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THE EFFECT OF FEMTOSECOND LASER PULSE IRRADIATION ON THE PROPERTIES OF ADVANCED MEDICAL GRADE PDMS POLYMER

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Abstract

The study investigates the effect of the femtosecond laser pulse irradiation on the modification and activation effects of medical-grade polydimethylsiloxane (PDMS) polymer. The motivation of the research is based on the continuous interest and variety of applications of the PDMS material in medicine and implantable neural interface devices. The PDMS is the preferred material due to its exceptional properties such as high biocompatibility and biostability, mechanical flexibility and stability, optical transparency from UV to near IR spectral region, and cost-effectiveness. The experimental investigation is performed by a femtosecond laser system with a pulse duration of 35 fs operating at a repetition rate of 1 kHz. Consistent sets of measurements are performed to analyze and characterize the effect of the laser beam parameters on the optical absorption, and surface morphology concerning the laser-treated zones. The morphology and the optical properties of the PDMS are investigated to activate its surface for successful metallization of the modified tracks. The reported findings and observations specify favourable results of the implementation of the ultrafast laser-based method for micro- or nano-processing of optically transparent biopolymers for interface devices in bioengineering technologies such as neural implants and interface applications.

Key words: femtosecond laser, ablation, PDMS, surface modification

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1. Introduction. Polymers are continuously sustaining their modern accent in almost all industrial, technological and biotechnological applications, e.g., semiconductor manufacturing and coatings, aircraft construction, waveguides, storage devices, optoelectronic devices in biomedicine, bioengineering, and biotechnology. Furthermore, extending their application to several new and high-technology environmental and industrial areas as engineering neural tissue from stem cells, a new generation of fibres, sensors, and biosensors [1–4]. The main reasons to be preferred materials are their resource efficiency and energy saving, easy and reliable processing capabilities for diverse styling, design, and property modifications. However, one should keep in mind that despite the excellent bulk physical and chemical properties, some of their properties such as low surface energy, hydrophobicity, and high electrical resistance, could cause limits to their applications, e.g., in nanotechnology and biotechnology. Among the enormous variety of polymer types nowadays, the PDMS is one of the high-performance polymers with its unique and desirable properties among them the ease of fabrication, cost-effectiveness, unique physical and chemical properties, tunable hardness, and optical transparency. The development of Neural prostheses and Hybrid Bionic Systems that link the human nervous system with electronic or robotic prostheses in recent years is used to restore the motor and sensory functions in disabled people and improve and facilitate human life. The medical grade PDMS is chosen as μ-channelled insulator carrier, among other polymers that can alleviate this issue because of its remarkable properties such as flexibility, chemical stability, good dielectric characteristics, and biocompatibility, suitable for long-term implantation with minimal tissue disruption. Furthermore, the PDMS become a preferred choice for fundamental studies in biology, physics, chemistry, and medicine, with various applications in neural implants and interface devices. This great diversity of applications of the medical grade PDMS requires surface modification to change its morphology and chemical composition, and thus functionalize the surface in the desired manner. Significant effort has been devoted to modifying PDMS through different methods going from physical to chemical changes. The surface modification methods include, e.g., plasma treatment, sol-gel strategies, chemical vapour deposition, protein absorption, grafting, coating, etc. [1,5–10]. The research investigations are focused on studying the processes of interaction and the material response to a certain method of treatment and corresponding application. Ultrafast laser processing is another extremely advanced method for direct and selective surface modification and functionalization of the PDMS surface and has become one of the most preferred. The ultrafast laser treatment could be further utilized to facilitate selective metalization of the activated areas [11]. The method is distinguished by its precise control of process parameters, absence of thermal effects relative simplicity, and flexibility compared to other conventional methods. The interaction of laser radiation with the material, regarding the material properties and laser beam parameters, can be easily predicted and optimized to

obtain an irreversible change in the surface properties (e.g., surface topography, crystalline structure, chemical composition, polymerization) and to increase its efficiency given the desired functionality.

It is of great importance the in-sign of the effect of the laser process parameters to be achieved precise control, significant miniaturization of the modification zones, reproducibility, and stability. Generally speaking, laser treatment is mainly based on the process in the ablation regime, where the reaction of the laser energy with the material results in a removal of the material above a certain threshold of laser fluency. This threshold depends simultaneously on the properties of the material and the laser beam parameters (e.g., wavelength and pulse duration). Thus, the knowledge regarding the processes that occur during and after irradiation with the laser pulses allows us to predict and therefore control the physical and chemical properties in the area of treatment following the specific application.

The present study concerns research of medical-grade PDMS polymer irradiated by femtosecond laser pulses for processing and selective surface functionalization to ensure further selective metalization of the activated zones. The effect of the laser processing parameters is investigated. The results of the formed ablation processed craters and channels, and their specific micro or nanostructured morphology are discussed.

The article is organized as follows. The Introduction section is followed by Section 2 presenting the used material, methods, and setup configuration. In Section 3 results and discussion are provided. The concluding remarks are given in Section 4.

2. Experimental settings and configuration. *Experimental setup.* The configuration of the experimental setup includes as the main part a femtosecond laser system (Spectra-Physics) and a further equipped periphery, including optical and optomechanical elements, as shown in Fig. 1. The femtosecond laser system consists of several units – an amplifier, a pumping laser, and an oscillator. The laser system is additionally equipped with an optical parametric amplifier. The Ti: Sapphire regenerative amplifier generates a pulse with a duration of $\sim$ 35 fs, a maximum pulse energy of $\sim$ 6 mJ, and operates at a 1-kHz repetition

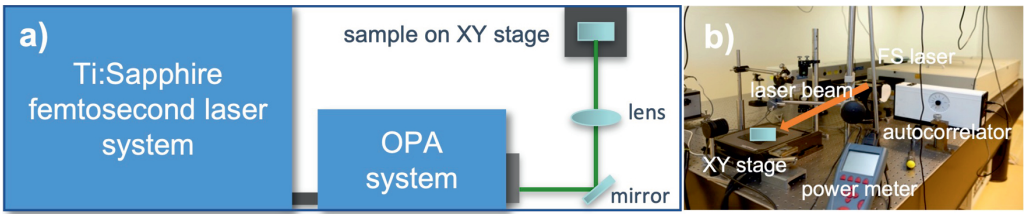


Fig. 1. Experimental setup: a) schematic representation of the experimental configuration; b) the included main periphery (e.g., planar XY stage, power meter, autocorrelator) performed during the experimental work and an arrow indication of the laser beam direction concerning the sample position

rate. The central wavelength of the laser system is 800 nm, while the optical parametric amplifying unit can generate pulses in a wavelength range from 240 nm to 2600 nm. The femtosecond laser is further equipped with a high-precision translation XY stage (Aerotech, Two-Axis Motor Stage), a power meter (Ophyr, Nova II), which covers a range of 300–1100 nm wavelengths, and 20 µJ–10 J impulse energies and optical and optomechanical elements. The laser beam is guided via ultrafast dielectric mirrors and focused on the sample surface by an achromatic lens with a focal length of 200 mm. The periphery equipment is used to perform experimental analyses and measurements as follows: (i) An autocorrelator system (GRENOUILLE model 8-20-USB) is used to control and monitor the main output parameters of the fs laser; (ii) A laser-beam profiler (Spiricon, Laser Beam Analyzer) is applied to analyze the laser beam distribution and measure and control the size of the beam; (iii) The PDMS samples are positioned on the XY planar stage to ensure smooth and precise translation of the sample through the laser beam focus. The moving speed of the XY planar stage is related to the number of pulses needed to achieve ablation at a unit area and laser repetition rate; (iv) The energy control is performed via the power meter and neutral energy filter.

Materials and methods. In this study a medical-grade polydimethylsiloxane (PDMS) type MED 4860, NUSil biopolymer films are used. The side size dimensions of the samples are in the range of 10×20 mm, where the thickness of the thin film samples is measured to be between 80 and 200 µm deposited on glass substrates. The PDMS samples are cleaned with ethanol solution, distilled water, and air stream drying before each laser treatment. The PDMS polymer, under investigation, is optically transparent in the UV-VIS-NIR spectral range. The medical grade PDMS polymer films are irradiated with wavelengths at 266 and 532 nm with 35 fs pulse duration and repetition rate of 1 kHz in an air environment. The laser parameters such as the number of laser pulses and laser energy are varied in a wide range of values.

The characterization and analyses of the laser-processed areas of the PDMS samples are performed by different analytical techniques including optical spectroscopy (Ocean Optics spectrophotometer) for measurements of the optical transmission in the near ultraviolet (UV), visible (VIS), and near-infrared (NIR) range of the spectra, optical microscopy (Zeiss Opton) for monitoring the visible permanent modifications of the surface and observation of the ablation depth, and scanning electron microscope (SEM) for the assessment of the laser tracks and surface morphology. After the laser treatment, the samples are further metalized with noble metal Pt by the electroless deposition technique (autocatalytic bath). The electroless plating process is based on a hydrazine hydrate reducer at an optimal concentration determined empirically. For more detailed information refer to our previous work [12].

3. Results. The native medical grade silicones as the PDMS is known that possess optically transparent properties from the near UV up to the NIR region

of the spectra. Consequently, the laser treatment of such materials is possible because of the effect of the incubation process attributed to increasing optical absorption due to the accumulation of laser energy caused by existing damages or defects below the surface. The incubation in the polymers is a result of the chemical transformations that occurred in the local laser-treated zone without consequent change to the bulk material properties. These modifications depend on the wavelength and the applied laser energy and appear after a certain number of pulses. On the other hand, this means that at a given wavelength and laser energy, the absorption increases during the laser irradiation with the initial incident pulses, i.e. a certain number of pulses is needed to be accumulated local chemical transformations and to reach the ablation conditions [13].

The investigated medical grade PDMS samples are modified employing lasers ablation in air through harmonics at 266 nm, and 532 nm of a 35 fs Ti: Sapphire laser. The PDMS is irradiated and modified under a variety of laser conditions, including different numbers of pulses, laser energy, and wavelengths. The main results of the laser processing findings presented in this work are performed mainly at wavelengths of 266 nm and 532 nm. The number of applied laser pulses is varied from 300 to 30 000. To achieve the ablation threshold and activate surface modification, the applied laser energy is found to be higher than 6 µJ at 266 nm wavelength and higher than 15 µJ for the case of 532 nm.

The study of the optical properties and morphology of PDMS samples irradiated at 266 nm has been recently published in our previous works [12,14]. It is demonstrated that with the increase of the laser pulse number the incubation occurs in the entire laser-treated area. Consequently, this leads to increased optical absorption and thus saturation of the incubation process. As a result it is found that the laser ablation starts efficiently. Optical microscope image analyses show treated PDMS sample at conditions of a wavelength of 532 nm, that the ablation depth is measured and is found that the incubation occurs with increasing absorption during the laser irradiation with an initial number of pulses higher than 800. It is found that in the case of laser treatment at wavelengths of 266 nm the initial number of pulses for effective ablation is higher than 300.

Measurements from an optical microscope are applied to investigate the visible permanent modifications of the surface and observation of the ablation depth, see Fig. 2. The presented treated samples correspond to laser treatment at a wavelength of 266 nm and laser energy at 6 µJ. The number of pulses is varied from 300 to 30 000. The measurements are obtained from the surface of the samples. The presented examples in Fig. 2 are for cases of laser pulse numbers of $N = 1000$, $N = 5000$, and $N = 30\,000$. It can be seen that no evidence of deposition of ejected material and heat-affected zone is observed near the ablation areas. The produced tracks are free of debris and with uniform nanostructured relief. The tracks formed in the number pulse range from 1000 to 5000 demonstrate profiles with regular contours and wide-opened symmetric shapes are formed as can be

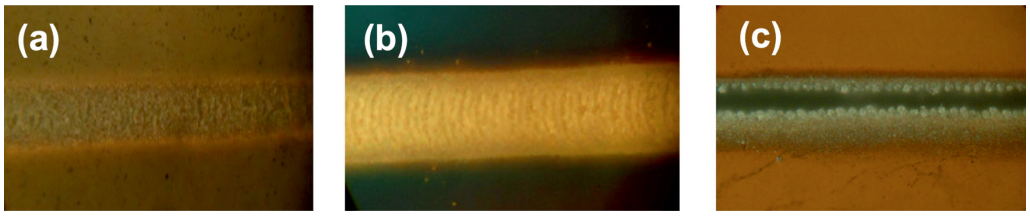


Fig. 2. Images from an optical microscope for treated PDMS samples with 266 nm generated wavelength and energy of 6 µJ. The number of pulses N is varied as follows: (a) $N = 1000$, (b) $N = 5000$, and (c) $N = 30\,000$ pulses

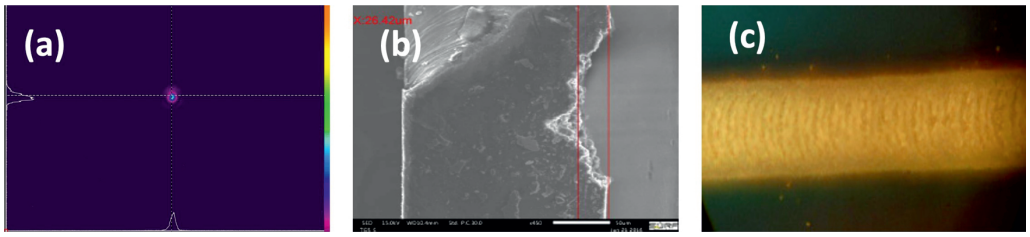


Fig. 3. PDMS irradiated at 266 nm with an energy of 6 µJ. (a) an image of a laser beam profile measured with a laser beam profiler; (b) SEM image of the sample demonstrating the shape of the produced profile at $N = 5000$; (c) linear profile along the laser propagation of the produced laser trace

seen from the examples given in Fig. 2 (a) and (b) and Fig. 3 (b). The case of Fig. 2 (c) shows a deeper trace due to the much higher energy deposited into the sample. On the side of the track could be observed the surface wave structured relief due to the overlapping laser pulses during the movement of the translation stage. The ablation at a lower number of pulses than 1000 is not efficient and the laser tracks obtained are not continuous along their longitudinal direction and lose their linear contours.

The case of the PDMS sample treated at pulse numbers $N = 5000$, at a wavelength of 266 nm, and laser energy at 6 µJ is shown in Fig. 3.

The measurements represent the laser beam profile, the morphological structure, and the laser-modified track. Figure 3 shows as follows: (a) the laser beam distribution and profile determined by the laser beam profile; (b) represents an SEM image of the sample demonstrating the wide-open symmetric shape of the produced profile; (c) the laser track of the sample along the laser propagation direction.

To perform and ensure uniform nanostructured laser traces is of great importance that the laser beam distribution is stable and preserves its Gaussian profile during the laser irradiation. Consistent and systematic analyses of the profile shape and stability of the laser beam are done for each sample under investigation.

The laser size spot is determined under each changed condition concerning the applied energy, number of pulses, and wavelengths. The beam preserves its

Gaussian profile and stability under the range of pulses from 1000 to 30 000. The spot size is measured to be $d = 30$ µm for $N = 1000$ pulses, and $d = 50$ µm for $N = 30\,000$ pulses and is measured to be the same for all performed measurements.

The samples are firstly modified by the laser treatment at different laser parameters, secondly analyzed by optical transmission and SEM analysis followed by the third step. Thus, preparing for metallization. Figure 4 represents an example of traces on the PDMS surface produced by the fs-laser processing at a wavelength of 266 nm irradiated at a wavelength of 266 and different numbers of pulses corresponding to (a) $N = 5000$, (b) $N = 10\,000$, and $N = 30\,000$. A selective metallization is performed without the application of masks or external templates. It demonstrates that a good quality and uniform coating deposition of Pt could be achieved. The metallization occurs on all the samples, although not with the same quality, the cracks in the case of (c) are visible. Several sets of new laser treatments have been performed to investigate the reason for the not reproducible uniform metallization process. The laser parameters have been varied in terms of laser energy, the number of pulses, and wavelengths. Up to now, no clear evidence for the relation between the laser parameters and the metallization step are observed. One of the authors' suggestions is that the used metallization protocol should be revised along with applied laser parameters, mainly the number of laser pulses and laser energy. It is important to note that the process of electroless metallization is an extremely sensitive method (e.g., chemical proportions in the solution, and temperature range). However, the importance here is that the applied femtosecond treatment demonstrates successful modification and activation of the PDMS surface. The functionalization of medical grade PDMS to facilitate the metallization process is observed and presented in this and previous works [13–15]. Apart from the concerns mentioned above, the femtosecond laser treatment is followed in most cases by a successful electroless deposition of Pt in the tracks, excluding sensitization by Sn and chemical activation by Pd usually preceding this process. In that manner, selective metallization is achieved without the use of masks or external templates. It is confirmed, as suggested by [16] that the time interval between laser treatment and metallization is not a critical process parameter to be considered.

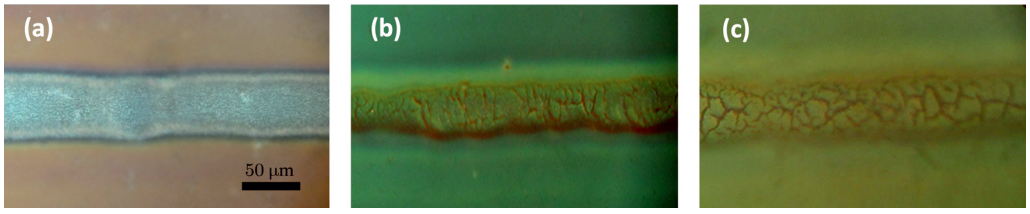


Fig. 4. Optical microscope images of the achieved PDMS tracks at a wavelength of 266 nm and a number of pulses (a) $N = 5000$; (b) $N = 10\,000$, and (c) $N = 30\,000$

4. Conclusions. This work reports results from investigating the effect of the femtosecond laser pulse irradiation on the modification and activation of the surface of a medical grade PDMS polymer in the UV and VIS range of the spectra. The high transparency of the PDMS is observed in the investigated spectral range from 266 nm to 532 nm. Consistent and systematic observations and analyses are performed to collect information on the effect of the laser beam stability and profile during the treatments. The optical absorption and the saturation caused by the incubation process concerning the change in the number of applied pulses, wavelengths, and laser energy are investigated. The study of the incubation process delivers a better understanding of the processes of femtosecond irradiation on PDMS surface and that significantly contributes to the increase of the efficiency of laser ablation, based on the influence of the laser parameters. The incubation occurs with increasing absorption during the laser irradiation with different numbers of initial pulses at a given wavelength. The efficient ablation of the PDMS polymer starts after the incubation occurred and ablation depth is defined at UV and VIS laser treatment. The results of the study demonstrate the successful high-quality metallization with Pt of the laser-treated tracks by electroless plating in the case of PDMS samples treated at 266 nm. This is an indication that for further successful activation and functionalization for metallization with care must be considered the applied laser parameters as well as the metallization procedures.

The authors aim in future research to perform the investigation concerning the structural properties of the medical grade PDMS and extend the study to the NIR spectral region.

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