

Supplementary Information

Mechanics of shape distortion of DLP 3D printed structures during UV post – curing

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Section S1. 3D Printing

We measured the intensity of UV at different points in the horizontal plane with the same distance from the projector. As shown in Fig S1, we projected rectangular and circular areas on the plane from the light source $H=9.9\text{cm}$. Central point and four edge points were selected in each pattern and the intensity on these positions were showed in right two charts. It can be found that the difference of intensity between points in rectangular is larger than that of in circular pattern. However, they are small enough that it's reasonable to treat the intensity of UV in a plane as uniform.

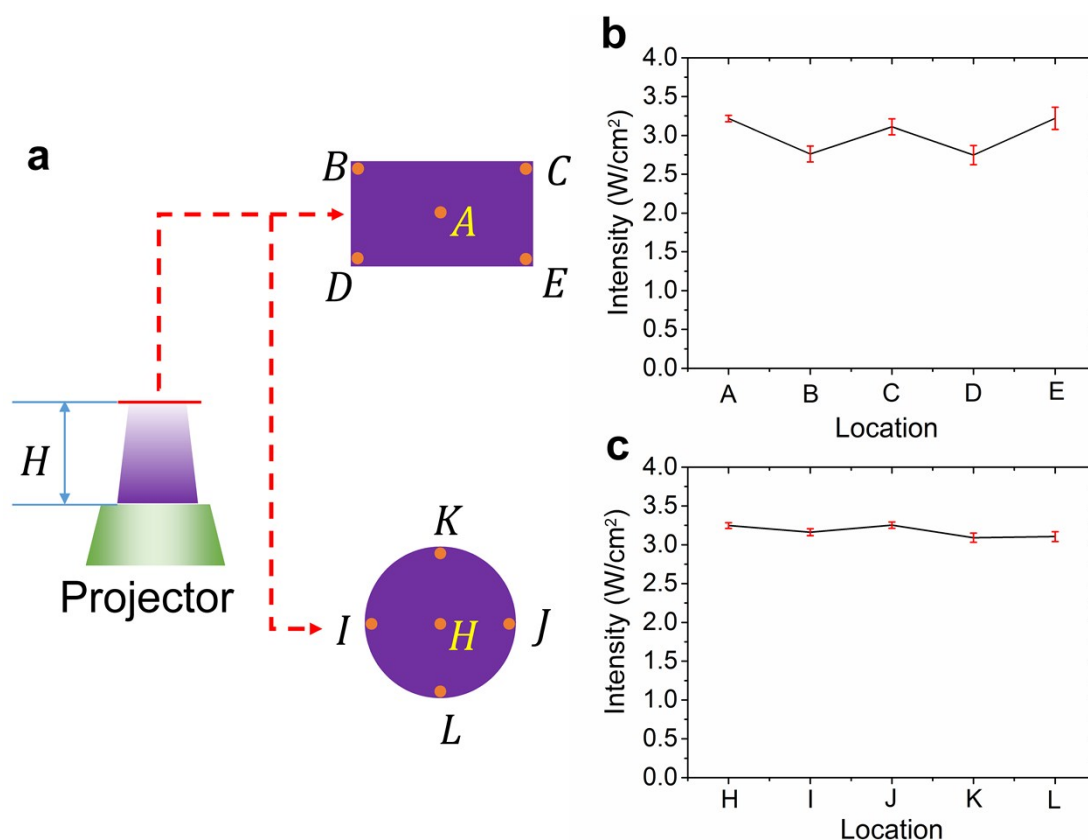


Figure S1. Measuring the differences of intensity in the same plane (a) Schematic diagram of measurements of intensity in different points in the same horizontal plane; (b)(c) Experimental results.

Section S2. Post-printing Irradiation

In this section, we describe the post-curing irradiation method after printing. As

shown in Fig. 1b, the printed strips were placed perpendicular to the horizontal plane and coincided with the marking line. We adjusted the distance L between projector and marking line to change the post-curing UV intensity received by samples. Digital camera (50D, Canon Inc, Japan) was used to record the shape distortion of samples. The intensity measurements at different distance was presented in S2. With the increase of the distance from the light source, the intensity of illumination decreases continuously.

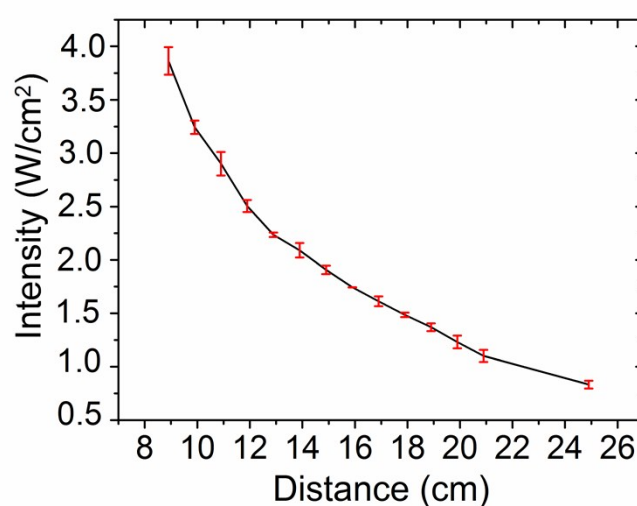


Figure S2. Post-cure intensity varied by changing the distance between strip and source.

Section S3. Explanation of parameters

In the free-radical photopolymerization action, the polymerization rate k_p and the termination rate k_{term} is not constant which can be influenced by the diffusion reaction and DoC. The DoC dependence of k_p is introduced through the variation of changeable viscosity with conversion and we use Buback's model to describe this characteristic. Besides, the termination is regarded as a combination of center-of-mass translation

diffusion and segmental diffusion.

They can be modelled as[1-4] :

$$k_p = \frac{k_{p0}}{1 + \frac{k_{p0}}{k_{p,D0}} e^{cp}}, \quad (S1)$$

$$k_{term} = \frac{1}{1/k_{t,SD} + \exp(cp)/k_{t,TD0}} + \frac{C_{RD}(1-p)k_{p0}}{1 + \frac{k_{p0}}{k_{p,D0}} \exp(cp)} \quad (S2)$$

k_{p0} refers to propagation without any diffusional contribution and $k_{p,D0}$ characterizes the diffusion-controlled part of the propagation reaction at zero conversion. c is a relative viscosity coefficient and p represents DoC. $k_{t,SD}$ is the segmental diffusion rate, $k_{t,TD0}$ refers to the translation diffusion-controlled rate at zero conversion and C_{RD} is the reaction diffusion proportion parameter.

k_p and k_{term} are critical factors to affect the degree of photopolymerization, which can lead to changeable modulus of materials. The modulus was modelled using an empirical function proposed by O'Brien et al. It shows that the modulus and DoC follow exponential relationship after the gel point and the calculation results fitted well with experiments data. It was modelled as:

$$E = E_d + E_c \exp\{b[p - p_c]\}, \quad (S3)$$

We use this cure dependent model to describe the evolution of modulus in printing and post-curing process. Here E_d , E_c and b were the experimental fitting values. p_c represents the gel point. Parameters used in the Eq. S1, S2, S3 are shown in Table S1 :

Table S1. List of theoretic model parameters[1]

Parameters	Value
$k_{p0}(m^3 mol^{-1} s^{-1})$	1.86048
$k_{pD0}(m^3 mol^{-1} s^{-1})$	9E+08
c	34.149
$k_{sD}(m^3 mol^{-1} s^{-1})$	4.39E+03
$k_{TD0}(m^3 mol^{-1} s^{-1})$	10024.43
$k_{p0}(m^3 mol^{-1} s^{-1})$	1.86048
$k_{pD0}(m^3 mol^{-1} s^{-1})$	9E+08
$E_d(MPa)$	3.321
$E_c(MPa)$	1.059
b	5.248

Section S4. Investigation of DoC inhomogeneity

We set the height of single-layer as $100\mu m$, printing UV intensity as 0.4 mW/cm^2 , printing time of single-layer as 1.0s. The distribution of printing UV intensity and DoC in the materials is shown in Fig. S3. Since the absorbance of photoabsorbers, UV intensity gradually decayed along the negative direction of Z axis, and finally approached to zero (Fig. S3a). The second and third layer would be influenced by the UV light from the first layer. Previous cured resin can continue to cure with the continuous illumination. In Fig. S3b, the X-axis represents the coordinate along printing direction, the Y-axis represents the Degree of Conversion of material (DoC). We use black curve to represent the DoC of the first layer. Then, when we printed the second

layer, the DoC of the first layer would be increased by the second UV irradiation, which was represented by the red line. The green line represents the effect of the 3rd layer of UV radiation on the first layer of solidification. The transmittance of resin will bring continuous UV irradiation to a single layer, and this kind of continuous irradiation will continuously improve its DoC.

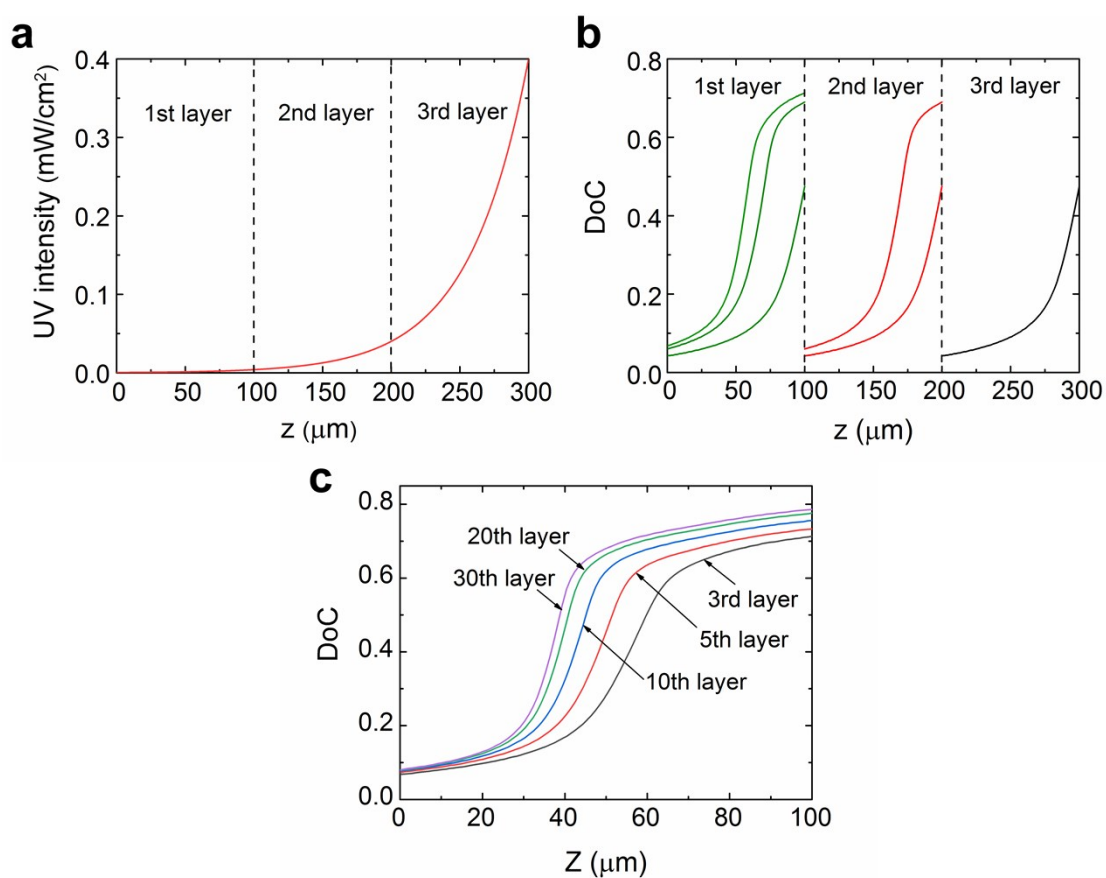


Figure S3. Calculating results of UV intensity and DoC during DLP printing process. (a) Variation of UV intensity through polymer of three printing layers; (b) Variation of DoC because of continuous irradiation; (c) Variation of DoC with the increase of printing layers.

In Fig. S3c, the five lines respectively represent the DoC of the first layer of resin when printing the third, 5th, 10th, 20th and 30th layers. With the continuous increase of the number of layers, the DoC of the first layer keeps increasing and finally tends to

be consistent. After the accumulation of enough layers, the DoC of each layer tends to be same. It is found by calculation that the DoC of each layer is close to the same after the accumulation of 30 layers. Therefore, the DoC of the resin of the first layer at the time of printing 30 layers is taken as the DoC of each layer of green-state samples, and the concentration of each component at this time is taken as the initial condition for each concentration at the beginning of post-curing.

Section S5. Printing parameters of samples

The printing parameters (printing time of single-layer T_0 , thickness of single-layer z^* , printing UV intensity I_0), post-curing UV intensity I' as well as the thickness of strips y^* of samples in Figures are listed in Table S2.

Table S2. Parameters of 3D printing and post-curing for samples

Figures	T_0 / s	$z^* / \mu m$	$I_0 (mW/cm^2)$	$I' (mW/cm^2)$	$y^* / \mu m$
2a, 3d	1.0s	100	0.4	0.8	0.5
3a, 4b	1.0s/1.2s	100	0.4	0.8	0.5
4d	2.0s	140/160	0.4	0.8	0.5
5b	1.0s	100	0.4	0.5/0.8	0.5
5c	1.0s	100	0.4	0.8	0.5/0.8
6a-d, f	1.5s	100	0.4	1.0	/
6e	0.7s	100	0.4	1.0	/