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Three-dimensional direct laser writing of acrylated epoxidized soybean oil

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Abstract

Direct laser writing (DLW) nonlinear 3D lithography allows precise (up to 100 nm resolution) manufacturing of mesoscale objects of polymers. Natural oils are rich in double bonds which can be cross-linked or converted to other functional groups. Plant based resins offer biodegradability and renewability, thus such substances recently became a popular target of researchers to replace common petroleum-derived plastics.
We investigate acrylated epoxidized soybean oil (AESO) as a great candidate for the DLW 3D lithography due to the high amount of various functional groups. Using femtosecond laser source (515 nm, 300 fs, 200 kHz), tight focusing (NA=0.8) and varying irradiation power *P*, scanning velocity *v* and distance between adjacent beam scans d_{xy} there was assessed a fabrication window for the AESO.
In this paper we present photostructuring of AESO (non-photosensitized) in 3D at micrometer precision. Evaluated and found optimal parameters showed great perspectives to apply AESO in DLW assisted additive manufacturing as a resin derived from natural resources potentially widely applicable fields such as biodegradable single disposal microfluidic devices, sensors, micro-optical, biomedical, lab-on-chip components.

Keywords: acrylated epoxidized soybean oil; photocross-linking; direct laser writing (DLW); two-photon polymerization (2PP)

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1. Introduction

Our developed direct laser writing (DLW) using ultrafast laser irradiation and its' induced multiphoton absorption and avalanche ionization allows nonlinear 3D lithography in polymers (Malinauskas et al., 2010, Parkatzidis et al., 2018). The technology ensures precise manufacturing of mesoscale objects (Jonušauskas et al., 2019). The mesoscale means, that achievable spatial resolution of a single feature can reach 100 nm or even less, while the whole structure can be in mm size – spanning within four orders of magnitude. This technological flexibility ensures DLW applicability in such areas as medicine for tissue engineering (Mačiulaitis et al., 2015, Ovsianikov et al., 2012), manufacturing of micro-optics for fibres (Žukauskas et al., 2014, Gissibl et al., 2016) and photonic crystals for light flow control investigation (Maigyte et al., 2013, Deubel et al., 2006), also various sensors (Tičkūnas et al., 2017) and lab-on-chip fabrication (Jonušauskas et al., 2018, Wu et al., 2009). The most affordable materials for DLW nonlinear 3D lithography are acrylates. The main advantages of acrylates are transparency for visible and IR light, radical polymerization, which allows precise control of the process, and material's properties adjustment using a mixture of different acrylates (Rekštytė, 2016). Also epoxies are used in DLW (Cadarso et al., 2011). They are solid during the process and are fully polymerized only after additional heating. Hydrogels are attractive due to their biocompatibility (Graham, 1998), biodegradability (Deshmukh et al., 2010) and permeability for oxygen, which is crucial for applications in medicine. New materials can be advantageous compared to the present ones. Recently, scientists are looking to replace existing petroleum-derived plastics to the ones obtained from natural resources (Zhu et al., 2016). Here plants take place of interest because they are an annually renewable and abundant raw material. For example, from soybean oil produced acrylated epoxidized soybean oil (AESO) has high amount of various functional groups such as the acrylic, epoxy and hydroxy groups, and is widely used in industry (Lebedevaite et al., 2019). AESO can be cross-linked using UV/VIS light and photoinitiator (Miao et al., 2016). In this study we demonstrate photoinitiator-free AESO laser polymerization, employing ultrashort pulses by multiphoton absorption and avalanche ionization initiated cross-linking.

2. Experimental

Pharos laser (515 nm, 300 fs, 200 kHz, Light Conversion Ltd, Vilnius, Lithuania), Galvano-scanners, 20× NA = 0.8 objective were employed to perform DLW 3D lithography experiments. A full description of the experimental setup can be found in a previous publication (Rekštytė et al., 2014). The aim was to figure out if AESO can be suitable for ultra-fast laser pulses initiated 3D polymerization in a confined space. At first, an investigation test to assess the optimal fabrication parameters was performed. A 3D model of so-called bi-layer woodpile structures was programmed. Each layer consisted of three 75 µm length (*l*) and 15 µm width (*p*) logs, separated with 15 µm width gaps (*d*). It resulted to total 30 µm period *T* (*T*=*p*+*d*). Each log was formed of multiple laser beam scans depended from the distance between scans d_{xy}. The layers were perpendicularly

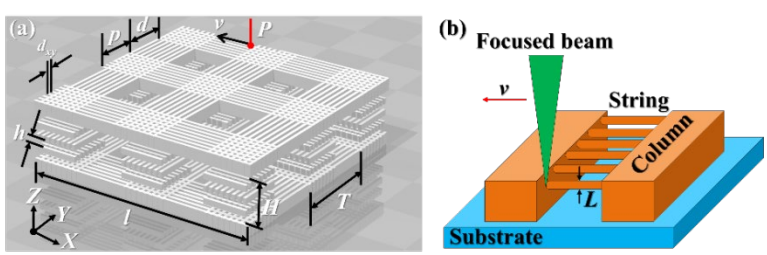

Fig. 1. (a) 75x75 μm^2 size bi-layer woodpile structure. *T* – period, *p* – log width, *l* – log length, *d* – distance between logs, d_{xy} – distance between scans, *H* – vertical column height, *h* – height between separate column segments, *P* – applied laser power, *v* – scanning velocity; (b) Resolution bridges model. Supportive columns fabricated on the glass substrate. Each string between columns is polymerized from a single laser beam scan. Focused laser beam is demonstrated in green colour. *L* – longitudinal string size (lateral one is not shown), *v* – scanning velocity.

orientated to the respect of each other and separated by vertical columns of 20 or 30 μm height (Fig. 1. (a)). The appropriate laser power (*P*), which corresponded to the light intensity (*I*) at the sample, the scanning velocity (*v*) and d_{xy} for the fabrication of structure were selected by scanning these parameters until well-defined structures of appropriate precision were obtained in a few minutes of writing time. The fabricated structures were characterized employing scanning electron microscope (SEM, Hitachi TM-1000, Tokyo, Japan). Secondly, the spatial resolution of formed objects in AESO was determined and its' dependency on laser power *P* and scanning velocity *v* was assessed. It was implemented using a method of so-called resolution bridges (RB). The idea was to form hanging strings between two supportive columns (Fig. 1. (b)). Each string is formed from a single laser beam scan. Depending on applied *P* and *v*, strings' lateral (*D*) and longitudinal (*L*) sizes differed. Using SEM, D and L were measured. Regarding to the assessed spatial resolution, there were fabricated structures, entirely made of single beam scan polymerized strings. As AESO is fluidic, during the DLW experiments it was placed between two glass slides to maintain it stable. After the exposure the samples were developed in 4-methyl-2-pentanone for 15 min, removing the uncured resin and leaving only the manufactured structures on the substrate to air dray. Using rotary pumped coater the samples were coated with 20 nm thickness silver layer to enhance SEM images.

3. Results

Bi-layer woodpile structures were manufactured varying laser power *P* in the range of 0.1-1.2 mW every 0.1 mW, scanning velocity *v* was set to 2.5, 5, 10 and 15 mm/s, d_{xy} – 0.25-2 μm every 0.25 μm. Used objective was 20 × NA = 0.8. SEM images of the formed woodpiles arrays are shown in the Fig. 2. Employing lower than 0.4 mW power, no structures were polymerized or they were too weak mechanically to withstand the development in the solvent. Well-defined structures of appropriate precision were achieved combining 0.4-0.8 mW *P* and 2.5 or 5 mm/s *v* (Fig. 2. (a) and (b)). Importance of d_{xy} parameter was revealed as well. In *v*=5 mm/s and *P*=0.4 mW case, structures with larger than 0.25 μm d_{xy} were not formed due to too low or absent overlap of adjacent scans. Increasing power to 0.5 mW or more, increases light intensity in the focus, too, resulting to bigger polymerized volumetric pixel – voxel. Thus structures with even 1.5-1.75 μm d_{xy} can be formed. In *v*=10 mm/s, 0.4-0.8 mW the power was insufficient to get well-defined structures and was required to be incremented (Fig. 2. (c)). Range of 0.9-1.2 mW was optimal for fabrication at recent *v*. Working with higher than 1.2 mW power, the optical damage of the material occurs. It starts to carbonize and form gas

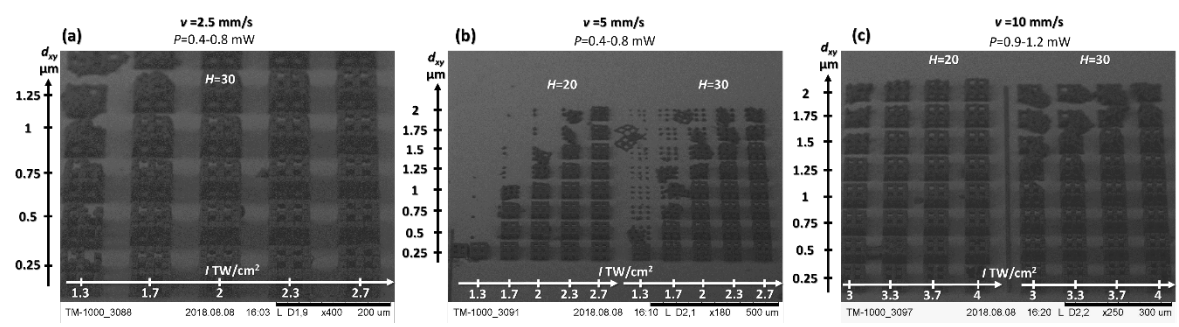

Fig. 2. SEM images of bi-layer woodpile structures arrays formed employing DLW. Used fabrication parameters were: (a) – *v*=2.5 mm/s, *P*=0.4-0.8 mW; (b) – *v*=5 mm/s, *P*=0.4-0.8 mW; (c) – *v*=10 mm/s, *P*=0.9-1.2 mW. To operate in mW units is experimentally convenient, but in general, the intensity *I* is more proper as it involves focusing conditions. Thus applied *P* is recalculated to *I* and demonstrated on white scale. Parameter d_{xy} is represented on black scale. Each woodpiles column and row is fabricated using certain *I* and d_{xy} values. *H* represents the height of the structures.

bubbles. To avoid this, *v* was increased up to 15 mm/s. However, no structures were produced in this case. Employing high speed, the polymerized material does not adhere well enough to the glass substrate and whole structures were washed away.

Further, RB method results are discussed. The supportive columns and the hanging strings were formed employing previously assessed fabrication parameters: *v*=5 mm/s, *P*=0.4 mW and d_{xy}=0.25 µm for columns and for strings – varying *v* in the range of 0.5-10 mm/s and *P* 0.4-0.6 mW. SEM images of RB are showed in Fig. 3.

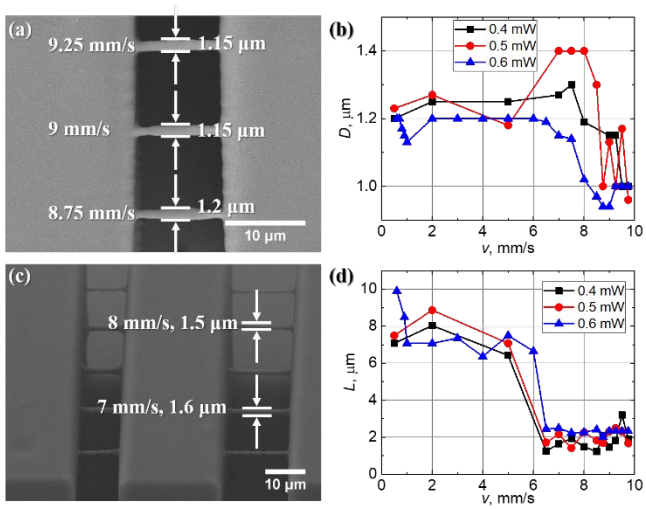

Fig. 3. (a) – demonstrates measurement of RB lateral *D* size. Top view. Applied power *P* to form strings was set to 0.4 mW, scanning velocity *v* and measured *D* are marked on the picture. (b) – *D versus v*. In the range of 2-6 mm/s, the lateral size of the string is approximately 1.2 µm. Increasing *v* up to 10 mm/s, *D* decreases to 1 µm. In the range of 0.4-0.6 mW, *D* remains comparable. (c) – measurement of RB longitudinal *L* size. View at 45 degrees angle. Applied *P* was 0.4 mW, *v* and measured *L* are marked on the picture. (d) – *L versus v*. In the range of 2-5 mm/s, the longitudinal size of the string is approximately 7-8 µm. Increasing *v* up to 10 mm/s, *L* decreases to 2 µm. Due to material softness, the strings' were twisted in respect of viewing point, what had an impact for deviation measuring *D* and *L*. Thus there is no significant dependence of *D* and *L versus P* in the range of 0.4-0.6 mW. (a) and (c) are SEM images.

(a) and (c). (b) and (d) demonstrates lateral *D* and longitudinal *L* sizes of the strings dependence on the *v*, when different *P* was applied. It can be seen, that *D* remains about 1.2 µm in the range of 2-6 mm/s and starts to decrease to 1.2 µm, when *v* is greater than 6 mm/s. It explains, why structures with higher than 1.25 µm distance between scans were not formed (Fig. 2. (b)).The same tendency is observed with *L* size. It remains between 7-8 µm, when used *v* is 2-5 mm/s, and decreases to 2 µm increasing *v*. The decrease in size appears due to lowered exposure when higher *v* is applied. *L* size is bigger than *D*, because of nature of focusing and can be explained by Rayleigh model. Variation of the *P* in the range of 0.4-0.6 mW had no meaningful difference in strings' dimensions. To observe *D* and *L* dependency on power, a wider interval of *P*

should be investigated. Moreover, it was noticed, that polymerized AESO is soft material. The formed strings were bent, twisted, stretched if the supportive columns have moved apart, sometimes adjacent strings tend to merged. It had a great impact of deviation measuring *D* and *L* as some strings appeared bigger due to their twist in respect of viewing point. Also such deformations confirms material's low storage modulus (4.76×10^6 Pa, Lebedevaite et al., 2019), which has to be taken into account while modelling 3D structures' geometry. Alternatively material mechanical rigidity can be increased by chemical modifications.

Finally, there were fabricated structures, entirely made of a single beam scan polymerized strings. The goal of this experiment was to reveal if the ASEO is a suitable material to form 3D objects with internal structure and features close to the resolution limit size. Object of 75x75 μm^2 consisted of ten layers. In every second layer the strings' orientation was perpendicular to the previous one. The distance between strings was set to 2 µm. The SEM image of such object is presented in Fig. 4. Although the geometrical shape was not well-defined, the structure maintained approximately strings and gaps of 1 µm width, resulting to the defined period of 2 µm.

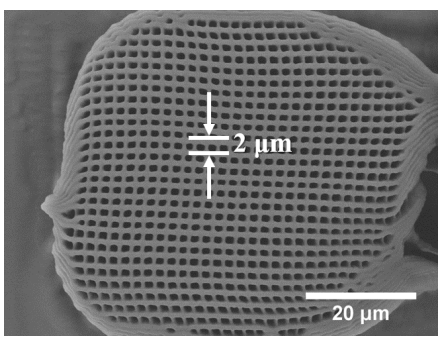

Fig. 4. SEM image of an object of 75x75 μm^2, fabricated of a single laser beam scan polymerized strings. Used parameters: *P*=0.35 mW, *v*=5 mm/s. Objective was 20x 0.8 NA.

4. Conclusions

Employing DLW 3D lithography experimental setup, multiphoton and avalanche ionization initiated polymerization of pure AESO was demonstrated. Optimal laser power *P*, scanning velocity *v* and distance between scans d_{xy} to fabricate well-defined woodpile structures in appropriate precision were assessed. Applying 0.4-1.2 mW power *P* (corresponding to 1.3-4 TW/cm^2 intensity *I*, when NA=0.8), 2-10 mm/s *v* should be used, while d_{xy}=0.25-2 µm. Spatial resolution was determined: 1 µm lateral and 2 µm longitudinal size features were achieved. 3D objects, consisted of such size strings, were fabricated. The strings' dimensions remained defined, while the whole object was deformed due to material softness. Since the photoinitiator- free plant-derived material was 3D cross-linked using ultrafast laser, it opens great perspectives to apply pure AESO in DLW as a resin derived from natural resources for rapid prototyping or additive manufacturing industries. However, for practical certain applications further systematic investigations is an ongoing research.

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