

Supplementary Materials for

Rapid, continuous additive manufacturing by volumetric polymerization inhibition patterning

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Supplementary Materials

Supplement 1: Derivation of Eq. 1

The intensity of a beam of light of a given wavelength at any distance (x) in an absorbing medium is given by the Beer-Lambert and is dependent on the incident intensity (I_0), the wavelength specific molar absorptivity of the absorbing species (ϵ), the molar concentration of the absorbing species (c), such that

$$I(x) = I_0 10^{-\epsilon c x}$$

The reaction rate for photopolymerization in the presence of a photoinhibitor has previously been shown to be dependent on the intensity of the initiating and inhibiting wavelengths, in this case blue and UV respectively, (I_{blue} and I_{UV}), the inhibition coefficient (β)—a constant that encompasses the ratio of inhibitor to initiator absorption cross section, quantum yields, and reaction rate constants—and the reaction rate constant (k). The reaction rate is thus

$$R_{poly} = k(I_{blue} - \beta I_{UV})^{0.5}$$

Combining the above terms yields an equation for the reaction rate as a function of the distance into the absorbing media, where

$$R_{poly} = k(I_{blue,0} 10^{-\epsilon_{blue} c_{blue} x} - \beta I_{UV,0} 10^{-\epsilon_{UV} c_{UV} x})^{0.5}$$

In the inhibition volume (IV), the rate of polymerization is zero since there is by definition no reaction, such that

$$\begin{aligned} 0 &= k(I_{blue,0} 10^{-\epsilon_{blue} c_{blue} x_{IV}} - \beta I_{UV,0} 10^{-\epsilon_{UV} c_{UV} x_{IV}})^{0.5} \\ 0 &= I_{blue,0} 10^{-\epsilon_{blue} c_{blue} x_{IV}} - \beta I_{UV,0} 10^{-\epsilon_{UV} c_{UV} x_{IV}} \\ I_{blue,0} 10^{-\epsilon_{blue} c_{blue} x_{IV}} &= \beta I_{UV,0} 10^{-\epsilon_{UV} c_{UV} x_{IV}} \end{aligned}$$

We can define the absorbance height at a given wavelength, h_i , as

$$\varepsilon_i c_i = 1/h_i$$

Substitution yields

$$I_{blue,0} 10^{-x_{IV}/h_{blue}} = \beta I_{UV,0} 10^{-x_{IV}/h_{UV}}$$

Rearrangement

$$10^{-x_{IV}/h_{blue} + x_{IV}/h_{UV}} = \beta \left(\frac{I_{UV,0}}{I_{blue,0}} \right)$$

Solving for x_{IV} yields

$$x_{IV} = \frac{\log_{10} \left(\frac{\beta I_{UV,0}}{I_{blue,0}} \right)}{\frac{1}{h_{UV}} - \frac{1}{h_{blue}}}$$

For the inhibition volume thickness to be identically zero, the numerator of equation S9 needs to equal zero, such that

$$\begin{aligned} 0 &= \log_{10} \left(\frac{\beta I_{UV,0}}{I_{blue,0}} \right) \\ 1 &= \frac{\beta I_{UV,0}}{I_{blue,0}} \\ \frac{1}{\beta} &= \frac{I_{UV,0}}{I_{blue,0}} \end{aligned}$$

This gives the minimum $\frac{I_{UV}}{I_{blue}}$ ratio which results in an inhibition volume.

Supplement 2: Derivation of Eq. 2

In a bottom-up 3D-printing application, the intensity of initiating light from the projection window is given by the Beer-Lambert Law, where

$$I_{blue}(x) = I_{blue,0} 10^{-\frac{x}{h_{blue}}}$$

Integrating this for all exposure times gives the total applied dosage for any vertical position, such that

$$E_{blue} = \int_0^{\infty} I_{blue,0} 10^{-\left(\frac{x}{h_{blue}}\right)} dt$$

Since the build head is translating at speed, s , the position relative to the print window is given by

$$x(t) = x_0 + st$$

Integrating over distance yields

$$E_{blue} = \int_0^{\infty} \frac{I_{blue,0} 10^{-\left(\frac{x}{h_{blue}}\right)}}{s} dx$$

Since the inhibition is generated by another wavelength of light we can define a new critical dose which is required to cure the polymer and overcome the inhibition, where

$$E_c^* = E_c + \int_0^{\infty} \frac{\beta I_{UV,0} 10^{-\left(\frac{x}{h_{UV}}\right)}}{s} dx$$

When the dose delivered by the blue light equals the critical dose the speed is at a maximum, since any additional dose is effectively wasted (i.e. $E_{blue} = E_c^*$), such that

$$\int_0^{\infty} \frac{I_{blue,0} 10^{-\left(\frac{x}{h_{blue}}\right)}}{S_{max}} dx = E_c + \int_0^{\infty} \frac{\beta I_{UV,0} 10^{-\left(\frac{x}{h_{UV}}\right)}}{S_{max}} dx$$

Combining the integrals, integrating and solving yields

$$\int_0^{\infty} \frac{I_{blue,0} 10^{-\left(\frac{x}{h_{blue}}\right)}}{S_{max}} - \frac{\beta I_{UV,0} 10^{-\left(\frac{x}{h_{UV}}\right)}}{S_{max}} dx = E_c$$

$$\frac{I_{blue,0} h_{blue}}{S_{max} \ln 10} - \frac{\beta I_{UV,0} h_{UV}}{S_{max} \ln 10} = E_c$$

$$S_{max} = \frac{I_{blue,0} h_{blue} - \beta I_{UV,0} h_{UV}}{E_c \ln 10}$$

This maximum rate is difficult to achieve owing to lingering lophyl radicals, mechanical properties of the curing resin, and liquid resin reflow into the inhibition volume. We can define an achievable maximum print speed, S_{max}^* , which is what is observed experimentally, as

$$S_{max}^* = \eta S_{max} = \frac{\eta (I_{blue,0} h_{blue} - \beta I_{UV,0} h_{UV})}{E_c \ln 10}$$

Supplementary Figures

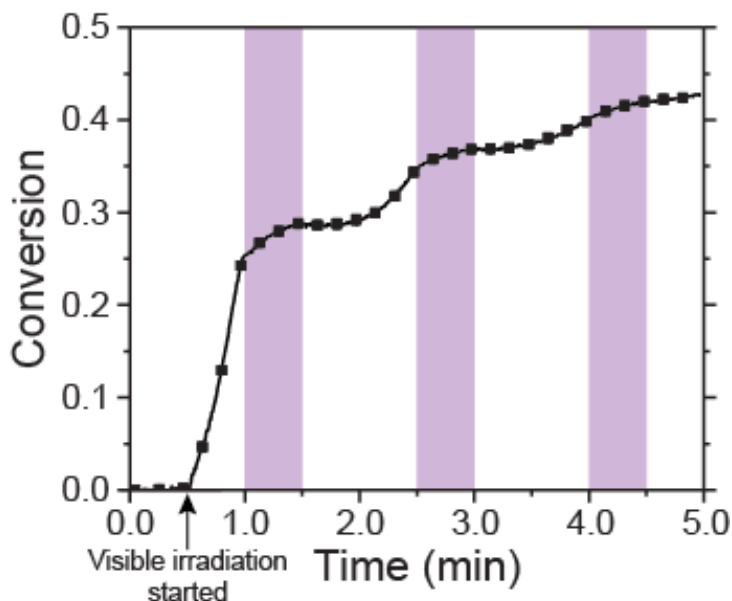


Fig. S1. Wavelength-selective photoinitiation and transient photoinhibition of methacrylate polymerization. Methacrylate conversion versus time for bisGMA/TEGDMA formulated with CQ/EDAB and *o*-Cl-HABI under continuous irradiation, starting at 0.5 minutes, with 470 nm @ 100 mW/cm² and intermittent irradiation with 365 nm @ 30 mW/cm² during the shaded periods as indicated. Rapid polymerization proceeds upon visible light irradiation, while the accumulation of lophyl radicals during the 30 second UV irradiation periods afford decreased polymerization rates. Upon cessation of UV irradiation, the polymerization rates recover after induction times of approximately 30 seconds owing to the relatively slow consumption of lophyl radicals by recombination.

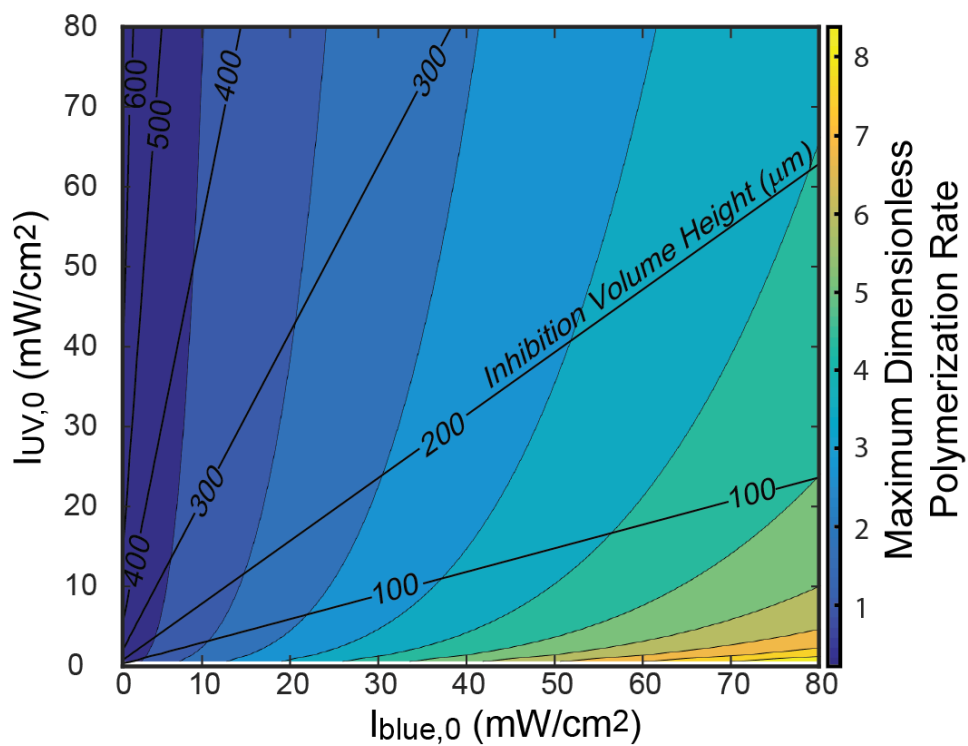


Fig. S2. Effect of incident UV and blue illumination intensities on inhibition volume thickness and polymerization rate. Adjustment of $I_{UV,0}/I_{blue,0}$ along an isorate line allows for adjustment of the inhibition volume thickness while maintaining the same polymerization rate. Additionally, raised polymerization rates can be attained for a given inhibition volume thickness.

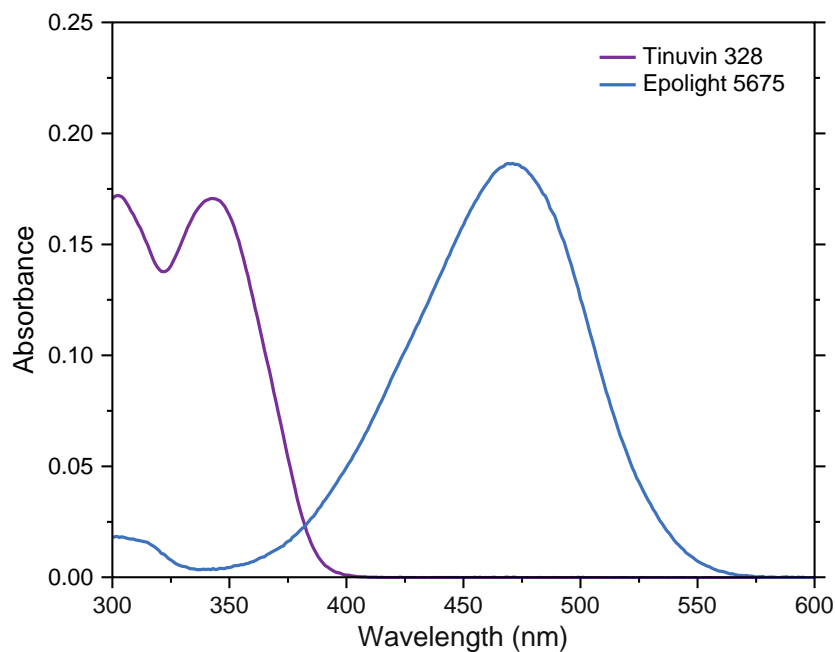


Fig. S3. UV-vis spectra of UV and blue light absorbers. The absorbance spectra of Tinuvin 328 and Epolight 5675 (1.1×10^{-4} M and 1×10^{-2} g/L, respectively) in isopropyl alcohol reveal no absorbance by Tinuvin 328 in the visible region of the spectrum and relatively low absorbance by Epolight 5675 in the near UV spectral region, enabling their use to independently control resin absorbance in the blue and near UV.

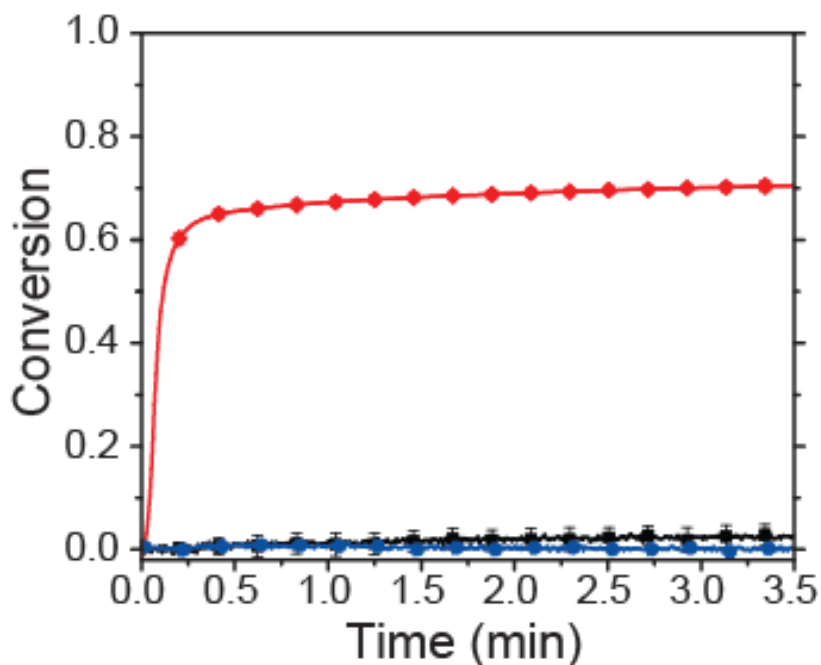


Fig. S4. Influence of co-initiator on *o*-Cl-HABI photoinitiation. Methacrylate conversion versus time for bisGMA/TEGDMA formulated with *o*-Cl-HABI and either no co-initiator (black line, squares), EDAB (blue line, circles), or MBT (red line, diamonds) under continuous irradiation with 365 nm @ 30 mW/cm². Whereas inclusion of MBT in the resin formulation results in rapid photopolymerization, the formulated methacrylate resin in the absence of a co-initiator exhibits negligible conversion upon UV irradiation. Similarly, no polymerization is observed during the irradiation of the resin formulated to include EDAB, indicating that the lophyl radicals are unable to generate polymerization-initiating radicals by hydrogen abstraction from the tertiary amine which can thus be employed as a CQ-selective co-initiator.

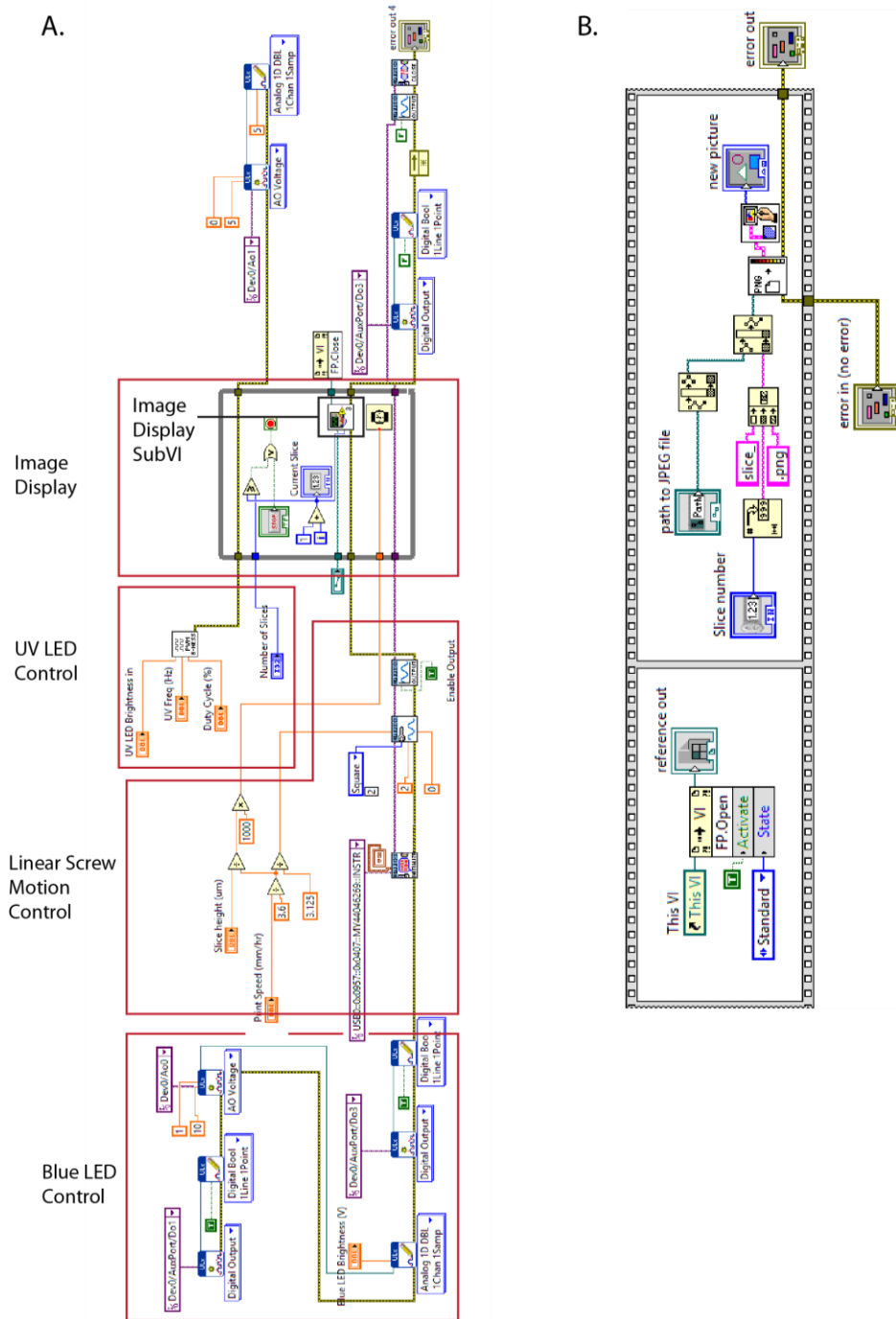


Fig. S5. LabVIEW 2014 VI block diagram. (A) The block diagram used for continuous printing. The blue and UV LED drivers, signal generator, and image generation were controlled using this VI during printing. **(B)** The image display sub-VI for projecting images.

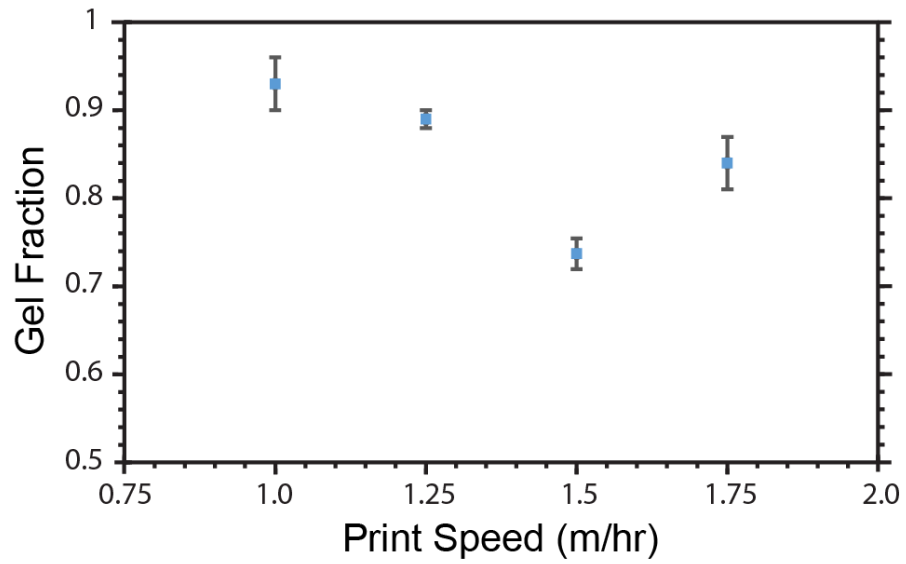


Fig. S6. Effect of print speed on the gel fraction of printed parts. Gel fraction versus printing speed determined using Soxhlet extraction for printing resins with $h_{blue} = 4500 \mu\text{m}$ and $h_{UV} = 100 \mu\text{m}$. Model used was a solid ($\phi = 0$) ASTM D638 Type V dog bone.