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Photopolymers with tunable mechanical properties processed by laser-based high-resolution stereolithography

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Abstract

Stereolithography (SLA) is a widely used technique for the fabrication of prototypes and small series products. The main advantage of SLA and related solid freeform fabrication (SFF) techniques is their capability to fabricate parts with complex shapes with high resolution. Although the spectrum of available materials has been widened in recent years, there is still a lack of materials which can be processed with SLA on a routine basis. In this work, a micro-SLA (μSLA) system is presented which can shape a number of different photopolymers with resolutions down to 5 μm in the xy-plane and 10 μm in the z-direction. The system is capable of processing various specifically tailored photopolymers which are based on acrylate chemistry. The materials processed for this work range from hybrid sol–gel materials (ORMOCER) to photo-crosslinked elastomers and hydrogels. The elastic moduli of these materials can be tuned over several orders of magnitude and range from 0.1 MPa to 8000 MPa. The reactivity of these monomers is sufficient for achieving writing speeds up to 500 mm s^{-1} which is comparable to commercial SLA resins. Various test structures are presented which show the suitability of the process for fabricating parts required for applications in micro-mechanical systems as well as for applications in biomedical engineering. Using the presented system, internal channels with a diameter of 50 μm and a length of 1500 μm could be fabricated. It was also possible to manufacture a micro-mechanical system consisting of a fixed axe and a free spinning turbine wheel.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Solid freeform fabrication (SFF) methods based on photopolymerization like stereolithopgraphy (SLA), digital light processing (DLP) or two-photon polymerization (2PP) offer several advantages compared to traditional manufacturing methods: there is no need for tools or masks and due to the fact that parts are built by stacking up thin layers of material, there is virtually no limit regarding the possible shape complexity of the fabricated parts. Although there is a large number of SFF-methods available, lithographic processes are most commonly used in the context of micro-machining. Lithographic SFF methods are capable of producing parts with excellent feature resolution and small layer thicknesses. The feature resolution of commercially available SLA- and DLP-systems is around 50 μm. The systems use either a ultraviolet laser beam (SLA) or a digital mirror device in combination with a high-pressure mercury lamp (DLP) to selectively irradiate a photosensitive resin. Where the light hits the resin surface, photopolymerization takes place and the resin solidifies. After one layer has been completed, the part is coated with a fresh layer of uncured resin and the process is repeated until the part is built.

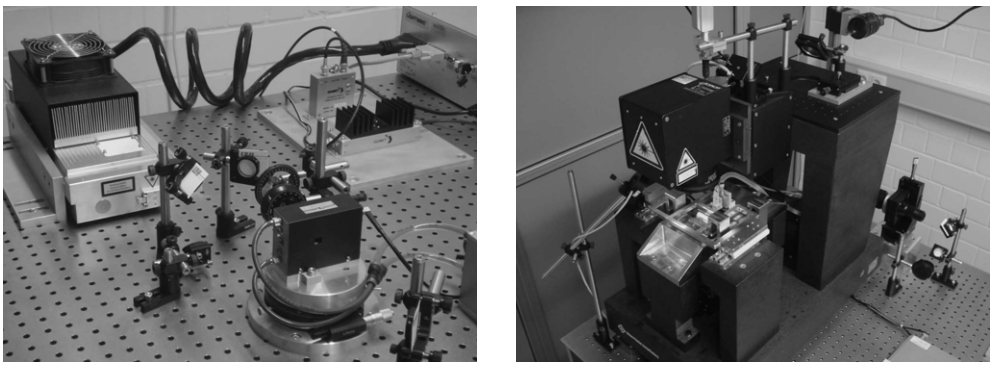

Figure 1. Optical setup with laser source and AOM (left image), and hard stone machining system with a laser scanner head, high-precision translation stages and processing chamber (right image).

Recent developments in the field of two-photon polymerization (2PP) have further improved achievable feature resolutions. Currently, 2PP is the SFF process with the best geometrical resolution [1, 2]. Wall thicknesses <300 nm have already been achieved [3, 4]. Main drawback of 2PP is the low writing speed. Compared to SLA (typical writing speed 200–500 mm s^{-1}) 2PP is at least one or two orders of magnitude slower (typically 0.5–2 mm s^{-1}). Currently used 2PP systems are furthermore limited in the maximum height of the fabricated parts (<1 mm) whereas there is virtually no limit for the build height in SLA systems.

For this work a new micro-SLA (μSLA) system with significantly enhanced feature resolution, compared to currently available SLA systems, was developed. With this system feature, resolutions down to 5 μm in the focal plane (xy-plane) and 10 μm in the direction of the incoming laser beam (z-direction) have been achieved. At the same time comparable writing speeds as in commercial systems could be demonstrated.

Other microfabrication techniques such as soft lithography using PDMS-moulds [5, 6] or mask-based lithographic processes offer significantly higher feature resolutions compared to μSLA, but they usually require the fabrication of expensive masks or moulds and they are highly limited when the fabrication of truly three-dimensional shapes is required. Especially in the field of micro-fluidics and biomedical engineering (e.g., scaffolds for tissue engineering), where minimum feature resolutions in the range of 1–10 μm are sufficient, and where complex shapes with severe undercuts are required, μSLA is therefore the potentially best suited manufacturing process.

Another benefit of using μSLA is the fact that the utilized photopolymers can be widely modified regarding their mechanical properties. By choosing different monomers and by changing the degree of cross linking the elastic modulus and the strength of the final product can be tailored quite easily. Additionally, by careful selection of specific monomers biocompatible and biodegradable monomers can be formed ([7–9]). Commercial SLA-resins are usually hybrid systems, containing acrylate-based monomers as well as epoxy-based monomers. The advantage of acrylate chemistry is the higher reactivity whereas epoxy-based resins exhibit significantly lower shrinkage. When macroscopic parts are manufactured by SLA, the degree of shrinkage usually limits the achievable accuracy of the final part. For microfabrication, shrinkage is less of an issue and the goal of this work is therefore to screen various acrylate-based resins regarding their suitability for μSLA. The formulations have been tailored to decrease the penetration depth of the incoming laser beams and to adjust the viscosity to a level that allows the coating of reasonably thin layers.

2. Microstereolithography system

2.1. Experimental setup

For this work, a custom made micro stereo lithography (μSLA) apparatus, capable for fabricating high-resolution structures has been deployed. Similar to conventional stereo lithography, parts are fabricated in a step-wise production cycle by scanning a focused laser beam over a liquid monomer surface after depositing a homogeneous layer of non-polymerized liquid on a substrate. By moving the substrate at precise increments inside a processing chamber that is filled with the liquid monomer, parts are built from the bottom to their top by selectively curing the areas that have to be solidified.

The μSLA system presented in this work is mounted on an optical table that carries the optical setup including the beam source and handling as well as a hard stone frame that carries high-precision translation stages, the processing chamber and laser scanning system (figure 1).

Four piezoelectric high-precision translation stages, offering an encoder-based resolution of 300 nm, are used for substrate positioning, polymer level error compensation and coating procedure. While positioning the substrate inside the processing chamber, the compensation mechanism moves in the opposite direction in order to keep the polymer level constant. A roller-coating device having a permanent contact with the polymer ensures the lamination of precise layers with a defined thickness. For illumination purposes, a frequency-tripled Nd:YAG oscillator operating at a wavelength $\lambda = 355$ nm with a maximum output power of $P_L = 20$ mW is used. Quasi-cw pulse trains of duration $\tau_P = 10$ ps are provided at a repetition rate of $\nu = 100$ MHz. An acousto-optic modulator (AOM) is used for fast time modulation of the laser beam in between irradiation cycles. The effective laser power used

during processing is aligned by a variable metallic ND filter. The laser beam is expanded and directed into a galvanometric scanning head. Two perpendicular oriented mirrors ensure the precise positioning of the laser beam on the polymers surface, with a calculated focal spot of approximately $f = 7.5\ \mu$m by using a telecentric scanning lens with a focal length of $f = 100$ mm. In order to precisely align the focal position of the laser beam on the polymers surface, the scanner head is mounted on a precision translation stage that offers the vertical position with a resolution of 1 μm. The automated production sequence is controlled by custom made software installed on a conventional PC. Like in conventional stereo lithography, digital files (STL-format) are generated from user-defined 3D-CAD models and sliced at constant increments among the z-axis. After slicing each generated layer (CLI-format) contains the information for layer fabrication. The μSLA setup is installed in a suitable laboratory environment with amber light.

2.2. Experimental procedure

For micro fabrication purpose, suitable substrates made of aluminium are mounted on the positioning platform that is subsequently moved into the starting position. A starting layer is coated and polymerized. Using the control software, the STL-files are virtually placed in the building room of the machine and sliced with constant increments. After allocating fabrication parameters (scanning speed v_s, hatch distance d_h, and laser power P_L) the automated production sequence is initiated. After the fabrication of the last layer is finished, the substrate with the built micro parts on top is removed from the processing chamber and cleaned in a chemical developer (2-propanol and 4-methyl-2-pentanone).

3. Materials

In this work, photopolymers based on acrylate chemistry are used to obtain lithographically fabricated parts. On one side, materials based on organically modified ceramics (ORMOCERs) were evaluated. Additionally, a number of purely organic systems, based on commercially available monomers, were evaluated in order to obtain a photopolymer which is compatible with the μSLA system described in section 2.1. Usually, such formulations are based on high molecular weight monomers with more than one reactive group that define the mechanical properties or in some special applications the biodegradation of the polymer. As these monomers are often highly viscous mono- and multi-functional reactive diluents are used to tune the processing viscosity of the formulation (figure 2). Additionally, by the number of reactive groups, the mechanical properties can be tuned even further. Generally, acrylate-based monomers are significantly more reactive than methacrylates. Advantages of methacrylates can be found in less toxicity and higher storage stability of the monomer and better mechanical properties. Absorption characteristics of the photoinitiator are essential as it has to meet the emission spectra of the light source. Generally, photoreactions occur from the less intensive $n-\pi^*$ transition, usually found at higher wavelength (320–360 nm) compared to the more intensive $\pi-\pi^*$ transition. In the presence of a solvent (water, poly (ethylene glycol)—PEG) the polymer network is swollen by the solvent molecules and the stiffness and strength of the overall structure is decreased. If required, inorganic particles (e.g., ceramic powders) can be incorporated in order to increase Youngs modulus or to equip the polymer with additional functional properties. Solvents as well as fillers will reduce the overall shrinkage during polymerization, thus increasing the shape accuracy of the produced part.

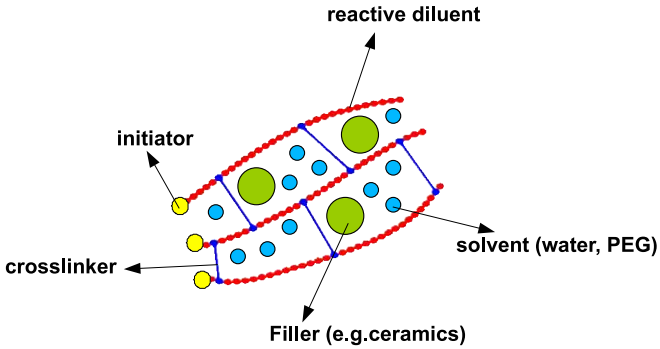

Figure 2. Basic building blocks of the utilized photopolymers.

3.1. Organically modified ceramics (ORMOCER)

ORMOCERs are hybrid polymers, that are synthesized by the sol–gel process [10], where for example diphenylsilanediol reacts with methacryloxipropyltrimethoxysilane. By controlled hydrolysis and condensation of the organically modified Si alkoxides, the sol–gel process is initiated. A radical photoinitiator (e.g., Irgacure 369, used as received from Ciba) is added after the removal of solvents at the end of the synthesis process. For the purpose of μSLA, the formulation has been adjusted by using additives to be introduced into the polymer and subsequently characterized, as published elsewhere [11].

The major achievement has been the effective increase of the process resolution in both vertical and lateral direction as well as the viscosity reduction of the applied monomer, thus avoiding high settling times. The curing depth cd could be adjusted in the range of $20 < cd < 80\ \mu$m below a cumulative laser fluence of $H_0 = 1000\ \mathrm{J\,cm^{-2}}$ (figure 3), when using 0.5% of ADM3 dye.

Generally, the lateral process resolution is mainly dependent on the focal spot size of the applied laser system. Due to this, the measurements have been performed in the focal plane only. Although out-of-focus irradiation may lead to enhanced resolution in the vertical direction, the degree of polymerization is lower, thus leading to instable layers. In our measurements, the lateral resolution has been improved up to factor 10 compared to a commercial SL apparatus. The measured curing width c_w of ORMOCER width varying parts of ADM3 is shown in figure 4. According to the graph, the curing width can be scaled by both changing the laser fluence H_0 and the concentration of the introduced dye material. In contrast to the curing depth c_d, the scaling of

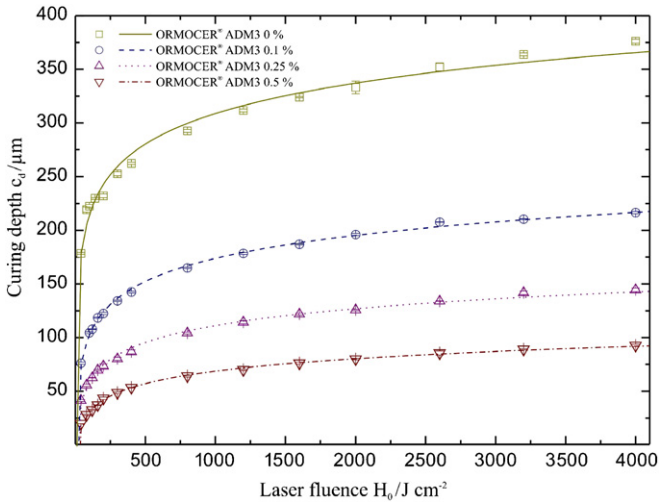

Figure 3. The curing depth c_d versus the laser fluence H_0 of modified ORMOCER with varying parts of ADM3 dye.

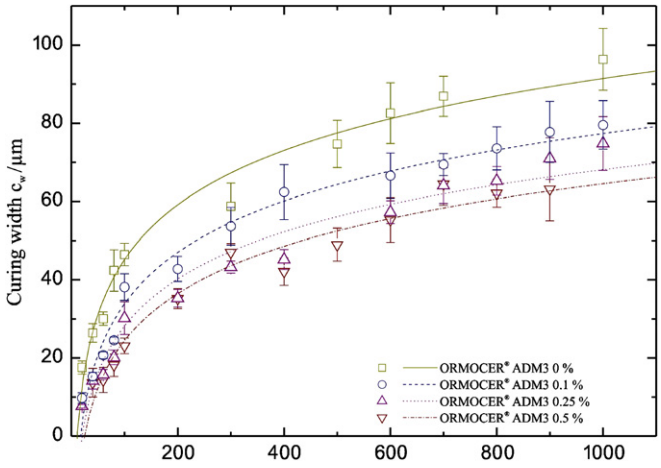

Figure 4. The curing width c_w versus the laser fluence H_0 of modified ORMOCER with varying parts of ADM3 dye.

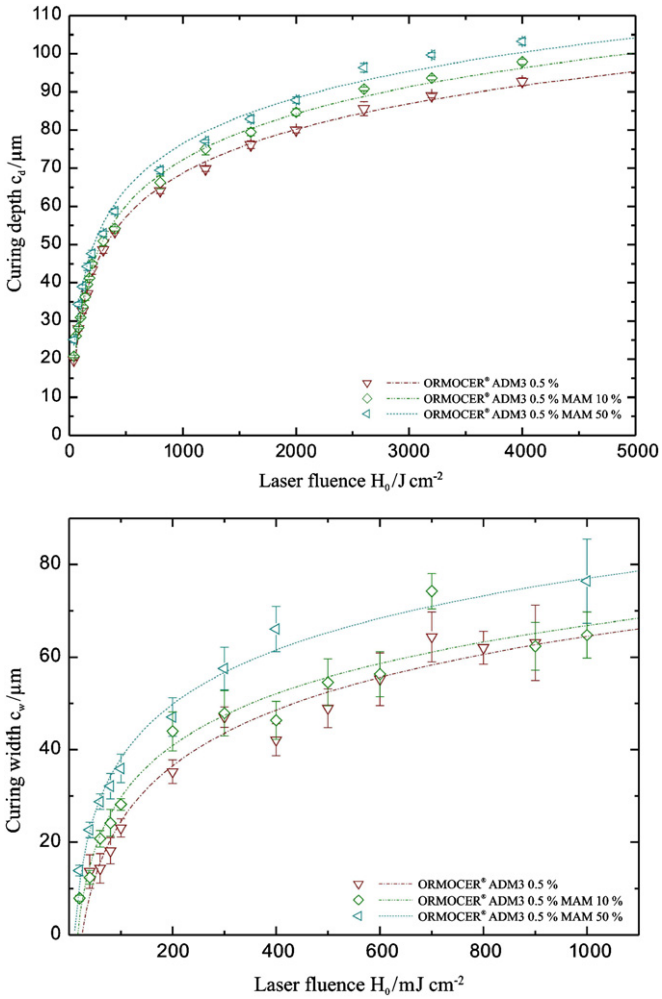

Figure 5. The curing depth c_d (top image) and curing width c_w (bottom image) versus the laser fluence H_0 of modified ORMOCER with 0.5 wt% of ADM3 and varying contents of a multi-functional acrylate monomer, which was used for viscosity reduction.

c_w is mainly achieved by the change of the laser fluence and less by the concentration of ADM3. At a laser fluence of 500 mJ cm^{-2}, a curing width of 70 μm is achieved without the use of an absorbing medium. In contrast to this, 0.5% of ADM3 leads to an increase of the resolution down to 50 μm at identical laser fluence. The smallest line structures which are developed without detaching from the applied glass substrate are around 7.5 μm in size and generated at a laser fluence H_0 of 20 mJ cm^{-2}. Before initiating the chemical development sequence, generated lines around 5 μm are detected via optical microscopy. However, during development, the fabricated lines detach from the substrate. Suitable processing resolutions for μSLA purpose could be achieved when using ORMOCER modified with 0.5% of ADM3 in the region of low laser fluence.

The influence of a multi-functional acrylate monomer (MAM) for viscosity reduction has been studied to detect possible changes in the process resolution. Additional curing measurements have been done after introducing 10 and 50% of the MAM into ORMOCER samples already modified with 0.5% of ADM 3. The following figures (figure 5) illustrate the change of both the curing depth and width when increasing the content of the MAM. Minor deviations towards a lower process resolution have been detected, however the gained resolution is still applicable for high-resolution stereolithography.

3.2. Organic acrylate-based resins

In order to further increase the materials spectrum available for μSLA, a number of acrylate-based monomers (figure 6) were used to obtain photopolymers with tailored chemical and mechanical properties. Depending on the utilized reactive diluents and cross-linker the reactivity as well as functional and structural properties can be tailored. Besides reactive groups the resin can also contain solvents to facilitate the fabrication of (hydro)gels. The utilized solvents for this work were water and PEG with a molecular weight of around 400.

For photopolymerization, the photoinitiator Irgacure 819 (IRG 819, figure 7) was used. To limit the penetration depth the UV absorber 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (DHDMBP, figure 7) was applied.

Table 1. Overview of photoreactivity and mechanical properties of the utilized materials. Renshape SL7570 [12] is mentioned as a reference material. All values were measured at room temperature.

Material	Young's Modulus E (MPa)	Bending Strength σ_b (MPa)	Viscosity η (mPa s)	Photoreactivity $t_{95\%}$ (s)	Photoreactivity H_{5s}/H_{tot} (%)
ETA/TTA 1:1	689	32	148	27	60
CEA/PEGDA/PEG 9:1:10	0.40[a]	0.15	21	10	73
PEGDA/UDMA 1:4	2,200	95	1,770	36	57
filled TTA/HEMA 4:1	8,000	70	28[b]	66	66
Ormocer	2,500		392	220	20
Renshape SL7570	2,600	95	210	107	22

[a] E and σ_b were measured in tension, since three-point bend tests were not possible due to the low stiffness of the samples. For the tensile test, PEG was exchanged with water.
[b] Viscosity and photoreactivity were measured with the unfilled material.

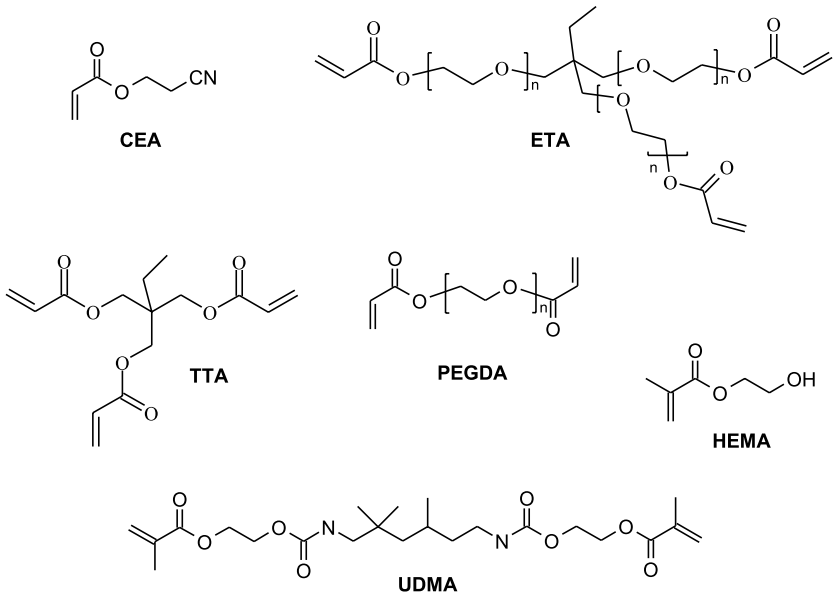

Figure 6. Utilized monomers.

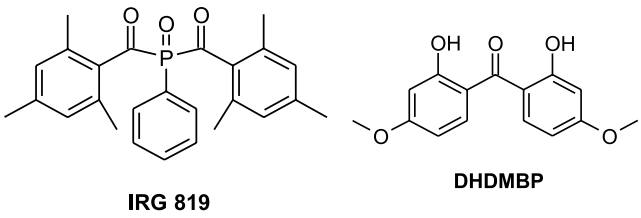

Figure 7. Utilized photoinitator (IRG 819) and UV-absorber (DHDMBP).

3.3. Photochemical characterization

Photo-differential scanning calorimetry (Photo-DSC) measurements of the photoresins were carried out using a Netzsch DSC 204 FI Phoenix ASC equipped with an EXFO OmniCure Series 2001 as a light source (filtered light with a wavelength of 280–450 nm and an intensity of 3000 mW cm^{-2}) similar to the method previously described [13]. From the Photo-DSC plots (heat versus time) the data from table 1 were obtained. $t_{95\%}$ is the time to reach 95% of the total conversion. H_{5s}/H_{tot} is the ratio between the formed heat after a time period of 5 s and the total heat of polymerization.

3.4. Mechanical properties

Due to the fact that the network density of the photopolymer can be varied to a large extent, the mechanical properties (strength, Young's modulus) of the final photopolymer can be tailored over a wide range. By adding solvents, which lead to the formation of a (hydro)gel, or by adding inorganic fillers, this range could be further expanded. Using the monomer formulations described in the previous section, silicone molds were filled and the liquid resin was exposed with UV-light. After photopolymerization, the beams were taken out of the mold for mechanical testing. Preferred method for the determination of strength and stiffness was three-point bending. The beams were 4 × 2 × 40 mm in size and were tested on a universal testing machine MTS Synergie 200. The CEA/PEGDA hydrogel was too soft for being evaluated in bending. For this material, a tensile test was employed.

The obtained values are shown in table 1. Renshape SL7570, a widely used resin for commercial SLA applications, is used as a reference material. The purely organic resins (ETA/TTA, PEGDA/UDMA) as well as the tested

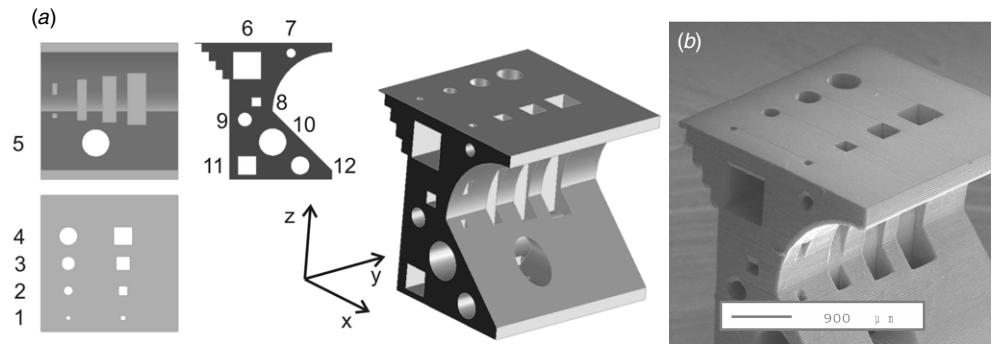

Figure 8. Three-dimensional CAD model for μSLA process analysis (left image). The structure was 1.5 mm in all directions with channel sizes ranging from 50 μm (1) to 300 μm for cylindrical and rectangular channels, respectively. SEM image of the fabricated part with a layer thickness of 10 μm (right image).

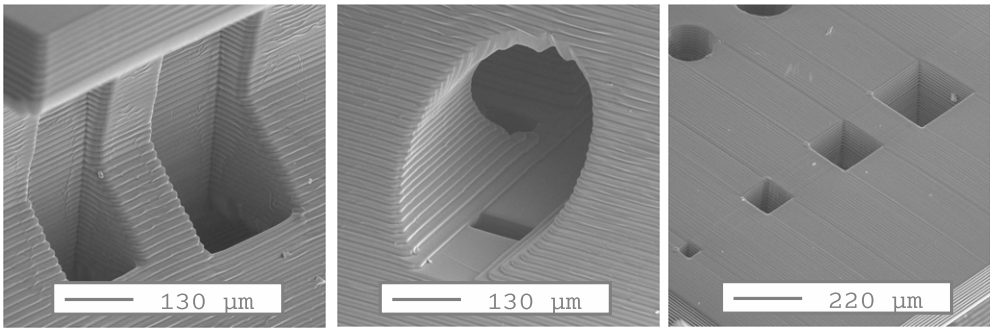

Figure 9. SEM detail images of the fabricated part, produced with a cumulative laser fluence of $H_0 = 208$ J cm^{-2}.

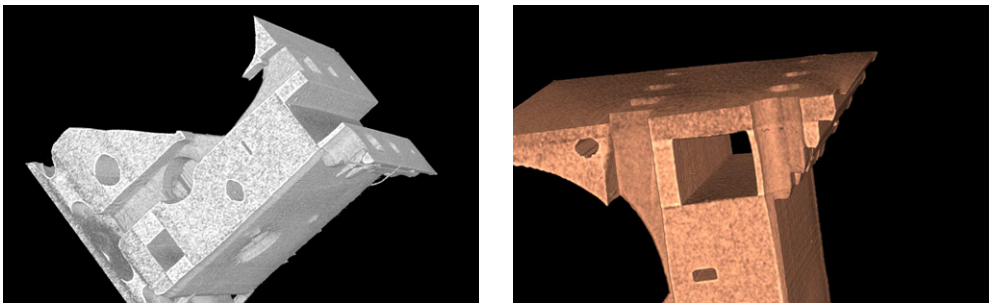

Figure 10. Virtual cross sections of the fabricated part made with micro computer tomography.

ORMOCER have values comparable to SL7570. By incorporating ceramic hydroxyapatite particles into the organic TTA/HEMA matrix, the Young's modulus of the material can be increased to a value of 8000 MPa without sacrificing the strength. For many applications, especially in biomedical and tissue engineering, soft materials with elastomer-like properties are required [14]. Such properties are accessible with photopolymers if the network density is low and large parts of the reactive monomer are replaced by a solvent. Using a mixture of nine parts CEA with one part PEGDA and ten parts of solvent (water or PEG), gels with low Young's modulus and sufficient reactivity for being structured with μSLA could be obtained. A Young's modulus of 400 kPa and a tensile strength of 150 kPa could be measured with these materials.

4. Results and applications

4.1. Process resolution of the μSLA system using ORMOCER

In order to distinguish the achievable μSLA process resolution, a three-dimensional CAD model with internal cylindrical and rectangular channels has been developed (figure 8(*a*)) and produced using the micro stereo lithography machine (figure 8(*b*)). For this study, the deployed material has been ORMOCER. The channel size of the model has been set from 50 μm (1) to 300 μm (5, 6) for cylindrical and rectangular channels, respectively. The edge length of the three-dimensional structure was 1.5 mm in all directions, consequently, the model consisted of 150 individual layers when using a layer thickness of 10 μm. Scanning Electron Microscopy (SEM) and Micro Computer Tomography (μCT)

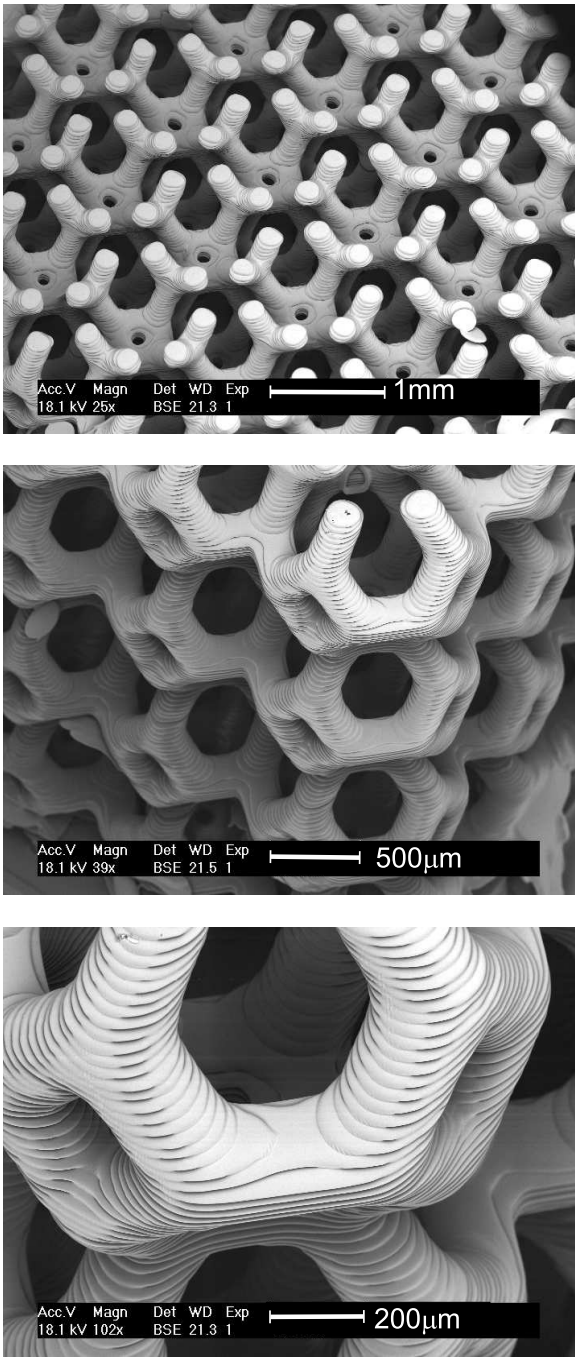

Figure 11. SEM images of the cellular structure made of ORMOCER.

have been used for determination of the achieved structural quality. Further optical microscopy was applied to distinguish the achieved precision.

Following a two-step analysis process, the fabricated structure has first been investigated regarding its general finish using a CamScan Series 2 SEM, operated at $U = 15$ kV and $P < 10^{-5}$ mbar. SEM detail images of the fabricated structure are shown in figure 4.2. It has been observed that the fabricated circular and rectangular channels are well defined and no liquid polymer residues remain on the structures surface or in the entrance region of the channels.

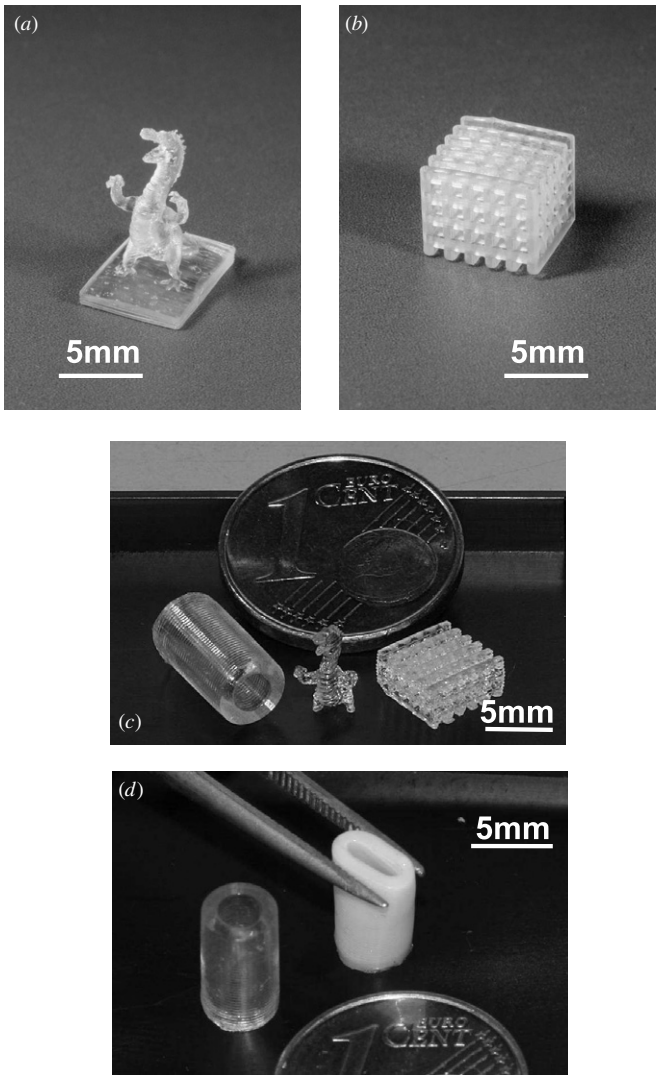

Figure 12. Photographs of test parts made of PEGDA/UDMA (*a*), (*b*) and CEA/PEGDA gels (*c*), (*d*). The elastomeric behaviour of CEA/PEGDA-hydrogel can be seen from the test tube compressed between the tweezer tips.

In order to gain access to the internal geometry of the structure, a 180 kV Micro Computer Tomography system from the type Phoenix x-ray Nanotom has been applied. Depending on both sample size and material, the Nanotom μ-CT achieves a maximum voxel resolution of approximately 500 nm. In the case of the fabricated structure, the detector magnification could be adjusted down to a voxel resolution of 2 μm, which was sufficient for analysing the internal structure geometry. Complete three-dimensional images could be generated at arbitrary slicing planes in a non-destructive fashion (figure 10). In that way, the internal morphology of the channels has been observed.

It has been found during inspection that all rectangular and cylindrical channels were free of any residue (liquids or solids). Additionally, it could be distinguished qualitatively that no deviations in shape of the channels occurred, e.g. the vertically arranged round channels where cylindrically shaped. The entrance diameters of the channels have been measured with optical microscopy by using both 20x and 50x objectives.

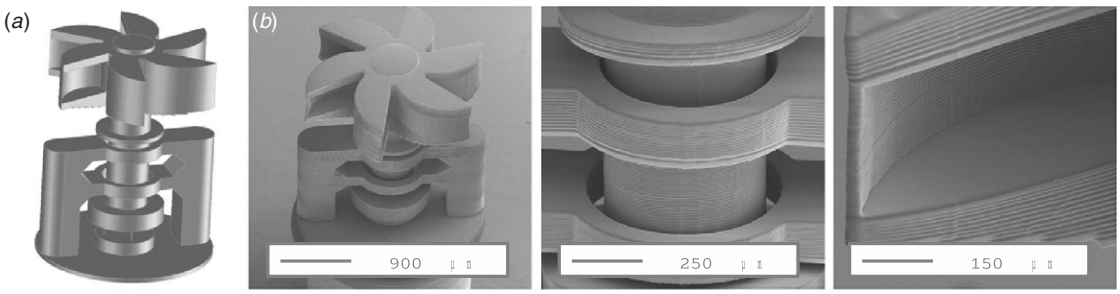

Figure 13. SEM image of a micro mechanical arrangement with movable components, produced with a laser fluence of $H_0 = 400$ J cm^{-2} and a layer thickness of 10 μm.

The achieved precision of the channels on the top surface of the structure has been better than 17 μm [15].

As a further benchmark structure a cellular structure, which has recently been analyzed regarding its mechanical properties [16], has been built with the above-described μSLA system. In figure 11 the corresponding SEM images are shown. The structure has been built with a layer thickness of 25 μm using ORMOCER resin. Due to the small penetration depth the undercuts are well resolved and beams with a thickness around 200 μm could be built successfully.

4.2. Process resolution of the μSLA system using acrylate-based resins and hydrogels

The materials described in section 3.2 were used to build various test parts depicted in figure 12. Compared to ORMOCERs the organic acrylates can more easily be tailored regarding their functional and structural properties, which makes them especially interesting for applications in biomedicine and tissue engineering. Compared to ORMOCERs and commercial hybrid resins (Renshape) the investigated acrylate-based resins react significantly faster (see $t_{95\%}$-values in table 1). It was therefore possible to fabricate structures with a write speed of 50–100 mm s^{-1} using a 2 mW laser beam. Drawback of the large fraction of highly reactive acrylate groups in the utilized resins is the increased shrinkage compared to ORMOCERs and commercial SLA resins such as Renshape. The feature resolution of all investigated resins was comparable, as long as the penetration depth is controlled properly by adding the appropriate amount of initiator and UV-absorber.

Special considerations have to be taken if hydrogel parts have to be fabricated. The CEA/PEGDA resins can be mixed with various amounts (up to 80 wt% could be achieved) of solvents (PEG), making them an ideal candidate for the fabrication of hydrogel structures. Due to the considerable evaporation of water, it is difficult to keep the resin level constant during the build process. It is therefore necessary to structure the parts using a resin containing solvents with high-boiling point T_b such as PEG 300 ($T_b \approx 200^\circ$ C). After the build process has been completed, the part was taken out and cleaned (figure 12(*c*)). In a last processing step the organic solvent is exchanged by water in order to achieve the final hydrogel part (figure 12(*d*)).

4.3. Micro-mechanical systems

Based on the CAD file displayed in figure 13 (left image) a micro mechanical arrangement with an integrated movable component could be produced without any assembly step. Gap distances between moving parts could be precisely fabricated down to approximately 75 μm. The roughness of the top surface has been measured to $R_z < 500$ nm.

5. Conclusion

Using a laser-based stereolithography setup a system with a beam diameter of 7.5 μm and a minimal layer thickness of 10 μm was developed. The system was screened using various commercially available resins (ORMOCER, Renshape) and specifically developed acrylate-based organic resins. The mechanical properties of the utilized resin can be tailored over a wide range, e.g. the elastic modulus E can range from 0.4 to 8000 MPa. The resins were screened regarding their rheological behaviour (viscosity) and their photoreactivity. It could be shown that parts with heavy undercuts and high-aspect-ratio internal channels (minimum diameter 50 μm and aspect ratio of 30) can be built. It was also possible to fabricate moving parts with clearances in the range of 75 μm.

Acknowledgments

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