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Optical properties of polydimethylsiloxane (PDMS) during nanosecond laser processing

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ABSTRACT

This article presents experimental investigations of effects of the process parameters on the medical grade polydimethylsiloxane (PDMS) elastomer processed by laser source with irradiation at UV (266 and 355 nm), VIS (532 nm) and NIR (1064 nm).

Systematic experiments are done to characterize how the laser beam parameters (wavelength, fluence, and number of pulses) affect the optical properties and the chemical composition in the laser treated areas. Remarkable changes of the optical properties and the chemical composition are observed. Despite the low optical absorption of the native PDMS for UV, VIS and NIR wavelengths, successful laser treatment is accomplished due to the incubation process occurring below the polymer surface.

With increasing of the fluence and the number of the pulses chemical transformations are revealed in the entire laser treated area and hence decreasing of the optical transmittance is observed. The incubation gets saturation after a certain number of pulses and the laser ablation of the material begins efficiently. At the UV and VIS wavelengths the number of the initial pulses, at which the optical transmittance begins to reduce, decreases from 16 up to 8 with increasing of the laser fluence up to 1.0, 2.5 and 10 J cm^{-2} for 266, 355 and 532 nm, respectively. In the case of 1064 nm the optical transmittance begins to reduce at 11th pulse incident at a fluence of 13 J cm^{-2} and the number of the pulses decreases to 8 when the fluence reaches value of 16 J cm^{-2}. The threshold laser fluence needed to induce incubation process after certain number of pulses of 8 is different for every wavelength irradiation as the values increase from 1.0 for 266 nm up to 16 J cm^{-2} for 1064 nm. The incubation and the ablation processes occur in the PDMS elastomer material during its pulsed laser treatment are a complex function of the wavelength, fluence, number of pulses and the material properties as well.

1. Introduction

Silicone-based elastomer polydimethylsiloxane (PDMS) is one of the most popular technical polymeric materials due to its advantageous properties: simple and inexpensive fabrication process, mechanical flexibility and stability, high dielectric constant and breakdown field, optical transparency in the UV, VIS and NIR spectral regions, high biocompatibility and biostability. PDMS is widely used in the fabrication of various micro-electro-mechanical systems (MEMS) and nano-electro-mechanical systems (NEMS) devices such as lab-on-a-chip, waveguides and memory-based devices [1–4], dielectric elastomer actuators [5], as well as in numerous pharmaceutical and medical applications [6–8]. Owing to its remarkable properties, the PDMS-elastomer is also used in biomedicine as encapsulation and/or as substrate insulator carrier for long term neural implants [9,10]. Highly flexible polymeric microelectrode arrays (MEAs) based on PDMS-elastomer scaffold composed by micro-channeled tracks as electrodes are applied as neural interfacing technologies for monitor and/or stimulation of neural activity [11–14]. Elastomeric MEAs can be rolled and flexed, thus offering an improved structural interface with neural tissues. Hence, the modification or structure formation of the PDMS elastomer surface opens an interesting research field for different applications.

Laser ablation of polymers is a well established process in industrial applications as an alternative to the traditional lithographic methods. Direct laser writing (DLW) based on multiphoton polymerization has been proposed for the production of 3D

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micro/nanostructures in 1997 [15]. UV, VIS and NIR ns- and fs-laser irradiation of PDMS-elastomer under ambient conditions is an easy and powerful method of micromachining allowing activation and functionalization of the surface without altering its bulk properties [3,15–28]. Laser micromachining is based on the laser direct ablation, which appears as a very suitable, low cost and versatile controlled processed parameters technique for the fabrication of tracks and complex 2D/3D structures with dimensions of several tens of microns or less in wide range of materials. Consequently, this approach allows the numbers of electrodes and pads to be increased by miniaturization of the tracks on the PDMS substrate and thus, to increase the nerve selectivity. After laser processing, selective metallization of the as-processed surface is obtained by immersion of the sample into autocatalytic bath containing metal ions (Ni or Pt) [27,28].

PDMS belongs to the specific class of polymers that are based on Si atoms. They are constituted of Si—O chains to which CH_3-radicals are fixed via Si—C bonding. In spite of the high transmittance in UV–VIS–NIR range of the spectra, it is possible to modify the surface of the PDMS elastomer by lasers irradiating in this range. This process is possible because incubation occurs below the surface by local chemical transformations. Apparently, the incubation effects are significant for the weakly absorbing materials such as the PDMS polymer. Under the laser exposure the polymer undergoes substantial degradation that alters its optical properties, making the material much more absorptive. It results in increase of the linear absorption coefficient and decrease of the laser fluence, which should be delivered in order the ablation to begin. Different mechanisms (photothermal and photochemical) are proposed in terms of the dependence of the dynamics of the etching process on the laser fluence, wavelength, pulse length, number of pulses (incubation), and the intrinsic properties of the polymer materials [29–33], and details of quantitative understanding are still controversial. Some authors declared that both photothermal and photochemical mechanisms contribute to the ablation at low laser fluences. Moreover, defects creation into the material, i.e. incubation, is considered as responsible for laser ablation of polymers.

In this work we seek to characterize and compare the optical properties of the PDMS elastomer processed by NIR, VIS, and UV pulsed ns-laser irradiation. The study is focused on understanding of the effects of three main process parameters – wavelength, laser fluence and pulse overlapping – on the optical absorption (incubation process), ablation depth, and chemical composition changes in order to activate the surface for further successful metalization of the tracks. Our work can enrich the discussion about laser induced changes in thin PDMS sheets which can be exploited in the context of the direct laser writing of microchannels for applications as microelectrode arrays (MEAs) in neural interfacing technologies for monitor and/or stimulation of neural activity.

2. Experimental

170 μm thick medical grade PDMS elastomer sheets (MED 4860) are irradiated with the fundamental frequency (FF, 1064 nm), second (SH, 532 nm), third (TH, 355 nm) and fourth (FH, 266 nm) harmonics of a Q-switched Nd:YAG (pulse duration $\tau = 15$ ns and repetition rate of 1–10 Hz) laser in air environment. The laser beam is focused normally on the PDMS surface by lens with focal length of 22 cm. The laser spot diameter is between 1.0 and 1.3 mm. The laser fluence increases from 0.5 to 16 J cm^{-2} depending on the laser wavelength applied. The data of the processing laser parameters are shown in Table 1. The samples are mounted on a stepper-motor *x*-*y* table with minimum step of 12.7 μm. The experimental setup configuration allows structuring of a single spot or a single line on the sample surface by pulsed laser ablation when the translational table is at standstill or the sample is translated along *x*- or *y*-axis, respectively. Single spot ablation is performed by applying of different number of pulses from 1 to 110 pulses with repetition rate of 1 Hz.

Table 1
Summary of the laser processing parameters. Comparison of the linear absorption coefficient and the average ablation depth. The absorption coefficient and the penetration depth are calculated according to the Beer–Lambert law, as the scattering is ignored, i.e. the values represent the linear absorption coefficient.

Wavelength	266 nm	355 nm	532 nm	1064 nm
Laser fluence (J cm^{-2})	0.5–1.0	2.0–4.0	7.0–10.0	13.0–16.0
α (cm^{-1})	14.9	7.38	3.58	2.86
Penetration depth (μm)	669	1354	2794	3502
Ablation depth (μm)	40	72	134	150

Continuous linear tracks are obtained by overlapping of each adjacent spot of the laser beam on the surface so as every unit of area is treated by 22 or 33 consecutive pulses. The moving speed of the *x*-*y* table is determined according to the number of pulses needed to perform at a unit of area and the laser repetition rate.

Before the laser treatment the PDMS samples are cleaned by the following steps: cleaning in a detergent solution using ultrasound bath; rinsing with deionized water; again cleaning with ethanol in ultrasound bath; and air stream drying finally.

The experimental techniques applied for characterization of the PDMS samples are: optical spectroscopy (Ocean Optics HR 4000 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 observation of any visible permanent modifications of the surface and measurement of the ablation depth; VK-9700K Color 3D laser Microscope (KEYENCE) for viewing and analyzing of the laser treated areas; μ-Raman spectroscopy (RMS-310 μ-Raman spectrometer (Photon Design)) equipped with laser source operating at $\lambda = 532$ nm for determination of the chemical composition and scanning electron microscope (SEM) SEM/FIB (Lyra/Tescan dual beam system) for the assessment of the laser tracks.

3. Results and discussion

We chose to work with thin medical grade PDMS sheets in accordance to the small size requirements of the potential application as implantable medical devices (neural or muscular surface interfacing). The changes of the optical properties of the PDMS samples after laser irradiation with different wavelengths (266, 355, 532, and 1064 nm) and different number of pulses in single spot ablation mode at various laser fluences are investigated by measuring of the optical transmittance (Fig. 1). It is known that the native medical grade silicones as PDMS elastomer are optically transparent from the near UV up to NIR region of the spectra. Laser treatment of such materials with wavelengths in this spectral region is possible because of the effect of incubation process attributed to increase optical absorption due to accumulation of damages or defects below the surface. It is considered that the incubation in the polymers is a result from the chemical transformations (intermolecular bonds breaking) occur in the local area laser treated without changing the bulk material properties. These modifications depend simultaneously on the wavelength and the laser fluence applied, and appear after a certain number of pulses. It means at given wavelength and laser fluence, the absorption increases during the laser irradiation with the initial incident pulses, i.e. certain number of pulses is required to accumulate local chemical transformations and to reach the ablation conditions.

In our experiments any visible permanent modification of the laser treated area of the PDMS surface observed by optical microscope at 625× magnification is defined as ablation. At a given

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