Supplementary Information for:

Linear Volumetric Additive Manufacturing of Polymer Structures via Light Initiated Direct Growth

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Curing resolution identification

With the aim of understanding curing resolution, photopolymerization speed based on the setup and printing material, we conduct a series of experiments. A set of squares are cured (as shown in Fig. S1) using different image sizes which range from 15 to 1000 pixels to explore the resolution
limitation and pixel size of the projector. All the squares are cured directly on top of a glass slide without any other constraint to imitate the real printing circumstance during the process. The minimum dimension of the accurately cured square is 300 μm and the pixel size is 20 μm/pixel. As discussed in the above section, an analytical model of optical energy distribution when light goes through solidified part and focuses on liquid photopolymer is required for printing accuracy. And the first step is to generate an energy distribution model of current light source. We assume the optical energy distribution of a pixel light beam fits the Gaussian distribution which is the general case for vat photopolymerization.

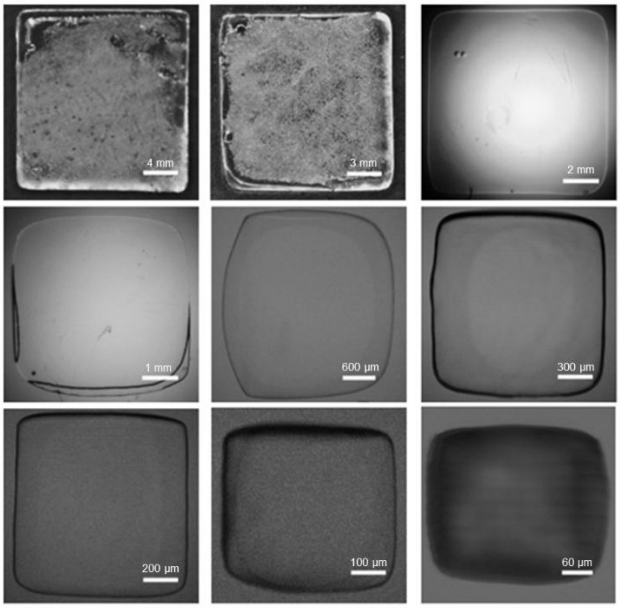

Fig. S1. The fabrication results of the squares with different dimensions ranging from 20 mm to 300 μm.

Light blending effect investigation

In order to have a better understanding of the light energy distribution in a projected image, the light intensity distribution on a 2-dimension plane is explored. First, single pixel with different gray scale levels is projected on the focused plane and pictures are taken for further image processing. By image processing, the light intensity data on XY plane for single pixel projection with different gray scale levels (illuminance) are obtained. To keep the evaluation standard same and illustration clear, the observed largest light intensity is set as 1 and the observed light intensity without any projection is set as 0. Then, all the light intensity is converted into relative values between 0 and 1. By fitting the light intensity data to a standard 2D Gaussian function as stated below, analytical models of light intensity distribution are built for all 5 gray scales Fig. S2a. With the purpose of investigation of the light energy accumulation effects, a series of pixels

are aligned on XY planes according to measured pixel size and the sum of light intensity on the XY plane is also calculated as shown in Fig. S2b. It is obvious that the maximum light intensity distributed on the XY plane will be larger than maximum light intensity of single pixel projection due to light blending effect. The blending effect exists because the light energy of single pixel illumination is not constrained inside the pixel aera. Therefore, the light intensity at a certain point (x, y) is not only contributed by a single pixel at that point but also several adjacent pixels around it, which leads to the result that the sum of light intensity is always larger than the light intensity of every single pixel at that position.

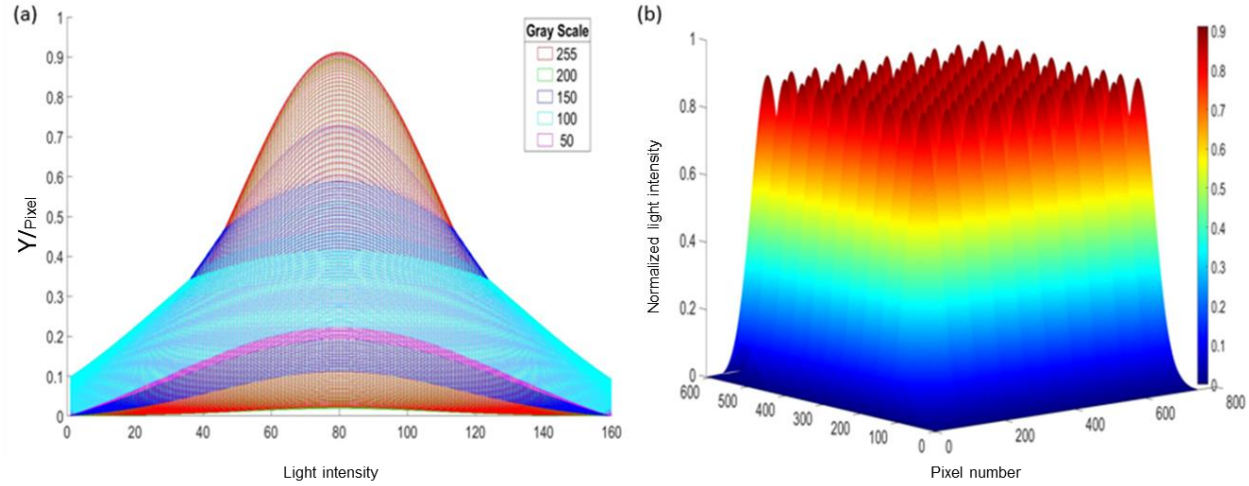

Fig. S2. The pixel blending effect (a) the Gaussian function models of light intensity distribution of single pixels of different gray scale levels and (b) the energy accumulation of the adjacent 10 x 10 pixels

Light initiated growth evaluation

In photopolymerization based additive manufacturing, there is a commonly used approach to improving curing accuracy which is to add dye in resin. Dye added inside photocurable resin will effectively reduce the depth of polymerization. So, with the aim of achieving functional micro scale printing, exploring the influence of dye concentration on curing characteristics is essential to be researched. Specifically, Oil Red O ($C_{26}H_{24}N_4O$) is used to control the depth of polymerization. The concentrations of dye are set as 0.01, 0.025, 0.05, 0.075, 0.1, 0.2, 0.3 and 0.4 wt. % to study the effects of dye concentration on characteristic penetration depth and max curing height. It is obvious that both relationships follow exponential function, as shown in Fig. S3c and S3d. To be specific, when the dye has a low concentration in the photopolymer, a slight increase in concentration will decrease the characteristic penetration depth and maximum curing height greatly, because at low concentrations the transparency of the mixture is still high and can be easily influenced by extra dye material. On the contrary, when dye concentration reaches a certain level, 0.1 wt.% specifically in our case, the additional dye has little influence on the transparency of the mixed solution because light is already hard to penetrate the red resin. Based on the obtained results, it is easy for researchers to use the presented method to achieve complex structures with small thickness.

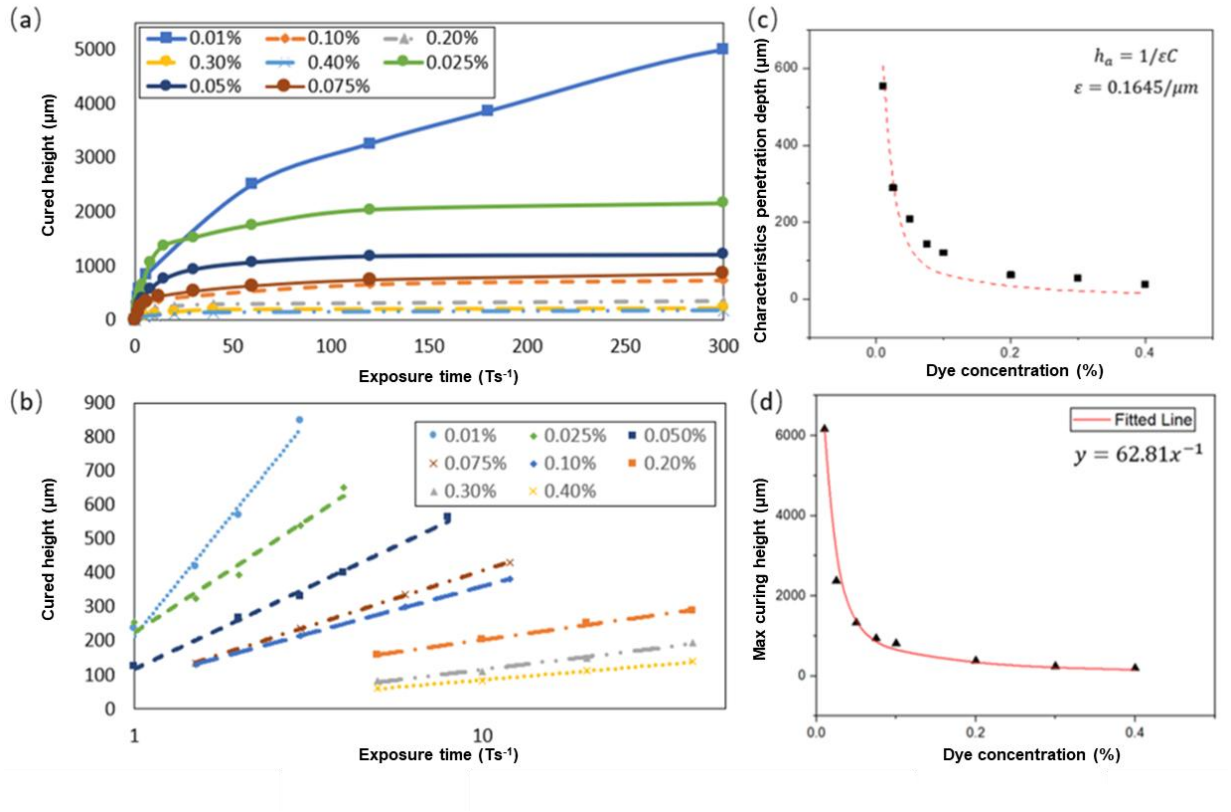

Fig. S3. (a) Cured height of print object with different dye concentrations. (b) Cured height of print object for resin with different dye concentrations in logarithmic coordinate. (c) Relationship fitting between characteristic penetration depth and dye concentration. (d) Relationship fitting between max curing height and dye concentration.

During macroscale printing, heat generation from light exposure and photopolymerization may cause localized temperature increases, affecting resin rheology and curing quality. We conducted a series of experiments to investigate thermal accumulation and its impact on resin flow behavior during macroscale printing. Our initial hypothesis was that thermal buildup during light exposure and photopolymerization, causing the partially cured gel to flow along with the part growth when the viscosity of the resin is low. To test this, we introduced a dye droplet into the resin as a visual tracer to monitor liquid movement. In control experiments without light exposure, the droplet remained stationary, indicating negligible flow. However, when light exposure was initiated without any mechanical stage movement, we observed a clear displacement of the dye droplet—despite the part growth not yet reaching its location (see Fig. S4a). This confirmed that thermal accumulation alone can induce resin flow. We prepared resin mixtures using BPAGDA and PEGDA at varying mass ratios and measured their viscosities (Fig. S5). These resins were then used in the LIDG printing process to fabricate test structures. The results showed that increasing resin viscosity significantly improved the top surface quality. When the viscosity exceeded a critical threshold, the dye droplet remained completely stationary under light exposure and stage movement, indicating suppressed resin flow (see Fig. S4b).

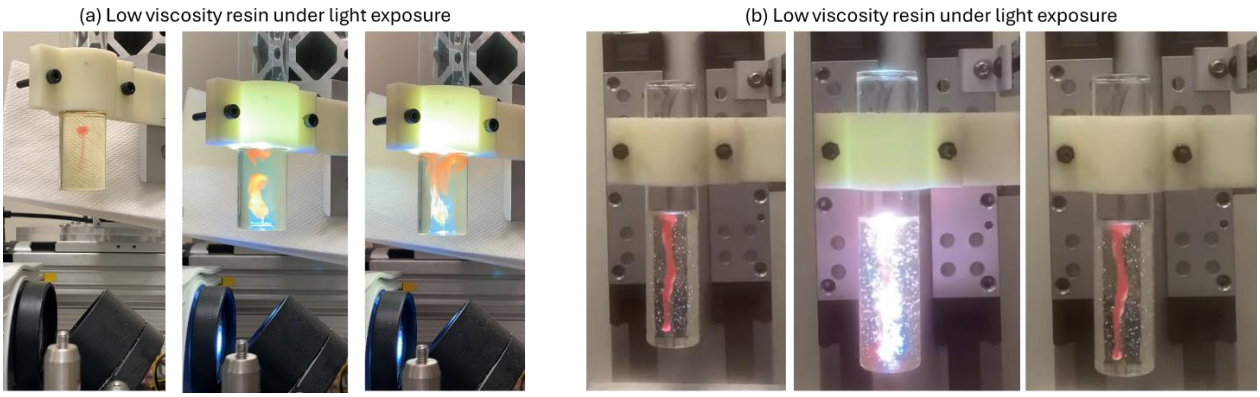

Fig. S4. the resin flow behavior of resin with (a) low viscosity and (b) high viscosity under exposure

Material viscosity investigation

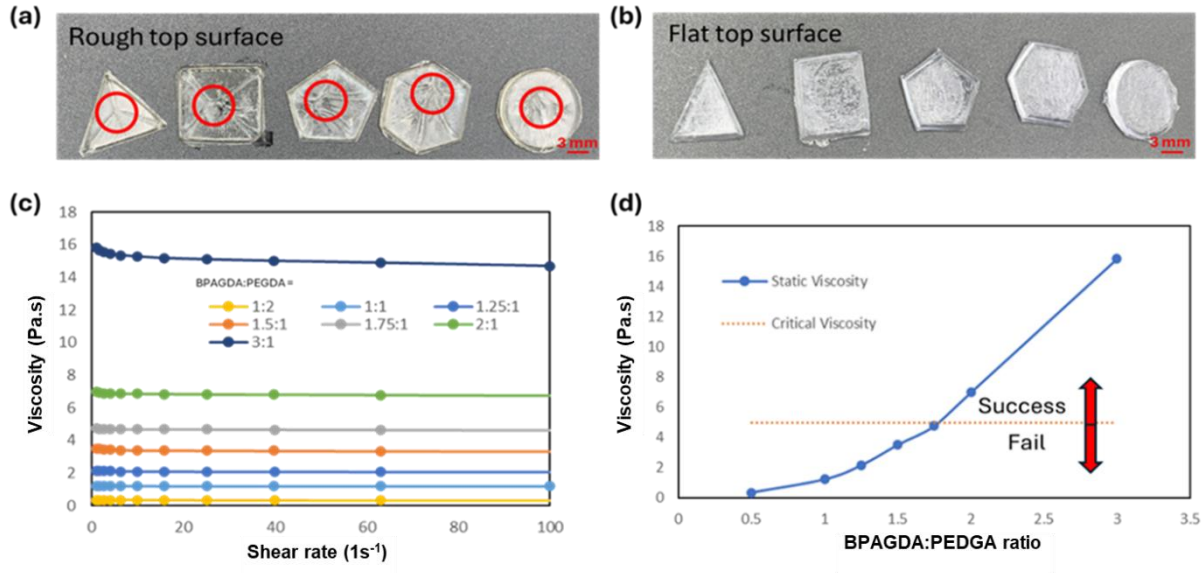

Fig. S5. (a) Structures printed with low viscosity resin (static viscosity = 0.35 Pa·s), (b) Structures printed with high viscosity resin (static viscosity = 6.97 Pa·s), (c) rheological behaviors of resin made with different weight ratio between BPAGDA and PEGDA; (b) static viscosity of resins made with different weight ratio between BPAGDA and PEGDA and critical viscosity.

However, undesired top features exceeding the base dimensions in constructions were observed (Fig. S5a), likely resulting from resin flow during exposure. To investigate the impact of exposure on liquid flow within the resin vat at varying viscosities, a selection of photopolymer resins was prepared by mixing different weight ratios of Bisphenol A glycerolate (1 glycerol/phenol) diacrylate (BPAGDA), a highly viscous substance, and Polyethylene glycol diacrylate (PEGDA), which exhibits a viscosity comparable to that of water. BPAGDA and PEGDA are frequently utilized in photopolymer resin formulations, and the rheological

behaviors of resins with varying BPAGDA/PEGDA ratios were investigated (Fig. S5c). Structures treated with these resins were examined to ascertain the critical viscosity, indicating that resins with viscosities greater than 5 Pa·s under static conditions as illustrated in Fig. S5d exhibited no undesirable surface characteristics (Fig. S5b). The weight ratio of BPAGDA to PEGDA at the critical viscosity was found to be 1.75. Moreover, it necessitates the optimization of energy distribution models and meticulous control of focus speed to prevent projection blurring. In the LIDG process, light must traverse cured structures to access the curing layer, resulting in the attenuation of optical energy during this penetration. Comprehending the attenuation characteristics of both solidified and liquid photopolymer is essential for determining the energy necessary for photopolymerization. The attenuation coefficients of solid polymer (μ_S = 0.0396 W/mm) and liquid resin (μ_L = 0.1489 W/mm) were ascertained using light intensity measurements, employing the Beer-Lambert Law. Moreover, light refraction is essential for modeling energy distribution in three-dimensional space, especially as liquid and solid photopolymers possess distinct refractive indices.

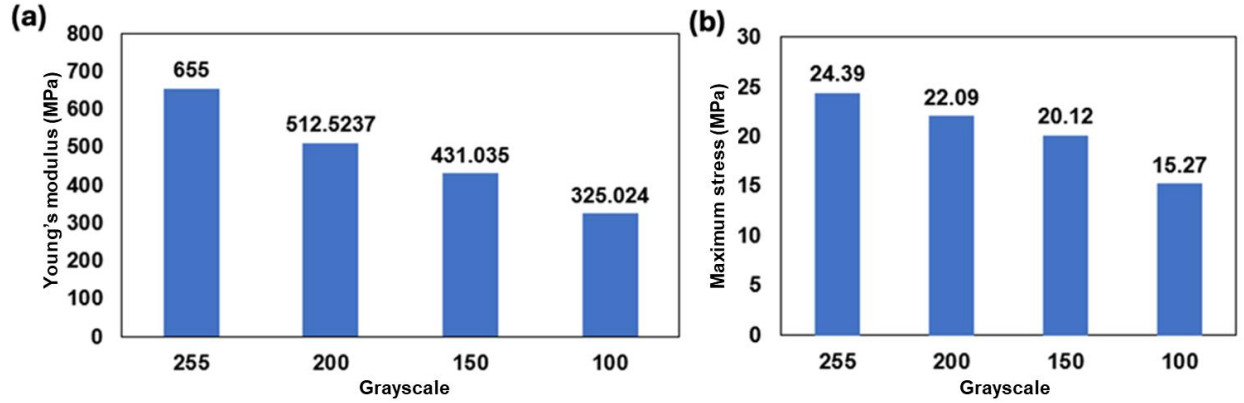

Fig. S6. (a) Average young's modulus of samples printed under different grayscale level; and (b) average maximum stress of samples printed under different grayscale levels.

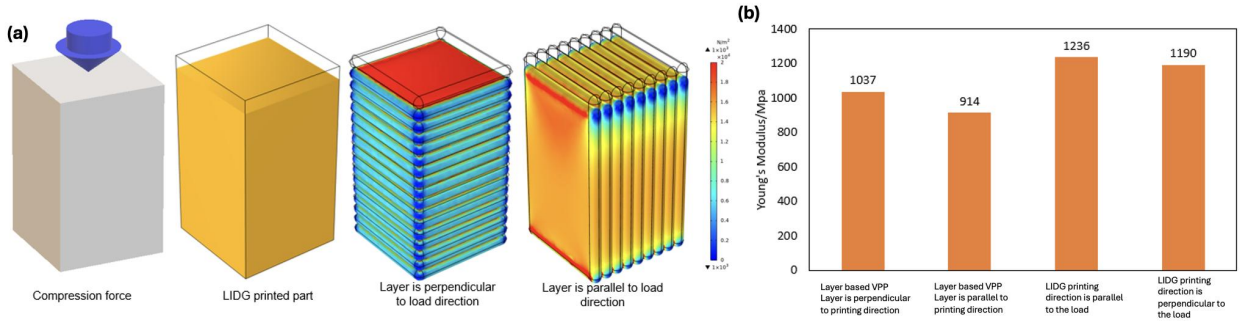

Fig. S7. (a) FEA simulation of the tensile test of the VPP and LIDG printed samples; and (b) the young's modulus of the VPP and LIDG printed samples

Supplementary Videos

SV1: Printing of the Tower via LIDG with Focus Adjustment

SV2: Printing of Macro and Micro Cylinders via LIDG without Focus Adjustment

SV3: Printing of the Macroscale Cylinder via LIDG with Focus Adjustment

SV4: Printing of the Microlens Array via LIDG with Focus Adjustment