IMPROVING ANISOTROPIC PROPERTIES OF OBJECTS PRINTED VIA STEREOLITHOGRAPHY

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Abstract -- Stereolithography (SL) is an additive manufacturing technique that involves using ultraviolet or visible light to solidify a liquid material into thin layers and subsequently build a 3D object layer upon layer. SL is a promising method for rapid prototyping and small to moderate volume production due to the ability to quickly create objects with intricate features at resolutions below 100 µm. However, widespread adaptation of SL faces several obstacles such as slow print speeds, unsuitable thermomechanical properties, and anisotropic properties. Herein, we quantify the anisotropic properties of digital light projection (DLP) SL by printing dogbones in a “vertical” orientation, where the long-axis is in the z-direction and compare those to dogbones printed in the “horizontal” dimension, where the long-axis is printed on the x-y plane. The modulus decreases by 33% when printed in a vertical orientation compared to horizontal prints. AIBN, a thermal initiator, was incorporated into the formulation to provide an additional method of radical generation during thermal postcure. Incorporation of AIBN and a thermal postcure led to a 22% increase in modulus for the vertical dogbones. These results work demonstrates the ability to modify anisotropic properties of objects printed via DLP SL using changes in formulation and postcure conditions.

Introduction -- Since its inception 30 years ago, stereolithography (SL) has become a valuable technology for rapid prototyping, customization, and manufacturing of intricate structures unavailable through other techniques.[1] SL is an additive manufacturing process that commonly utilizes UV-initiated polymerization to selectively cure resins into layers of solid materials, subsequently building an object layer by layer and capable of printing objects with feature sizes down to the scale of 10 to 100 micrometers.[2] However, widespread adaptation of SL technologies faces many obstacles including slow print speeds, unsuitable thermomechanical properties, and inadequate resolution and fidelity.[3] Currently, little fundamental understanding exists relating material properties and processing conditions to the resolution, printing speed, and mechanical properties of the heterogeneous 3D printed structure. Understanding this relationship will lead to faster print speeds and higher resolutions, increasing applications of 3D photocured systems.

Advances in SL technologies have enabled a variety of industrial and biomedical applications.[4] The initial systems developed and patented by Charles W. Hull in 1986 are more commonly known as “top-down” SLA stereolithography. In these systems, a UV scanning laser is used to polymerize a layer of resin on a platform present in a vat of liquid photopolymer. The platform is then lowered a set distance and the scanning laser continues to build the object layer by layer, polymerizing through the air/resin interface. Within the last few years, “bottom up” digital light projection stereolithography (DLP) has been developed and allows for larger objects to be manufactured with less resin. In “bottom up” SL, a digital micromirror device is used to reflect UV light in precisely controlled patterns which pass through a transparent window to polymerize a layer of photopolymer resin on a platform. The platform is then raised a set distance and the next layer of the object is cured. The advance from “top down” to “bottom up” SL is important because of the decreased fabrication time with DLP technology, the ability to create larger structures with less wasted resin due to smaller vat requirements, and an increase in pixel resolution from hundreds of micrometers to tens of micrometers.

The SL process relies on a number of variables that influence the final structures and properties including designed model features, resin formulation, light intensity, layer illumination time, layer thickness, and postcure, among other variables.[1] In order to get the highest z-axis resolution and fastest print times, layers are often illuminated until the full depth reaches gel-point and has enough green strength to hold the desired structure. This large conversion gradient can lead to poor mechanical properties, and high concentrations of extractable components due to low monomer conversion.

While less pronounced than other 3D printing methods (such as fused deposition modeling), the conversion gradient in the SL fabrication process still results in anisotropic structures, particularly for objects created using DLP technologies. Since two-dimensional layers printed using DLP are formed simultaneously, intralayer adhesion tends to be much more uniform than interlayer adhesion, creating objects with structure and properties that vary when measured in the x-y dimension versus the z dimension. This effect is less pronounced in laser scanning SLA systems, as the fabrication process essentially builds objects point by point rather than layer by layer, but is still present due to the attenuation of light through a single layer.

One common method to increase overall conversion and alleviate anisotropic properties is to expose the 3D printed object to a UV postcure.[5] This theoretically causes all the unreacted resin to reach its full conversion and make the structure and properties much more isotropic in nature. In practice, the common inclusion of UV blockers in stereolithography formulations enhances the attenuation of light as described by the Beer-Lambert Law and makes it difficult for the UV light to penetrate the depth of the object. This results in a shell of full conversion forming around the object, where the first few hundred micrometers are fully cured but with little to no effect on the inner portions of the objects.

In this work, we quantify the anisotropic properties of an acrylate formulation printed using DLP stereolithography by measuring the mechanical properties of tensile dogbones printed with the long axis in the x-dimension and comparing those results with samples with the long axis printed in the z-dimension. A trithiocarbonate reversible addition-fragmentation chain transfer (RAFT) agent is added to the formulation to modify the network formation and increase interlayer adhesion. Additionally, we incorporate different thermal initiators and a thermal postcure step to fully cure objects created using DLP stereolithography. The results of this work demonstrate the importance of postcure in diminishing anisotropic properties and increasing the overall conversion of these formulations.

Materials and Methods- The acrylate formulation used is composed of equal parts of a tetrafunctional acrylate (40 wt%, SR494 obtained from Sartomer) and a tetrafunctional urethane acrylate (40 wt%, Ebecryl 8210 obtained from Allnex), with a monofunctional urethane acrylate acting as a reactive diluent (20 wt%, Genomer 1122 obtained from Rahn). Additionally, a UV photoinitiator (1.0 wt%, TPO diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide) and UV blocker (0.16%, Mayzo OB+ (2,2'-(2,5-thiophenediyl)bis(5-tertbutylbenzoxazole)) obtained from Sigma) were added to the formulation to allow for polymerization. To study the effects of a thermal postcure, azobisisobutyronitrile (AIBN, Sigma) was added to the formulation at 0.4 wt% and 1.0 wt%.

3D printed dogbones were prepared (5 mm x 20 mm x 0.25 mm, W x L x T) with an Autodesk Ember DLP 3D printer (405 nm LED, ~20 mW/cm^2) using the model acrylate formulation. The first layer was illuminated for 8 seconds, four burn-in layers illuminated for 4 seconds, and the remaining layer illuminated for 1.8 seconds each. To determine the effect of postcure on the anisotropic properties, the samples were UV postcured with a medium-pressure mercury arc lamp at 50 mW/cm^2 for 10 minutes. To determine the effect of thermal postcure using a thermal initiator, a 2-factor, multi-level design of experiments was conducted with tensile bars cured for one hour at 65 °C, 90 °C, 115 °C, or 140 °C. To determine the effect of a thermal initiator on the anisotropic properties, samples were exposed to both thermal and UV postcure for 1 hour at 140 °C and 10 min at 50 mW/cm^2, respectively.

Mechanical properties were determined using a TA Q800 Series dynamic mechanical analyzer in tensile mode. Stress-strain testing was performed in the tensile mode at a constant temperature (30ºC) from 0 N to 18 N with a force ramp rate of 1.5 N/min.

Results and Discussion- In this work, we aimed to quantify the effect of anisotropic structure on the mechanical properties of objects printed via DLP stereolithography. Herein, we examine the underlying cause of anisotropy and alleviate the effects through the use of a thermal initiator, AIBN. A two-factor, multi-level, full-factorial design of experiments was used to identify the conditions at which incorporation of a thermal initiator had the largest effect. The mechanical properties of 3D printed dogbones postcured under these conditions were then measured to determine the effect of a thermal initiator and thermal postcure on the anisotropic properties of this system.

While SL is unique in its ability to convert liquid resins to complex 3-dimensional structures, it still faces significant challenges with respect to unsuitable thermomechanical properties and anisotropic structure. Figure 1A shows a schematic that illustrates the absorption of light through each layer, a major cause of anisotropy. The effect of this attenuation of light can be seen in Figure 1B, where objects that were printed in different orientations were imaged using SEM. In the object on the left, each layer can be distinctly seen and features a sawtooth design on the edge of the object that is absent from the object imaged on the right which features a smooth surface with no visible layers.

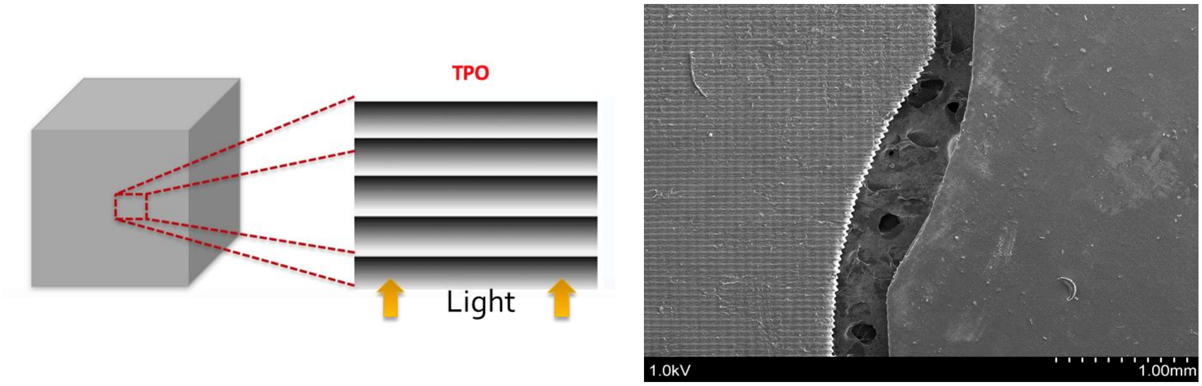

Figure 1. Left- a schematic showing how the attenuation of light through a layer can cause anisotropic properties. Right- an SEM image of dogbones 3D printed vertically (left) and horizontally (right).

In photopolymerization, monomer conversion is proportional to the dose of light used to cure the resin. Therefore, the attenuation of light through a layer in DLP SL causes a gradient of monomer conversion, where the bottom of the layer is closer to the light source and thus is exposed to higher light intensity than the top of the layer, subsequently reaching a higher conversion than the rest of the layer. This causes the portion of the layer than receives the highest intensity of light to form the extended portion of the sawtooth structure, while the top of the layer forms a retracted version. These jagged edges can act as stress concentrators that further compound the issues and affect observed mechanical properties.

Figure 2 shows the stress-strain plots for objects printed in orthogonal orientation and quantifies the effect of the anisotropic structure shown in Figure 1. The specimens printed in the “horizontal” orientation, where the long axis of the object is along the x-y plane, has a much higher modulus than the sample printed in the “vertical” orientation, where the long axis of the object is printed in the z-dimension. The higher modulus persists through a UV postcure designed to penetrate the full depth of the object and ensure that monomer conversion was the same between the two samples.

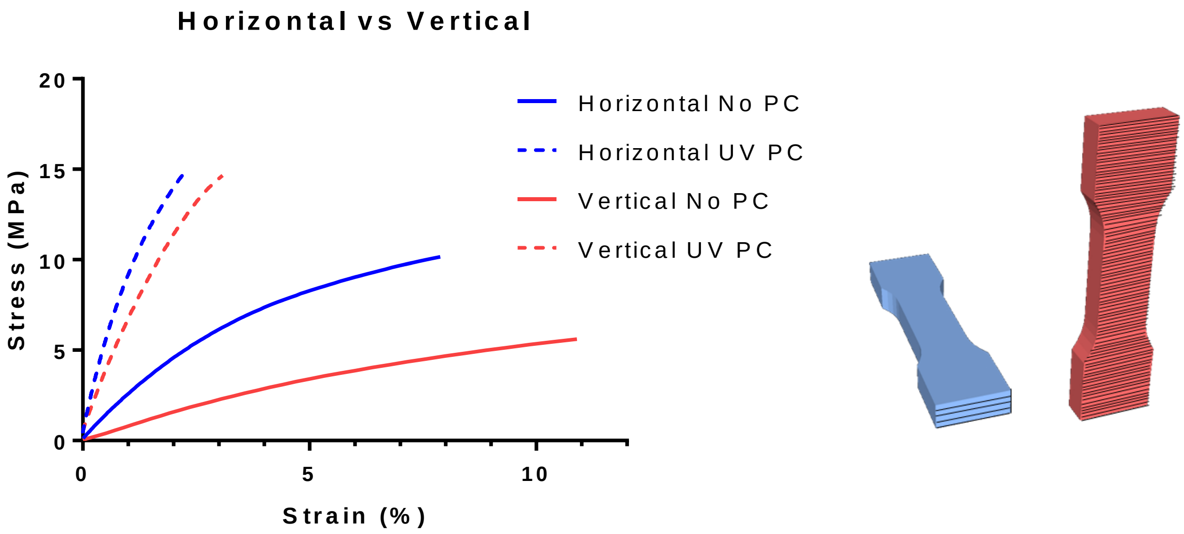

Figure 2. Stress-strain plots of dogbones printed using the acrylate formulation. Dogbones were printed in a "horizontal" orientation where the long-axis of the specimen is along the x-y plane (blue), and a "vertical" orientation where the long-axis is in the z-dimension (red). Results are shown with no postcure (solid lines) and with a UV postcure (dashed lines, 10 min at 50 mW/cm^2).

The decrease in modulus for vertical dogbones compared to horizontal dogbones that persists after UV postcure indicates the anisotropic structure imaged in Figure 1B plays a significant role in the final mechanical properties. Prior to UV postcure, the samples printed in a horizontal orientation have a modulus nearly three times higher than vertical samples, while their strain at break is approximately 25% lower. Additionally, the stress at break for horizontal specimens is nearly twice as much as those printed vertically. These results show that the anisotropic nature of DLP SL is a significant factor in the properties of the green state with no post treatment. The degree to which print orientation affects the properties in this state is due to the conversion gradient along the axis in which the force was applied for tensile testing. In the vertical prints, weak points occur approximately every 50 µm where areas of lower conversion are adhered to areas at high conversion causing the properties of the bulk material to more closely resemble those of the incompletely reacted resin. The horizontal prints do not have the same weak points along the tensile axis and therefore exhibit properties of a more highly cured polymer.

Upon UV postcure, the anisotropic properties remain, although the discrepancy between the two orientations is much lower. In this case, the modulus of a horizontal dogbone is approximately

25% higher than a vertical dogbone, while the strain at break remains roughly 25% lower. The stress at break is significantly modified by a UV postcure and is roughly equivalent for both samples. These results indicate that the anisotropic properties cannot be completely reduced through UV postcure. Additionally, the similar stress at break between the two orientations indicates that the edge effects seen on the vertical sample are likely not the cause of the decrease in modulus. If the sawtooth edges were acting as stress concentrators, the vertical samples would undergo premature breakage resulting in lower stress and strain at break rather than the results seen. Therefore, the role of the sawtooth edges can be seen as negligible and no further processing is needed to create smoother edges.

The specimens tested were designed to be thin enough for the UV postcure to penetrate through the depth of the material, causing the entire object to reach full conversion. However, the decreased modulus for vertical prints that persists through UV postcure, indicates that the materials may not be fully crosslinked. To further overcome this and enable the materials to more fully react, we incorporated a thermal initiator (AIBN) into the formulations along with a thermal postcure. A full-factorial design of experiments was used to test the effect of initiator concentration and postcure temperature to more fully understand the conditions at which the thermal initiator would be most effective. To isolate the effects of the thermal initiator, experiments were performed on samples that were printed in the horizontal orientation and underwent a thermal postcure only.

Figure 3 shows the stress-strain plots for two AIBN concentrations, at four temperatures each. The initial concentration of 0.4 wt% was chosen to match up with the wt% of photoinitiator present in the system, and 1 wt% was chosen to ensure enough initiator was present to reach high conversion through a thermal postcure. AIBN has a thermal half-life of six minutes at 101 °C, roughly the middle point of the temperatures chosen. A range of temperatures from 65 °C to 140 °C was selected to ensure full understanding of the effect of temperature on the degree of cure that occurs through a thermal postcure.

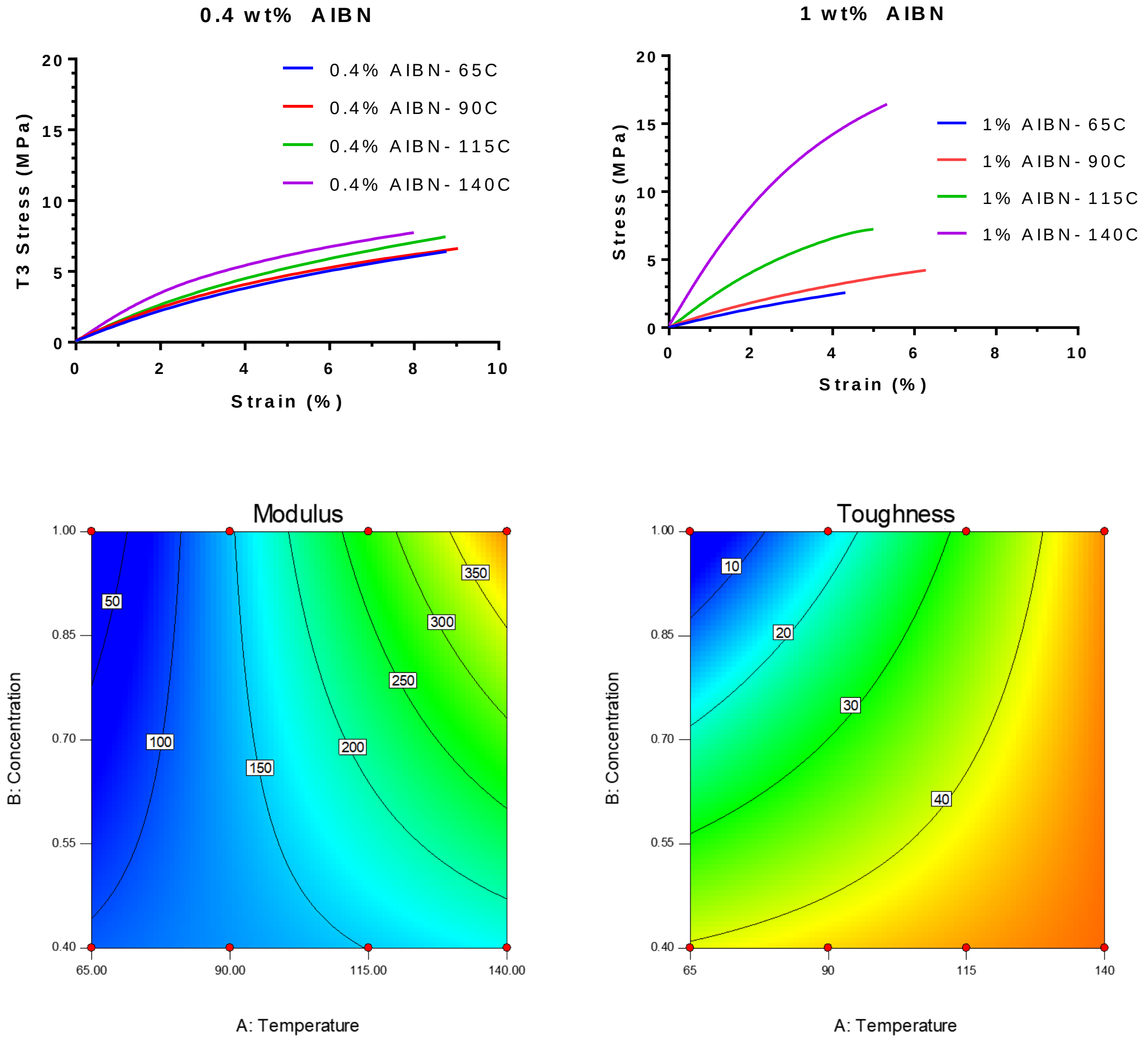

Figure 3. Stress-strain plots for the acrylate formulation with 0.4 wt% AIBN (**A**) and 1.0 wt% AIBN (**B**) after thermal postcure only. The results were incorporated into a 2-factor, multi-level, full-factorial design of experiments with response surfaces shown for the modulus (**C**) and toughness (**D**).

Figure 3A shows the results for the acrylate formulations with 0.4 wt% AIBN through the full range of temperatures. Interestingly, all of the samples produce roughly the same results at this concentration with the samples cured at 140 °C showing a slightly higher modulus. This behavior indicates that at 0.4 wt%, the concentration of AIBN is not high enough to impact the mechanical properties and therefore has a small effect on the final conversion after postcure.

Figure 3B shows the stress-strain results for the acrylate formulation with 1.0 wt% AIBN. The incorporation of higher levels of AIBN appear to have a large impact on the strain at break, causing all of the samples to break at lower strain compared to those at lower concentration. Additionally, the samples cured at lower temperatures exhibit a similar modulus to the systems with 0.4 wt% AIBN, further verifying that little to no extra reaction is occurring at low concentrations and low temperatures. The modulus begins to increase at 115 °C and has a very large increase when the samples are postcured at 140 °C, indicating that higher concentrations and temperatures are necessary for an effective thermal postcure. Figure 3C illustrates the effects of both temperature and concentration on the modulus, with the highest concentration and temperature tested correlating with the highest modulus. However, this behavior doesn't fully measure the impact of the concentration since the higher level of AIBN caused a lower strain at break for all temperatures. To account for these differences, the toughness was calculated and the response surface is shown in Figure 3D. The toughness increases as the postcure temperature increases, reaching a maximum around 140 °C, independent of concentration. The increased toughness for the lower concentration samples is due to their high elongation, while the increased toughness for the higher concentration samples is due to their high modulus.

Based on the design of experiments performed in Figure 3, it was determined that formulations with 1.0 wt% AIBN and postcured for 1 hour at 140 °C have the largest effect on the acrylate conversion, due to the increased modulus observed. These conditions were selected for further testing to determine the ability of a thermal initiator to improve the anisotropic properties of 3D printed structures. Dogbones were then printed using this concentration in both horizontal and vertical orientations.

Figure 4 shows the stress-strain results after both UV and thermal postcure, for both orientations. The modulus for horizontal dogbones is very similar with and without AIBN, indicating that any extra conversion resulting from the thermal postcure plays little role in the mechanical structure and resulting properties. For vertical dogbones, incorporating a thermal initiator and thermal postcure appears to play a role in the final mechanical properties. When AIBN is included in the formulation, the modulus of vertical samples increases by approximately 22% after both a UV and thermal postcure. Additionally, the strain at break decreases by about 15% and the stress at break increases by 12%, reaching the same stress at break value as horizontal samples. Although the modulus for a vertical dogbone increases when AIBN is included, it is still 15% lower than the modulus of corresponding horizontal dogbones. While AIBN is able to effectively decrease the anisotropic properties in DLP SL, the anisotropy still remains. As discussed earlier, the sawtooth structure on the edges of the vertical sampless may have an effect on the measured properties, but this explanation is not supported by the data.

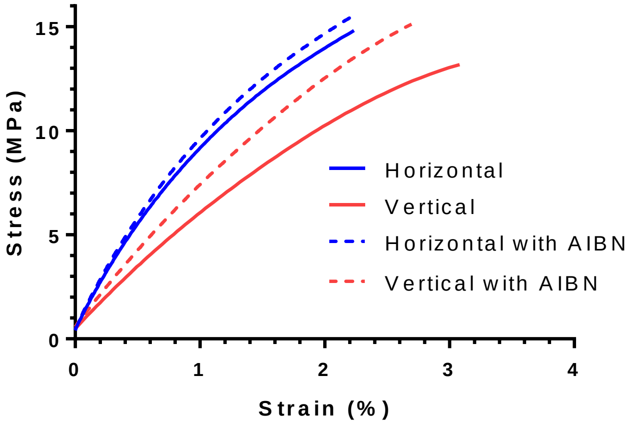

Figure 4. Stress-strain plot comparing dogbones after both a UV postcure (10 min at 50 mW/cm^2) and a thermal postcure (140 °C for 1 hr). Dogbones were printed in both the horizontal (blue) and vertical (red) orientations, without AIBN (solid lines) and with 1.0 et% AIBN (dashed lines).

Conclusions- In this work, we determined that objects printed in the horizontal orientation, where the long-axis is along the x-y plane, have a modulus that is 300% higher than objects printed in the vertical orientation, where the long-axis of the object is printed along the z-axis. The magnitude of the anisotropic properties is decreased through UV postcure but still remains significant, as UV postcured horizontal dogbones have a modulus that is 25% higher than their vertically printed counterparts. To further decrease the effect of print orientation, a thermal initiator was incorporated into the formulation and we performed a design of experiments to understand the effect of concentration and postcure temperature. Of the conditions tested, it was found that using 1.0 wt% AIBN and a thermal postcure at 140 °C had the largest effect on the modulus. Horizontal and vertical dogbones were prepared using this formulation and the modulus for the vertical dogbones increased by 22%, but the modulus was still 15% lower than the horizontal dogbones. These results demonstrate that incorporation of a thermal initiator and thermal postcure is capable of decreasing the effect of anisotropy in DLP SL, but further steps are needed to completely eliminate anisotropic properties.

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