Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 132–135
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Two-photon polymerization of an Eosin Y-sensitized acrylate composite

Maria Farsari [a,*], George Filippidis [a], Kyriaki Sambani [a], Theodore S. Drakakis [a], Costas Fotakis [a,b]

[a] *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 71110 Heraklion, Crete, Greece*
[b] *Department of Physics, University of Crete, Greece*

Received 2 November 2005; received in revised form 18 November 2005; accepted 22 November 2005
Available online 27 December 2005

Abstract

We report two-photon polymerization of an acrylate composite using a femtosecond laser at 1028 nm. The composite consists of an acrylate monomer, a free-radical co-initiator and a photo-sensitizer. The material is transparent to infrared laser radiation and absorbs strongly in the visible. By scanning the tightly focused laser beam, we employ two-photon absorption to polymerize and selectively solidify the material.

Two photo-polymerization of organic composites permits the construction of complex-shaped three-dimensional structures of sub-micron resolution. Due to their versatile optical and chemical properties and the ability to mix them with active molecules, the materials described in this work are particularly useful for a variety of applications such as photonic devices, actuators and micro-fluidic devices. In addition, as both the single photon and the two-photon wavelengths are not in the ultraviolet part of the spectrum, this technique is particularly promising for incorporation into the photo-polymer of active molecules that are sensitive to UV radiation.

Keywords: Two-photon polymerization; Eosin Y; Acrylate monomer

1. Introduction

Two-photon polymerization is a very powerful and relatively simple technique for producing complex, three-dimensional structures from a liquid photosensitive material. When the beam of a femtosecond, infrared laser is tightly focused into the volume of a photo-polymerizable composite, the polymerization process can be initiated by non-linear absorption within the focal volume. By moving the laser focus in a three-dimensional manner through the liquid, three-dimensional structures can be fabricated. The technique has been used with a variety of acrylate and epoxy materials [1–5] and several components and devices have been fabricated such as photonic crystal templates [5,6], microrotors driven by laser tweezers [7], mechanical devices [8,9] and microscopic models [10,11].

Up to now the laser systems used were mostly Ti:Sapphire femtosecond lasers, while previous studies have demonstrated the feasibility of two-photon polymerization from new efficient initiators using an Nd:YAG microlaser at the fundamental and second harmonic wavelength [12,13]. We show that two-photon polymerization can also be achieved by employing a compact femtosecond laser oscillator operating at 1028 nm and a polymeric composite whose components are readily available. As both the single photon and the two-photon wavelengths are far from the UV, this technique is particularly promising for incorporation into the photo-polymer of active molecules that are sensitive to UV radiation [14]. To our knowledge this is the first time two-photon polymerization has been demonstrated using a femtosecond laser operating at a 1028 nm wavelength.

2. Materials composition

The photo-polymerizable system used in this work is an acrylate-based photo-polymer, which has been used in the past for single photon stereolithography [15–18]. It consists of three basic components: a sensitizer dye, an amine co-initiator and a multifunctional acrylate monomer. Pentaerythritol triacrylate (PETIA, Aldrich, Fig. 1a) forms the backbone of the polymer network. *N*-methyldiethanolamine (MDEA, Aldrich, Fig. 1b) is used as a co-initiator and Eosin Y (2-, 4-, 5-, 7-tetrabromofluorescein disodium salt, Aldrich, Fig. 1c) as sensitizer dye. This system is particularly sensitive in the spectral region from 450 to 550 nm, where the two-photon absorption window for the 1028 nm laser lies.

* Corresponding author. Tel.: +30 2810 391342; fax: +30 2810 391318.
E-mail address: mfarsari@iesl.forth.gr (M. Farsari).

1010-6030/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2005.11.025

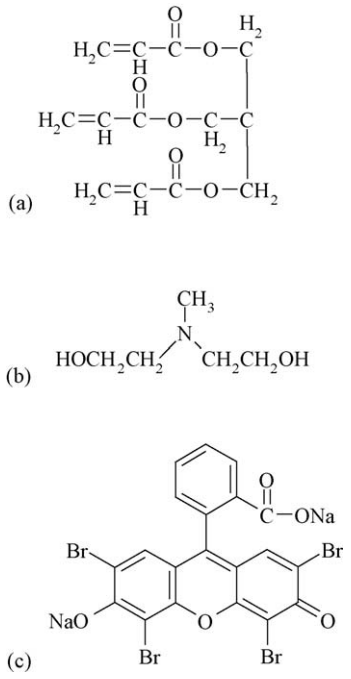

Fig. 1. Molecular structures of the different components of the photo-polymerizable composite: (a) PETIA, (b) MDEA and (c) Eosin Y.

The process of single photon polymerization has been extensively described in Ref. [19]. Similarly, the two-photon polymerization reaction is initiated through a radical process. Two components are involved in radical formation: a dye capable of absorbing two-photons of infrared radiation and an amine that can be oxidized by the triplet state of the dye. Once the radicals trigger the polymerization, the monomers polymerize, developing into a three-dimensional network.

The work reported in this paper has been obtained with the following reference formulation: pentaerythritol triacrylate 10 ml: *N*-methyldiethanolamine 0.1 ml: Eosin Y 10 mg (dissolved in 0.5 ml of methanol).

3. Experimental set-up

The set-up for the fabrication of three-dimensional microstructures by two-photon microstereolithography is shown in Fig. 2. The laser used is an Amplitude Systems t-pulse laser femtosecond oscillator operating at 1028 nm. This source is a compact diode-pumped femtosecond laser oscillator delivering a train of high energy, short duration pulses. The average power of the laser is 1 W, a pulse duration of less than 200 fs and a repetition rate of 50 MHz.

The photo-polymerized structure is generated using an *x*–*y*-galvanometric mirror digital scanner (Scanlabs Hurryscan II), controlled by SAMLight (SCAPS) software. The scanner has been adapted to accommodate a high numerical aperture focusing microscope objective (Nikon 50×, N.A. = 0.8). The lateral resolution of our objective is given by $r = 0.61\lambda/\text{N.A.} = 785$ nm and the axial resolution by $r = 2\lambda n/(\text{N.A.})^2 = 3.2$ μm. Movement on the *z*-axis is achieved with a single-axis piezoelectric stage (PI) and beam control with a mechanical shutter (Uniblitz). The piezoelectric stage and the shutter are computer controlled via a National Instruments LabVIEW program. Beam intensity control is achieved using neutral density filters. A CCD camera is mounted behind a dichroic mirror for online monitoring of the two-photon polymerization process. This is possible as the refractive index of the originally liquid photo-polymer changes during polymerization, so that the illuminated structures become visible during the building process.

4. Results

Fig. 3 shows the normalized absorption spectrum of the PETIA/MDEA/Eosin Y composite, taken using a Cary

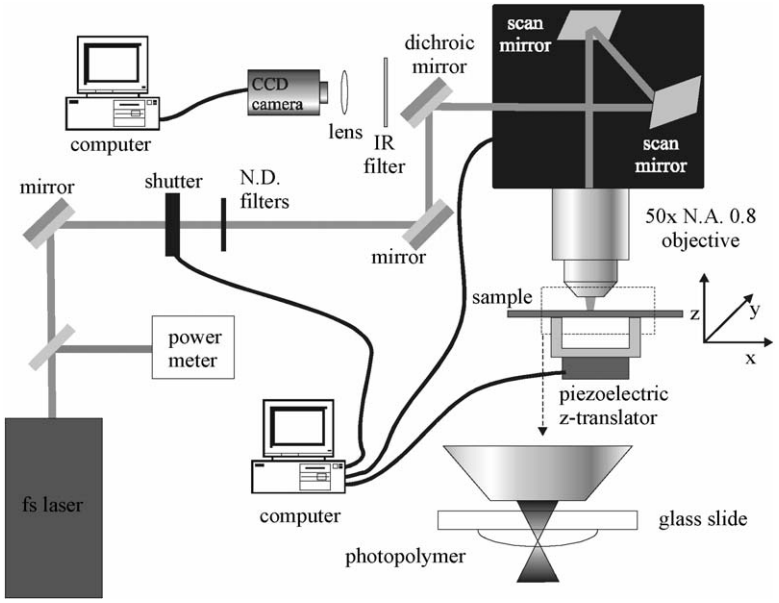

Fig. 2. Experimental set-up.

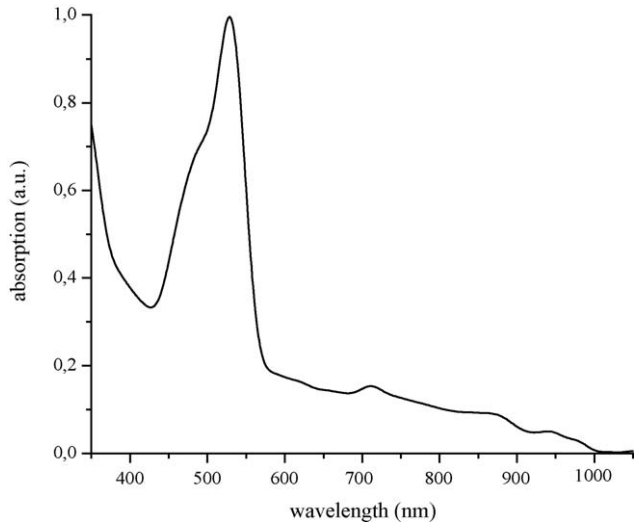

Fig. 3. Normalized absorption spectrum of the photo-polymerizable composite.

50 UV–vis/IR spectrometer. The material exhibits no absorption above 1000 nm and absorbs very strongly in the green spectral region, where the two-photon absorption window of the laser used lies. The absorption in the green is due to the addition of Eosin Y.

The three-dimensional structures are fabricated layer-by-layer bottom up with the last layer attached to the coverslip. As the material is very viscous and the build process lasts less than a minute there are no issues with material drifting.

The first component built by two-photon polymerization consists of 9×10 square cells array. The component is built by repeating the same pattern over 15 layers with a 1 μm separation thickness. The separation thickness is smaller than the axial focal length of the lens; this was done so that there is adequate adhesion between the layers.

The galvo scanning speed used in all cases is 7 mm/s. For the same galvo speed, several laser powers were investigated. The lowest laser energy per pulse that appeared to polymerize the material was found to be 2.5 nJ, which corresponds to a laser fluence of 0.13 J cm^{-2}. The components presented in this paper were made using this minimum laser pulse energy.

After the completion of the component building process, the sample was developed for approximately 20 s in methanol. No further curing was carried out. Following the washout the samples were coated with a few nanometers thick palladium layer and their structural properties were investigated in a scanning electron microscope (SEM). The results are depicted in Figs. 4 and 5.

Fig. 4 shows an 850× magnification of the component where the effect of distortion due to polymer shrinkage can be clearly seen. Fig. 5 depicts a 4000× magnification of the central area of the component. It can be seen that the resolution is approximately 1 μm, slightly larger than the focused beam waist.

Figs. 6 and 7 show two other built components, a hollow gear and a filled gear. Both these components we built with the same conditions described earlier.

All the components built appeared to suffer from distortion due to shrinkage. This is a well-documented problem in con-

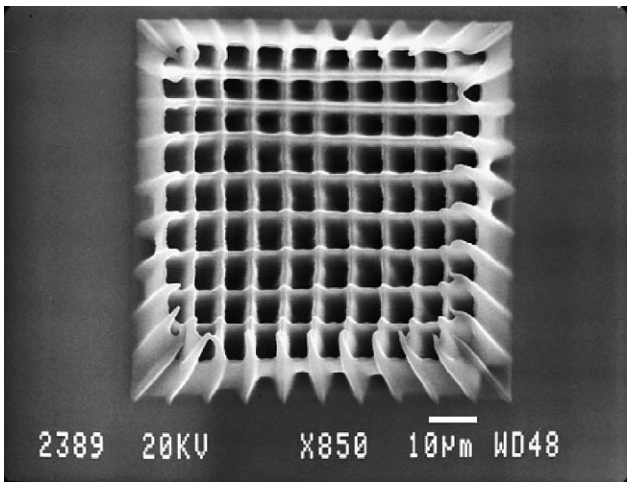

Fig. 4. SEM image of the component built by two-photon microstereolithography. The component was scanned using 15 layers at 7 mm/s and layer spacing 1 μm. The laser pulse energy used was 2.5 nJ.

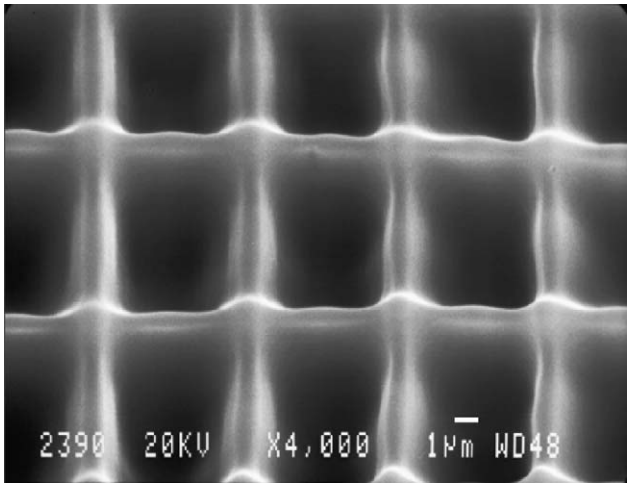

Fig. 5. A magnification of a feature of the component of Fig. 4.

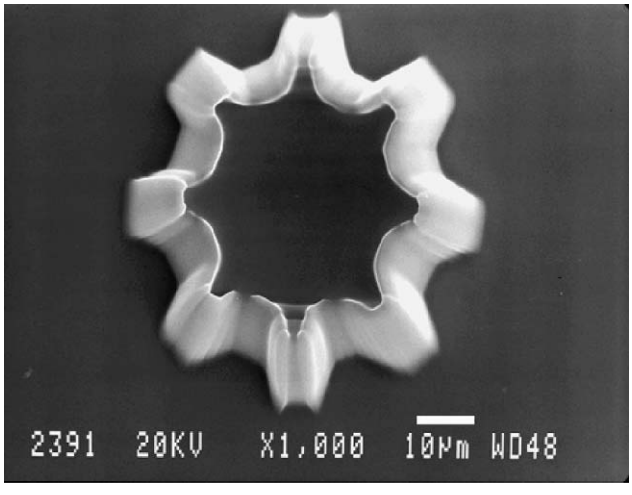

Fig. 6. A hollow micro-gear.

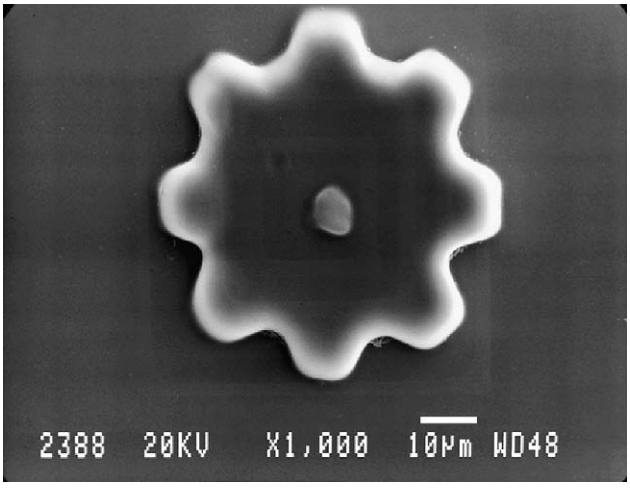

Fig. 7. A filled micro-gear.

ventional stereolithography [20,21]. The industry addresses it by engineering both the resins and the technique used. On the materials front, the problem is greatly reduced by using a mixture of oligomers as the polymer backbone; when oligomers photo-polymerize the volume reduction is smaller compared to monomer polymerization. In addition, nowadays mostly epoxy resins are used, which suffer less from shrinkage effects [22]. Materials engineering is not, however, adequate for the shrinkage to disappear. Therefore, it is necessary for components and building sequences to take into account the amount of shrinkage.

5. Conclusions

We have demonstrated two-photon polymerization of a polymer composite using a femtosecond laser at 1028 nm. The photosensitive liquid consists of an acrylate monomer, a free-radical co-initiator and a photo-sensitizer. It was feasible to fabricate three-dimensional structures of 1 μm resolution to the Eosin Y-sensitized acrylate composite. The material and the innovative method of multi-photon polymerization are promising for incorporation into the photo-polymer of active molecules that are sensitive to UV radiation. All the components built appeared to suffer from high shrinkage, with the most likely reason being the use of monomers instead of oligomers.

Acknowledgments

Maria Farsari would like to thank Prof. B.N. Chichov and A. Ovsianikov of the Laser Zentrum Hannover e.V. for many helpful discussions.

References

[1] S. Maruo, O. Nakamura, S. Kawata, Three-dimensional microfabrication with two-photon-absorbed photopolymerization, Opt. Lett. 22 (1997) 132–134.
[2] S. Kawata, H.B. Sun, T. Tanaka, K. Takada, Finer features for functional microdevices—micromachines can be created with higher resolution using two-photon absorption, Nature 412 (2001) 697–698.
[3] X.M. Duan, H.B. Sun, K. Kaneko, S. Kawata, Two-photon polymerization of metal ions doped acrylate monomers and oligomers for three-dimensional structure fabrication, Thin Solid Films 453 (2004) 518–521.
[4] L.H. Nguyen, M. Straub, M. Gu, Acrylate-based photopolymer for two-photon microfabrication and photonic applications, Adv. Funct. Mater. 15 (2005) 209–216.
[5] M. Deubel, G.V. Freymann, M. Wegener, S. Pereira, K. Busch, C.M. Soukoulis, Direct laser writing of three-dimensional photonic-crystal templates for telecommunications, Nat. Mater. 3 (2004) 444–447.
[6] H.-B. Sun, S. Matsuo, H. Misawaa, Three-dimensional photonic crystal structures achieved with two-photon-absorption photopolymerization of resin, Appl. Phys. Lett. 74 (1999) 786–788.
[7] P. Galajda, P. Ormosa, Complex micromachines produced and driven by light, Appl. Phys. Lett. 78 (2001) 249–251.
[8] H.-B. Sun, K. Takada, S. Kawata, Elastic force analysis of functional polymer submicron oscillators, Appl. Phys. Lett. 79 (2001) 3173–3175.
[9] T. Tanaka, H.-B. Sun, S. Kawata, Rapid sub-diffraction-limit laser micro/nanoprocessing in a threshold material system, Appl. Phys. Lett. 80 (2002) 312–314.
[10] M. Straub, L.H. Nguyen, A. Fazlic, M. Gu, Complex-shaped three-dimensional microstructures and photonic crystals generated in a polysiloxane polymer by two-photon microstereolithography, Opt. Mater. 27 (2004) 359–364.
[11] J. Serbin, A. Ovsianikov, B. Chichkov, Fabrication of woodpile structures by two-photon polymerization and investigation of their optical properties, Opt. Express 12 (2004) 5221–5228.
[12] I. Wang, M. Bouriau, P.L. Baldeck, C. Martineau, C. Andraud, Three-dimensional microfabrication by two-photon-initiated polymerization with a low-cost microlaser, Opt. Lett. 27 (2002) 1348–1350.
[13] C. Martineau, G. Lemercier, C. Andraud, I. Wang, M. Bouriau, P.L. Baldeck, New initiator for two-photon absorption induced polymerization with a microlaser at 1.06 μm, Synth. Met. 138 (2003) 353–356.
[14] A. Athanassiou, M. Varda, E. Mele, M.I. Lygeraki, D. Pisignano, M. Farsari, C. Fotakis, R. Cingolani, S.H. Anastasiadis, Combination of Microstructuring and Laser-light Irradiation for the Reversible Wettability of Photosensitised Polymer Surfaces, ISNM, University of Cyprus, 2005.
[15] S. Sainov, C. Ecoffet, DJ. Lougnot, Evanescent wave holographic recording in a photopolymer, J. Mater. Sci.: Mater. Elect. 14 (2003) 855–856.
[16] C. Triger, C. Ecoffet, D.J. Lougnot, Replication of patterns on nanometric polymer films obtained by photopolymerization by evanescent waves, J. Phys. D: Appl. Phys. 36 (2003) 2553–2558.
[17] A. Bertsch, J.Y. Jézéquel, J.C. André, Study of the spatial resolution of a new 3D microfabrication process: the microstereophotolithography using a dynamic mask-generator technique, J. Photochem. Photobiol. A: Chem. 107 (1997) 275–281.
[18] P. Schaeffer, A. Bertsch, S. Corbel, J.Y. Jézéquel, J.C. André, Industrial photochemistry XXIV. Relations between light flux and polymerized depth in laser stereophotolithograph, J. Photochem. Photobiol. A: Chem. 107 (1997) 283–290.
[19] A. Espanet, C. Ecoffet, D.J. Lougnot, PEW: photopolymerization by evanescent waves. II. Revealing dramatic inhibiting effects of oxygen at submicrometer scale, J. Polym. Sci.: Part A: Polym. Chem. 37 (1999) 2075–2085.
[20] P.F. Jacobs, Rapid Prototyping and Manufacturing: Fundamentals of Stereolithography, Society of Manufacturing Engineers, Dearborn, Mich, 1992.
[21] D. Karalekas, A. Agelopoulos, Study of shrinkage strains in a stereolithography cured acrylic photopolymer resin, J. Mater. Process. Technol. 136 (2003) 146–150.
[22] M. Farsari, S. Huang, R.C.D. Young, M.I. Heywood, P.J.B. Morrell, C.R. Chatwin, Four-wave mixing studies of UV curable resins for microstereolithography, J. Photochem. Photobiol. A: Chem. 115 (1998) 81–87.