Applied Surface Science 257 (2011) 5389–5392

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Two-photon polymerization of an epoxy–acrylate resin material system

R.J. Winfield*, S. O'Brien

Tyndall National Institute, Lee Maltings, Prospect Row, Cork, Ireland

ARTICLE INFO

Article history:
Received 31 May 2010
Received in revised form
22 September 2010
Accepted 12 October 2010
Available online 23 October 2010

Keywords:
Two-photon polymerization (2PP)
Material system
Epoxy
Acrylate

ABSTRACT

Improved material systems are of great interest in the development of two-photon polymerization techniques for the fabrication of three dimensional micro- and nano-structures. The properties of the photosensitive resin are important in the realisation of structures with submicron dimensions. In this study investigation of a custom organic resin, cross-linked by a two-photon induced process, using a femtosecond Ti:sapphire laser, is described. A structural, optical and mechanical analysis of the optimised material is presented. The influence of both material system and laser processing parameters on achievable micro-structure and size is presented as are representative structures. Parameters include: laser power, photo-initiator concentration and material composition.

1. Introduction

Laser 2-photon polymerization (2PP) has attracted much attention as a tool for the fabrication of complex three dimensional structures with submicron resolution [1–7]. The writing technique uses the fact that polymerization only occurs within the very high intensity focal volume of a laser delivered through a high numerical aperture objective lens. In this way polymerization is localized in three dimensions with the use of a single beam.

Central to the technique is the use of a material that is suitable for photopolymerization. Several systems have been reported including acrylates, epoxies and inorganic–organic hybrid systems [1,6,8–10]. The important attributes for any materials system in this application are: efficiency of writing, resolution and stability. This was, for example, why the inorganic–organic hybrid materials attracted much interest. In fact, apart from materials that have zero shrinkage [10], contraction is a typical phenomenon reported by several authors (see for example [11]).

In recent years the use of positive tone epoxy systems has become popular [12,13]. In particular the SU8 resin system is widely used as it is commercially available and does not require synthesis before use. This is an epoxy resin that combines the qualities above however the structures are written as a latent image that cannot readily be monitored in situ and requires a heating and development step. Resolutions as high as 30 nm have been reported [13]. Negative tone acrylate systems have also been widely reported. Commercially available resins (for example, SCR 500, JSR Company) have been used to write structures using 2PP. Baldacchini et al. [14] reported the development of a non-commercial acrylate-based resin.

In this paper we report the use of an epoxy/acrylate hybrid resin that combines the ease of a photopolymerizable negative tone resist with the benefit of an epoxy system. It is based on formulations that have been reported for use in high resolution nanoimprint lithography [15]. In this paper an epoxy source has been added and the photoinitiator replaced by one with a proven 2-photon absorption at the laser wavelength. The polymerization is a two-step process that uses Ti:sapphire femtosecond laser to cross link the acrylate group followed by thermal cross-linking of the epoxy group. We present the writing characteristics of the material and give examples of periodic structures that were written using this process.

2. Experimental

The laser system used in the evaluation of the epoxy–acrylate resin has been described previously [9] and is shown in Fig. 1. It comprised a fs laser, projection system, XYZ stage control and a CCD monitoring system. The laser was a Spectra Physics Mai Tai Ti:sapphire fs laser operating at a wavelength of 795 nm. The pulse duration was ~100 fs at a pulse repetition frequency of 80 MHz. A quarter wave plate was used to transform the linearly polarized beam to circular polarization.

The projection system used a beam expander to overfill a high numerical aperture oil immersion objective with numerical aperture 1.25 and ×100 magnification. The average power of the laser

* Corresponding author. Tel.: +353214904377; fax: +353214904058.
E-mail address: richard.winfield@tyndall.ie (R.J. Winfield).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.10.044

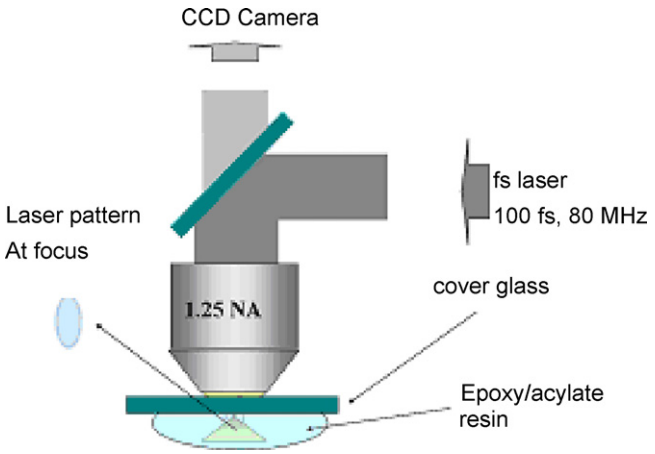

Fig. 1. Laser system.

was varied using neutral density filters and the exposure gated by a Uniblitz LS3ZM2 shutter.

The sample movement was provided by an XYZ stack of piezoelectric stages (Physik Instrumente (PI) GmbH). Because an oil immersion objective was used, with short working distance, the epoxy–acrylate resin was mounted inverted on the stage platform to separate it from the index matching fluid. The substrate was a 120 μm thick glass slide.

The material used for 2-photon polymerization was prepared by mixing Ebecryl 265 (Cytec), which is an aliphatic urethane triacrylate diluted with TRPGD, with the modulator trimethylol propane ethoxylate triacylate. This was primarily done for ease of handling and efficiency of mixing subsequent components of the system. Since Ebecryl 265 is extremely viscous, it would be very difficult to achieve a homogenous mixture without the addition of the modulator to reduce viscosity. Also, effective removal of unpolymerized material from the polymerized network would be extremely difficult in the case of a highly viscous resin. 3-Glycidoxypropyl trimethoxysilane was then added epoxy source, followed by addition of 4,4-bis (diethylamino) benzophenone as a photo-initiator. The mixture was allowed to degas over night before use.

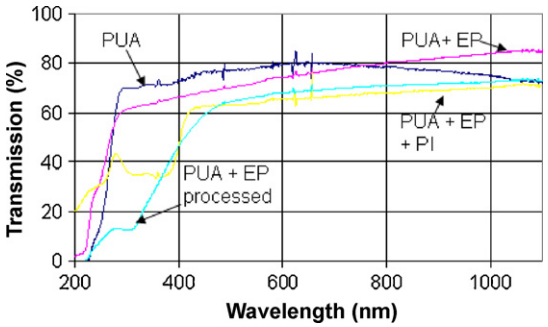

Fig. 3. UV–vis transmission spectrum.

The components of the resin most likely to affect the polymerization characteristics are the photoinitiator concentration and the ratio of the epoxy source to the Ebecryl 265 acrylate. In order to study the effect of photoinitiator concentration on the dimensions of the polymerized structure a series of samples were prepared with photoinitiator concentrations of 0.5, 1.0 and 2.0 wt.%. For this series the concentration of 3-glycidoxypropyl trimethoxysilane was 6.0 mol%. To investigate the effect of the epoxy component the photoinitiator concentration was held constant at 1 wt.% and samples were prepared with 3-glycidoxypropyl trimethoxysilane concentrations of 0, 6.0 and 30 mol%. After laser exposure, the unpolymerized resin was dissolved in isopropyl alcohol leaving the polymerized structure written in the acrylate system. The sample was then placed on a hot plate (10 min at 60 °C) to thermally cross link the epoxy group.

Spectral measurements were also made on thin film samples using an Agilent 8453 UV–vis spectrometer. In the case of the UV–vis experiments, representative samples were prepared by spin coating quartz discs with: ebecryl, ebecryl with modulator, ebecryl-modulator with photo-initiator and finally the UV processed material. The resulting films, except the UV processed film

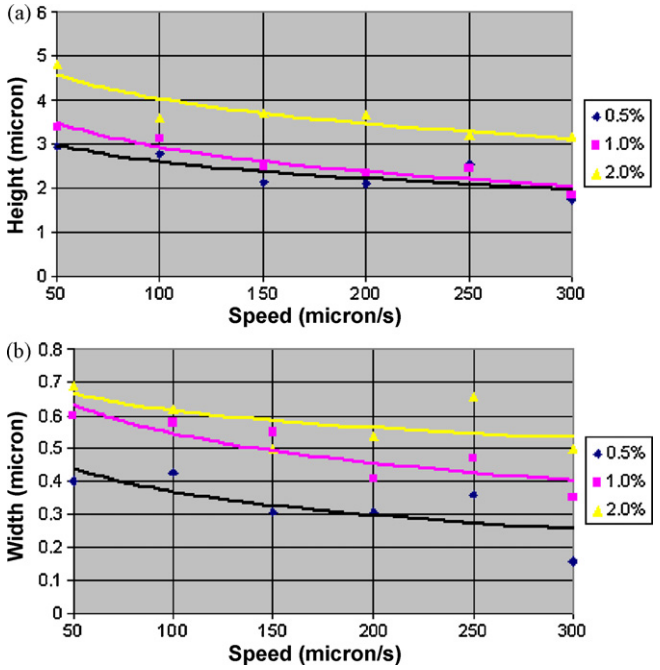

Fig. 2. Resin writing characteristics for different photoinitiator concentrations: (a) height, (b) width.

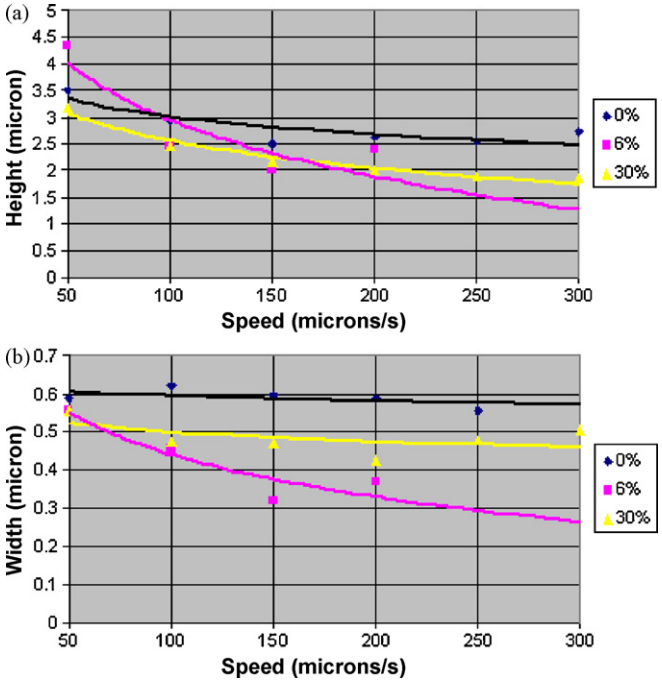

Fig. 4. Resin writing characteristics for different epoxy concentrations: (a) height, (b) width.