Supplemental Materials

Zero-Support 3D Printing of Thermoset Silicone via Simultaneous Control of Both Reaction Kinetics and Transient Rheology

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1. Formulation

The formulation was developed to ensure that the silicone began to crosslink shortly after mixing, had a yield stress, and was extrudable in a high resolution nozzle. In addition to the Dragon Skin 10 Very Fast silicone itself, which was chosen because its cure rate at ambient conditions was the fastest available in the Dragon Skin family without the addition of an accelerator, other Smooth-On additives were used to ensure desired behavior. The first additive was a thickener and thixotropic additive (Thi-Vex), used at maximum recommended concentration in the mixture to ensure yield stress characteristics. The second additive was a thinner (Silicone Thinner) used to reduce viscosity and ensure flow through a high resolution nozzle. One might ask: why would both a thickener and thinner be used? An explanation of the qualitative behavior of the formulation is available in Figure S1. When thinner was used in the mixture without Thi-Vex, the silicone would flow too rapidly to retain filament structure when printing. When Thi-Vex is added with thinner, the formulation still benefits from the lowered viscosity but retains structure after mixing. Without thinner, the silicone is difficult to print with high resolution nozzles. Though the exact chemistry of the silicone formulation is proprietary, this formulation functions well for 3D printing this highly elastic material. A 27 gauge nozzle (315 µm inner diameter) was the highest gauge the silicone would flow through.

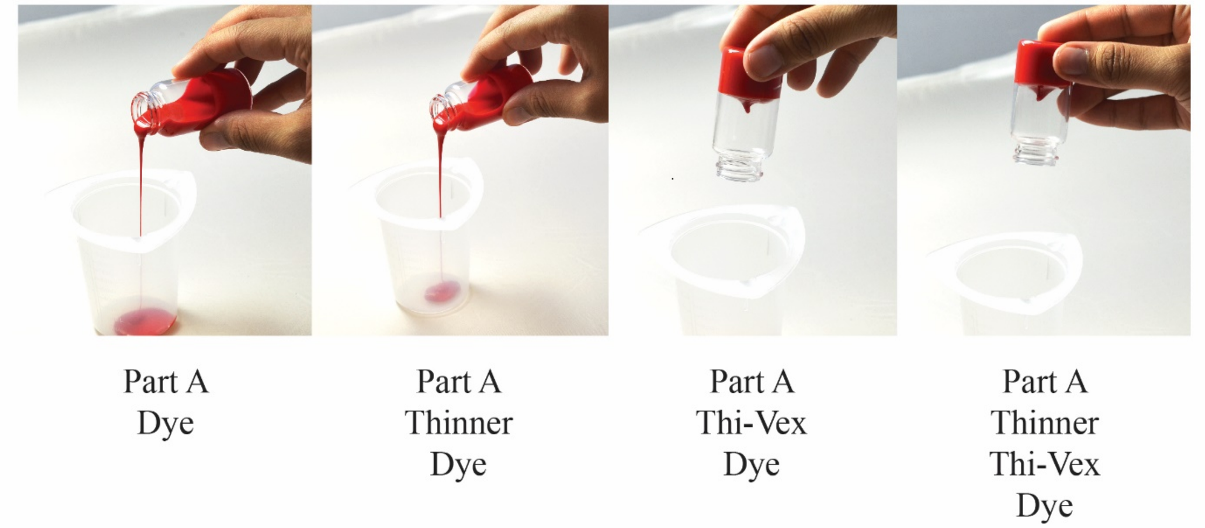

Figure S1. Formulation differences. Qualitative differences between additives are noticeable when trying to pour the formulation. Thi-Vex increases the yield stress of the silicone, and Silicone Thinner reduces viscosity for extrusion.

2. Viscous and Elastic Modulus Behavior During Curing

The formulation of the silicone helps retain structure in the print in addition to the temperature increase because the silicone is elastic modulus dominated throughout the printing process. This means that even if the silicone is extruded after short periods of time, the mixture is a gel that will allow for some stacking of layers. The growth of the elastic modulus G' over the viscous modulus G'' is shown in Figure S2. The growth of G' over G'' is tracked through $\tan(\delta)$ in the main manuscript.

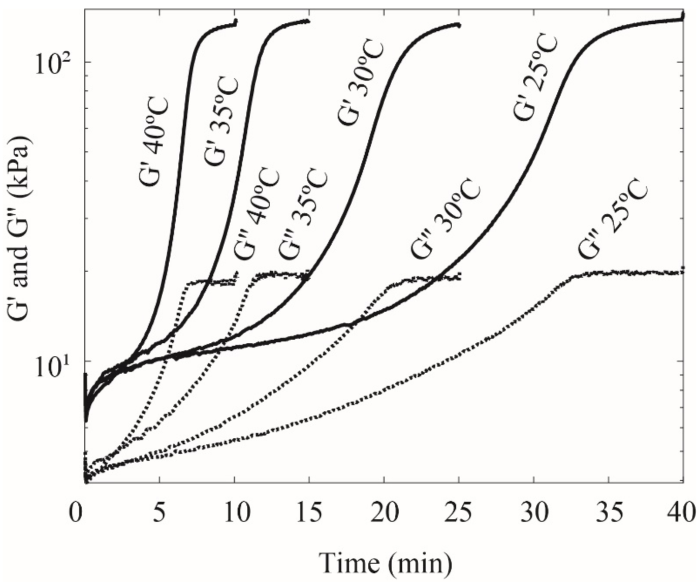

Figure S2. The silicone is G′ dominated throughout the curing process, but the structure in the silicone for layering starts when G′ starts to grow faster than G″.

3. Normal Force Methods

Normal force was tested by loading a mixed sample into the rheometer, setting the plate gap to 1 mm, and compressing the sample at 1 μm/s until a gap height of 900 μm was reached (deformation of 10% from 1 mm gap). This test was started at different times (increments of 1 minute up until the normal force neared the limits of the machine). The sample was not compressed until the specified start time was reached. Layer height held above a deposited portion of silicone was calculated using the normal force data by translating the information into a height of silicone using geometry (40 mm wide disk with height of 1 mm) and average density. Density (1.06 g cm^{-3}) was calculated by averaging the reported densities from each component's technical document based on weight percent of each component in the formulation.

Normal force testing was performed up until 10% deformation (Figure S3), but 1% deformation is used as an acceptable amount of deformation in a print to estimate how much weight the printed silicone can hold (Figure S4). In Figure S4, the data points are the value of the equivalent silicone height (calculated from normal force) at 1% deformation, and the dotted lines are the growth of the silicone height values up to each data point. The purple data is at 30°C and the orange is at 35°C. Polynomial trend lines are shown as predictors of layer height. By the time the start of the test passes the 8 minutes after mixing mark, in approximately 10 seconds after the start of the test, the amount of silicone that a deposited layer can hold plateaus around 10 cm at 30°C.

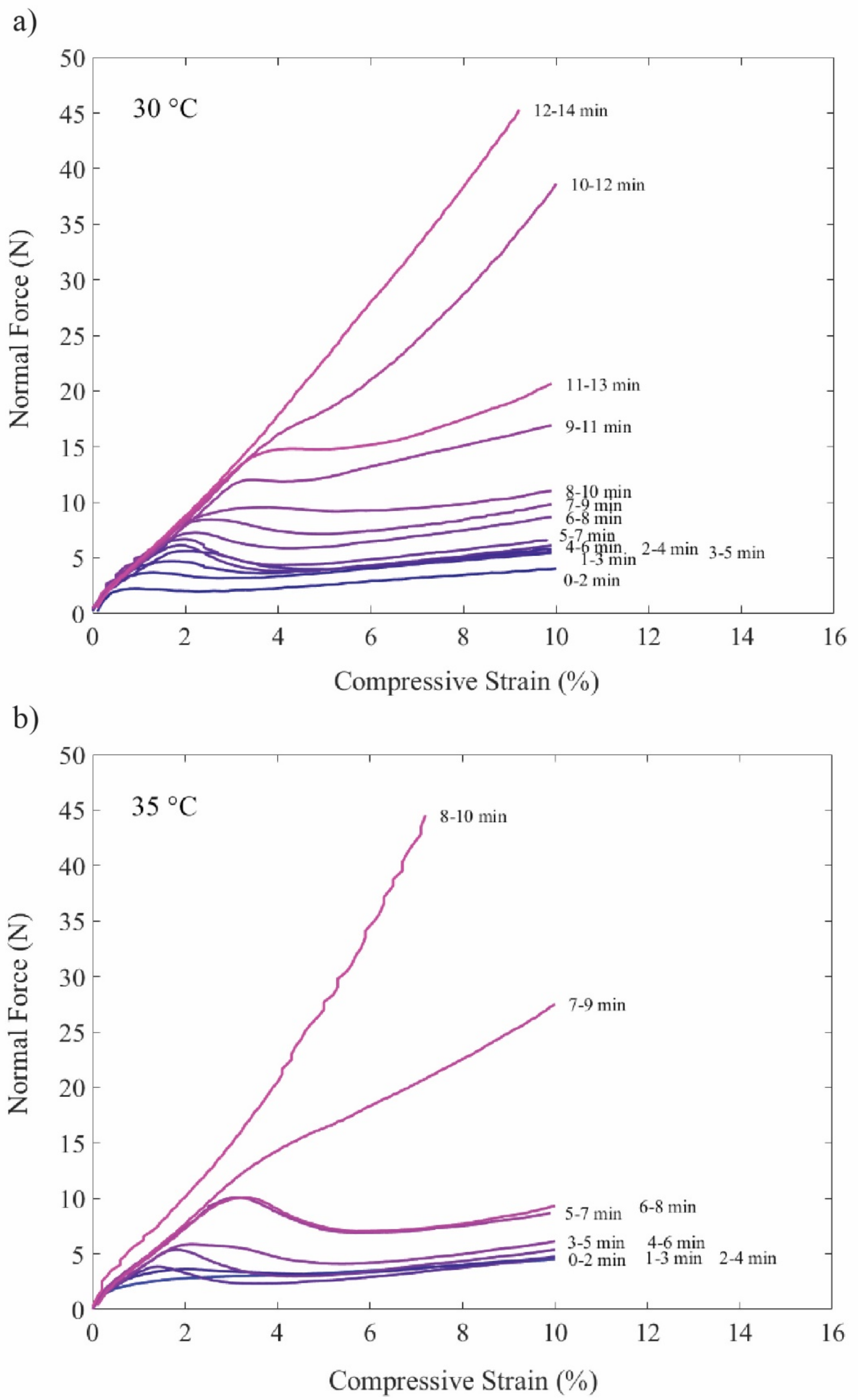

Figure S3. Normal force data for 30°C and 35°C tests. Darker colors are tests started closer to mixing, lighter colors are tests started farther from the mixing time. The 25°C and 40°C temperatures were not tested because they would not work well with the printer system.

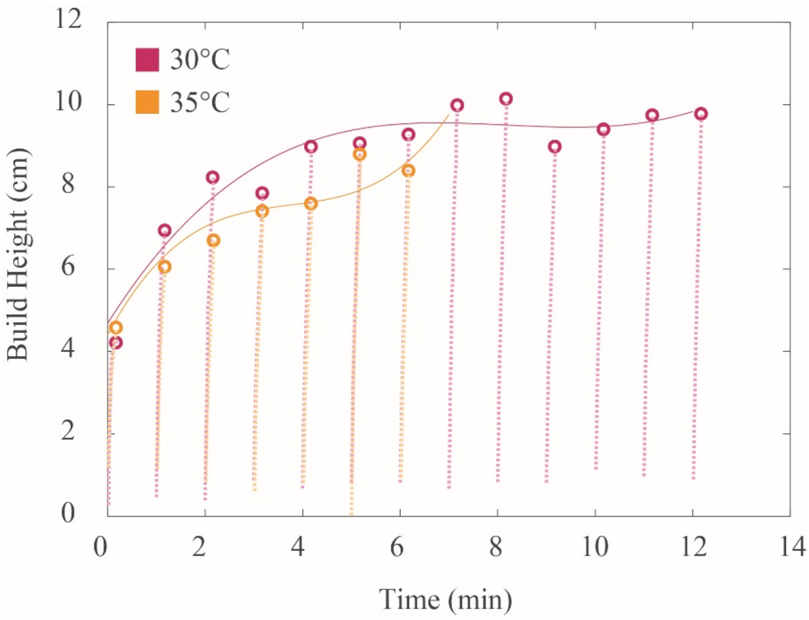

Figure S4. Silicone height held based on normal force. Normal force values were translated into silicone height held above the sample via geometry and density calculations described below. The normal force values used in the calculations are from the zero to 1% of deformation (0-10 μm) range in the test. Polynomial trend lines were overlaid in an attempt to serve as a predictor of weight a layer could hold at these time ranges. The area is the area of the 40 mm diameter parallel plate rheometer geometry. Density is estimated to be 1.06 g/ml based on data from technical document and density averaged by volume percent of each element in the formulation.

$$Build\ Height = \frac{F\ (\frac{kg*m}{s^2}))}{g\left(\frac{m}{s^2}\right)} * \frac{Vol\ (m^3)}{mass\ (kg)} * \frac{1}{Area\ (m^2)} * \frac{100\ cm}{1\ m} \qquad \text{(Equation S1)}$$

4. Spanning Tests

Spanning characterization was performed by printing filaments across a 5 mm high triangular rig. The speed of travel of the extruder head was 600 mm/min. The rig was placed so that the filaments were printed at a 90° angle from the base of the rig. The triangular gap of the rig ranged from 1-30 mm. Each filament was measured for spanning distance across the gap and vertical depression from the top of the rig.

Spanning tests were performed within the temperature boundaries of our custom printer (Figure S5). Because the G' of the silicone between 25°C and 30°C is the same for about the first 10 minutes, the spanning is expected to be similar because the residence time of the mixer is 3.4 minutes and the silicone is sure to be extruded by 10 minutes. The equation used for this comparison comes from Smay et al.[28]. As seen in Figure S5, spanning behavior overlaps for all three temperatures. The length of span can be estimated by solving for L in the model.

G' was also noted when tracking spanning behavior. In this system, the spanning lengths of the filaments are limited because G' stayed in a similar range until t_2 (11.1 minutes). For 2 – 12 mm gaps, the polymer has a 0.2 mm – 1.7 mm sag distance from the horizontal (Figure S5). Sag distance could be designed based on the acceptable range of deviation from the STL model.

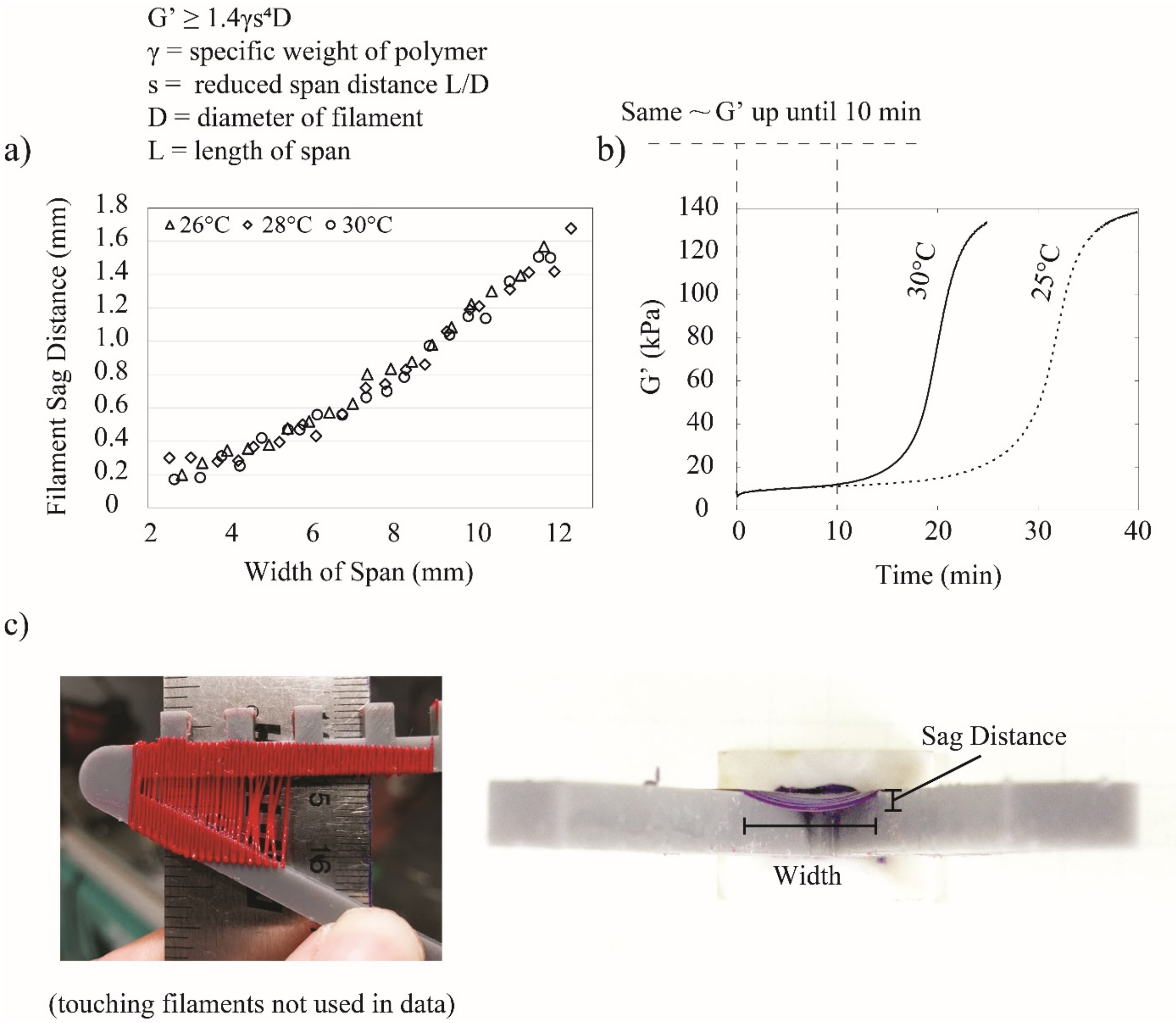

Figure S5. (a) The spanning characterization confirmed the assumption that when G′ is the same (here, across 3 temperatures), and the filament dimensions are the same, the spanning results will overlap. (b) The G’ values for 25°C and 30°C do not clearly differentiate for the first 10 minutes of testing. (c) Filaments were printed on top of a 5 mm tall spanning rig (photo is an example only, spanning filaments used for data did not touch).

5. Line Height Profilometry

Line width and height characterization were performed on a ZeScope Optical Profilometer at 5x magnification. The boundary where the scan did not reflect was assumed to be the start of the silicone filament edges, and the height was determined via maximum z value. Filaments were printed at 600 mm/min approximately 1 mm above the glass plate to ensure no deformation took place from the nozzle pressing into the lines. For each temperature, the heated chamber, build plate and glass plate were at the set temperature for at least 20 minutes before printing. Filaments were extruded at temperatures of 26°C, 28°C and 30°C to ensure no clogging would take place.

Line profilometry on the silicone shows increasing height with increasing temperature (Figure S6). This is indicative of the silicone retaining structure at higher temperatures due to increased cure percent after extrusion. The silicone also tends to flow slightly faster in warmer temperatures, which, along with mechanical vibrations in the printer, can lead to slight variation in filament diameter when deposited. As seen in Figure S6, the width differences between filaments at different temperatures are not statistically significant. Line profilometry results were used to guide the selection of G-code filament widths and layer heights for the demonstration prints. Unoptimized printed hollow eggshell models in Figure S6 demonstrate the improvement of print fidelity as the operating temperature is increased when using the same G-code file. The CAD model is presented for qualitative shape comparison. The hollow egg prints are difficult to print near the top of the model due to the relatively thin wall (2.5 mm) and reduced time between layers which means a more uncured state. However, with further optimization, model geometries and printer paths in G-code can potentially overcome these limitations.

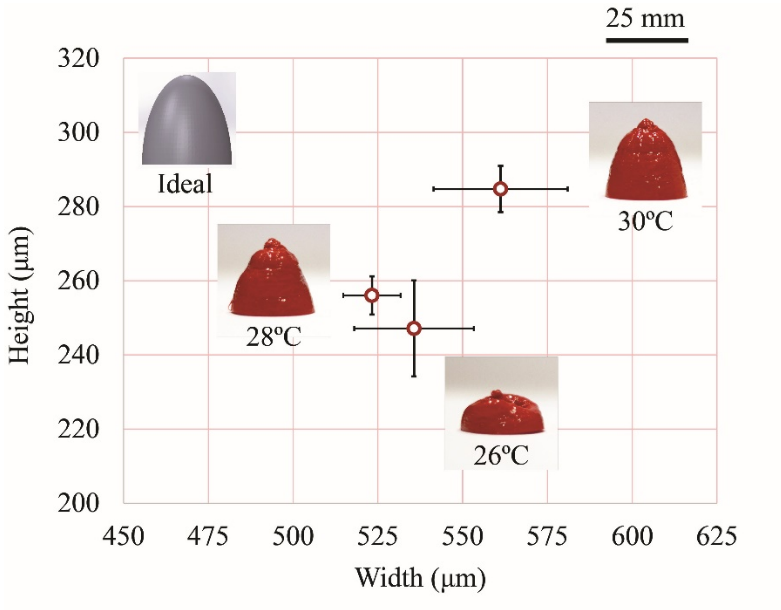

Figure S6. Line profilometry performed on silicone extruded onto glass at the same speed (600 mm/min) at 26°C, 28°C, and 30°C show that at 30°C the filament height increases. Width is variable but differences are not statistically significant. This could be due to small mechanical oscillations in the extruder and slight flow variations possible when heating the uncured silicone. These values are used as a basis for starting to choose G-code parameters for filament extrusion width and height. Non-optimized hollow eggshell models were printed with the same G-code parameters as a demonstration of the role that increased temperature played in improving print quality.

6. Yield Stress Methods

The yield stress testing is described in more detail in the main document, but this supporting information shows how the yield stress points were chosen. Yield stress was determined to be the first local maximum in a stress growth test. Data from 30°C and 35°C is shown in Figure S7. The yield stress values are noted in the data with a star. Samples that did not yield within the rheometer limits (see the last run in each graph) are not shown in the main manuscript.

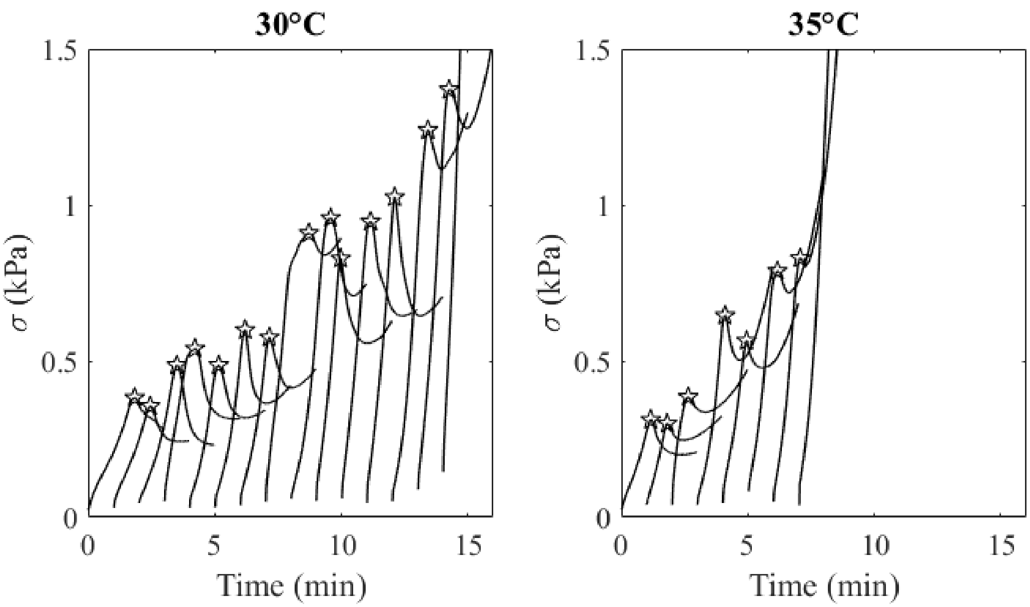

Figure S7. Yield stress data was taken using a rotational rheometer for 30°C and 35°C after determining that the silicone would cure too quickly at 40°C for the printer system and at 25°C curing would occur too slowly for practical print times. The yield stress was determined using the first local maximum of the stress curve (starred points). These data also display the transient nature of oscillatory stress growth in the curing silicone.

7. Equations for Yield Stress and Silicone Height graphs

Equations for predicting yield stress and silicone height at a certain time of cure are determined by fitting a polynomial curve to the maxima data. The following equations can be used to help predict the stress or height (normal force) for the system based on manufacturing needs:

For y = yield stress (kPa), x = time (min)

$y_{30} = 0.076042x + 0.16909$

$y_{35} = 0.095912x + 0.16406$

For y = Silicone Height (cm), x = time (min)

$y_{30} = 0.0096774x^3 + -0.23719x^2 + 1.8815x + 4.686$

$y_{35} = 0.049379x^3 + -0.55416x^2 + 2.2246x + 4.4062$

8. Slicing and G-code

Because this is a continuously extruding material, the extra travel paths where material would retract in a thermoplastic filament system prove troublesome if not handled properly. 3D structures created with purposeful manipulation of G-code (the computer commands that direct the operation of the 3D printer) ensure that little extra material is deposited on the print and layer height and width are appropriate to the short-term equilibrium position of a printed filament determined via line profilometry testing. Ideally the printing paths of the extruder do not pass over previously printed areas within the same layer. More explanation of G-code strategies will be included in the operating manual for the open source printer release.

9. Printer Schematics

The silicone 3D printer was custom-made using: (1) a Taz 6 3D gaantry (Lulzbot), (2) an isothermal chamber surrounding the printer with a PID-controlled heater, (3) a dual syringe pump (PHD ULTRA™ 4400, Harvard Apparatus), (4) a custom-designed extruder with a high-resolution luer lock nozzle (315 µm inner diameter, Techcon), and (5) a high resolution video camera (Grasshopper3, FLIR). The mixer used a custom-designed reamer turned by a small DC motor (34:1 Metal Gearmotor 25Dx52L mm LP 12V, Polulu) (Figure S8). The environmental control box keeps the entire printer as isothermal as possible to enable us to match the isothermal characterization data with the resulting print layer behavior. The syringe pump flow rate is constant and is not controlled by any mechanism to start or stop flow. Measurements of the flow rate coming out of the nozzle at 30°C were performed multiple times and averaged to estimate an actual flow rate of approximately 0.063 mL/min. Adequate mixing was determined when two contrasting colors blended with no visible streaking. Options to start and stop flow rate or control the path planning in order to improve print quality are left to future work. The 3D gantry is an off the shelf model with slight alteration of the firmware to accommodate the extruder and nozzle of slightly different size for homing in the z axis. The custom extruder/mixer files are meant to be extremely user friendly and easy to assemble. All of the component CAD designs will be available as open-source files. The camera is used as a tool to analyze filament as it comes out of the nozzle and spreads onto the print. With the video camera it is easier to diagnose print problems (slowing of flow due to clogging, improper alignment, improper layer height, etc.).

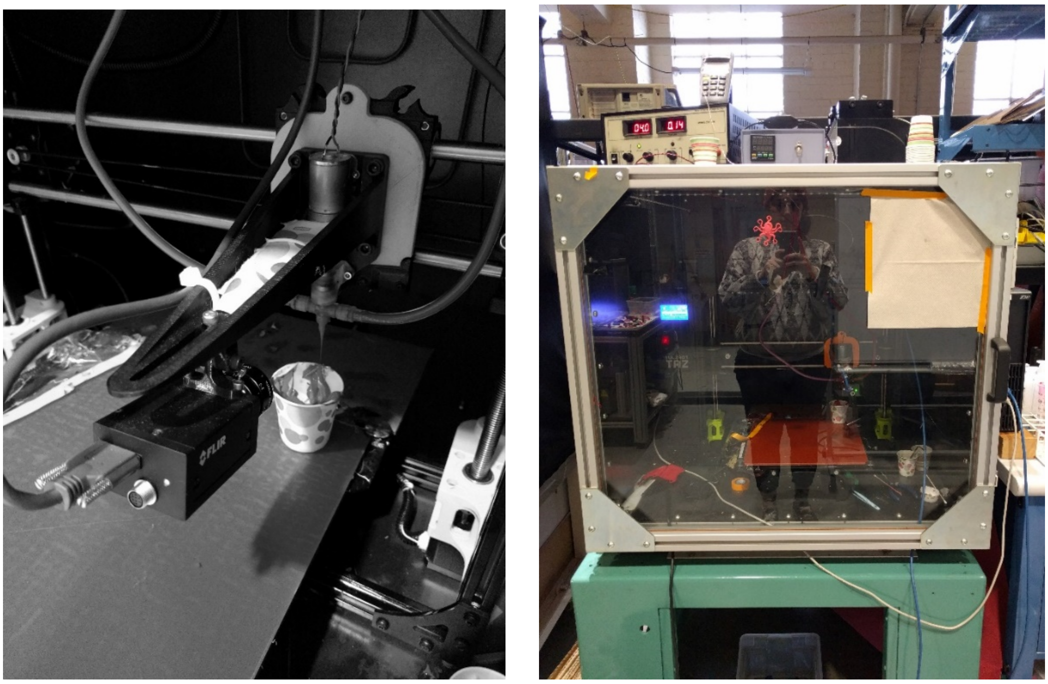

Figure S8. General printer appearance. More information, including how to build the entire system, will be released as open-source content.

Movie S1. Formulation behavior during printing. This movie shows the printing process and explains how the curing framework facilitates 3D printing of thermoset silicone.