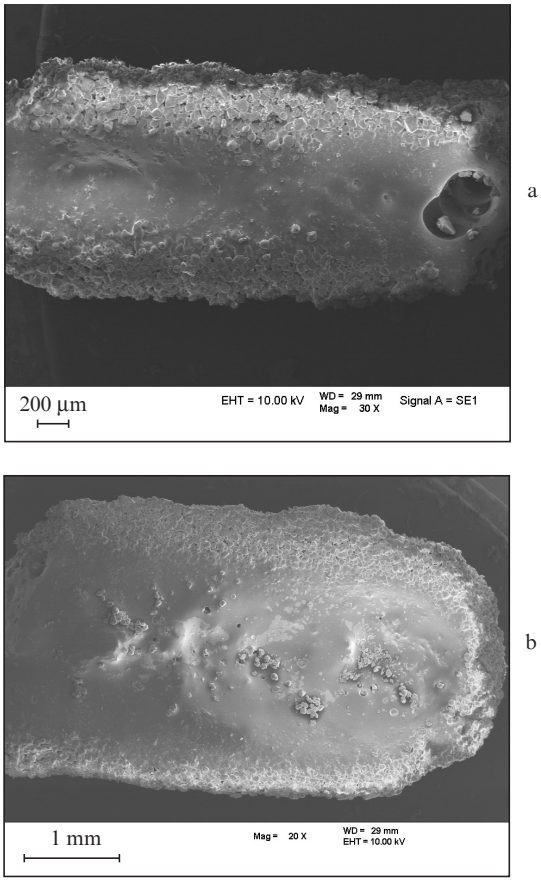

Figure 5. Microphotographs of the fragments of polymer filaments sintered in a polymer powder wetted with water at W = (a) 0.3 and (b) 2.5 W.

The structures, sintered in dry powders, are dense and homogeneous, while the structures, produced in wetted powders, possess pores of different size, from units to tens of micrometres. In the process of sintering without water polymer particles melt due to the absorption of laser radiation, fuse, and take a symmetric oval shape because of the surface tension. In the wetted powder the initial heating and melting occurs due to the absorption of radiation by water, and the numerous pores appear in the sintered structure due to both water evaporation and water 'embedded' inside of the sintered volume. The cross section of a filament, sintered in a wetted powder, is crescent-shaped. This shape is determined by the fact that the most part of the radiation is absorbed in the thin (~0.1 mm) surface layer, and the heating of lower layers of the powder is

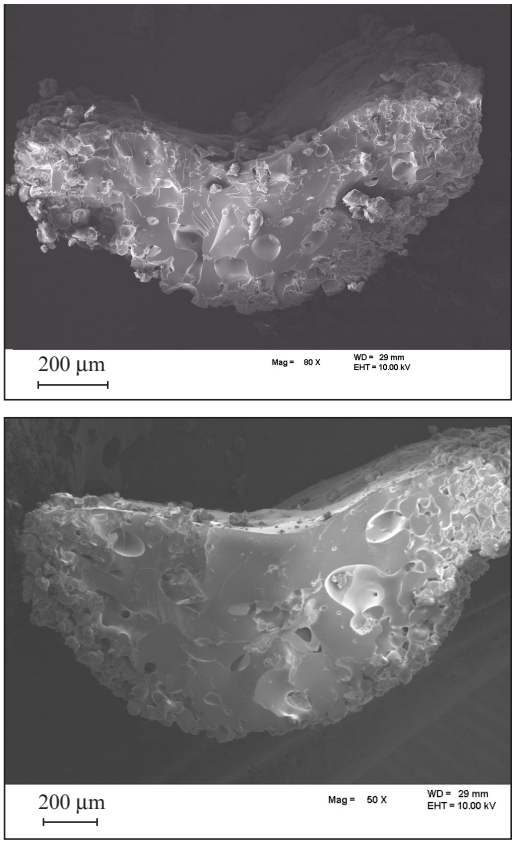

Figure 6. Microphotographs of cross sections of polymer filaments sintered at $W =$ (a) 0.3 and (b) 1.0 W in a polymer powder wetted with water.

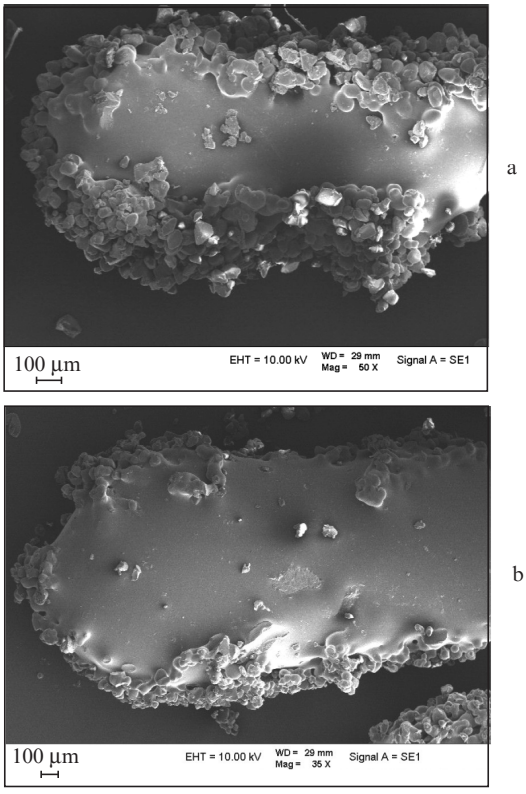

Figure 7. Microphotographs of the fragments of polymer filaments sintered in dry powder at $W =$ (a) 0.4 and (b) 0.8 W.

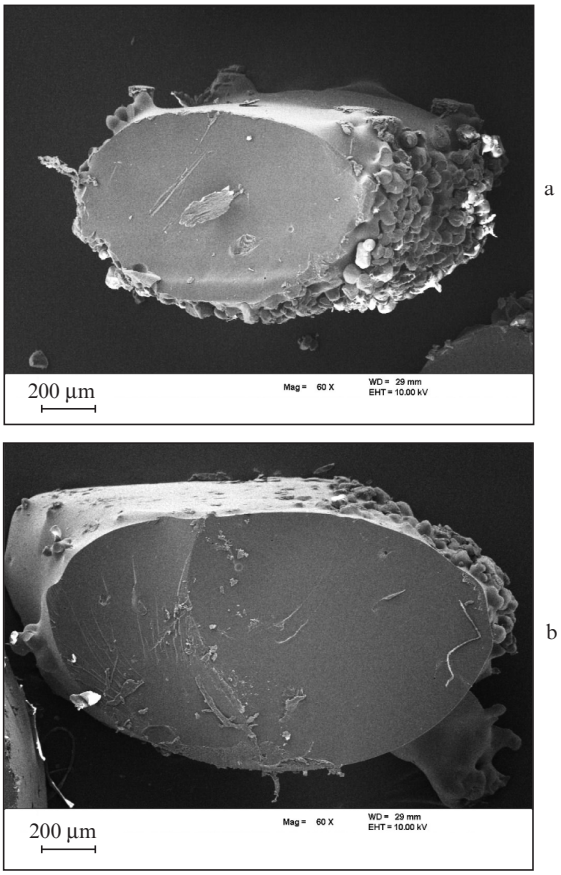

Figure 8. Microphotographs of cross sections of polymer filaments sintered in dry powder at $W =$ (a) 0.4 and (b) 0.8 W.

due to the heat diffusion. In the process of water heating and evaporation, polymer particles are pushed from the maximal intensity zone of the radiation beam to the periphery. This effect is stronger expressed in the sintering of thin powder layers.

Figure 9 presents the filaments formed in the course of laser radiation scanning over the layer of a wetted powder 0.5 mm thick at different radiation powers. Under these conditions the fast heating and water boiling occurs that causes the displacement of the material from the zone of maximal heating. One can also observe the fluctuations of the absorbed energy, caused by the shielding and distortion of the laser beam by water vapours. For the radiation powers, exceeding the threshold values by 2–4 times, the sintered filaments are homogeneous along the entire length of the laser track (Fig. 9, track 1).

The cross sections of the structures, sintered using water, smoothly increase with increasing laser radiation power. Figure 10 presents the measured dependences of the sintering depth (at the cross section centre) and the maximal width of the cross section of the structures on the laser radiation power.

The measurements have shown that the sintering of dry polymer particles yields filaments of smaller width, and the depth of sintering is greater than for wetted particles. For the structures sintered from dry particles, one can observe a sharper decrease in the cross section with decreasing laser radiation power.

The restriction of the polymer heating temperature is an important aspect of using water for the sensitized sintering of

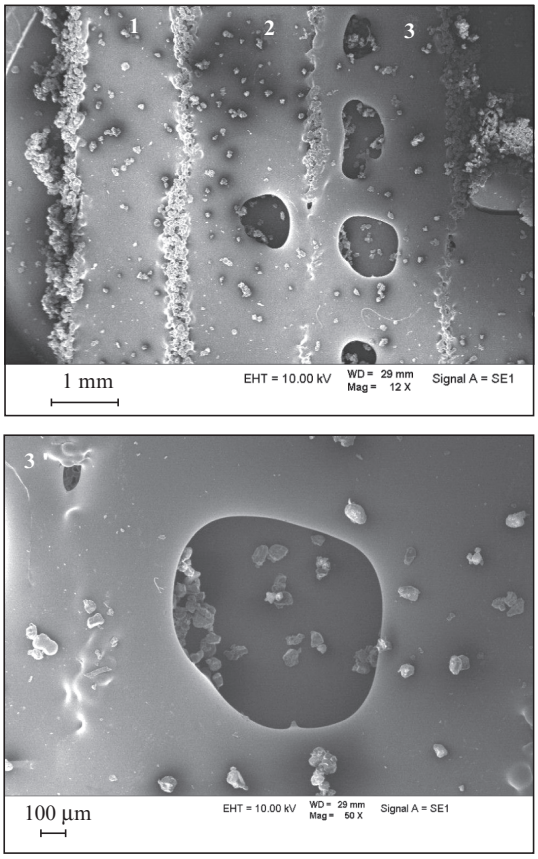

Figure 9. Microphotographs of (a) the structures sintered at a laser beam scanning velocity 1 mm s^{-1} and a radiation power (*1*) 0.5, (*2*) 1.0 and (*3*) 1.5 W (3), and (b) the magnified fragment of the structure sintered at $W = 1.5$ W.

polymer powders in the SSLS method. The wetting of particles with water that has a sufficiently high heat conduction coefficient ($\alpha = 1.5\times10^{-7}$ m^2 s^{-1}) protects the polymer from thermal destruction and formation of toxic components.

The SSLS method is aimed at producing construction matrices for tissue engineering with given shape, porosity and biodegradation rate. Using SSLS one can model the porosity and porous structure scale within wide limits both by controlling the energy parameters of the sintering process and by specifying the trajectory of the laser radiation beam.

Figure 11 presents a photograph of the sample with a cell matrix structure sintered in the powder wetted with water. The separation between the matrix lines was 3 mm. For the laser radiation power $W = 0.8$ W the width of the filaments and the size of the gaps between them were virtually the same and amounted to ~1.5 mm. In the cross section of the sintered matrix, one can observe the increased thickness at the places of filament crossings, since the laser radiation acts on these places twice. In the considered case, the thickness of the powder layer was equal to 1.5 mm and did not restrict the growth of the sintering depth in the course of multiple scanning of radiation over the same points on the layer surface. For thinner layers of powder the sintering depth will be determined by the layer thickness and will not depend on the number of laser radiation passages through the given point of the surface.

Figure 10. Dependence of the cross section width of sintered structures (*1*, *3*) and the sintering depth (*2*, *4*) on the laser radiation power for the sintering in water-wetted polymer powder (*1*, *2*) and in air (*3*, *4*).

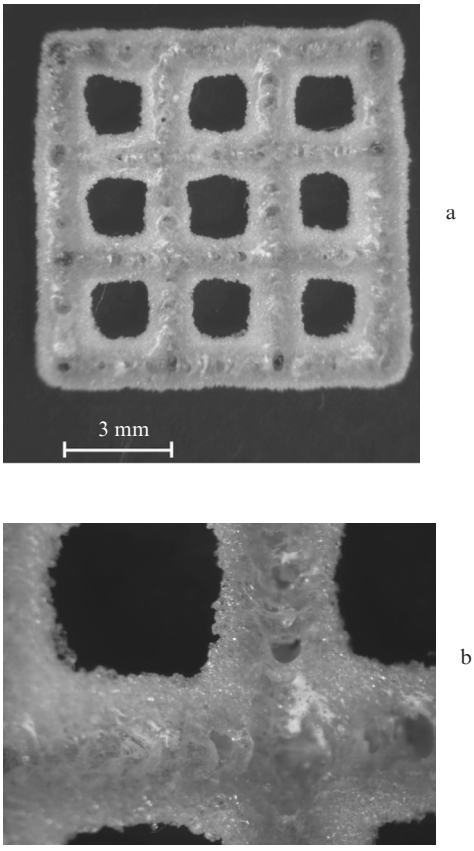

Figure 11. (a) Photograph of the matrix structure sintered in the wetted powder at $W = 0.8$ W and (b) its magnified fragment.

4. Conclusions

Thus, a new scheme for the SSLS of thermolabile polymer particles has been developed based on the use of water as a sensitizer of laser heating and particle sintering. The sintering has been stimulated using a thulium fibre laser with a wavelength of 1.94 μm, corresponding to the strong absorption band of water. The method of sintering the powders of the hydrophobic bioresorbable polymer poly(lactide-co-glycolide) after modifying the surface of its particles with an aqueous solution of HA has been developed. The dependences of the cross sections of filaments, sintered in dry and

wetted poly(lactide-co-glycolide) powders, on the laser radiation power have been obtained. The proposed method can be applied to produce matrices of tissue engineering constructions, including thermolabile materials in their composition.

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References

1. Deckard C. US Patent 4,863,538 (1989).
2. Shishkovskii I.V. *Lazernyi sintez funktsional'nykh mezostruktur i ob'emnykh izdeliy* (Laser Synthesis of Functional Mesostructures and 3D Articles) (Moscow: Fizmatlit, 2009) p. 424.
3. Vershinina E. *Atomnyi Ekspert*, (5-6), 56 (2014).
4. Rimell J.T., Marquis P.M. *J. Biomater. Res., Part B*, **52**, 414 (2000).
5. Tan K.H., Chua C.K., Leong K.F., et al. *Biomaterials*, **24**, 3115 (2003).
6. Coole T., Cruz F., Simoes J., Bocking C. In: *Advanced Research in Virtual and Rapid Prototyping* (London: Taylor and Francis, 2005) p. 147.
7. Popov V.K., Antonov E.N., Bagratashvilli V.N., et al. *Materials Processing for Properties and Performance (MP3)*, **3**, 332 (2004).
8. Antonov E.N., Bagratashvilli V.N., Whitaker M.J., et al. *Adv. Mater*., **17**, 327 (2005).
9. Antonov E.N., Bagratashvili V.N., Howdle S.M., et al. *Laser Phys.*, **16**, 774 (2006).
10. Kanczler J.M., Mirmalek-Sani S.-H., Hanley N.A., et al. *Acta Biomater*., **5**, 2063 (2009).
11. Minaev V.P. *Lazernaya Meditsina*, **16** (3), 57 (2012).
12. Cui D., Sun F., Zhuo J., et al. *World J. Urol.*, **32** (3), 683 (2014).
13. Polder K.D., Harrison A., Eubanks L.E., Bruce S. *Dermatol. Surg*., **37**, 342 (2011).
14. Kou L., Labrie D., Chylek P. *Appl. Opt.*, **32**, 3531 (1993).
15. Shtil'man D.I. *Polimery medico-biologicheskogo naznacheniya* (Polymers of Medical and Biological Purpose) (Moscow: Akademkniga, 2006) p. 400.
16. Tjia J.S., Aneskievich B.J., Moghe P.V. *Biomaterials*, **20**, 2223 (1999).
17. Yoo H.S., Lee E.A., Yoon J.J., Park T.G. *Biomaterials*, **26**, 1925 (2005).
18. Volkov Z.V. *Fiz. Khim*., **13**, 225 (1939).
19. Zisman W.A. *Advances in Chemistry*, **43**, 1 (1964).