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# Additive manufacturing by UV laser direct writing of UV-curable PDMS

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## Abstract

The combination of photo-curable polymers and laser direct writing technique established one of the well-known technologies in the field of additive manufacturing. Recently, 2D/3D structuring of an elastic polymer material is required as an advanced technique for various different research fields. In this study, we have demonstrated UV laser photo-polymerization of elastic 2D/3D structures using UV-curable Polydimethylsiloxane (PDMS). In this technique, UV curable PDMS was locally polymerized to fabricate 1D and 2D single layer structures, as well as 3D multi-layer structures with resolution in micrometer-scale and structure dimension in millimeter-scale. In addition, a hybrid technique of aerosol jet printing followed by UV laser direct writing was developed to realize 2D patterning of thinner UV curable PDMS layer without solvents. The polymerized PDMS had good transparency and elasticity as same as common thermal curing-type PDMS. The hybrid technique of aerosol jet printing followed by UV laser direct writing achieved the thinnest layer thickness of UV curable PDMS as small as 1.6  $\mu\text{m}$  on the free-form surface.

Keywords: UV-curable PDMS, UV laser direct writing, Aerosol jet printing, Additive manufacturing;

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## 1. Introduction

Polydimethylsiloxane (PDMS) is one of the well-known organic materials in the industrial and research fields. PDMS is getting attention due to its attractive properties such as physical elasticity, chemical inertness

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and non-toxicity, and optical transparency. Therefore, application of PDMS is widely spread in bio-applications [1,2], optics [3-5], mould and soft-lithography [6,7], and micro fluidics [8-12]. In applications using PDMS, popular fabrication methods include the replica moulding process by thermal curing and rapid prototyping by photo-chemical reactions based on two-photon polymerization. In the moulding process, a master mould is prepared for an original pattern with PDMS transferred into it to form the casted structure. Thus moulding process using PDMS is excellent at mass production. However, thermal curing type PDMS is not suitable for selective polymerization, as the entire process area will become polymerized leaving a thin film of PDMS on the process area. On the other hand, the fabrication method of PDMS structures using photo-chemical reactions can be done by laser direct writing (LDW). LDW can fabricate the required structure directly from computer-aided design (CAD) data. So far, the photo-polymerized PDMS is locally done through laser induced thermal curing or addition of photo-initiators in PDMS via avalanche ionization induced by two-photon absorption using femtosecond laser pulses [13-17]. However, the two-photon polymerization process can achieve resolution on a nano scale, with a process area of only hundreds of micrometers. Therefore, the PDMS structures fabricated in the past literature mentioned above concerning two-photon polymerization has not been reported the basic characteristics like transparency and elasticity yet, since the fabricated structures were too small to evaluate the characteristics. Recently, several companies have released commercially available UV curable PDMS products. As a result of the improved cost performance for high power UV light sources, photo-curable elastomers have received a surge of attention as an alternative for conventional thermal curing types of PDMS [18-20]. The commercially available UV curable PDMS is designed to polymerize at UV wavelengths, making it a suitable material to discuss the photo-chemical reaction between the UV curable PDMS and a UV laser. In LDW of UV curable PDMS, a tightly focused UV laser beam scans the UV curable PDMS, resulting in localized photo-polymerization with free-form shape. In this paper, we demonstrate the fabrication of 2D and 3D structures in UV curable PDMS by LDW. In addition, thin layer coatings of UV curable PDMS using Aerosol Jet Printing (AJP) without the use of solvents has been demonstrated. The hybrid 2D patterning of UV curable PDMS using UV LDW and AJP techniques enables us to print on free-form surfaces as well as 2D pattern over complex geometries.

## 2. Experimental setup

### 2.1. UV laser direct writing

Figure 1 shows a schematic illustration of the experimental setup for 2D/3D structuring using UV curable PDMS. A UV curable PDMS (KER-4690 A/B, Shin-Etsu Silicones Europe B.V.) which is in a pre-mixed condition

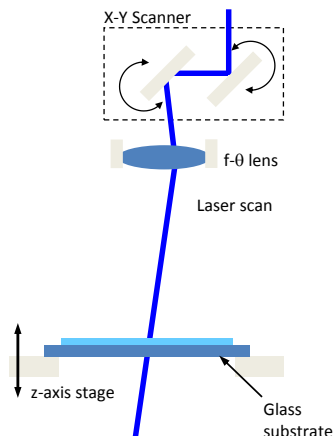


Fig. 1. Schematic illustration of the experimental setup for 2D/3D structuring using UV curable PDMS

of the two components (50/50 wt.% mixture of A and B) was used in the experiments. For the photo-curing process, a continuous wave UV laser system (Cobolt AB, Model Zouk™, CW 20 mW, 355 nm) was used. Timing of the laser irradiation and laser power were adjusted by an acousto-optic modulator (AOM) and neutral density (ND) filters. The laser beam was scanned by an x-y galvanometric mirror scanner (Hurry SCAN 14, SCANLAB AG) and positioned in its z-axis by a high-resolution linear stage (MT105-50 LM, Feinmess Dresden GmbH). The motion of the scanner for 2D patterning of laser irradiation was controlled by SAMLight (SCAPS) software and CAD data. The laser beam was focused on the sample surface with 103 mm focal-length F-Theta lens.

## 2.2. Aerosol Jet printing system

Figure 2 shows the fluid flow schematic of the Aerosol Jet Printing system (Optomec Inc.) with a dual atomizer module. As the unique feature of this setup, the two aerosol jet streams are mixed in a controlled ratio. The system contained two Atomizers which contain a heater and a material reservoir individually. One of the material reservoirs holds liquid Material A and the other holds Material B, which can be pre-mixed condition in the Aerosol Jet System. The aerosol particles were individually generated from each atomizer and created a dense aerosol stream through the virtual impactor. The temperature inside of each material reservoir was held constant with the heater in order to maintain constant viscosity of the materials for stable atomization. Tubing from each virtual impactor channeled the two aerosol jet streams to the Y-shape connecting tube where they converged. Finally, a homogeneously mixed aerosol jet stream was ejected from a nozzle head with elongate output aperture (3.0 x 0.5 mm<sup>2</sup>). The aerosol jet stream is surrounded with nitrogen Sheath gas to focus and collimate the stream into a tight beam and prevent clogging inside the

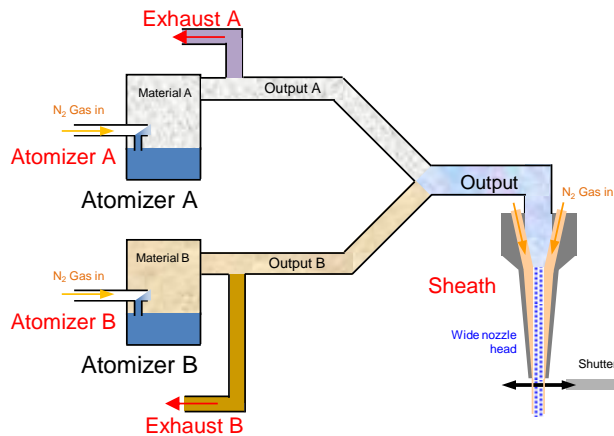


Fig. 2. Fluid flow schematic of the Aerosol Jet Printing system with a dual atomizer module

nozzle head. The gap distance between the nozzle head aperture and the substrate was kept at 3 mm. The combination of a computer-controlled stage and a mechanical shutter enabled a uniform coating of UV curable PDMS layer, 3 mm in line width, on a glass substrate. After coating, the UV curable PDMS underwent photo-curing process by UV laser direct writing shown in Fig.1.

### 3. Results and discussion

#### 3.1. 2D/3D structuring of UV curable PDMS by UV laser direct writing

The absorption of the UV curable PDMS was evaluated on a 5 mm thick sample by a spectrometer (UV-1650 PC, Shimadzu Europe). Figure 3 shows the absorption spectrum for wavelengths of 320 nm to 610 nm. The UV curable PDMS appears an absorption range at wavelengths shorter than 455 nm. At the relevant wavelength of 355 nm, the absorption was 0.131, which is enough absorption for a photo-chemical reaction in volume.

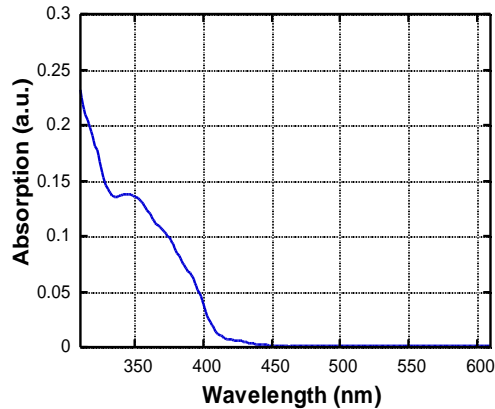


Fig. 3. Absorption spectrum of UV curable PDMS

As an example of the UV curable PDMS fabricated by laser direct writing, Fig. 4 shows the polymerization of line arrays for widths of 29.1  $\mu\text{m}$  with a pitch of 230  $\mu\text{m}$ . Before laser irradiation, UV curable PDMS was spin coated onto a glass substrate at 4000 rpm for 60s, making a layer thickness of 14.4  $\mu\text{m}$ . Each line was produced at a laser power of 4.5 mW and laser scanning speed of 500 mm/s, with 750 laser irradiation cycles. After laser irradiation, the structures are not stable enough for development as they are not fully polymerized. Thus, the structures were treated by post-baking for 10 minutes at 50°C in an oven to

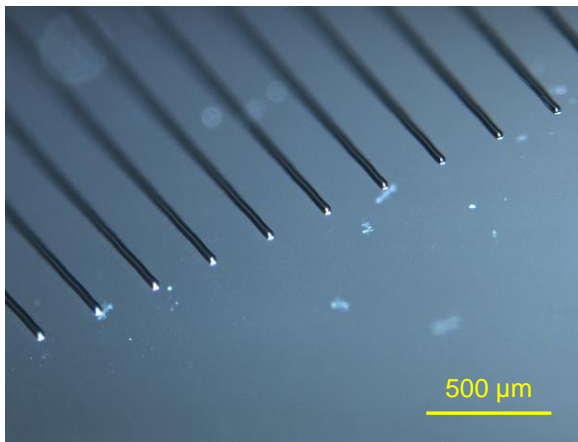


Fig. 4. Photo-polymerization of a line array with widths of 29.1  $\mu\text{m}$  and a pitch of 230  $\mu\text{m}$

accelerate the polymerization reaction only at the exposed areas. The structures were then developed with Tetrahydrofuran (THF) to wash away unpolymerized liquid. The lines are sharp and uniform in their widths, height, and smoothness, indicating repeatable and stable polymerization in the UV curable PDMS. There is no distortion in the lines, showing good adhesion to the glass substrate and physical stability during the development process.

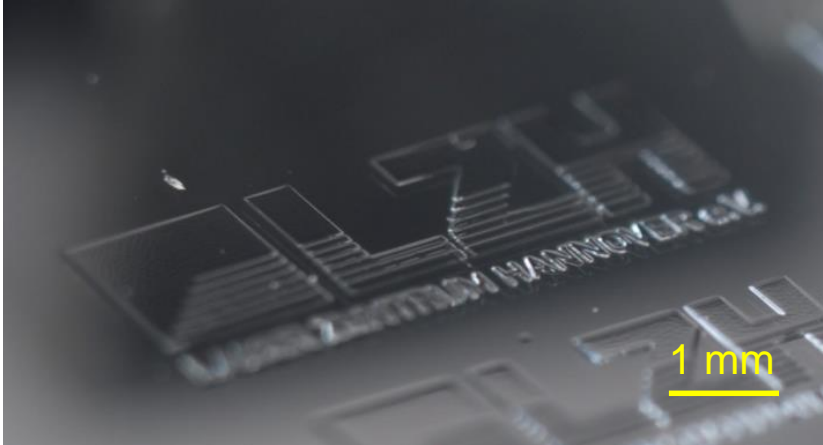


Fig. 5. 2D patterning of the “Laser Zentrum Hannover” logo

An instance of the patterning that can be achieved in 2D structures with UV curable PDMS is demonstrated on the glass substrate. Figure 5 shows 2D patterning of the “Laser Zentrum Hannover” logo. The sample was irradiated with a laser power of  $843 \mu\text{W}$  on glass substrates spin coated in UV curable PDMS. The 2D structures, with a size of 6.00 mm by 2.23 mm, had adhesion taking place in both planar directions. The polymerized PDMS retained its transparency. The samples also had very smooth outer surfaces and good sharpness at all corners and edges. As well, good localized polymerization occurred, as is shown in the ability to produce very small gaps for the striped part of the LZH logo. On all samples, there was no deformation due to shrinkage effects.

Demonstration of 3D structuring was done with the creation of a spider web style net shown in Fig. 6. The spider web style structure was fabricated by two layer process. In each layer, liquid UV curable PDMS was dropped into a circular frame (diameter of 15 mm and a height of 3 mm) on a glass substrate. The dropped UV curable PDMS layer was irradiated at a laser power of  $843 \mu\text{W}$  in a spider web pattern as the first layer. Then, the second layer was dropped into the frame and irradiated again at  $843 \mu\text{W}$  to form the posts on the spider web pattern. Thus, the entirety of the structure was able to be built in a two layer process. The discrepancy between the technical drawings measurements of the net and the actual measurements, about  $200 \mu\text{m}$ , was due to the width of the laser beam, and can be adjusted by the laser exposure conditions. After post treatment, the structure was turned over so the posts supported the full weight of the web part. The structure was again able to maintain its transparency and had smooth outer surfaces. Due to the absorption depth of the UV curable PDMS shown in Fig. 2, a 3 mm thick layer can be polymerized without a layer by layer process. Thus, pillars on the web structure with an aspect ratio of 2 could be obtained. The polymerized PDMS was strong and flexible, even in the thinnest 0.39 mm section. For the demonstration of the elasticity of the structure, 1.49 g steel ball was held in the netting of the structure. The demonstration appeals the strength and elasticity of the polymerized UV curable PDMS. The netting was able to return to its original shape after the steel ball was removed.

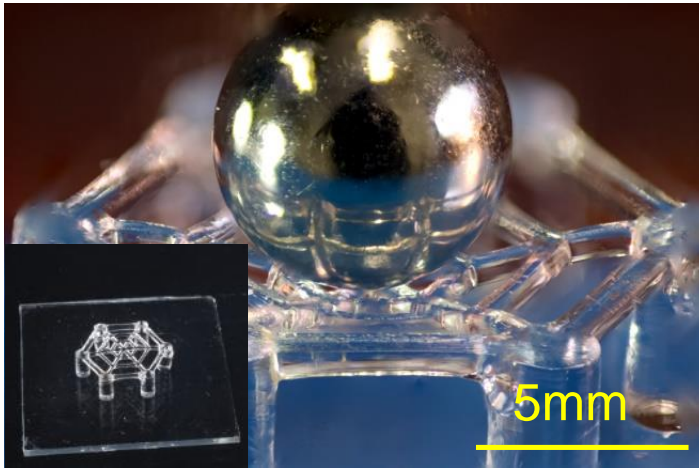


Fig. 6. Multilayer spider web structure holding steel ball

### 3.2. Hybrid 2D patterning of UV curable PDMS using UV laser direct writing and aerosol jet printing techniques

In the pre-mixed condition of UV curable PDMS, the standard mixing ratio of Material A and B is designed to set at 1:1 in order to undergo a complete photo-chemical reaction. The flow of aerosol jet stream from dual atomizer module was optimized to be mixing ratio of 1:1 by controlling the individual flow rates in each Atomizer, Virtual impactor, and Sheath gas as well as the material temperature, so that both deposition rates were 0.17 mg/min, and a combined deposition rate of 0.34 mg/min was obtained as expected. Once the ideal parameters for material mixing were determined, the AJP technique could be combined with UV LDW to selectively polymerize the thin film. For 2D patterning, it is important to determine the achievable resolution in the X-Y and Z directions. To determine the resolution in Z, the aerosol jet printing nozzle-moving speed can individually control the layer thickness of the produced coating. The achievable layer thickness of a coating has been demonstrated and compared to the results of spin-coated samples to show

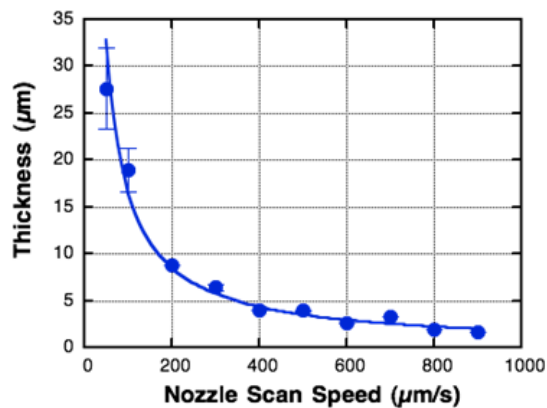


Fig. 7. Layer thicknesses of PDMS on glass substrates coated by AJP at various nozzle-scan speeds

the advantage of AJP.

Figure 7 shows the dependence of the layer thickness on the nozzle-moving speed at a deposition rate of 0.34 mg/min. The PDMS layer was photo-polymerized under a UV LED lamp (Dymax BlueWave®, Model QX4™, RediCure™ 365 nm) after coating and then put into an oven at 155 °C for 15 min to accelerate polymerization. The layer thickness was measured from the cross-sectional images of the samples that were viewed under the optical microscope (Leica Microsystems Switzerland). Increasing the nozzle-moving speed resulted in a decrease in the printed layer thickness. The minimum layer thickness achieved was 1.6 μm using a nozzle-moving speed of 900 μm/s shown in Fig. 8. The layer thicknesses achievable with the AJP system are very difficult and take longer processing time in the case of spin-coating technique. In addition, the morphology of the coated layer with minimum thickness indicated uniform thickness similar to that of coated by spin-coating technique. The dependence of layer thickness on the nozzle-moving speed indicates that there is a difference in graph forms for a speed region lower than 400 μm/s versus a speed region higher than 400 μm/s. In the case of lower speed region, the deposition of excess UV curable PDMS has an influence of migration caused by stream pressure of the aerosol jet on the substrate. Namely, the particles in the aerosol jet stream are provided to direct underneath the nozzle head, but excess material migrated as over-coating of the surrounding area. Thus, the form of graph shows a curved line. On the other hand, a higher nozzle-moving speed does not provide excess material to the substrate, so that the layer thickness linearly decreases as the nozzle-moving speed increases.

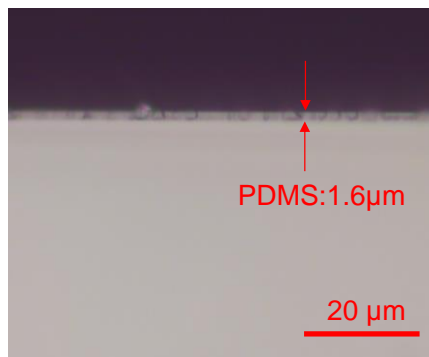


Fig. 8. Uniform coating of PDMS on glass with a thickness of 1.6 μm coated by AJP at a nozzle-moving speed of 900 μm/s

After the thin-film coating of PDMS was made by AJP, localized polymerization for 2D patterning was demonstrated using a UV LDW process. Figure 9 shows an optical microscope image of a grid pattern with a pitch of 750 μm fabricated by hybrid 2D patterning using UV curable PDMS. The thin film PDMS layer was coated onto the glass substrate by AJP with a nozzle-moving speed of 500 μm/s and a deposition rate of 0.34 mg/min. The square grid pattern was scanned onto the coated surface at a laser power of 1.5 mW and a scanning speed of 500 mm/s. The pattern was iterated over by the laser, scanning 8000 times. After laser irradiation, the sample was put into an oven at 50 °C for 15 min to accelerate the polymerization at only the laser-exposed areas. After the thermal treatment, the unpolymerized area was washed away with THF. The fabricated PDMS grid pattern shows localized polymerization of straight uniform lines with sharp contrast between polymerized and unpolymerized areas. The dimension of the grid pattern which corresponded to the original CAD data did not indicate shrinkage effect even after the development process using THF. Additionally, the patterned PDMS lines have good adhesion to the glass substrate.

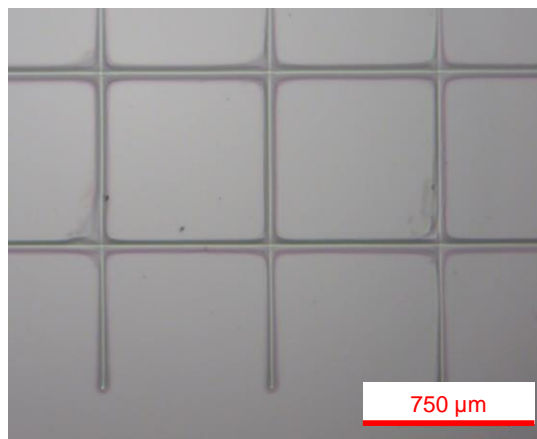


Fig. 9. Fabricated 2D patterning of a square grid with a pitch of 750  $\mu\text{m}$



Fig. 10. LZH logo ( $3.00 \times 8.07 \text{ mm}^2$ ) printed on a freeform cylindrical surface with an outer diameter of 14.8 mm

Hybrid 2D-patterning using aerosol jet printing was realized not only 2D patterning on flat surfaces, but also on a free-form surface. Figure 10 shows the  $3.00 \times 8.07 \text{ mm}^2$  LZH logo printed onto a cylindrical glass bottle. AJP was carried out to make a uniform layer of UV curable PDMS onto a glass cylinder with an outer diameter of 14.8 mm. The large area coating was made by iteration of the coating once length-wise along the cylinder then rotating the cylinder. The coating was operated at a nozzle-moving speed of  $200 \mu\text{m/s}$  and a deposition rate of  $0.34 \text{ mg/min}$ . Due to the curvature of the glass bottle, the edges of the coating are an extra  $0.15 \text{ mm}$  away from the nozzle. Since the aerosol jet stream from the nozzle is collimated, there is no focus point and the coating of material can be uniform over free-form surfaces in a distance range of 3 to 12 mm between nozzle and substrate. The coated bottle was irradiated with a  $1.5 \text{ mW}$  laser with a scan speed of  $500 \text{ mm/s}$ . The 2D pattern of the LZH logo had a hatching parameter of  $1 \mu\text{m}$  in only one direction and was irradiated 25 times. The  $103 \text{ mm}$  F-Theta lens that was used enabled a tightly focused beam diameter over the whole range of small deviations over the surface of the bottle. After laser irradiation, the sample



was placed in an oven at 70 °C for 20 min to help the polymerization reaction at the irradiated areas. Finally, THF was used to wash away the remaining unpolymerized material. The resulting pattern showed good adhesion to the curved substrate and clearly displayed the LZH logo.

#### 4. Conclusion

In conclusion, the fabrication of 2D/3D structuring using an UV curable PDMS has been demonstrated by laser direct writing technique. PDMS structures were obtained with a lateral resolution of 15.7  $\mu\text{m}$ . The fabricated structures had good physical strength and elasticity. In addition, the structure maintained transparent appearance and smoothness without deformation of surface morphology due to shrinkage effects. The UV curable PDMS used in this experiment had an absorption depth longer than 3 mm. This long absorption depth enabled the achievement of a high-aspect ratio of 3 by curing in single step laser irradiation. Furthermore, hybrid 2D patterning of UV curable PDMS with laser direct writing and aerosol jet printing has been developed. The unique combination of UV curable PDMS and aerosol jet printing enables full control over the mixing ratio between two materials resulting in a reliable coating process. This technique also allows us to produce a 1.6  $\mu\text{m}$  uniform thin-film layer coating of UV curable PDMS on free-form surface without solvents, which is a more flexible way than conventional spin-coating techniques using pure UV curable PDMS. The laser direct writing process can achieve maskless patterning of UV curable PDMS. The combination of laser processing and AJP makes patterning on free-form surfaces possible. Thus, these new approaches using UV curable PDMS are promising for wide and more flexible applications in additive manufacturing and thin-film coating techniques.

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