Wednesday 2-5

Effects of Curing Rate on the Temperature Increase of Photopolymer Resins

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2.671 Measurement and Instrumentation
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Abstract

3D printing is a quickly moving field, on its way to being viable for mass manufacturing. A current roadblock to increasing print speed is the risk of overheating the resin and causing a fire. As an exothermic reaction, it is useful to characterize the effect of the curing rate on the heat of photopolymerization. A thermal imaging camera was used to measure the temperature of the top layer of resin for a prototype 3D printer. Curve fitting was used to correlate the temperature change to the duration of the print, and then the rate of temperature change during a print to the layer time, or print speed. This showed a maximum temperature increase rate of 0.159±0.034ºC/s and a negative proportional relationship between temperature increase rate and print speed of -0.171±0.067ºC/s^2.

Keywords: Thermosetting Resin, Additive Manufacturing, Temperature, Photopolymerization

1. Introduction

Additive Manufacturing (AM), commonly referred to as 3D printing, is a burgeoning industry. Valued at $20.4 billion in 2023, with continuing advancements in printing technologies, Additive Manufacturing is expected to continue its explosive growth at a compound annual growth rate of 23.5% through 2030 [2]. The technology offers many attractive benefits over conventional manufacturing techniques. Among these are the ability to print complex structures, unit-specific customization, and minimization of waste [3]. Despite these benefits, 3D printing has had limited adoption as a viable mass-manufacturing method due to its high process variation and low throughput [4]. As a result, it is imperative to increase speed, and, in hand, throughput, to bring 3D printing into the mass-manufacturing space.

MIT's own Professor John Hart has himself ventured into the 3D printing stage through co-founding ventures in VulcanForms Inc. and Desktop Metal. Most recently, Fabri Inc. has received his guidance with the goal of pushing Additive Manufacturing to its absolute limit in terms of speed and scale. Fabri has developed a prototype 3D printer and has achieved a print speed of up to 24 inches per hour, a rate unmatched in the industry. The next roadblock for this technology is the potential of reaching the flash point temperature of the 3D printing resin in use. Were this to happen, the entire resin reservoir would polymerize, an expensive mistake, or worse, start a dangerous fire. Therefore, the effect of print speed on temperature needs to be studied further.

The temperature of the 3D print at the top layer of the photopolymer resin bath was measured, and the rate at which the print's build plate was lowered into the resin bath, known as the Layer Time, was varied. Three prints were monitored at each of five distinct specified Layer Times, 0.750, 0.600, 0.450, 0.300, and 0.150 seconds all using a standardized print geometry. The temperature of each test sample throughout the duration of the print was plotted against the time that the print took. Additionally, for the duration of each test, the ambient temperature of the surroundings of the experimental setup was measured in order to account for any fluctuations in temperature between different experiment dates. Then, the rate of temperature increase was correlated with its respective Layer Time. This analysis will be used to inform whether a print will safely be completed considering its initial temperature, print duration, and layer print time.

2. Background and Theory

Additive Manufacturing processes are typically classified into seven main groups: vat photopolymerization, material jetting, binder jetting, directed energy deposition, material extrusion, sheet lamination, and powder bed fusion [5]. These methods vary widely in the manner by which each achieves the creation of the final product, such as using ultrasonic welding in Sheet Lamination, to employing lasers to sinter metal in Powder Bed Fusion [6], but, in general, they all progress by sequentially placing layers of material one on top of the other. Of these methods, the printer used in this study performs a type of Vat photopolymerization known as Digital Light Processing (DLP) and thus, this process is the topic of interest.

2.1 The Digital Light Processing Method

Developed in the 1980s, Vat photopolymerization was the first form of 3D printing [7]. It prescribes the use of a UV light source to selectively polymerize, or cure, photosensitive materials such as liquid photopolymer resin [5]. The two most common sub-processes of vat photopolymerization are Stereolithography (SLA), and Digital Light Processing (DLP). The more commonly commercially available SLA uses a focused laser beam and a scanning mirror to trace the contours of a part [8]. On the other hand, DLP uses a UV light projector to flash the image of the full part layer onto the resin and cure it all at once (Fig. 1). This key difference is what makes DLP a much faster method to manufacture at scale than SLA [9].

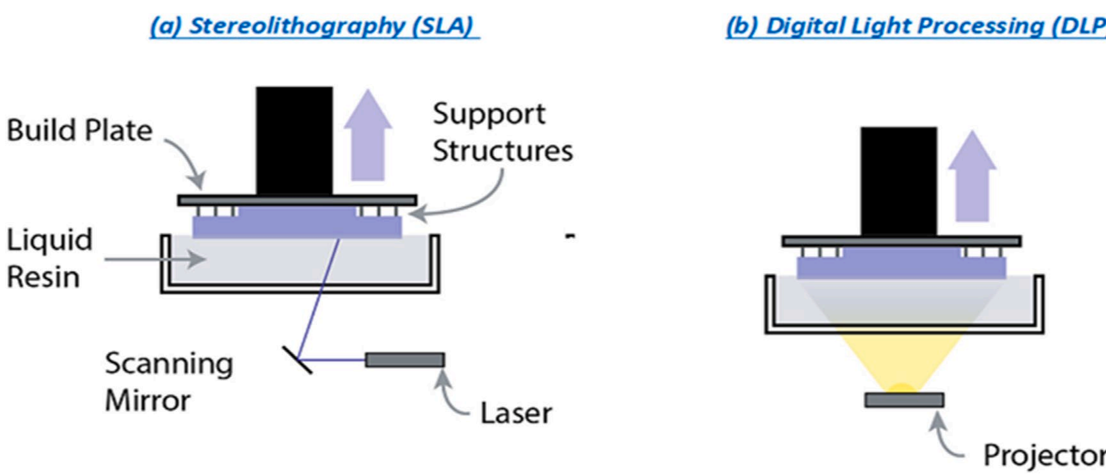

Figure 1: Differences between the setup for an SLA 3D printer (a), and that of a DLP 3D printer (b) [5]. An SLA printer uses a laser source accompanied by a scanning mirror to trace the print geometry. A DLP printer uses a UV light projector to display and cure the entire layer at once. This distinction allows DLP to print equally complex parts at a much faster rate than SLA.

Because the entire layer is cured at once, DLP requires that the photopolymer resin be as flat as possible in order to ensure high part quality. Ideally, the photopolymer resin would quickly flow and reach a steady state before the next layer is projected, but in practice, this process is too slow and is sped up by using a blade to recoat the part with a fresh resin layer [10]. This method is also time consuming and far from perfect, so the next step in DLP manufacturing is to forego the wait time and push forward to faster and faster build rates. For this reason, it is important to characterize the effects of printing faster on the maximum temperature of the resin. This will prevent the flashpoint from being reached, which, were that to happen, would ignite a dangerous chemical fire.

2.2 Curing Process of Photopolymers

Photopolymers are materials that change their physical or chemical properties through interaction with light [11]. Photopolymer resin is typically comprised of three components: monomers, oligomers or binders, and photoinitiators. The main components of the resin are monomers and oligomers. When a layer of resin is exposed to UV light, the photoinitiators are decomposed, yielding free radicals that react with monomers and oligomers, providing crosslinking to produce long polymer chains [5]. This reaction propagates until the polymer chain encounters a free radical or if it binds to another polymer chain (Fig. 2) [12].

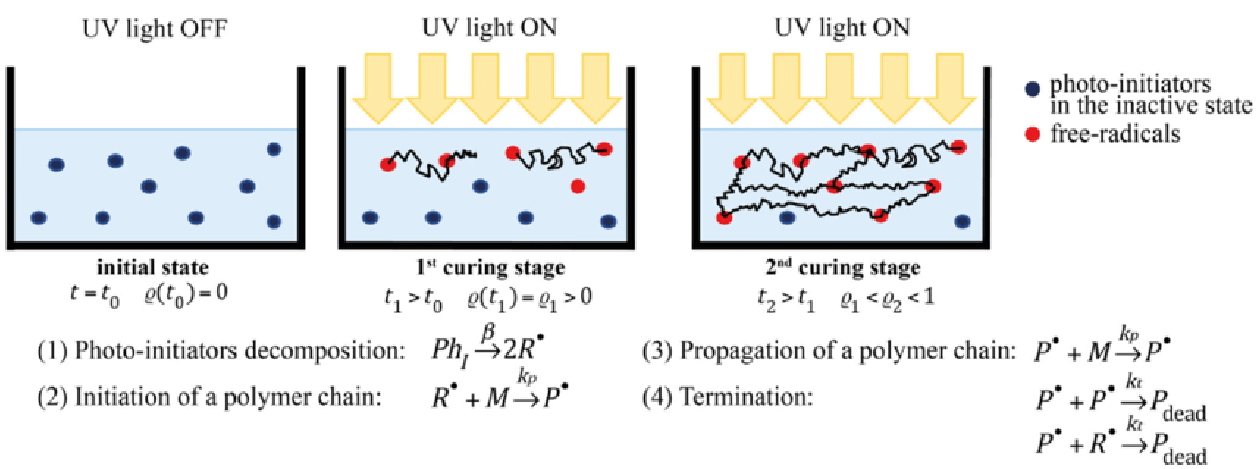

Figure 2: The process of photopolymerization reactions. In the first stage, the photopolymer resin is inactive. Once irradiated by UV light, the photoinitiators decompose into free radicals. These free radicals react with the monomers and oligomers of the resin causing cross-linking and the propagation of polymer chains [12].

Photopolymer resins are specified for the wavelength of light that will cause the photopolymerization reaction to occur. The wavelength of light of the 3D printing system, then, is what guides the choice of an appropriate resin [13]. For this study, the photopolymer resin reacts to UV light with a wavelength of 405nm.

2.3 Previous Study into Photopolymer Temperature

Photopolymerization is an exothermic reaction. Since the entropy for the chain itself decreases, energy must be dissipated to increase the entropy of the surroundings, obeying the second law of thermodynamics. One study found that the photopolymerization rate is affected by the ambient temperature and the UV light intensity. They quantified the total specific heat of photopolymerization reactions by exposing test samples to UV light with intensity of 20 mW/cm^2 for ten minutes. They found the specific heat of the reaction to be $h_{tot} = -404.43\ J/g$ [14].

However, the current work is aimed at quantifying a volumetric effect on maximum temperature, rather than the effects of irradiation intensity and ambient temperature on the material properties of a print, so this further work is warranted.

3. Experimental Design

In order to characterize the rate of temperature increase for the photopolymer resin, a thermal imaging camera was placed above the 3D printer's build plate, and an external temperature probe was used to measure ambient temperature in case of any unexpected thermal fluctuations in the printer's environment.

3.1 3D Printing Setup

The study was conducted using a prototype 3D resin printer developed by Steven Davis '24 for his startup Fabri, Inc. As a DLP printer, the system uses projectors to display the entire layer of the print on the surface of the photopolymer resin in 405nm UV light.

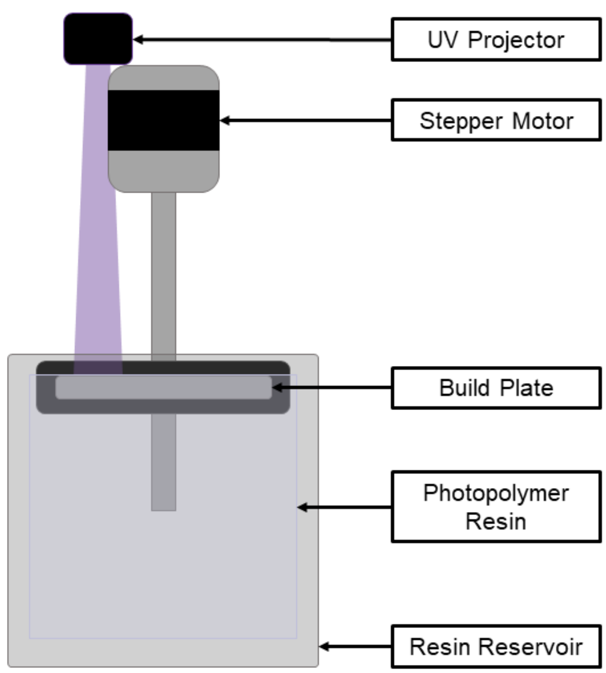

Figure 3: Schematic of the Fabri Inc. 3D printer.

Quantifying the curing rate of a 3D resin print was approximated by controlling the volume that was printed. A strip of 1.59 × 50.8 × 15.9 millimeters (1/16 × 2 × 5/8 inches) was chosen as the test sample. To progress through the print, the printer uses a servo motor to control the depth of the build plate into the photopolymer resin as shown in Fig. 4.

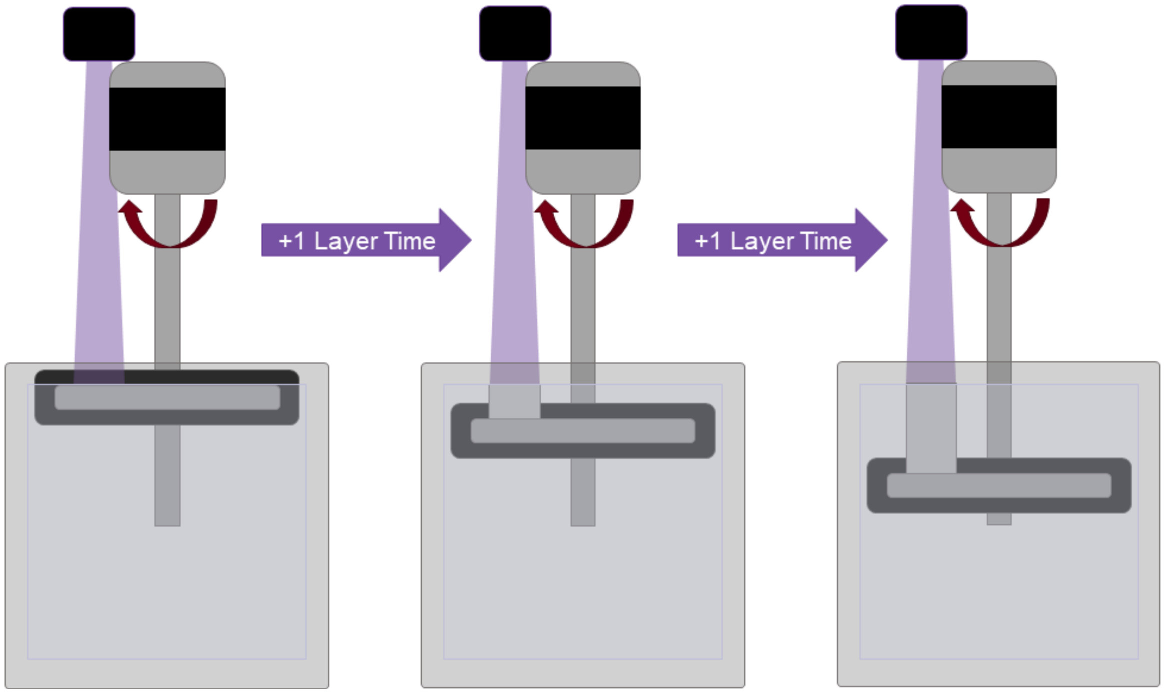

Figure 4: The stepper motor lowers the build plate by 50 microns into the reservoir of photopolymer resin. The time between each of these movements is specified as the Layer Time. Layer times of 0.750, 0.600, 0.450, 0.300, and 0.150 seconds were studied. As the build plate is lowered, the next layer of the print cures where the resin is in contact with the UV light, and the 3D-printed object increases in height.

The stepper motor lowers the build plate 50 microns deeper into the photopolymer resin after a specified time referred to as the Layer Time. As the build plate is lowered, the next layer of photopolymer resin is cured where it is in contact with the UV light, thus adding a layer to the test sample. Since the volume printed is standardized, the five Layer Times studied, 0.750, 0.600, 0.450, 0.300, and 0.150 seconds, provide a good proxy for the curing rate of the resin.

3.2 Thermal Imaging Setup

The thermal camera selected to measure the maximum temperature of the top layer of the test prints was a TOPDON TC001. It was mounted directly above the printer's build plate, next to the projectors facing down. This thermal camera is able to measure temperatures between -20°C and 550°C, and it offers automatic data logging capabilities [15]. The full specifications for the thermal camera are summarized in Table 1. Additionally, a Vernier Temperature Probe (TMP) was used to record the ambient temperature throughout the duration of each print. It was placed neatly on a tabletop near the printer.

Table 1: Relevant specifications for the Thermal Camera

Specification	Value
Resolution	256 × 192 Pixels
Frame Rate	25 Hz
Data Logging Rate	1 Hz
Temperature Range	20℃ to 550℃
Temperature Accuracy	±2℃
Temperature Resolution	0.1℃

To take data, in the viewing window of the camera's software, a measurement rectangle was selected, and the software automatically tracked the highest and lowest temperatures it sensed within the rectangle. Temperature data was logged to a Microsoft Excel spreadsheet, and a plot was automatically generated. The provided software also averaged the two data sets and provided that information as well. However, as the measurement rectangle could not be perfectly recording the test sample strips and *only* the test sample strips, the average temperature data recorded by the thermal camera was not representative of the temperature of the print, for the neighboring resin that was not being cured remained at a constant temperature for the duration of the print. Furthermore, the danger of fire comes from the photopolymer resin reaching its flashpoint temperature, in this case, 110℃, so the maximum temperature was of most interest. In addition to automatic data logging, the thermal camera can simultaneously record video and capture still images as shown in Fig. 5.

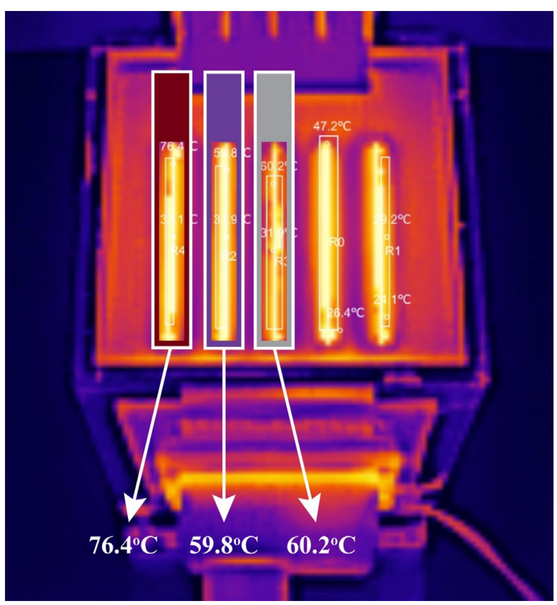

Figure 5: Thermal camera view of the printer's build plate for the print with a Layer Time of 0.600s. The maximum temperature of each of the three test sample strips, differentiated by their location on the build plate, was recorded every second of the print and logged into a Microsoft Excel spreadsheet.

The temperatures of three test sample strips, differentiated by their location on the build plate, were recorded throughout the duration of each print for each Layer Time setting. First, the specified Layer Time was input into the printer. Then, the logging was started for each of the test strip locations, and the ambient temperature recording was started. Then, the print command was sent to the 3D printer. Upon completion of the print, all data logging was stopped. The build plate resurfaced out of the resin, and it was removed, cleaned, and replaced to start the next print.

4. Results and Discussion

The maximum temperature of each test sample strip was recorded throughout the duration of a print. It was shown (Fig. 6) that the temperature of the top layer of photopolymer resin increased linearly from beginning to end.

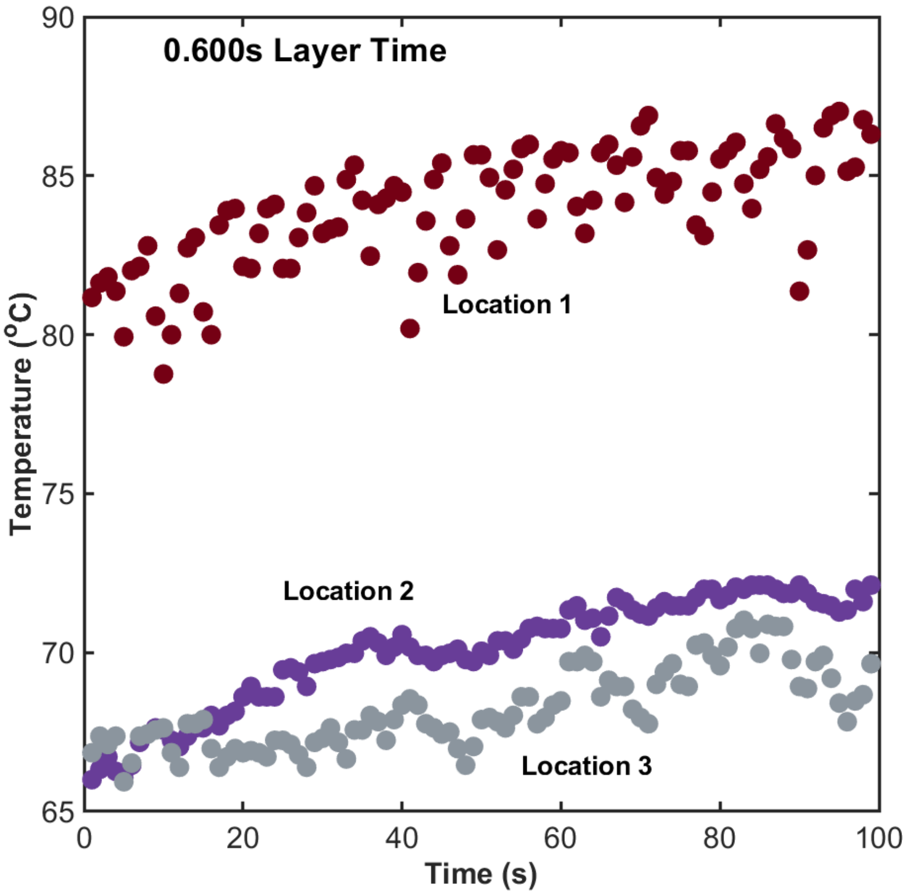

Figure 6: Temperature trend for the three print locations during the 0.600s Layer Time print. All three test sample strips showed a linear increase in temperature throughout the duration of the print. Two of the samples had an initial temperature near 65°C, and they both reached a final temperature near 70°C. The other sample had a higher initial temperature but had a similar change in temperature as the other two.

The temperature of the photopolymer resin in the three test sample locations showed a linear increase in temperature. Two of the samples had comparable initial temperatures near 65℃, and likewise, they both had similar temperatures at the end of the print near 70℃. The sample at location one had a higher beginning and ending temperature, but a similar ΔT of approximately 5℃. A linear fit was attempted to quantify the similarities between the trials, shown in Fig. 7.

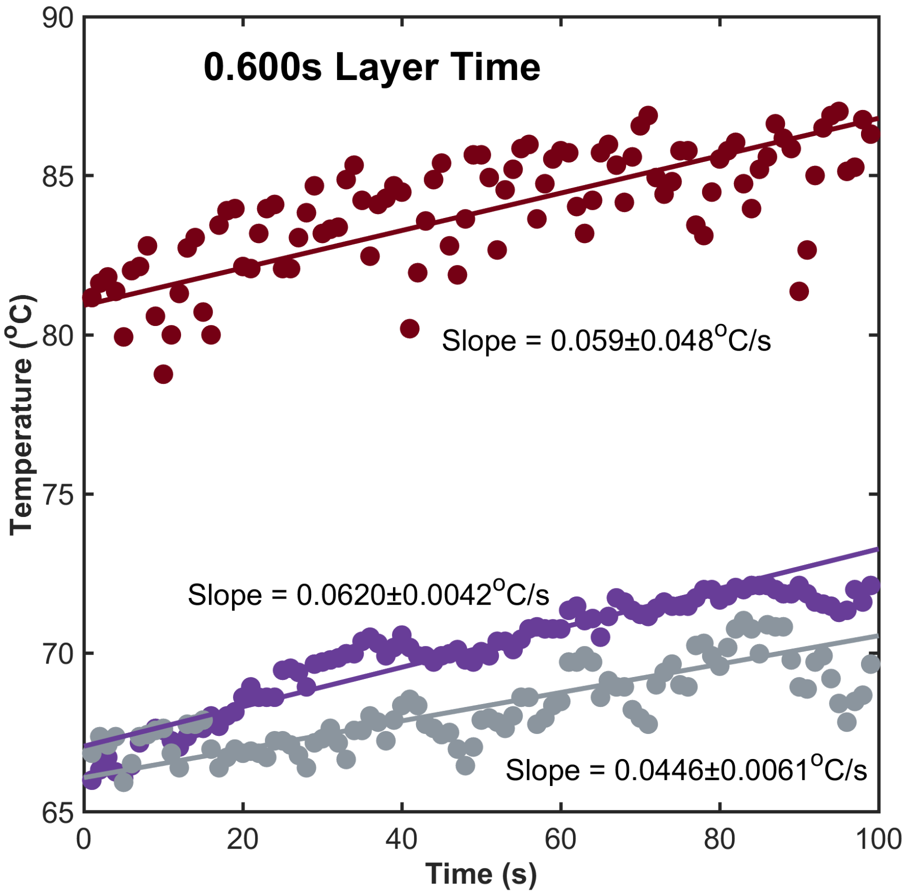

Figure 7: Linear fits for the three test samples for the 0.600s Layer Time setting overlaid on their respective temperature data. Location 2 had the greatest rate of temperature increase of 0.0620±0.0042℃/s, and Location 3 the lowest at 0.0446±0.0061℃. All three sample locations have similar slopes within a factor of 1.39.

Applying a linear fit to the temperature data for each sample yielded slopes of 0.059±0.048℃/s for Location 1, 0.0620±0.0042℃/s for Location 2, and 0.0446±0.0061℃/s for Location 3. The difference between the two extremes is a factor of approximately 1.39. Similar curve fitting was applied to all three test samples for the five selected Layer Times. The slope and uncertainty were determined for each, and the data was compiled in a plot to visualize and understand the relationship between the rate of temperature increase and the associated Layer Time, shown in Fig. 8.

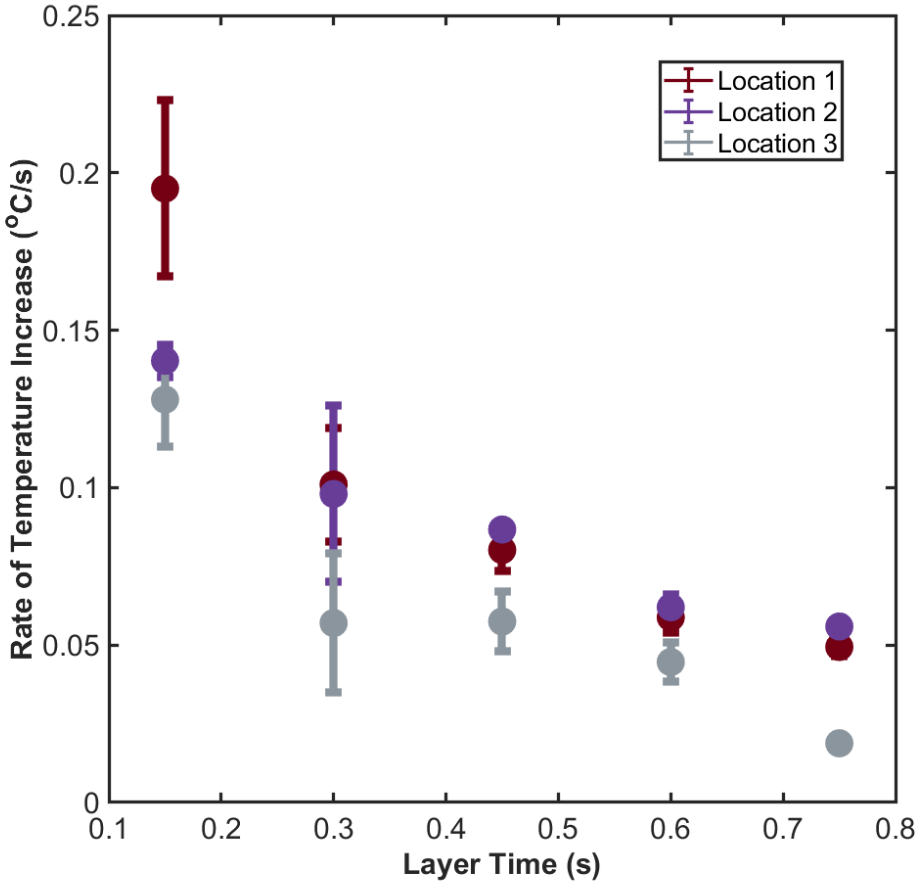

Figure 8: The slopes found from creating a linear fit to the temperature data show a linear relationship between the Layer Time and the Rate of Temperature Increase of the photopolymer resin. The error bars show the uncertainty in the linear fit's slope associated with each individual test sample with 95% confidence.

Plotting the slopes found from creating linear fits for the temperature data of each test sample for all Layer Times revealed yet another linear relationship. The Layer Time and the rate of temperature increase of the photopolymer resin have a negative proportional relationship. The error bars show the uncertainty in the linear fit's slope associated with each individual test sample. Furthermore, generating a linear curve fit for this data would produce a model that would be able to predict the maximum rate of temperature increase for the specific photopolymer resin used in this study. This relationship is shown in Fig. 9.

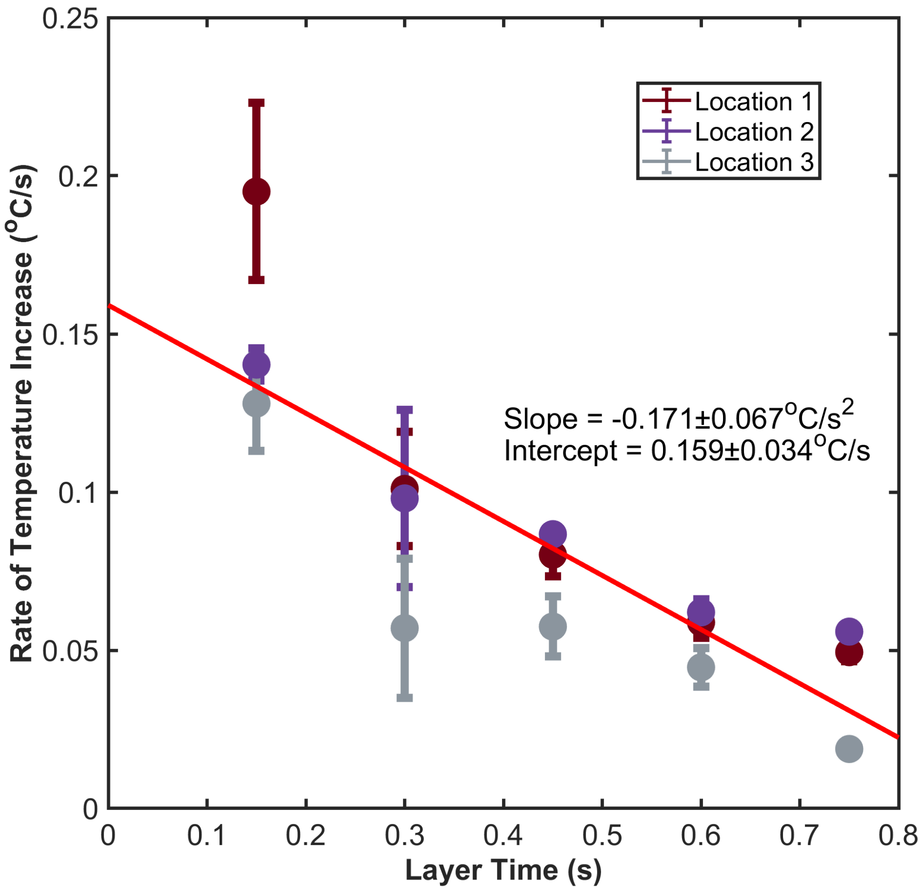

Figure 9: A linear fit applied to the various trials' rates of temperature increase. The intercept of this graph shows the theoretical maximum rate of temperature increase possible for this resin and a print with the same geometry. At "Continuous Printing," that is, a Layer Time of 0 seconds, the resin's temperature will increase at a rate of 0.159±0.034℃/s.

Applying curve fitting to the fifteen total samples studied yielded a linear fit with a slope of -0.171 ± 0.067℃/s^2 and an intercept of 0.159±0.034℃/s. This linear fit can be used as a predictive model to characterize the rate of temperature increase for arbitrarily small Layer Times. Thus, for "Continuous Printing" (i.e. 0 second Layer Time), the photopolymer resin will be increasing in temperature at a rate of 0.159±0.034℃/s.

Some clear limitations of this study are the narrow, namely one, breadth of photopolymer resins considered. Other resins likely have different heat capacities, which would make the correlations for the linear fit parameters different. Another similar limitation is that the volume printed per layer may affect the rate of temperature increase as well. A layer thickness of 50 microns is fairly standard and provides a good surface finish for a part, but printing other cross-section geometries, or at different scales may affect the maximum temperature of the print. However, the procedure for taking those factors into account is much the same as what was done here, so the groundwork has been set, and has already yielded vital information that can inform users of DLP printers looking to maximize their throughput safely.

5. Conclusions

Analysis of the data with a linear curve fit showed a negative proportional relationship between the Layer Time and the rate of temperature increase for photopolymer resin. At a continuous printing rate (i.e. 0 second Layer Time), the top layer of the resin will heat up at a rate of 0.159±0.034℃/s.

This information can be represented as a predictive model that informs users whether or not a print will cause the resin to reach its flashpoint. For a print that takes 300 seconds, the resin's temperature will increase by 48±10℃/s. That means that, for a resin with a flashpoint temperature of 110℃, the maximum safe starting temperature for such a print is 52℃!

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