Published in final edited form as:

Adv Eng Mater. 2018 December ; 20(12): . doi:10.1002/adem.201800876.

Understanding and Improving Mechanical Properties in 3D printed Parts Using a Dual-Cure Acrylate-Based Resin for Stereolithography

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Abstract

Application of 3D printed structures via stereolithography (SLA) is limited by imprecise dimensional control and inferior mechanical properties. These challenges are attributed to poor understanding of polymerization behavior during the printing process and inadequate post-processing methods. The former via a modified version of Jacob's working curve equation that incorporates the resin's sub-linear response to irradiation intensity is addressed by the authors. This new model provides a more accurate approach to select 3D printing parameters given a desired z-resolution and conversion profile along the depth of the printed part. The authors use this improved model to motivate a novel material design that can be post-processed to be indistinguishable from the polymer at 100% conversion. This approach employs a dual initiating system in which photo-initiated printing is followed by a thermal post-cure to achieve uniform conversion. The authors show that this approach enables fast printing times (10 s per layer),

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

exceptional horizontal resolution (1–10 microns), precise control over vertical resolution, and decreased surface corrugations on a 10's of microns scale. The techniques described herein use an acrylate-based SLA resin, but the approach can be extended to other monomer systems to simultaneously achieve predictable properties and dimensions that are critical for application of additive manufacturing in load-bearing applications.

Keywords

Jacob's working curve; mechanical properties of 3D printed parts; post-cure; stereolithography; 3D printing

1. Introduction

Stereolithography (SLA) affords high spatial resolution,^[1] short build times,^[2] and a broad range of available chemistries.^[3] It has been used to manufacture a wide range of parts, such as molds for orthodontic Invisalign plastic inserts,^[4] scaffolds for tissue engineering,^[5] and the skeleton structure of biohybrid robots.^[6] While the technology has proven to be invaluable in manufacturing complex parts, a better understanding of the photochemical processes governing the material response in 3D printing is needed for the development of structures with predictable material properties and dimensions.

3D printing was originally introduced as a rapid prototyping technique. In this application, the mechanical performance and dimensional tolerances of the finished object are secondary to the appearance.^[3] Therefore, the mechanical and chemical properties of materials patterned using SLA 3D printing techniques have not been studied in depth.^[3] Nonetheless, both dimensional accuracy and mechanical performance of the final part are required to increase the scope of SLA from prototyping to the fabrication of operational parts that require mechanical performance.

The properties of parts printed by SLA are intimately derived from the SLA process, summarized in Figure 1. Here, a computer aided design (CAD) file is sliced into two-dimensional images that are sequentially projected by a spatial light modulator (SLM) onto the surface of a precursor resin. The resin is held between a motorized build platform and a transparent window coated with polydimethylsiloxane (PDMS). The coating prevents adhesion between the part and the window by maintaining a thin layer of oxygen to inhibit polymerization.^[2,7] A 3D part is manufactured by projecting a 2D slice on the resin surface for a designated exposure time, lowering the build platform by a designated thickness, and repeating the process iteratively until the 3D CAD structure is reconstructed (Figure 1).

Light penetration and cure depth are controlled by a photoabsorber in the resin formulation. The photoabsorber results in an exponential decay in light intensity, defined by Beer-Lambert law,^[8] leading to a gradient in conversion within each printed layer that varies from $\approx 100\%$ at the top to the gelation threshold at the bottom. This variation causes a material and mechanical gradient within each layer and is responsible for the inferior properties of the final structure compared to the bulk material.^[8–10] Variation of conversion within each

layer causes the surface to exhibit a saw-tooth corrugation with amplitude on the order of 10 microns. Also, 3D printed parts fail at lower strains than samples of fully converted resin.^[11]

Post-processing is employed to raise conversion and improve the mechanical properties of 3D printed parts, commonly via UV exposure as well as thermal curing.^[12] The former does not improve the interior of the part due to the presence of absorber. Thus, the final printed properties remain inferior to those of the fully converted material (Figure 2).^[3,13–15] The latter has been studied using epoxy-based resins, but these require higher energies for photopolymerization than acrylate-based resins, leading to increased print times.^[12] These approaches do not address the root cause of mechanical inferiority, and achieving equivalent material properties in 3D printed parts remains challenging.

The fabrication of geometrically accurate parts with predictable mechanical properties is critically important for the success of SLA 3D printed parts. To this end, this work investigates a) processing parameters that lead to inferior mechanical properties to provide a more predictable understanding of the final properties of 3D printed parts and b) development of a dual-cure system that achieves 3D printed parts with mechanical properties matching that of material properties of polymer at 100% conversion. A multi-functional acrylate-based resin was used for this study, which is composed of poly(ethylene glycol) diacrylate (PEGDA), pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), and the photo-initiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO). A dual cure system is introduced with the inclusion of a thermal initiator, 2,2'-Azobis(2-methylpropionitrile) (AIBN). This formulation was chosen to serve as a model material for multi-functional acrylates commonly used in SLA applications.^[3,6,16,17] Overall, this work describes methods to characterize SLA materials to predict local conversion within the printed part, the role of post-processing on the mechanical properties, and finally the development of a novel SLA resin formulation based on a dual-cure system using light and thermal cures to achieve mechanical properties that are indistinguishable from the material properties of the polymer at 100% conversion.

2. Results and Discussion

2.1 Mapping the Relationship between Intensity and Time to Predict Conversion

SLA is made possible by light absorption of the resin such that an incident optical intensity applied for a defined exposure time converts a finite thickness of monomer into polymer. This thickness, known as the cure depth, is dependent on the polymerization kinetics. The relationship between the two exposure parameters, intensity and time, and cure depth is typically understood by the “working curve” model introduced by Jacobs.^[13] However, this model overly simplifies the photochemical reactions by assuming that SLA resins are “reciprocal,” meaning that the resin response depends only on the product of intensity (I) and time (t). This assumption generally fails for radically-initiated photopolymers.^[18] While primary photochemical reactions such as absorbance and initiator cleavage follow the first order scaling of reciprocity, radical polymerizations are known for their sub-linear dependence on light intensity due to subsequent bimolecular radical termination.^[19,20] Further, the reaction proceeds through a distinct sequence of events: oxygen inhibition, light-induced polymerization, and dark polymerization. Each region follows kinetics that are

distinct and often not described by optical energy dose ($I \times t$), which is commonly used in the working curve. Here we apply knowledge of polymerization kinetics to derive an improved working curve model for acrylate-based resins to enable a more accurate prediction of conversion across the 3D printed part.

We first explore the polymerization regime. it is known that the rate of polymerization is related to light intensity by a power law^[21] such that monomer conversion (C_p) is proportional to the product of intensity raised to a power and time, $I^m t$. The exponent, m , varies depending on the radical termination mechanism.^[18,22] in this work, the conversion of the PEGDA/PETMP resin was monitored as a function of time by real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) for a range of intensities. Conversion is plotted as a function of time and intensity using a scaling factor m of one assuming reciprocity in Figure 3a. Conversely, the same data can be collapsed on to a single master curve by a fit to the scaling factor, $m = 0.68 (\pm 0.01)$, as shown in Figure 3b.

The regime corresponding to oxygen inhibition is also important to the working curve, since it predicts the intensity and time required to overcome the oxygen inhibition threshold. For multi-functional monomers which gel at very low fractional conversion, formation of a crosslinked gel occurs very quickly after this threshold. in this work, we approximate these two exposures to be the same. This point can be identified by extrapolating the data in Figure 3b to a conversion of zero to find the critical exposure time (t_c). In typical resins that contain only acrylates, this critical time scales linearly with light intensity due to primary radicals and propagating radicals that react with oxygen to form peroxide radicals, which do not participate in the polymerization process. However, a small concentration of the thiol PETMP monomer as used here reduces oxygen inhibition through chain transfer from the peroxy radical to the thiol.^[23] This process leads to thiol-based crosslinks during the inhibition period, which scales with light intensity by a factor between 1 and $m = 0.68$. This critical exposure, E_c , can be written following a similar scaling relationship. We introduce a new scaling exponent, n , for this region of the polymerization, as follows:

$$E_c = I^n t_c \quad (1)$$

The scaling factor n was determined by plotting critical time (t_c) as a function of light intensity and fitting to a power law. (Figure 3c) Minimizing the variance in $I^n t_c$ gives a scaling factor of $0.86 (\pm 0.02)$. The constant E_c for the PEGDA/PETMP resin was determined to be $17.2 (\text{mWcm}^{-2})^{0.86} \text{ s}$.

Accounting for these two distinct phases and their scaled intensities, a simplified model was derived to predict final fractional conversion (C_p) including both polymerization during illumination and in the dark as a function of intensity and time:

$$C_p(I, t) = \begin{cases} 0 & \text{if } t \leq t_c(I) & \text{(inhibition)} \\ R_p(I)(t - t_c(I)) & \text{if } t_c(I) < t < \frac{1}{R_p(I)} + t_c(I) & \text{(propagation)} \\ 1 & \text{if } t \geq \frac{1}{R_p(I)} + t_c(I) & \text{(saturation)} \end{cases} \quad (2)$$

where,

$$t_c(I) = E_c I^{-n} \quad (3)$$

$$R_p(I) = kI^m \quad (4)$$

R_p is the intensity dependent rate of fractional conversion with units of one over time, k is a constant given by the slope in Figure 3b, and I is intensity at a given depth. The model captures the experimental data (Figure 3d) describing C_p as a function of intensity and time across the entire range of exposure conditions. This model can thus be used to predict conversion given any range of intensities and exposure times.

This master curve for conversion can be combined with the Beer-Lambert law to derive an improved version of Jacob's working curve. For multifunctional macromers, gelation occurs rapidly after the inhibitory period is overcome such that it can be used to approximate the conditions for the onset of gelation. Thus, a modified working curve, which incorporates the scaling exponent for oxygen inhibition, can be found from Equation (3) as

$$C_d = \frac{D_p}{n} \ln \left(\frac{I_0^n t}{E_c} \right) = \frac{D_p}{n} \ln \left(\frac{E_0}{E_c} \right) \quad (5)$$

where C_d is the cure depth, I_0 is the incident optical intensity, t is the exposure time, n is the scaling factor for the oxygen inhibition regime, E_0 is the exposure at the surface, and D_p is the penetration depth. Beer's Law defines the penetration depth of light into the resin at which the intensity drops to $1/e$ by

$$D_p = \frac{1}{\sum a_i [A_i]} \quad (6)$$

where a_i is the molar extinction coefficient of species i and $[A_i]$ is the molar concentration of species i . UV-vis spectrophotometry allows for the experimental determination of a_i and $[A_i]$ is a known quantity. A semi-log plot of C_d versus I_0^n produces a straight line with a

slope of D_p/n and an x-intercept of E_c . The new working curve can be used to determine the two resin constants D_p and E_c . Note that Equation (5) has a form similar to the Jacob's model only because the exposure time to reach gel, Equation (3), is related to intensity via a power law and that the Jacob's model is recovered when $n = 1$.

The validity of the modified working curve in Equation (2) was investigated by quantifying the depth of cure through a series of isolated 3×3 mm square-shaped photoexposures of the resin. The exposure time was varied for a constant intensity and the cure depth measured using a confocal reflection microscope for optical profilometry.^[24] Figure 3e shows the mean cure depth as function of incident exposure E_0 .

The critical exposure found from FTIR data and Equation (3) of $E_c = 17.2 \text{ (mWcm}^{-2}\text{)}^{0.86} \text{ s}$ can be compared to the x-intercept of the data in Figure 3e which predicts $E_c = 13.2 \text{ (mWcm}^{-2}\text{)}^{0.86} \text{ s}$ will yield a cure depth of zero. The difference of these two values can be explained by the sensitivity of E_c to the differing spectra of the light sources used in the FTIR and printer. Conversely, the slope of the working curve is largely insensitive to spectrum. The penetration depth found from UV-vis and Equation (6) of $D_p = 37 (\pm 1.8) \text{ }\mu\text{m}$ matches well with the slope of the modified working curve model which predicts $D_p = 38 (\pm 2.9) \text{ }\mu\text{m}$.

These results demonstrate a modified working curve that accounts for sublinear behavior in photopolymerizable SLA resins. Since t_c depends sublinearly on intensity, many of the curves in this work do not use units of energy dose, and instead use the product of a scaled intensity and exposure time for each regime. This most-general case can be simplified as necessary, for example, when the inhibition kinetics are reciprocal ($n = 1$) or the resin is not inhibited ($t_c = 0$). However, most acrylate and methacrylate chain polymerizations are subject to oxygen inhibition, and exhibit more than one regime.^[25] Thus, this model can be extended to a wide range of materials as long as the regimes, and corresponding scaling factors are established via the characterization methods above. Moreover, with an accurate working curve, a better understanding of the polymerization kinetics as a function of depth is achieved where conversion, and hence material properties, can be described at any location in the 3D printed layer.

2.2 Post-Processing Effects on Mechanical Properties

Post-processing of SLA parts typically consists of a solvent (e.g., ethanol) used to remove unreacted monomer followed by UV exposure to raise conversion. However, an inevitable consequence of the conversion gradient in each layer is the presence of unreacted monomer. This leads to two potential applications of solvent as illustrated in Figure 4a. One can employ either a quick solvent "rinse" to remove surface monomer or a longer "soak" to remove monomer from the interior of the 3D printed part. A solvent rinse minimizes shrinkage in the low conversion regions since much of the monomer is retained in the volume. However, the presence of this monomer can cause plasticization, which lowers the modulus of the printed part.^[26] Conversely, a part, that is, solvent "soaked" to remove the unreacted monomer does not experience plasticization, but exhibits conversion-dependent shrinkage that creates a saw-tooth corrugation at the surface and stresses within the printed part, as illustrated in Figure 4b.

To study the effects of conversion on mechanical properties in a controlled manner, optically thin 3D cylindrical constructs (3 mm height, and 3 mm diameter) were fabricated without absorber. These were exposed, using the model of Equation (2), to achieve a conversion that ranged from the gel point to full conversion. Samples were treated with each of the two post-processing conditions. The “rinse” post-processing condition was performed by submerging the constructs in a large volume of ethanol after fabrication for a short period of time (≈ 1 s). The “soak” post-processing condition was performed by submerging the constructs in a large volume of ethanol for 72 h. All of the structures were then swollen to equilibrium in phosphate buffered saline (PBS) for 48 h before mechanical testing. The compressive moduli of hydrated constructs are shown in Figure 4c.

The data demonstrate that solvent soaked constructs increase in modulus as exposure increases to ≈ 40 MPa (i.e., the modulus of fully converted polymer), while solvent rinsed structures achieve a maximum modulus of ≈ 24 MPa. Before this maximum there is a crossover point at 25% conversion (Figure 4b), where samples soaked have a lower modulus than those that were rinsed. There are two phenomena that can explain these differences. At the lower conversions, high molecular polymer chains form, but which not all of the chains are covalently connected to the network. These chains, however, can act as effective crosslinks through entanglements and contribute to the overall crosslinking density leading to a higher modulus. When these chains are removed during the solvent soak, the effective crosslinking is reduced and hence the modulus is lower.^[26] At higher conversion, the presence of unreacted monomer, which acts as a plasticizer, has a greater effect on the mechanical properties.^[27,28] Thus, the modulus is lower in the solvent rinse, due to the presence of unreacted monomer, when compared to the solvent soak. The resultant plasticization constrains the maximum modulus of the part to 24 MPa.

To summarize, there are two important findings. A solvent soak that removes unreacted monomer results in a modulus gradient within each layer that varies from ≈ 0.6 to ≈ 40 MPa. Conversely, for a solvent wash that leaves most unreacted monomer within the part, the modulus variation is less from ≈ 10 to ≈ 25 MPa. Regardless, the overall mean modulus is significantly lower than the polymer at full conversion.

2.3 Improved Conversion and Mechanical Properties with Thermal Post-Cure

To achieve full conversion throughout the volume of the part that cannot be achieved by UV post-cure due to the presence of the photo-absorber (see Figure 2), we introduce a dual-cure material system. This enables a thermal post-processing step to achieve uniform high conversion and improved mechanical properties. A thermal initiator, AIBN was introduced into the PEGDA/PETMP resin with the photoinitiator TPO both at a 0.05 wt%. The thermal initiator (AIBN) did not show polymerization at the wavelength used (405 nm), indicating that it is an orthogonal process of radical initiation (Figure S2). To understand how the first-stage conversion caused by photopolymerization affects the final conversion after thermal polymerization, RT-FTIR was used to monitor conversion as a function of photo-exposure and subsequent heating times. Figure 5a shows two typical results, where photopolymerization and subsequent dark cure reaches 10%, and 60%. After final conversion from photopolymerization is reached, thermal treatment begins at $t = 200$ s, and

is able to further drive conversion. These results indicate that the implementation of a thermal post-cure can lead to full conversion regardless of the initial level of conversion.

To demonstrate the efficacy of the proposed material and post-processing method, single optically-thin layers were printed to represent material properties at various depths within a photo-absorbing layer. These uniform samples were tested for compressive modulus using a traditional mechanical tester. Samples of a control with no thermal initiator and the proposed dual-cure material were photo-exposed to various fractional conversions using Equation (2). The control samples were soaked in ethanol for 72 h to remove unreacted monomer and maximize modulus, as shown in Figure 4. The dual-cure samples were rinsed in ethanol to remove surface monomer but leave AIBN, heated, then subject to the same 72 ethanol soak to be directly comparable to the control. Both samples were swollen in DPBS to equilibrium. As shown in Figure 5b, samples with no thermal post-processing show a strong dependence of modulus on exposure conditions due to the variable crosslink density caused by partial conversion. Conversely, the dual-cure samples experience a significant increase in the compressive modulus when heated, up to a factor of 62 for the lowest initial conversion. Critically, the dual-cure samples reach a compressive modulus equal to that of the fully converted material for all first-stage conversions. In contrast, the control samples only achieve the maximal modulus when the photo exposure is sufficient to achieve full conversion.

To determine the post-processing method's effect on solvent plasticization, uniform samples of the control and the dual-cure material were soaked in ethanol for various timepoints. The dual-cure samples were rinsed in ethanol, heated, and then soaked in ethanol for the same 24 h, 72 h, and 2 weeks as the control. After the solvent soak, both sets of samples were swollen in DPBS to equilibrium before mechanical testing. Figure 5c shows that plasticization is still observed in the dual-cure samples after a 24 h solvent soak. Although the mechanical properties are significantly improved at all soak times, these results indicate that a solvent soak is still necessary to reach maximum modulus. This is consistent with the hypothesis that unattached species have a plasticizing effect and cause a reduction in stiffness. These results demonstrate that unreacted monomer and polymer chains need to be removed from the network to achieve maximum mechanical properties.

2.4 Improved Mechanical Properties of SLA 3D Printed Parts

Here we apply the knowledge gained in the materials characterization above to an SLA 3D printed part using the PEGDA/PETMP resin and dual cure approach. The larger exposure area (5×10 mm) necessitated a lower intensity. To compensate, a higher photoinitiator concentration was used, while keeping the thermal initiator concentration constant. Since initiation rate is proportional to the product of incident intensity and the photoinitiator concentration ($[PI]$), we predict E_c for $[PI] = 0.008$ M to be $5.2 \text{ (mWcm}^{-2}\text{)}^{0.86}\text{s}$, and use Equation (5) to determine a D_p of $36.8 \text{ }\mu\text{m}$.

To demonstrate that the proposed dual-cure material and process improves the mechanical properties of multilayer SLA parts, we fabricated pillar structures connected by a lattice on each side using the proposed dual-cure material and a control with no thermal initiator. The solvent post-processing methods matched that described in Section 2.3. The structure is

made up of 200 μm diameter pillars at a 25% volume fraction, attached by a lattice of ≈ 120 μm thickness on top and bottom, with a total height of 1.7 mm. The intensity and time were chosen to yield a minimum feature size in z of $C_d = 120$ μm to satisfy the structural parameters. Stage motion in the z direction was chosen to be 25 μm per layer such that the expected conversion variation from the top to bottom of a printed layer was 100 to 60%. This significantly reduces the sawtooth corrugation but, as shown in the electron micrograph of Figure 6, it is still prominent in the control samples. The use of the dual-cure material further reduces the corrugation due to an increase in conversion along the depth. Figure 6 shows SEM images for parts fabricated using SLA photoinitiation with no thermal initiator as a control (left) and for parts where the dual-cure material was implemented (right). Figure 6a and b demonstrate that both sets of samples are able to maintain vertical resolution in the 120 μm range, regardless of post cure. The arrows in Figure 6c and d point to the detectable difference in the saw-tooth corrugation at the edge when comparing the two conditions. Figure 6e and f magnify the layering effect, and how it changes after a thermal post-cure is implemented. The uniformity in conversion that results from the dual-cure material and the post-processing method reduces the differential shrinkage/swelling that causes the ridged pattern.

To assess the change in mechanical properties of multi-layer parts after a thermal post-cure, we performed unconfined compression experiments on both 3D printed samples of the proposed dual-cure material and a control with no thermal initiator. Figure 6g shows the compressive modulus are significantly increased from 7 to 15 MPa when implementing a thermal cure. The 15 MPa modulus of the printed part is expected given the 40 MPa material modulus and 25% volume fraction of the dry pillars.

3. Conclusion

In this work, we developed a new dual-cure acrylate resin that can be thermally post-processed to improve the overall mechanical properties and create 3D printed structures with properties that match the material polymerized in bulk. We used this resin to 3D-print geometrically accurate parts with mechanical properties that were equivalent to fully converted polymer. We showed that the response of our PEGDA/PETMP material to SLA processing fits a modified working curve model, which allows the design and fabrication of arbitrarily shaped 3D-printed parts with improved mechanical properties. The resin and process presented here overcome the limitations associated with conventional UV post curing and enables the fabrication of mechanically robust, dimensionally accurate 3D structures. Although the demonstration was performed in an acrylate-based resin, our technique is applicable to other SLA resins that exhibit a sublinear response to intensity and undergo radical polymerization, proving useful for both characterizing the material response, and designing new materials with enhanced mechanical performance.

4. Experimental Section

Materials:

PEGDA 700 (Aldrich), PETMP (>95%, Aldrich), Diphenyl-(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 97%, Aldrich), 2-(2-hydroxyphenyl)-benzotriazole

derivative (Tinuvin[®] CarboProtect[®], BASF Company), 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), Dulbecco's Phosphate Buffered Saline (DPBS, Corning) without calcium and magnesium. The AIBN was mixed prior to performing the experiment to avoid degradation.

RT-FTIR:

PEGDA 700 and PETMP were mixed at 99:1 wt% with 0.05 wt% TPO as a photoinitiator to enable free radical photo-polymerization of the acrylate groups under UV-vis exposure. FTIR was utilized for kinetic analysis using a Nicolet 6700 FTIR spectrometer (Madison, WI) with a KBr beam splitter and an MCT/A detector. This analytical technique was carried out to gauge the real-time conversion of monomer into polymer. The sample was placed in a 1 mm thick silicone mold between glass slides. A 400–500 nm filter was used and the samples were irradiated with light passing through the filter. The light intensities used for this study were 6.75, 12.5, 25, 50, and 75 mWcm⁻² and conversion was monitored by the disappearance of the double bond (C = C) peak of the acrylate at 6200 cm⁻¹ in the near-IR range. (Figure S3) The feasibility of a thermal post cure was investigated through the use of RT-FTIR by photopolymerizing samples with 0.05 wt % AIBN under irradiance intensities of $I = 25 \text{ mWcm}^{-2}$ for $t = 4 \text{ s}$, and $I = 50 \text{ mW cm}^{-2}$ for $t = 1 \text{ s}$ to achieve a final conversion near 60% and 10%, respectively (before thermal cure). The samples were then heated to $100 \pm 5 \text{ }^{\circ}\text{C}$.

Custom-Built SLA System:

This study used a custom-built projection SLA system for 3D printing. This SLA uses an LED ($\lambda = 405 \text{ nm}$, SOLIS-405C, Thorlabs) as a light source and a spatial light modulator (1920×1152 Analog SLM, Meadowlark Optics) as the programmable mask. (Figure S1.) An acrylates glass slide is used as the build-stage. A neutral density filter ($\text{OD} = 4$) is used with index-matched immersion oil (Type B, Cargille Laboratories Inc.) to prevent any back-scattering. The PDMS window was prepared using the Sylgard 184 Silicone Elastomer Kit (DOW CORNING) mixed at a 10 parts to 1 part ratio. The mixture was degassed and cured between two glass slides with a 1 mm spacer at room temperature for 24 h.

Cure Depth Measurements:

PEGDA 700 and PETMP were mixed at 99:1 wt% with 0.05 wt% TPO as a photoinitiator to enable free radical photopolymerization of the acrylate groups under UV-vis exposure, and 0.8 wt% Tinuvin[®] CarboProtect[®] as a photoabsorber. UV-vis (Tinuvin[®] CarboProtect[®]): $\lambda_{\text{max}} (\epsilon) = 405 \text{ nm}$ ($5800 \text{ M}^{-1} \text{ cm}^{-1}$), and UV-vis (TPO): $\lambda_{\text{max}} (\epsilon) = 405 \text{ nm}$ ($250 \text{ M}^{-1} \text{ cm}^{-1}$). This precursor solution was placed between a methacrylate functionalized glass slide, and a rain-X coated glass slide separated by a 254 μm spacer. A $3 \times 3 \text{ mm}$ square digital image was projected onto the functionalized slide with a 405 nm LED light source at an intensity of 15 mWcm^{-2} . Seven samples were fabricated to investigate the effect of exposure conditions on cure depth by varying exposure times (4, 6, 12, 18, 24, 48, and 96 s) ($n = 3/\text{group}$). The samples were soaked in ethanol for 72 h. The Cure depth was measured through the use of a custom-built optical profilometer as described by Glugla et al.^[24]

Solvent Post-Processing:

To compare solvent rinse to solvent soaked, 3×3 mm cylinders were fabricated using the SLA. The prepolymer resin was contained between two glass slides separated by a 3 mm silicon spacer. A 3 mm diameter circle digital image was projected onto the top of the glass slide for varying exposure times. The material used for fabricating the 3×3 mm cylinders did not contain the pigmented absorbing species; therefore, these cylinders were optically thin samples. The solvent rinsed structures ($n = 8/\text{group}$) were exposed at an irradiance intensity of $I = 9.9 \text{ mWcm}^{-2}$ for varying exposure times (3, 4.5, 9, 13.5, 18, and 35 s), rinsed with 100% ethanol, and subsequently swollen to equilibrium in DPBS for 48 h. The solvent soaked structures were exposed at an irradiance intensity of $I = 11.25 \text{ mW cm}^{-2}$ for varying exposure times (2.5, 3, 5, 7, 10, and 15 s), and were soaked in 100% ethanol for 72 h, and subsequently swollen to equilibrium in DPBS for 48 h.

Thermal Post-Cure:

To implement the thermal post cure, 3×3 mm cylinders fabricated as described above were rinsed with 100% ethanol after fabrication. Any remaining ethanol and monomer on the surface of the printed structure was removed. The cylinders were then placed in an oven at a temperature $105 \pm 5^\circ \text{C}$ under vacuum for 1 h. Each construct was subsequently soaked in 100% ethanol for 72 h.

Mechanical Tests:

Compressive testing was conducted on a Mechanical Testing System (MTS; Eden Prairie, MN). Hydrogels ($n = 8/\text{group}$) swollen to equilibrium in PBS were tested in unconfined compression at a constant strain rate of 0.03 mm s^{-1} to failure (3 mN pre-load; total load cell capacity of 250 N). Testing fixtures were lubricated to minimize friction at sites of sample contact. The stress and strain data were analyzed to yield three values: the true modulus, the secant modulus and the tangent modulus. The “true modulus” is the slope of the linear region of points of the true stress-true strain curve. True stress and true strain take into account the changing cross-sectional area of the sample, which is most appropriate for large strains ($>5\%$). True stress and true strain are calculated from the raw stress-strain curves, assuming a Poisson’s ratio of 0.5 as is typical with hydrogels. The secant and tangent moduli were calculated from engineering stress and strain data, which assumed no change in cross-sectional area. The slope of the secant line drawn from 7% to 10% strain finds the secant modulus, while the tangent modulus is the slope of a line tangent to the curve at 10% strain. The three moduli values were found to differ by less than 1 MPa. Herein, we report the tangent moduli.

3D Printing Pillar Structures:

PEGDA 700 and PETMP were mixed at 99:1 wt% with 0.25 wt% TPO as a photoinitiator, and 0.8wt% Tinuvin[®] CarboProtect[®] as a photoabsorber. The structures printed with the dual-initiating resin were made up of the same components, but 0.05 wt% of AIBN was added to the resin. The CAD design was composed of $200 \mu\text{m}$ in diameter pillar structures connected by a lattice on each side ($n = 3/\text{group}$). The structure was sliced into sixty-eight $25 \mu\text{m}$ layers to form a structure with a height of 1.7 mm before swelling. Each layer was

exposed for 10s at an irradiation intensity of $I = 15 \text{ mWcm}^{-2}$ as measured by a power meter at $\lambda = 405 \text{ nm}$ where the power was $3.7 \pm 0.1 \text{ mW}$ for a 0.0025 cm^2 square image. (Model 2936-C, Newport). The bottom lattice was exposed for four layers creating a $100 \mu\text{m}$ thick lattice. The subsequent 63 exposures created the pillars, and the last layer exposed the lattice for the top, creating an overhanging feature of $\approx 120 \mu\text{m}$ in length.

Structural Characterization:

Investigations on the layering within 3D printed parts were performed on a scanning electron microscope (SEM, Hitachi SU3500). Prior to analysis, the samples were dried using 100% ethanol at 25°C for 1 h. The dried samples were coated with platinum before being analyzed on the SEM using the secondary electron emission mode at an accelerating voltage of 5 kV. Images acquired by SEM demonstrate that the post-processing step does not affect the structural integrity of the printed parts (Figure S4).

Statistical Analysis:

Moduli are expressed as mean $\pm$ one standard deviation (SD). All of the single layer mechanical tests were conducted on eight replicates. A two-way ANOVA (Analysis of Variance, Minitab) method was used to determine the differences observed among the groups (Photocure compare to photo and thermal cure); $p < 0.05$ was considered significant. The multi-layer mechanical tests were conducted in triplicate and a Student's t-test (Microsoft Excel) was performed to assess statistical significance ($p < 0.05$) comparing moduli of structures that were thermally post-cured and structures that were not.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

Kevin Eckstein and Andrew Tomaschke provided support with evaluation of mechanical testing results. Jennifer Coulombe assisted with statistical analyses. Research reported in this publication was supported by the National Institute of Arthritis and Musculoskeletal and Skin Diseases of the National Institute of Health under Award Number 1R01AR069060 and by the National Institute of Child Health and Human Development of the NIH under Award Number 1R21HD090696. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. The authors also acknowledge support from a NSF Graduate Research Fellowship award to ACU.

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Figure 1. Stereolithography diagram, where a 3D CAD file is sliced into 2D layers of a desired thickness, and prepolymer resin is photopolymerized with a light source in the UV range. The absorber required for overhang features causes an exponential decay in light intensity along the depth of each exposed layer.

Figure 2.

A multilayer structure can be post-processed to achieve higher mechanical properties. The current go-to method is the use of a UV oven. While this method may achieve higher mechanical properties, it is limited by the “candy-shell” effect caused by the presence of absorber, where only a thin layer on the outside of the structure is hardened. We propose using a thermal initiator to perform a post-cure in order to drive the entirety of the material to high conversion.

Figure 3.

a) Acrylate monomer conversion as a function of intensity and exposure time as measured by real-time Fourier Transform Infrared (RT-FTIR). Reciprocity would cause these curves to overlap when plotted versus energy dose, the product of light intensity and time; instead we find that the material has a sub-linear response to intensity and conversion is dependent on a scaled intensity. b) Acrylate monomer conversion as a function of the product of scaled light intensity and exposure time. c) Critical time for gelation as a function of light intensity with the fit parameters of $E_c = (17.2mWcm^{-2})^n s$ and $n = 0.86$. d) Measured conversion as a function of predicted conversion C_p , where a master curve allows us to predict conversion given intensity and time. e) Cure depth measured as a function of surface exposure, E_0 , plotted on a semilog scale. Here, the x-intercept of the plot is E_c and the slope of the plot is the D_p/n . The modified model is compared to the experimentally measured cure depth.

Figure 4.

a) Every 3-D Printed part must undergo a solvent post-processing step in order to get rid of unreacted material. To investigate the impact of solvent post-processing, we fabricated single layer structures without absorber to represent infinitely small sections within an absorber containing layer. b) Exposing the structure to solvent for a small amount of time through a rinse of 5mL of 100% Ethanol generates a reduced compressive modulus, that is, likely due to plasticization. In contrast, when the structure is exposed to the solvent for a time greater than that of equilibrium swelling (e.g., 48 h), the structure is able to achieve properties that are comparable to the bulk properties of the polymer at 100% conversion ($P < 0.001$). The crossover point at low exposures is a result of entangled chains which likely contribute to the mechanical properties of the gel that were rinsed with the solvent. We hypothesize that the solvent soak at low exposures is causing a reduced modulus because the solvent acts as a plasticizer when the crosslink density is low, and the solvent-polymer interaction is greater than the polymer-polymer interactions. c) Schematic representation of a solvent rinse versus a solvent soak in a 3D printed part.

Figure 5.

a) RT FTIR data shows that the prepolymer can reach full conversion in both the case that the conversion is originally low ($\approx 10\%$) or high ($\approx 60\%$). b) A circular pattern of 3mm diameter was exposed on the surface of the resin to create 3×3 mm cylinders through optical exposure. The thermal post-cure allows the uncured pre-polymer to reach full conversion and significantly increase the mechanical properties of a single 3D printed layer in structures with predicted conversions less than one ($P < 0.001$). Material that was photopolymerized to complete conversion exhibits no significant increase in modulus, as expected. c) Single layer 3D printed parts were exposed to a predicted fractional conversion of approximately 0.1 and one group was thermally post-cured. Both groups were then soaked in 100% ethanol for varying times. The thermally post-cured samples exhibited plasticization at a 24 h soak. Although conversion has increased after the post-cure process, a small amount of free polymer chains may be acting as a plasticizer. Regardless, the thermal post-cure is still able to increase the modulus from 0.6 to 25 MPa in the thermally post-cured samples after a 24 h soak ($P < 0.001$).

Figure 6.

SEM images for multi-layer 3D printed parts fabricated via custom SLA. a), b) Photo-cured structure compared to thermally post-cured multi-layer construct. c), d) Thermal post cure causes decreased layering effects of SLA by increasing uniformity of conversion in depth. e), f) Smoothing out effect of thermally post-cured pillars as compared to heavy layering effect seen in only photo-cured pillars. The lack of differential shrinkage/swelling in post-cured structures may lead to layer-to-layer uniformity, causing a nearly featureless surface on the pillar, as compared to structures that were not post-cured. g) Multi-layer constructs were fabricated using SLA. The structure was composed of a 25% volume fraction of 200 μm pillars attached to a lattice on the top and the bottom. Three samples were fabricated for each condition (i.e., thermally and not thermally post-cured) and a statistically significant increase in compressive modulus was observed for samples following a thermal post-cure.