Optical 3D Micro- and Nano-formation of Bioplastics

SUMMARY

The present technology allows printing complex 3D micro- and nano-structures from environmentally friendly plant-derived material – acrylated epoxidized soybean oil (AESO). Non-toxicity and high biodegradability enable application in biomedicine, micro-optics and nanophotonics.

BACKGROUND

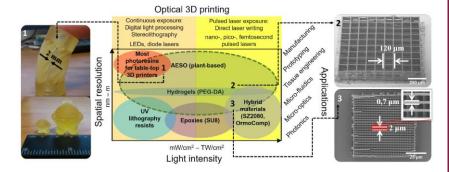
3D printing is a simple, low-cost and flexible additive manufacturing technique to create complex structures that cannot be cut, assembled or carved. It is especially useful in rapid fabrication of micro- and nano-structures to be used in health area, nanoelectronics, nanophotonics, etc. The most popular materials for optical 3D printing – epoxy and acrylic resins, have good mechanical properties, but are derived from petroleum, may have toxic ingredients, have low biodegradability, and therefore limited scale of applicability.

Currently, soybean oil is one of the most promising materials to replace petroleum-derived resins. AESO can be polymerized by ultraviolet / visible light using appropriate photoinitiators and cross-linking agents, majority of which are petroleum-derived.

TECHNOLOGY

The present technology is based on polymerization of plant-derived AESO resins using ultrashort laser pulses. We use pure AESO resin or AESO mixed with a photoinitiator (vanillin dimethacrylate (VDM) or vanillin diacrylate) to obtain mechanical and thermal properties that are sufficient for practical application in 3D optical printing.

Using Direct Laser Writing (DLW) 3D lithography technique, photo-crosslinking can be achieved by tightly focusing ultrashort laser pulses into AESO resin, thus initiating a polymerization reaction. Selectively exposing material to laser radiation allows creating fully 3D structures with submicrometer spatial resolution. The smallest achieved spatial features are 1 µm with a throughput of 6900 voxels per second. Since the 3D cross-linking of the plant-derived materials is initiated using ultrafast laser induced multiphoton absorption and avalanche ionization, it does not require the usage of any photoinitiator, thus enabling green 3D micro-printing [1]. Recent studies have proved that AESO resin can be used in 3D printing structures of any size with all types of optical / laser printing equipment (state-of-the-art laser setups or widespread table-top 3D printers) [2].



TECHNOLOGY READINESS LEVEL

TRL 4 - technology validated in the laboratory.

INTELLECTUAL PROPERTY

Invented in cooperation between Vilnius University and Kaunas University of Technology by: M. Lebedevaitė, J. Ostrauskaitė, E. Skliutas, M. Malinauskas.

PUBLICATIONS

[1] M. Lebedevaite, J. Ostrauskaite, E. Skliutas, M. Malinauskas. Photoinitiator Free Resins Composed of Plant-Derived Monomers for the Optical μ -3D Printing of Thermosets. Polymers 2019, 11(1), 116. https://doi.org/10.3390/polym11010116.

[2] E. Skliutas, M. Lebedevaite, S. Kasetaite, S. Rekstyte, S. Lileikis, J. Ostrauskaite, M. Malinauskas. A Bio-Based Resin for a Multi-Scale Optical 3D Printing. Sci Rep 10, 9758 (2020). https://doi.org/10.1038/s41598-020-66618-1.



BENEFITS

- Bio-friendly: 3D micro-printing from plant-derived, non-toxic and highly biodegradable material.
- DLW technique does not require the usage of any photoinitiators.
- Mechanical and thermal properties are sufficient for practical application for table-top and industrial grade optical 3D printing.
- The smallest spatial features are 1 μm with a throughput of 6900 voxels per second.
- Non-toxicity allows application in biomedicine.
- Avoidance of photoinitiators reduces auto-fluorescence while performing microscopy.
- AESO can be used in printing structures of any size with all types of optical / laser printing equipment

APPLICATION

The present technology can be used in various applications:

- Printing 3D cell-growth scaffolds;
- Microscopy (in vitro or in vivo);
- > Biomedicine;
- Micro-optics:
- Nanophotonics;
- General optical 3D printing;
- Prototyping.

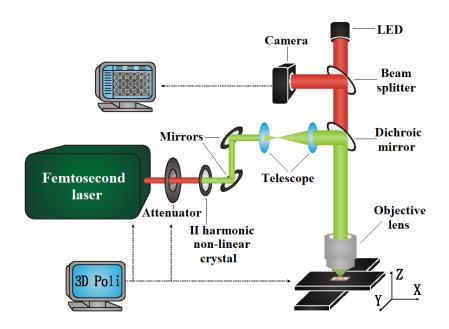
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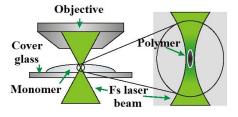
Technical information: Direct Laser Writing 3D Meso-Scale Lithography

DLW 3D MESO-SCALE LITHOGRAPHY SETUP

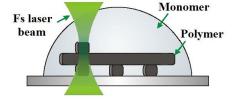


DLW 3D MESO-SCALE LITHOGRAPHY PROCESS

(I) photopolymerization reaction is initiated in the focal spot of the beam



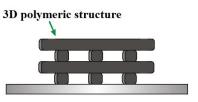
(II) polymeric structure is directly written by moving the sample in regard to the focal spot



(III) organic developer washes unexposed material



(IV) 3D free-standing structure is obtained on a glass substrate





Direct Laser Writing (DLW, a.k.a. Two-Photon Polymerization, Multiphoton Processing) lithography is a technique of precise additive manufacturing, accomplished by illuminating positive-tone negative-tone or photoresists via femtosecond pulsed light. This technique allows producing features on a of nanometres photosensitive material, without the need to use complex electron beam or UV optical systems or photomasks (see DI W fabrication setup).

This technique relies on a multiphoton absorption process in a material. Typically its two-photon absorption when a simultaneous absorption of two-photons of the twice longer wavelength within the ultra-confined volume within a material restricted by the focus of a laser beam. It occurs once intensities of high order reached (typically of TW/cm2). At the focal point of the laser beam a photochemical such reaction, as photopolymerization induced crosslinking), occurs (see I). In liquid resins, this process leads to liquid-to-solid transition (see II). By manipulating the position of the focal point in respect to volume of the modified material, e.g. by moving the stage (substrate) and/or scanning the beam. 3D structures materialized.

After the laser 3D structuring, the unexposed resin is dissolved in a developer (see III) and the fabricated structure is revealed (see IV).

More details are available elsewhere: M. Malinauskas et al., Nanophotonics lithography: a versatile tool for manufacturing functional three-dimensional micro-/nano-objects, Lith. J. Phys. 52(4), 312 (2012)