INFLUENCE OF FEMTOSECOND LASER PROCESSING PARAMETERS ON THE SURFACE MORPHOLOGY AND WETTABILITY PROPERTIES OF POLYLACTIC ACID

Albena Daskalova*, Liliya Angelova1, Xavier Carette2, Rosica Mincheva3, Jean-Marie Raquez2, Anton Trifonov3, Ivan Buchvarov3
1Institute of Electronics, Bulgarian Academy of Sciences, Sofia, Bulgaria
2Laboratory of Polymeric and Composite Materials (LPCM), University of Mons, Place du Parc, 23, B-7000, Mons, Belgium
3Faculty of Physics, St. Kliment Ohridski University of Sofia, Sofia, Bulgaria
*e-mail: albdaskalova@gmail.com

Abstract. Polylactic acid (PLA) is a very attractive material for applications in the field of regenerative medicine and tissue engineering, as it is a biocompatible and biodegradable synthetic polymer, whose morphological properties can be finely tuned via laser processing. Ultra-short pulse laser treatment is a non-invasive method for optimizing the surface properties of engineered biomaterials. The method offers controlled porosity of the treated biomaterial tailored specifically for implantation needs. In this research, we investigated the interaction of femtosecond laser radiation with PLA stacks while varying the output laser parameters in order to estimate their influence on the morphology of the PLA samples. The induced microstructural features were characterized by thickness measurements and SEM, EDX and FTIR analyses. In order to evaluate the hydrophilicity of the treated surface, water contact angle (WCA), measurements were also performed. Topography modification of the PLA substrates could essentially improve this material’s bioactivity properties, which, after proper optimization of the laser parameters, could make its biomedical applications even more successful.

1. Introduction
Regenerative medicine and, in particular, tissue engineering represent the basis of today’s and tomorrow’s medicine [1,2]. In this field, the polylactic acid (PLA) is a very attractive newly emerging material with the potential to become a basic one, as it is an easily produced biocompatible and biodegradable polymer, whose morphological qualities can be further improved [3,4]. In their exhaustive review, Khoddami et al. [5] explained in detail all the advantages of PLA as a promising material for bone tissue engineering – PLA interacts well very easily with the host bone cells when it is implanted [6,7]. This fact makes it an ideal candidate for contact surface material between the natural bone and the external implant and for a bone scaffold substrate, as the ideal engineered matrix should be composed of biomaterials that closely mimic the structure and qualities of natural bone extracellular matrix [8,9]. The mechanical properties of PLA are similar to those of bone tissues and, what is more, it is amenable to processing and degrades into natural metabolites, which makes it nontoxic for the organism [10]. Ultra-short pulse laser treatment is a non-invasive method that perfectly fits into the idea of optimizing the surface properties of cell-engineered matrices, as it can offer strictly controlled porosity of the treated biomaterial tailored specifically for implantation, without adding unnatural physical or chemical components to the scaffold created. This topography-reforming biocompatible technique successfully overcomes the limitations associated with the application of other physical and chemical methods since the side effects caused by the interaction of fs laser pulses with biological tissues are minimized. Moreover, ultra-short pulse laser treatment provides a porous cell scaffold, with precisely varied dimensions of the created interconnected pores (1 ÷ 500 μm), providing diffusion of oxygen and nutrients, as well as cell viability, adhesion, movement and tissue ingrowth into the engineered ECM [11,12].

The main goal of this study is to acquire initial knowledge of the porosity and morphology of PLA samples after ultra-fast laser modification in view of future design and preparation of porous PLA-based cell matrices, which could form the basis for creating effective bio-interfaces between the tissues of the recipient and the foreign implant. For this purpose, fs modified microstructured polymer
scaffolds were investigated by SEM, EDX and FTIR. Wettability measurements of treated and non-treated surfaces were performed. The thicknesses of the samples before and after the ultra-fast laser modification were also compared.

2. Material and methods

2.1. Sample preparation
The PLA is supplied by Nature Works (PLA 4060D) and is amorphous with a $T_g$ of around 60 °C. PLA pellets were prepared via heat compression molding using a Carver 4122 12-12H manual heated press. The pellets were first vacuum-dried overnight at 60 °C, then inserted in the mold (a 0.5-mm thick square). The following compression procedure was used: at 180 °C, 3 min of contact, several steps of degassing, and 2 min at 12 bar. The material was cut into 4×4 cm² squares.

2.2. Laser treatment
The femtosecond ($\tau = 150$ fs) laser modification of the prepared PLA samples was performed by a Quantronix-Integra-C Ti:sapphire laser system oscillating at a central wavelength of $\lambda = 800$ nm and 0.5-kHz repetition rate. The applied energy and number of laser pulses were varied as follows: $F = 0.42$ J/cm² and 0.34 J/cm²; $N = 2, 10, and 30$. The experiments were performed in air and the setup was controlled by LabView software. The sample was positioned normally to the laser beam on a high-precision XY translation stage and processed by scanning the laser beam over the material’s surface at precisely defined separation intervals in order to optimize the PLA surface texturing.

2.3. Thickness measurement
The thickness of the tested samples was measured before and after the laser treatment to determine the penetration depth of the fs pulses applied. For this purpose, a coating meter (coating thickness gauge VA 8042) was used, with every value quoted representing the average of 10 separate measurements.

2.4. SEM-EDX analysis
The surface morphology and elemental composition before and after the fs laser treatment were analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) (TESCAN/LYRA/XMU, respectively). The samples were gold-sputtered and several images were taken for every modification investigated. The corresponding elemental composition [wt. %] was also defined.

2.5. WCA evaluation
Water contact angle evaluation of the control and fs-modified PLA was performed at room temperature by a homemade installation in air – 1 μl dH₂O drop was applied on the samples surface and images were taken every 0.5 s for 9 s. The contact angles were measured using the ImageJ software. All contact angle values were averaged according to the patterning type.

2.6. FTIR analysis
A Fourier-transform infrared (FTIR) spectrophotometer (IR Affinity-1, Shimadzu, Kyoto, Japan), working in the range from 4500 cm⁻¹ to 500 cm⁻¹ was used to obtain the IR transmittance spectra [%] of the prepared probes to evaluate the chemical bonds alterations after laser treatment relative to the control sample surface.

3. Results and discussion
The surface morphology of the PLA sheets after femtosecond irradiation at different fluences and multiple number of laser pulses is presented below. Figure 1 shows representative SEM images and the corresponding EDX elemental composition [wt. %] of a control PLA sheet and PLA sheets patterned by $N=2, 10, and 30$ fs pulses and laser fluence $F = 0.34$ J/cm² and 0.42 J/cm².
Comparing panels (a) and (b) of Figure 1 one can easily see that the laser-processed PLA samples exhibit a microporous granular morphology for all parameters of fs modification.

After processing by $N = 2$ at $F = 0.34 \text{ J/cm}^2$, adhesion of raised spatters around the sides of interaction zone is seen. Increasing $F$ from 0.34 J/cm$^2$ to 0.42 J/cm$^2$ results in smoother zones, while increasing the number of applied laser pulses from 10 to 30 leads to the formation of through holes. Using either value of $F$ and the highest number of laser pulses initiates the creation of self-formed complex frameworks. The microstructures generated when using a large number of pulses exhibit a periodicity. This result could have positive effect on cells’ behavior, as the modification affects the scaffold morphology in depth and thus provides a greater porosity in the volume. The slight variation in the $[C]$ and $[O]$ [wt. %] with changing $N$ and $F$ of the fs pulses could be explained with the breakage of weak chemical bonds, which does not affect the elemental composition of the samples, as no elements uncommon for PLA are observed in the EDX data, Figure 1(c). In this way, the ultra-fast laser processing provides precise control of the shape and the size of the hierarchically connected pores without affecting the chemical composition of the biomaterial in order to further resemble the natural cellular environment. The results from the WCA measurements show that the material changes its wettability properties. The WCA values of the control sample was measured to be $\theta = 74^\circ$. 

**Figure 1.** SEM images of PLA matrices (a) patterned with $N = 2, 10, 30$ and $F = 0.42 \text{ J/cm}^2$ (first row) and $F = 0.34 \text{ J/cm}^2$ (second row); (b) control PLA surface; (c) EDX elemental composition [wt. %] of the corresponding samples.
Increasing the number of laser pulses to \( N = 2 \) for both laser fluences applied reduces the average contact angle. When using a large number of pulses to modify the material, the initial WCA values are the highest in the first second compared to the WCA obtained from patterns acquired with fewer \( N \); this corresponds to a morphology having a micro-scale hierarchical structure, Figure 2 (a and b). The microstructures on the processed PLA surface obtained under irradiation with multiple pulses have a decreased thickness (Table 1); thus, when the water droplet bounds to the surface, it undergoes heterogeneous wetting. Due to the increased surface roughness, vapor pockets may be trapped underneath the liquid. This heterogeneous wetting is usually described by the Cassie-Baxter (CB) model, which is proved by the values obtained for WCA for \( N = 30 \).

In this way, the functionality of the cells implant may be further improved, as control over cells adhesion and movement could be achieved. Apart of that, hydrophilic grooved biomaterials have improved surface qualities, making them a preferable choice for covering traditional long-lasting bone implants.

![Figure 2](image)

**Figure 2.** WCA evaluation of fs-modified PLA samples (a, b) and image of the water droplet on the surface of fs-modified PLA, \( N = 10, F = 0.34 \text{ J/cm}^2 \) after 0.5 s (c) and 5 s (d).

The thickness of the tested samples before and after laser treatment is quoted in Table 1. As can be seen, the thickness of the laser modified surface areas decreases as the number of applied laser pulses is increased. This finding is in agreement with the morphological examinations and is due to a melting of the solid polymer matrix and severe ablation leading to formation of wells and islands with conical-like shape when the surface temperature suddenly increased during the ablation. The partially melted phase is followed by resolidification, which affects the processed region thickness in the case of high laser fluence values (\( F = 0.42 \text{ J/cm}^2 \)).

| PLA | Thicknesses [\( \mu \text{m} \)] | PLA | Thickness [\( \mu \text{m} \)] |
|-----|----------------------------------|-----|--------------------------------|
| Control | 501 | Control | 501 |
| \( N = 2, F = 0.42 \text{ J/cm}^2 \) | 491 | \( N = 2, F = 0.34 \text{ J/cm}^2 \) | 472 |
| \( N = 10, F = 0.42 \text{ J/cm}^2 \) | 486 | \( N = 10, F = 0.34 \text{ J/cm}^2 \) | 459 |
| \( N = 30, F = 0.42 \text{ J/cm}^2 \) | 479 | \( N = 30, F = 0.34 \text{ J/cm}^2 \) | 448 |
Table 1. PLA samples thickness measurement before and after fs modification with different fluence and number of pulses applied.

The FTIR spectroscopy results (Figure 3) after fs laser treatment compared with the untreated PLA [13] confirm the lack of changes in the chemical composition of the samples. The shapes of the spectra from the processed PLA areas for both fluences and different number of applied laser pulses do not show discrepancies, the only difference being the intensity of the peaks. The regions of interest are visible in all spectra of the fs-modified PLA. The maximum at 3600–4000 cm\(^{-1}\) characteristic for the PLA corresponds to O–H bond stretching. The peaks detected at 1750 cm\(^{-1}\) and 1180 cm\(^{-1}\) correspond to the C=O stretching and the C–O–C stretching of PLA. They are clearly visible in all PLA spectra. The band at 1780 cm\(^{-1}\) is attributed to stretching of the C=O bond. The carbonyl peak at 1650 cm\(^{-1}\) is also well defined.

![FTIR spectra of PLA matrices after fs laser irradiation.](image)

Figure 3. FTIR spectra of PLA matrices after fs laser irradiation.

4. Conclusion

Formation of a smooth surface is observed on the PLA surface when the least number of irradiating pulses is used. The generation of micro-scale hierarchical structures due to the emission of gas-phase products when the number of laser pulses is drastically increased lead to configurations of self-formed periodical structures. The results obtained confirm that fs laser irradiation is a promising surface processing technique for future design of porous PLA-based cell matrices, which could be the basis for creating effective scaffolds. The modification of the PLA substrates topography could essentially improve the bioactivity properties of this material, which, after a proper optimization of the laser parameters, could make its biomedical applications even more successful.

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