

Multi Laser Volume Stereolithography, a new Freeform Fabrication Method

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Zusammenfassung

A new method creating 3D objects within photopolymer resin has been developed which promises quality enhancement in the field of 3D printed transparent objects. In contrast to common additive manufacturing techniques the volumetric object is not build layer by layer at the surface of the resin. Instead the object is built up within the volume of the resin. This method, called Multi Laser Volume Stereolithography (MLVS), enables hardening of the resin only at the exterior surface of an object. All focus points of six lasers are overlapped in one voxel to cure the resin. Moving this overlap area around the contour of the object hardens the outer shell of the object and leaves the inner material fluid. The method promises higher productivity and higher resolution than current layer by layer techniques. The process and its validation by experiments are presented.

Keywords 3D Printing, Photopolymers, Polymerisationsverfahren - Stereolithographie (SL), Rapid Prototyping, Stereolithography, UV curing

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1. Introduction

Additive Manufacturing, often called 3D printing, is one of the most successful inventions in the field of rapid fabrication and prototyping. Originating from the incentive of hobbyists and tinkerers in the 1980th [1], 3D printing is established nowadays in commercial production. The opportunity to generate objects in a fraction of common manufacturing times attracts nearly every industry segment. The most common application is the production of prototypes, but increasingly customized ready for sale products are being produced [2]. Including dental implants, human skin and oral drugs to name a few [3, 4, 5, 6].

Generally, 3D printing is based on *additive manufacturing* methods whose basic principle is to assemble layers with equal thickness [2]. The contouring of each layer is given by a two-dimensional plane. These planes are created by slicing the 3D-CAD drawing which provides the data of the object. Layers will be stacked and bonded together which finally results in the formation of the desired workpiece. Producing the 3D object directly from the CAD design file without the need of adaptation to the manufacturing process is a unique selling point of additive manufacturing. Depending on the field of application an appropriate printer system can be chosen out of a multitude of commercially available printer variations with fixed specialized properties. Depending on the printing process there exists a vast variety of surface and material qualities. Techniques and printing qualities variate from fast but less stable to more complex and costly.

Before starting explanations of the new method, called *Multi Laser Volume Stereolithography* (MLVS), a short introduction to the field of commercial *additive manufacturing* techniques is given in order to put attention onto the unique attributes of MLVS.

1.1. Overview Additive Manufacturing

The most common 3D printing techniques can be categorized by elucidating three methods by the names of: *Selective Laser Sintering (SLS)*, *Color and Plastic Jet Printing (CJP/ PJP)* and *Stereolithography (SLA)*.

Selective Laser Sintering is a technique based on laser beam melting of powder or granulate layers to stable objects [7, 8]. The dry material is spread homogeneously over the entire printing area in thin layers. A laser melts material by tracing the contouring of each layer. Bulk material that remained unmelted can be reused. Synthetic materials like polyamid, metal- or ceramic powders are used for SLS. Applied laser types are CO₂-, Nd:YAG- or fiber-lasers. SLS and variants of SLS using electron- or infrared-beams processing plastic or metal powder, are summed up in the category of *Melting- and Sintering processes* [9]. *Color Jet Printing (CJP)* is based on the 2D ink-jet printer technology [10, 11]. The ink-jet print head spreads a liquid binding agent over the surface of a powder bed. Whereas the powder serves as underfilling and bulk material, the ink-layers form the resulting 3D object. One after another a layer of white powder is spread over the surface area, followed by the printing head complementing the binding agent over a defined area to form the contour of the current object layer. By using binding agents in the original object color, there is no need for further coloring. Due to inevitably resulting of interstitial space between ink lines the object has to be infiltrated with wax or epoxy resin to achieve a mechanical stability.

Plastic Jet Printing (PJP) is a 3D printing technology that operates with thermoplastics [2] and works by the principle of extrusion. A printer head extrudes beads of the used material (filament) under heat and pressure. The objects arises layer wise without the need of filling material. Support pillars are necessary to realize laterally protruding structures. These supports have to be integrated in the CAD file beforehand. The described principles of CJP and PJP are also related to *Multi-Jet-Modeling*, *Thermo Jet* or *Direct Metal Printer*.

Stereolithography (SLA) is also based on a layer-wise process [2]. Materials used for SLA are photosensitive epoxy or acrylic based synthetic resins. Furthermore two methods of SLA can be distinguished namely *Solid Ground Curing* and *Laser Stereolithography*. *Solid Ground Curing (SGC)* works by the principle of covering. A mask covers the area that does not belong to the current object layer. An ultraviolet-light source irradiates the liquid photosensitive material at the uncovered areas. Supporting pillars are not required, areas not belonging to the object are filled with wax applied by a separate mechanism. Whereas the SGC technique cures an entire layer, *Laser Stereolithography* is based on a point wise curing process, which will be explained in more detail in 1.2.

In conclusion, conventional 3D printing is based on piling up layers with more or less equal thickness. The layers will be stacked and bonded together and finally result in the formation of the desired object. Due to the layer by layer growth of the object, *staircase effects* are commonly observed [12] depending on the layers thickness.

These defects cannot be avoided completely and need to be considered in the CAD. Eventually vertical printed structures are less precise compared to structures in horizontal line. This circumstance is illustrated in Figure 1. In the following, a closer look to 3D printing with focus on *Laser Stereolithography* is given. Stereolithography and the polymerization process are explained leading over to the optimized *Laser Stereolithography* method the *Multi Laser Volume Stereolithography (MLVS)* developed in the course of this project.

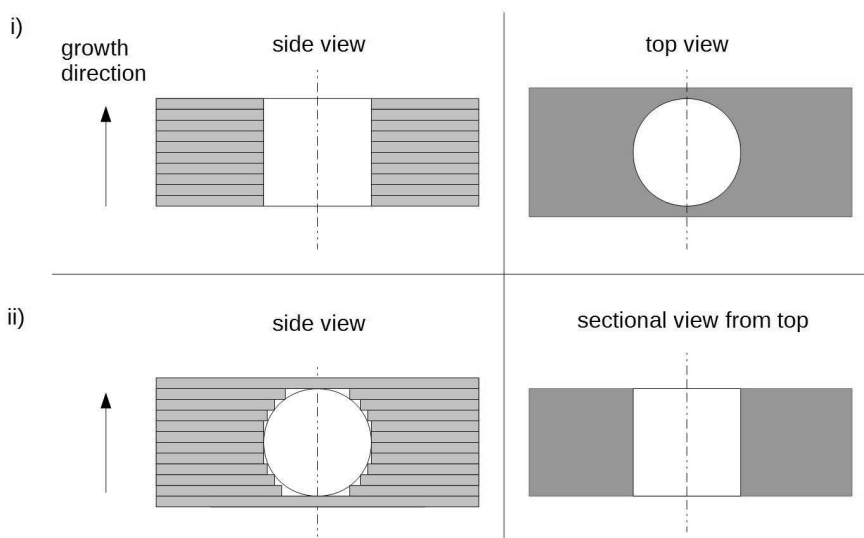


Fig. 1 Schematic drawing of a hole i) in growth direction; ii) perpendicular to growth direction to illustrate the staircase effect. Effect is explained more in detail in [2].

1.2. Laser Stereolithography (LSLA)

Laser Stereolithography, also referred to as *Laserinduced Stereolithography*, is based on the principle of building chains of molecules in photopolymer resin by irradiating with a short-wavelength laser [2]. The laser is focused to the resin's surface. Layer by layer the laser traces the contour given by a two-dimensional CAD design. Molecular chain building in resin is named polymerization and photo-polymerization in case of initialization by photons. At the focal point the laser energy exceeds the threshold needed for starting the polymerization process which causes the hardening of the resin. In summary, polymerization is the process of unsaturated molecules reacting to polymers leading to molecular chains.

Commonly, photopolymer resins are acrylate based and consist of tough low cross linked monomers compounded with photo-initiators. The laser generates a *critical energy* at the resin's surface to start polymerization [13, 14]. At the beginning of polymerization the initiators decompose into their radicals with a single electron in its outer shell. In the growth reaction phase the highly responsive radicals react with carbon atoms bounded in monomers. This reaction leaves another single electron in the outer shell of the monomer and leads to a further reaction. The reaction terminates if no reactive particles are in range of the radicals either due to the lack of further bonding abilities or due to the fusion of two polymer chains. Furthermore the increase of the resin's temperature terminates chain building when exceeding a certain limit. The *ceiling temperature* [1] is defined to be the temperature where polymerization and depolymerization (decomposing polymer chains back into monomers) are in counterbalance.

Each specific initiator is sensitive to photons of a specific wavelength and ionizes by irradiation with an adequate light source. The resulting radicals are responsible for chain building guaranteeing the curing of restricted areas in order to create structures at the resins surface. The responsiveness of the resin can be expressed by the transfer constant C .

$$C = \frac{k_{trans}}{k_{increase}} \quad (1)$$

K_{trans} defines the energy per time induced by the laser and $k_{increase}$ the resulting number of polymer chains [15]. A high number of initiator molecules results in a high polymerization rate of the resin. The *critical energy* yielded by the laser and needed for polymerization depends on the resins composition. The penetration depth depends on the absorption of the laser radiation due to the resin. This absorption is a function of the laser wavelength. The energy $E(x)$ that remains in a depth x can be calculated with the help of the Beer-Lambert-equation [16]:

$$I(x) = I_0 \cdot e^{-\alpha(\lambda) \cdot C \cdot x} \quad (2)$$

$I(x)$ is the intensity at the position x in the resin. I_0 indicates the intensity at the thickness $x = 0$ (initial intensity) and the concentration of the sample is indicated with C . The extinction coefficient $\alpha(\lambda)$ depends on the specific wavelength (λ) and is defined as:

$$\alpha(\lambda) = - \frac{dI}{dx} \cdot \frac{1}{I} \quad (3)$$

dI indicates the light attenuation and dx the distance. The penetration depth is defined as the distance x_{pd} , where the intensity I_0 is lowered to $I_{pd} = I_0 \cdot e^{-1}$ [17].

The resolution of 3D objects created by LSLA is depending on the diameter of the focal point. Focusing the *critical surface energy* at a small area increases the resolution.

1.3. Processing Principle of LSLA

The main component in common LSLA setups is a short wavelength laser irradiating perpendicular to the surface of a resin reservoir. A metal grid serving as a ground plate of the object is placed under the resin's surface, such that the grid is wetted by resin. Tracing the contour of the first layer with the focused laser beam the object is fixed to the ground plate. Sinking downwards the ground plate causes the just cured layer to be moistened by resin. These steps are repeated until all layers of the 3D object are finished. Craning structures are in need of additional supporting pillars. These supporting structures have to be integrated in the CAD design and are made of the same material as the object. They have to be removed from the finished

object in a second production stage. A post curing process of the resin is recommended to reach the full mechanical strength.

2. Multi Laser Volume Stereolithography (MLVS)

The basic principle of *Multi Laser Volume Stereolithography* (MLVS) corresponds to the LSLA method of laser induced polymerization. It is based on the hardening of photopolymer resin by laser radiation. Focusing on the main problems of SLA, the new method should avoid its most evident drawbacks. These drawbacks are the *staircase effect* and the *shrinkage*. The *staircase effect* results from the layer process on which all 3D printing technologies are based. This effect appears in form of steps where smooth curves are required for the object. *Shrinkage* is an effect that occurs in relation with photopolymer resin. Cured structures contract in contact to oxygen and cause an uneven surface. *Multi Laser Volume Stereolithography* superimposes several laser beams, focused to one point within the volume of the resin. The number of laser beams is essential, as well as the intensity and wavelength. Several beams with low intensity are essential to stay below the *critical energy* for polymerization. Moreover the resin needs to have a low absorption at the laser's wavelength to allow a large penetration depth. At the superposition point the *critical energy* is exceeded and polymerization starts.

By MLVS the curing process is done in the bulk resin material instead of hardening the surface of resin like it is executed in the case of LSLA.

Volumetric objects arise within the resin. The focused superimposed laser beams are directed as a whole to trace the outer shell of the desired object. This enables hardening of the object's shell. The bulk material inside can stay liquid and can be cured posterior under an ultraviolet light source. Structural inequalities inside the cured volume, caused by the conventional layered process, can be avoided. It should be possible to fabricate optical components like lenses in high quality due to a perfect homogeneity of the inner material. Losses of resolution or *staircase effects* due to the layer process decrease or vanish completely.

2.1. Processing Principle of MLVS

3D printing with the MLVS method can be achieved by using an interaction of several single laser beams to cure single points in the volume of the resin. More precisely, the initial point of the object is cured at an arbitrary position within the resin reservoir and can grow from here to all sides. Whereas the laser beam in LSLA systems is restricted to the surface of the resin, or in other words to the interface between air and resin, in the case of MLVS each laser beam has to pass the volume of the resin to reach the target interaction point.

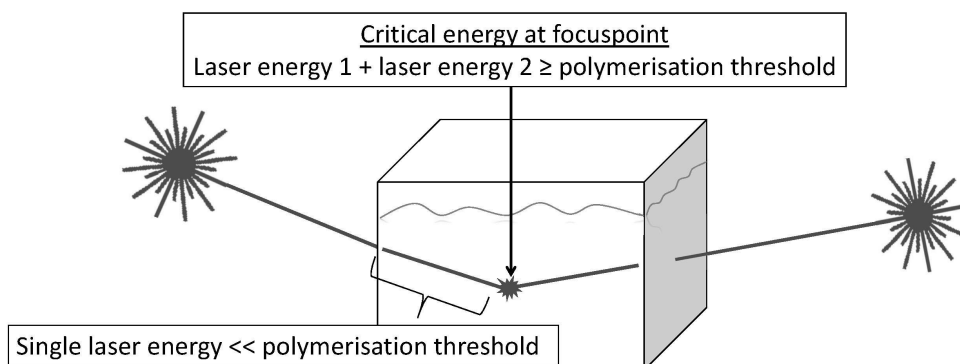


Fig. 2 Schematic drawing of two laser beams focused into a photopolymer reservoir to one target point (voxel).

A laser beam crossing the resin reservoir towards the target point that produces an energy equal or higher than the *critical energy* would cure a needle along its beam path. Consequently the laser intensity of one beam has to be much lower than the *critical intensity*. Only the sum of overlapping laser beams in the interaction point should exceed the critical value to enable polymerization if additionally the exposure time is large enough. This is illustrated in figure 2. A big advantage of this technique is the ability of printing objects with solid surfaces which are still liquid in the enclosed volume. A final curing process of the whole object takes place afterwards and can also be realized outside the printing system, which speeds up the production process. Structural inequalities inside the cured volume, caused by the conventional layered process, can be avoided. Having pointed out the characteristics of MLVS it is advisable to have a closer look at the polymerization process. A commercial resin, *Formlabs CLEAR Photopolymer Resin for Form 1* [18], for 3D printing was used for exploration of the MLVS. It consists of methacrylated oligomers, methacrylated monomers and Photoinitiators.

As described above, the progress of building molecule chains is complex and depends on a number of factors. The energy of a single laser beam should be as low as possible to prevent initiators from building radicals outside the interaction point. The build-up mechanical setup to realize the MLVS used a six laser version. Laser wavelength is 445 nm. The energy of each laser beam has been determined to stay just below the polymerization threshold. Anyhow, initiators outside the focus point occasionally absorb photons and form radicals. These radicals only lead to scattered compounds or very short chains, since the induced energy is too low for long chain growth. Long polymers can only arise if sufficient energy is available. This fact must be taken into account in case of longer production times, as the bulk material changes for a continuance.

One solution to minimize adverse chain building could be the prevention of laser beams crossing the resin at the same point twice. Obviously this is hard to realize. MLVS suggests crossing the same point in a time interval long enough to let the monomers diffuse and to extinguish the active side of the undesired chains. Instead of a continuous radiation a defined pulsed laser radiation is used. The pulse duration ought to be as long as needed to cure one voxel of the desired volume. During the off-phase the laser interaction point can be moved and repositioned. This pulse duration time should be precalculated for each point of the CAD object which has to be cured.

2.2. Polymerization threshold

The *critical energy* to cause radicals and start chain building is defined slightly over the polymerization threshold. Due to the fact that the threshold depends on the resin's composition it has to be identified in a first step. An easy method to measure the progress of polymerization is a spectral analysis (optical spectroscopy). Most photopolymer resins show a high absorption of radiation with short wavelength (UV light). Figure 3 shows the absorption spectrum of *Formlabs CLEAR* for example.

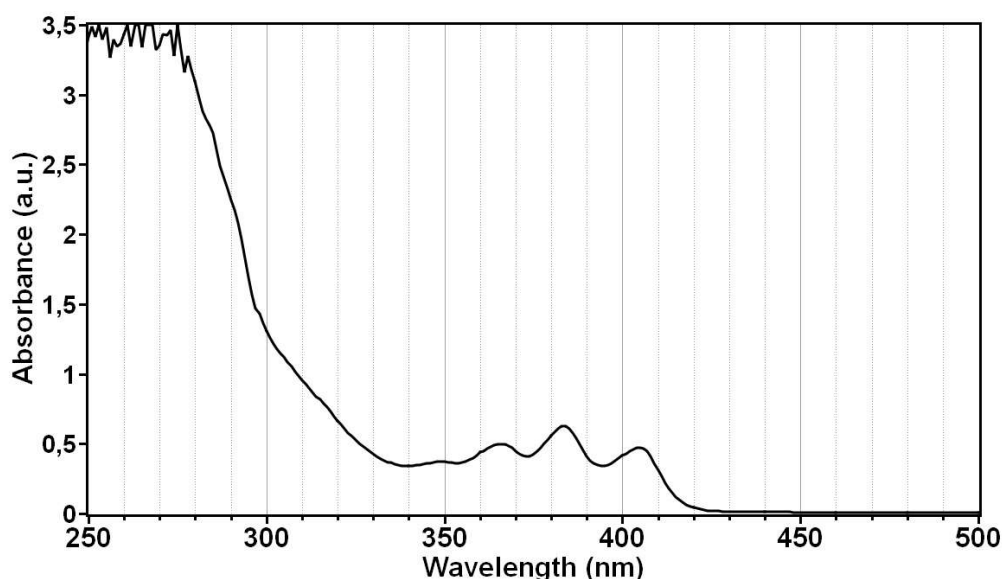


Fig. 3 Spectral absorbance of Formlabs CLEAR resin diluted with Tetrahydrofuran. Measured with a SPECTROstar[®] Nano (sensitivity: OD range 0 to 4 OD).

In the following the used measurement setup and process is described. A cuvette with resin was placed in an open spectrometer setup with a wide spectral range. A laser beam with a wavelength of 445 nm is widened till it illuminates the cuvette's width. The laser intensity is set constantly to 50 mW. The graphs in figure 4 demonstrate the behavior of the resin during irradiation. Fixing the laser power to a constant value the resin is irradiated by the blue laser in intervals of one second. After every interval the spectral transmission was measured. Increasing of exposure time yields decreasing of the transmission of the resin at 425 nm. This wavelength corresponds to the increasing absorbance of *Formlabs CLEAR* resin nearest to the irradiation wavelength. To determine the degree of conversion of the resin alteration of absorption over irradiation/exposure time was measured.

Figure 5 shows the deviation of every value at 425 nm to the reference value measured at the beginning (exp. time: 0 sec). As it can be seen in figure 5 polymerization starts at about 5-6 seconds irradiation time indicated by the steep increase. The liquid photopolymer resin polymerizes into a stable structure. For MLVS the behavior of resin under laser irradiation can be classified into four phases. In the first phase the induced power is too low to evoke any reaction within the resin. At a specific power scattered chains emerge or link up, but the induced energy is too low to end up in long chains. This determines phase two. In the field of 3D printing the third phase is relevant. Complete polymer chains arise to build stable structures. Finally polymerization reaches the fourth phase and no radicals are left to build chains. The resin is now completely hardened.

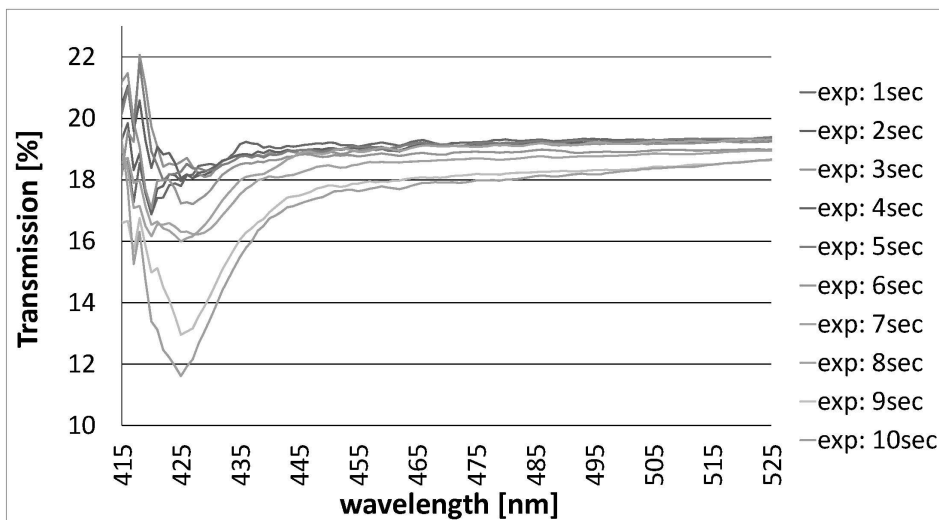


Fig. 4 The graphs show the spectral measurements at exposure time intervals from 1 to 10 seconds. Uncured resin was used as reference.

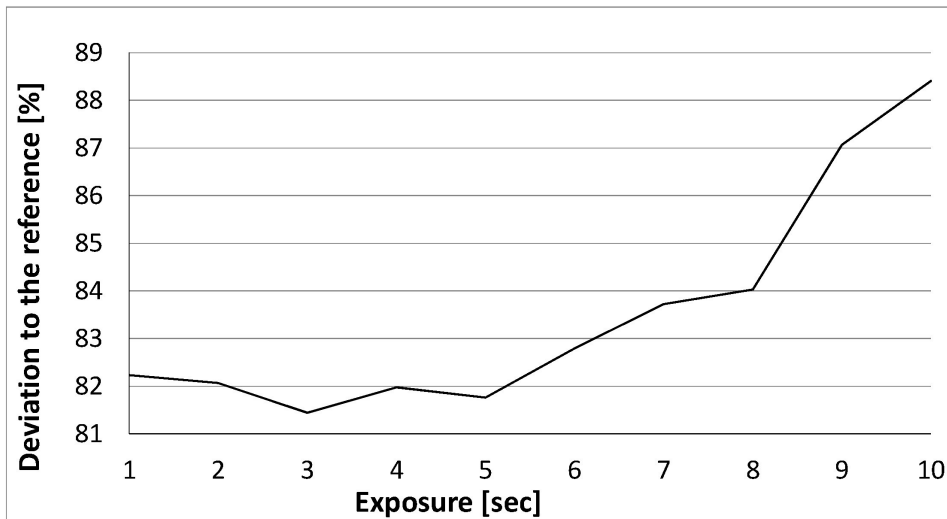


Fig. 5 The curve progression of the deviation of the transmission value at 425 nm to the reference value for the exposure intervals from 1 to 10 seconds is shown.

2.3. MLVS setup for feasibility studies

The setup which is presented in the following, facilitates a feasibility study for MLVS. The intention is to confirm the theory and idea of MLVS for 3D printing. A strong focus has been put onto the adaption of resin specific attributes. The required laser energy has to be defined and adjusted considering the diameter and transversal intensity distribution of the laser beam. Furthermore, the volume of the resin reservoir effects on the intensity of particle diffusion. It is assumed that the diffusion varies from an intense activity in the middle of the resin volume to less activity nearby the walls.

Figure 6 illustrates the components of the MLVS setup. The setup includes six lasers which are mounted on one base plate. Each laser can be adjusted in vertical and horizontal direction. Furthermore the focus position of each laser diode can be regulated. As mentioned earlier all laser diodes have a wavelength of 445 nm and a maximum output of 100 mW. The laser's electronic is integrated in an individual electronic board and placed right behind each laser. The base plate with the six lasers is further mounted on an optical bench in order to align the lasers towards the resin reservoir.

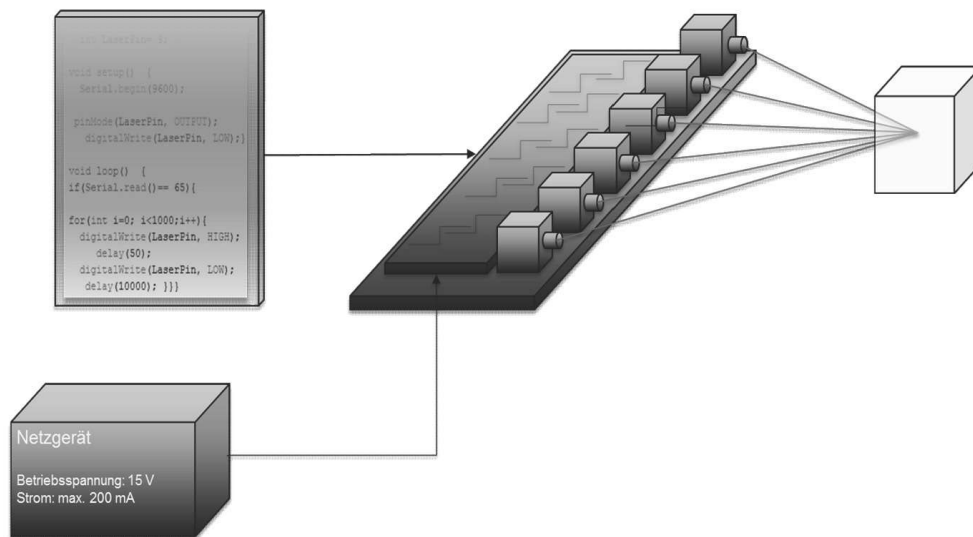


Fig. 6 Schematic illustration of MLVS components. Microcontroller (upper left), power supply (lower left), 6 lasers with electronic components (middle), resin reservoir (right).

The electronic board of each laser includes two input connectors. The main power supply and the modulation input. Laser output can be adjusted almost linearly from 0 % to 100 %. Exposure times of about 10 ms are possible by an external modulation control. This external control unit is realized by a μ -controller board with analogue input and output connectors. The μ -controller can be programmed by C/C++. A programmed loop alternates the analogue output in the predetermined frequency for exposure and pause time.

2.4. Laser adjustment

The right adjustment and focus of all laser beams was realized by the use of a high-resolution camera sensor. The first step was to focus each laser to the same focal plain. This plain is defined to be the distance in which the resin reservoir is placed. To protect the camera pixels from the high energetic laser beams a density filter is placed in front of the camera sensor. It can be assumed that the focus shift caused by the refraction at the glass filter is equal to the focus shift caused by the resin reservoir. The camera sensor is connected to a display in order to observe the overlapping of the laser beams. In step two all lasers were arranged to strike the focal plane in the same point and to overlap each other in the same point as illustrated in figure 7. The display shows an isolated circle with a diameter of 0.5 mm in best case.

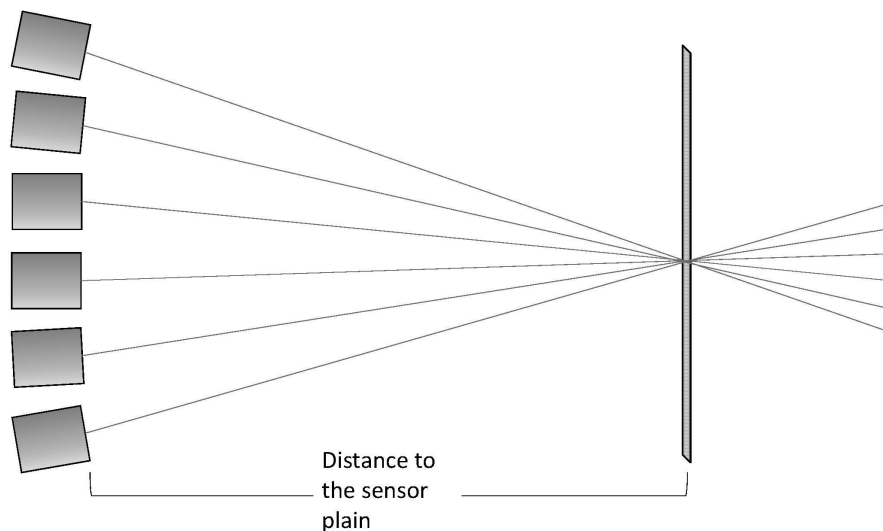


Fig. 7 Schematic illustration of the lasers focused to the sensor plain.

Each laser needs to be adjusted to the same intensity. The laser intensity at the focal point was measured and verified to match the required value.

2.5. Results

The experiment was performed using the setup as explained above. All components are placed at an optical bench. Lasers are focused to join at the center of the resin reservoir. Exposure routine was set to cure single voxels interrupted by a pause time of 10 sec. The positioning of all laser beams close together but not overlapping leads to a result as illustrated in figure 8. The close proximity of the beams leads to polymerization of short individual lines.

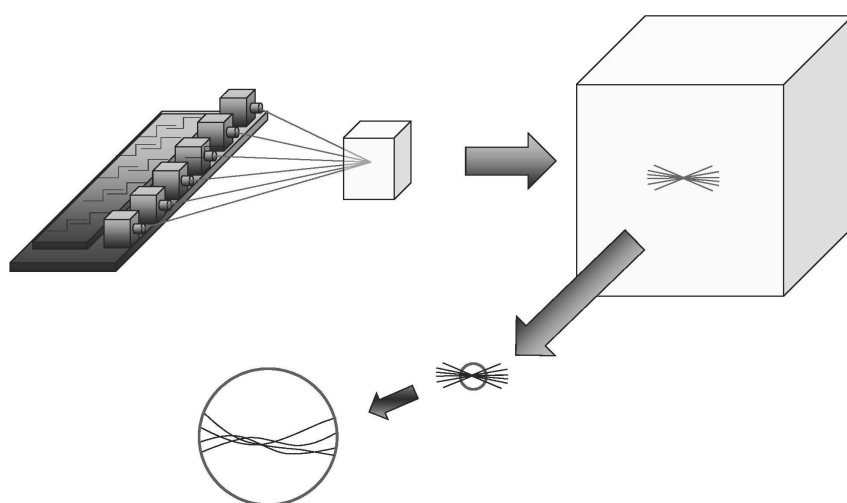


Fig. 8 Schematic illustration of the result in the case of imprecise adjustment of the laser beams. Laser beams don't overlap in one point.

Repeating the experiment with adjusted laser beams tackled the problem leading to a more promising result. It was possible to cure isolated voxels, as illustrated in figure 9.

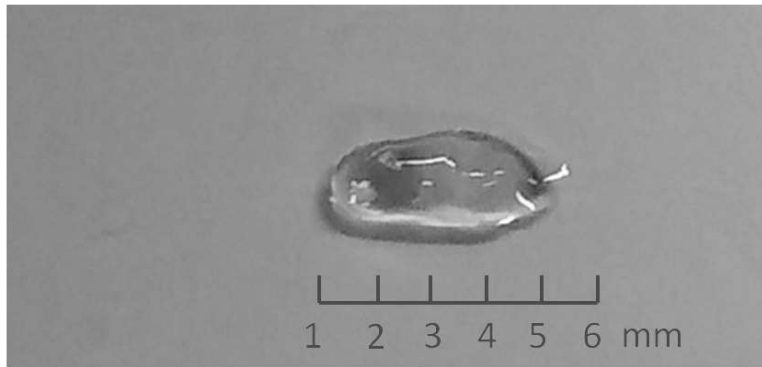


Fig. 9 Isolated voxel cured within CLEAR photoreactive resin.

Having a closer look at the cured structure the shape is identifiable as an elongated oval. The thinner ends of the cured oval point in the same direction as the lasers axis. Line structures disappeared and the voxel shows a homogeneous surface. Further attempts in order to show the possibility of printing more complex structures like lines or rectangles are in progress and will be part of further papers.

3. Conclusion

Multi Laser Volume Stereolithography involves a new approach in freeform fabrication. This approach promises the avoidance of the layer process utilized by all common 3D methods. Staircase effects and the need of support pillars could vanish. Moreover, the realization of liquid-inside objects could be conceivable. The contraction of polymer resin being in contact to oxygen can be easily avoided. The basic idea of Multi Laser Volume Stereolithography is to cure structures amid a photopolymer resin filled reservoir. Taking advantage of the properties of the resin in terms of the polymerization threshold, particle diffusion and spectral absorbance is the key component of MLVS. Thereby MLVS becomes outstanding in cost efficiency and flexible applicability. A guidance to the measurement of these properties is given. Moreover, the experimental proof for technical feasibility of MLVS has been made.

A modified setup to realize the curing of complex structures is in progress. This setup includes a replacement of the mechanical mounting brackets for the lasers with an electronic shifting system to enable movement in all spatial directions.

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[1] Normally a processing temperature of 25° C to 30° C is chosen to be below the *ceiling temperature* [2]

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