

**Structural stability of thermosets during material extrusion additive
manufacturing**

A Dissertation Presented for the

Doctor of Philosophy

Degree

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DEDICATION

I dedicate this work to my wife, Dacey Romberg, whose love, patience, willingness to learn about “polymers,” and tenacious editing made this dissertation possible; to my parents, Thea and Doug Romberg, whose love and support helped me persevere through many difficult times; and my cat, Isabelle Cockrill, who was always interested in a spirited game of fetch when I needed a break.

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ABSTRACT

Over the past decade, the scale of polymer additive manufacturing has been revolutionized with machines that print massive thermoplastic parts with greater geometric complexity than can be achieved by traditional manufacturing methods. However, the heat required to print thermoplastics consumes energy and induces thermal gradients that can reduce manufacturing flexibility and final mechanical properties. With the ability to be extruded at room temperature and excellent compatibility with fibers and fillers, thermoset resins show promise to decrease the energy consumption, expand the manufacturing flexibility, and broaden the material palette offered by large-scale polymer additive manufacturing. However, structural instability in the uncured state has limited the scale of thermoset printing. This dissertation develops models to predict instabilities in printed thermoset structures and evaluates in-process chemically initiated curing to suppress instability.

First, instability is studied using direct ink writing to print thin walls with epoxy-based composite resins. Assuming these complex, viscoelastic resins exhibit elastic-plastic behavior, mechanical models based on measured rheological properties are shown to accurately predict collapse height, linking rheological properties to stability. This study helps estimate the scaling limits of thermoset additive manufacturing.

Second, unsupported, overhanging walls are printed with an epoxy-based composite resin. Again, assuming elastic-plastic behavior, an analytical beam bending model, finite element analysis, and rheological properties are used to predict the yield

height and deflected profile of an unsupported overhanging wall. The predicted yield height and deflected profile agree with experimental observations. This study generalizes the link between rheological properties and structural stability, provides tools to analyze overhanging walls, and emphasizes scaling limitations.

Finally, a custom-built, large-scale printer is used to mix organic peroxide with vinyl ester resin immediately before deposition to initiate curing and suppress collapse. A stable processing window is revealed, where curing keeps pace with the rate at which layers are stacked on the print. Outside the stable processing window, successful printing is affected by pre-gel collapse, transient thermal behavior, and warpage. Preliminary modeling efforts are presented and motivate future research.

These studies advance large-scale thermoset additive manufacturing by providing ways to predict structural instabilities and evaluating one way to address instability.

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Attachment 23: Video of a wall with programmed $\alpha = 35^\circ$ (Raw profile - alpha-35 Sample1.mov).

Attachment 24: Video of a wall with programmed $\alpha = 40^\circ$ (Raw profile - alpha-40 Sample3.mov).

Attachment 25: Video of a wall with programmed $\alpha = 45^\circ$ (Raw profile - alpha-45 Sample4.mov).

Attachment 26: Video of a wall with programmed $\alpha = 50^\circ$ (Raw profile - alpha-50 Sample4.mov).

Attachment 27: IR video of LT0.68 without fans (0_68 without fans - IR.mov).

Attachment 28: IR video of LT0.68 with fans (0_68 with fans - IR.mov).

Attachment 29: IR video of LT2.25 without fans (2_25 without fans - IR.mov).

Attachment 30: IR video of LT2.25 with fans (2_25 with fans - IR.mov).

Attachment 31: IR video of LT4.50 without fans (4_5 without fans - IR.mov).

Attachment 32: IR video of LT4.50 with fans (4_5 with fans - IR.mov).

Attachment 33: IR video of LT6.50 without fans (6_5 without fans - IR.mov).

Attachment 34: IR video of LT6.50 with fans (6_5 with fans - IR.mov).

1 CHAPTER 1: INTRODUCTION

1.1 Additive manufacturing background

The origin of additive manufacturing (AM) is often credited to Chuck Hull and his patent of stereolithography in 1986 [1]. The past four decades have seen many inventions that similarly leverage the unparalleled control offered by automated machines to build complex parts in a layer-by-layer fashion. To expedite communications about process methodology, the American Society for Testing and Materials (ASTM), along with the International Organization for Standardization (ISO), categorized seven broad classes of AM [2]. This dissertation focuses on the *material extrusion* category, which describes the process by which material is extruded through an orifice and selectively deposited. Thermoplastics are the most common feedstock used in material extrusion. However, this work explores thermoset printing, which shows promise to address some of the challenges faced by thermoplastics in large-scale material extrusion.

1.2 Behavior of polymers

Polymers are often split into two categories – thermoplastics and thermosets. These two classes are defined by their material properties, which are governed by the interactions of their base polymer molecules (or *chains*). In thermoplastics, polymer chains are formed by covalent bonds. These chains form bonds with other chains through secondary bonding, like van der Waals bonding. Temperatures above the glass transition temperature, T_g , of the polymer can break these weak intermolecular bonds and enable

conformational changes. This freedom increases the mobility of the thermoplastic molecules, allowing them to slide past each other, reducing the rigidity of the polymer [3-5]. The ability to transition thermoplastics to a viscous state and then back to a glassy state enables the extrusion and controlled deposition of material required for 3D printing [3, 5]. Much like thermoplastics, molecules in cured thermosets are formed by covalent bonds; however, these molecules interact differently. Rather than being held together only by weak van der Waals forces, thermoset molecules form covalent bonds between molecules when they are cured. These intermolecular bonds are often referred to as *crosslinks* [3]. These crosslinks are not easily broken by heat, resulting in a material that cannot be melted and recycled by traditional means [4]. A conceptual comparison between the molecular arrangement of thermoplastics and cured thermosets is shown in Figure 1. In the context of thermoset printing, the polymer usually begins in a soft viscoelastic state that allows for extrusion at room temperature. After deposition the crosslinking reaction is initiated, causing the material to transition to the elastic state required for a solid, final part. A variety of methods can be used to induce crosslinking during the printing process or after it has been completed, including heated curing [6-16], chemical initiation [17, 18], ultraviolet curing [19, 20], and frontal polymerization [21]. This wide range of curing and solidification options provides unique flexibility that can be leveraged in AM.

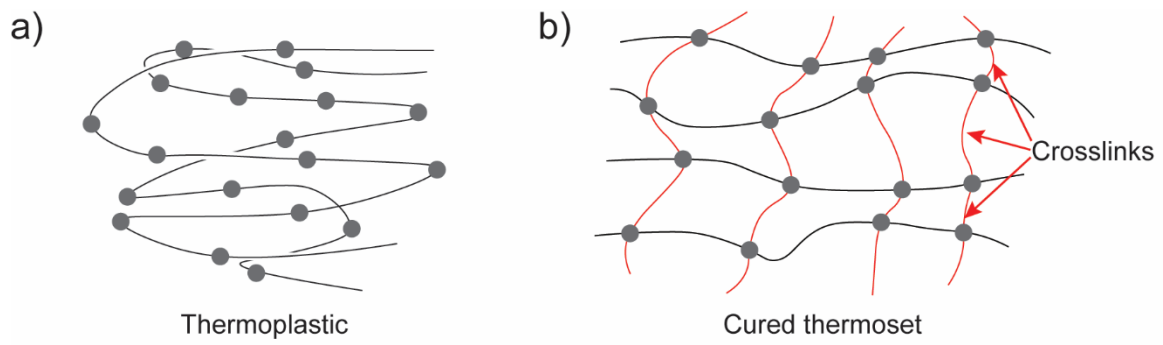


Figure 1: Conceptual illustration showing the molecular structure of polymers. a) Thermoplastic. b) Cured thermoset.

1.3 Large-scale thermoplastic material extrusion

In 2014, collaboration between Oak Ridge National Laboratory (ORNL) and Cincinnati Inc. produced the Big Area Additive Manufacturing (BAAM) system, which utilizes a 6 m x 2.4 m x 1.8 m build envelope and revolutionizes the scale of AM [22-35]. Figure 2 shows the BAAM and a conceptual processing schematic. By processing affordable pelletized feedstock (\$2-10/kg) and depositing material at a high rate (50 kg/h) within a large build envelope (6 m x 2.4 m x 1.8 m), the BAAM system has widened the application range for thermoplastic printing beyond small parts produced by typical desktop and medium-scale Fused Filament Fabrication (FFF) machines [22, 32]. This advancement has also provided an alternative to traditional manufacturing of large parts. Focusing on tooling, the BAAM machine can facilitate the rapid production of large, lightweight molds with complex features that are cost-prohibitive to produce using conventional subtractive methods [30]. The weight and size of raw billets of material can pose logistical issues during transportation. Further, the machining step is known to be time consuming and geometrically restrictive. These constraints result in long lead times (on the order of months) and less-effective tools. On the other hand, the BAAM system decreases lead times and enables production of more geometrically complex tools. Since the invention of the BAAM, other large-scale thermoplastic machines have been designed including, MasterPrint (Ingersoll Machine Tools, Inc., Rockford, IL) [<https://en.machinetools.camozzi.com/products/additive-manufacturing/additive-manufacturing-machines.kl>], Large Scale Additive Manufacturing (LSAM) (Thermwood

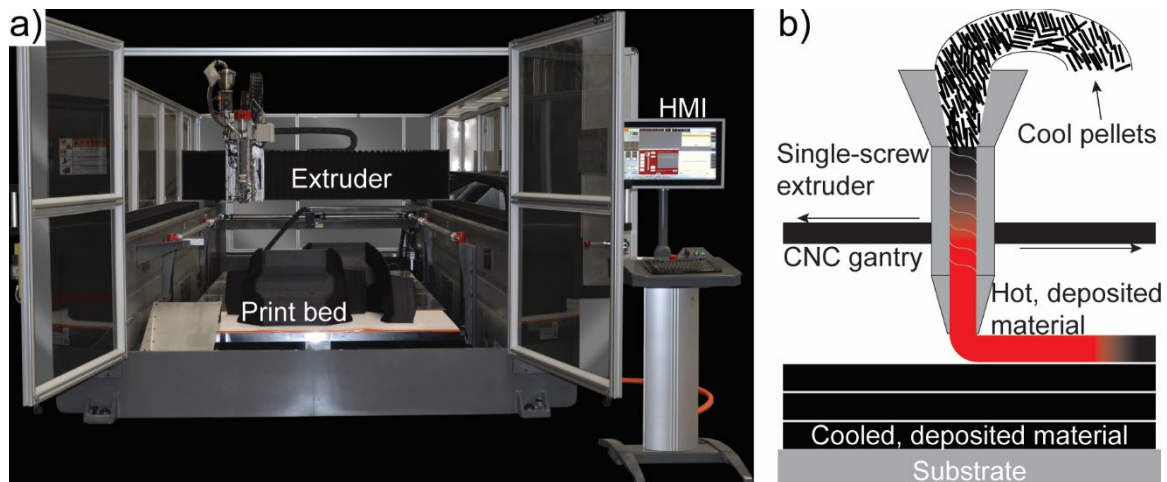


Figure 2: Explanation of the BAAM system. a) The BAAM system. b) Conceptual diagram illustrating the pelletized feedstock, the extrusion process, and the deposition process.

Corporation, Dale, IN) [http://www.thermwood.com/lmam_home.htm], and the Large-Scale Bio-Based Additive Manufacturing system (University of Maine, Orono, ME) [<https://composites.umaine.edu/large-scale-bio-based-additive-manufacturing/>]. This approach has enabled the production of many complex, near-net-shape parts at scales orders of magnitude larger than that of common small-scale printers, including vehicle bodies, a submarine hull, a boat, an excavator cab, a pavilion, and many molds [23-31].

Although large-scale thermoplastic printing provides a combination of scale and geometric flexibility unparalleled by any traditional manufacturing system, it poses challenges inherent to its processing approach. Fundamentally, thermoplastic printing requires elevated temperatures to transition the polymer into a viscoelastic state conducive to extrusion. Additional energy costs are associated with applying heat. This heat results in thermal gradients as hot material is deposited on top of material that has been allowed to cool. Thermal gradients lead to residual stresses, resulting in warpage [32, 34, 36, 37]. The cooling of previously deposited layers immobilizes molecules, hindering molecular diffusion across layer boundaries and forming poor interlayer bonds. Coupled with residual stresses, poor bonding can lead to delamination where the weak interface separates [34, 38]. Ultimately, these behaviors limit the scale at which printing can occur. A 1D, finite-difference thermal model constructed by Compton et al. [34] showed excellent agreement with experimental results of printing thin, long thermoplastic walls. This work demonstrated that to avoid warpage and delamination, layer times should be short enough to keep the previous layer from cooling below the T_g of the

material. Sustaining this surface temperature becomes difficult with large parts that require long layer times. Moreover, the heavy extruder required to heat the material limits the maximum translation rate of the print head [39]. Even if the layers are deposited quickly enough, the reduced temperature of previous layers affects the final properties of the part and other aspects of the process. Poor molecular diffusion between layers results in anisotropy in the z-direction [22, 32, 33, 40, 41]. Printing advanced thermoplastics for high-temperature applications, such as autoclave tooling, exacerbates these thermal issues, since these feedstocks are used for their higher T_g values and require even higher extrusion temperatures [35]. Further, toolpath flexibility is limited as the extruder risks collision if it returns to places with cooled, hard material. After deposition, the hard material is also unreceptive to the placement of disparate parts that can add multifunctionality. These challenges motivate research of AM processing options that do not require heated extrusion.

1.4 Large-scale thermoset material extrusion

To explore solutions that do not require heated extrusion, a large-scale thermoset material extrusion machine, called Reactive Additive Manufacturing (RAM), with a build envelope of 4.9 m x 2.4 m x 1.0 m was developed in collaboration with Magnum Venus Products [39, 42, 43]. Thermoset polymers can be extruded at room temperature, making them ideal candidates for material extrusion AM at ambient conditions. This dissertation focuses on addressing the challenges associated with thermoset printing, as well as the performance of the final product.

The design of the RAM expands on a small-scale process called Direct Ink Writing (DIW). DIW is a technique that emerged in the late 1990s under the name “Robocasting” – a portmanteau of “robotic” and “slip casting” or “gel casting” [44]. To achieve DIW, a syringe with a nozzle is mounted on a computer numerically controlled (CNC) gantry. Pressure is applied to extrude the material at room temperature. The deposition of the material is prescribed by the g-code provided to the CNC gantry. Key material characteristics are required to achieve printing using this approach. First, the material must be *shear thinning* (meaning viscosity decreases as shear rate increases) to enable extrusion at achievable pressures. Second, the material must exhibit a *yield stress*, τ_y , meaning the material will not flow below a critical value of stress. The yield stress allows the material to maintain shape after deposition [6, 7, 45]. Therefore, fluids with Bingham plastic behavior (Figure 3), which exhibit both shear thinning and a yield stress, are ideal candidates for DIW.

At some point after deposition, the material must crosslink and solidify to permanently maintain shape. Crosslinking can happen during the print under ambient conditions, in the case of a chemically initiated resin. For latent-cure systems, the reaction occurs after the print when the material is cured in an oven. Additionally, a combination of in-process and post-print curing can be utilized to obtain the desired printability and output properties. This work considers the printability of material systems that do not include in-process curing. It also presents the printability and output

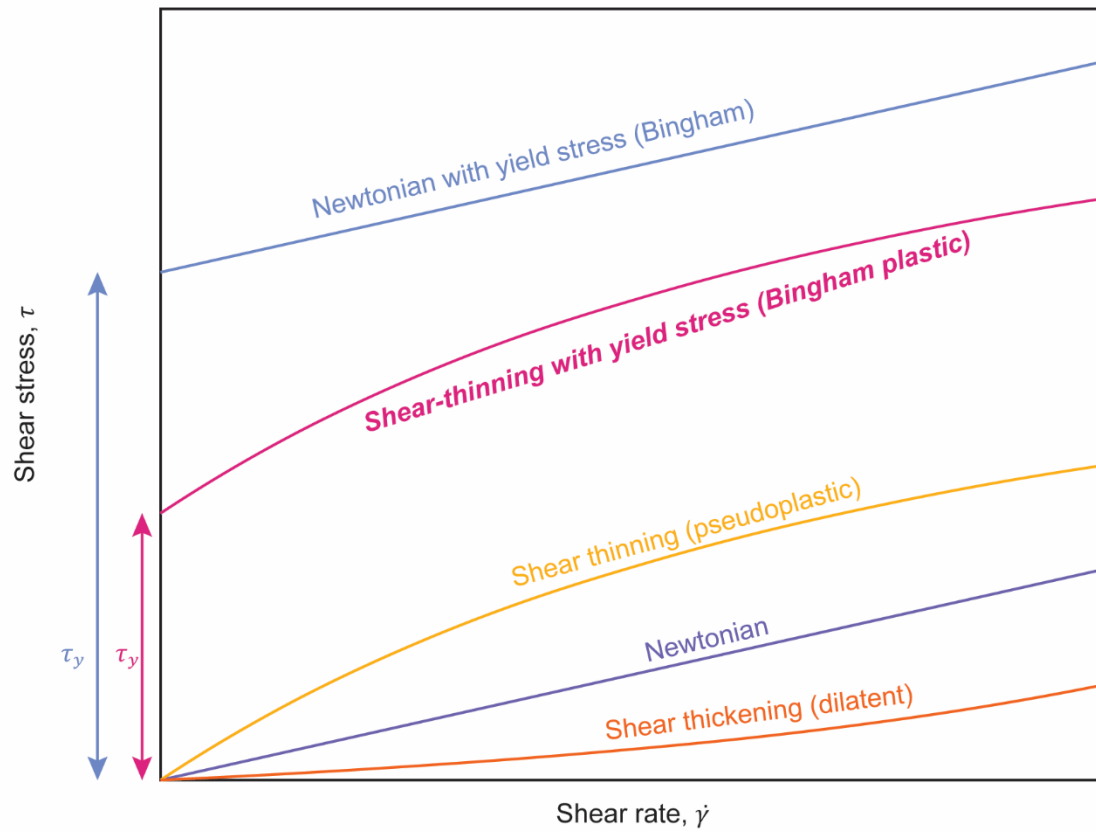


Figure 3: Flow behavior of different classes of viscous and viscoelastic materials

properties of a system designed for the large scale that uses in-process chemical initiation to cure the resin during the print.

While providing comparable mechanical properties and decreasing the energy required to achieve extrusion [18, 46], chemically initiated thermoset printing at ambient conditions is expected to offer solutions to some of the thermal issues observed in thermoplastic printing. Reducing thermal gradients promises to diminish residual stresses, warpage, and delamination. Decreasing the likelihood of these failure modes improves scalability because long layer times become less prohibitive. Since bonds can form across layers, thermoset printing has shown potential to improve adhesion between layers [17], which may reduce the anisotropy typically associated with 3D printing [18]. The reactive nature of thermosets also decouples the deposition temperature from the maximum operating temperature of the final product, making the production of parts with high temperature resistance more practicable. This system also shows promise to allow greater flexibility during production. The elimination of a heavy extruder offers the opportunity to increase print speed [17, 18]. The ability to tailor reaction kinetics of thermosets provides opportunities unavailable to rapidly cooling thermoplastics. Preliminary testing on the RAM system has shown that delayed crosslinking is expected to provide a couple of benefits. First, more complex structures can be achieved since the deposition head can return to a location without risk of collision with hardened material. This feature provides excellent potential to create functional cellular structures with highly cohesive nodes [43, 46]. Second, the uncured deposited material is particularly

receptive to placement of objects [47], allowing for more flexible incorporation of multifunctionality than thermoplastics. Although preliminary tests on the RAM system have shown promise to provide more flexibility than thermoplastic printing, most of the improvements expected from thermoset AM come from observations on scales much smaller than those suggested here. The following sections explain additional benefits of thermoset materials, challenges of scaling up thermoset material extrusion, why chemical initiation has been chosen to increase scale, and the material system proposed to achieve chemical initiation.

1.5 Thermoset DIW material extrusion

The flexibility of DIW has enabled developments for a wide range of materials on the small scale, including elastomers [11, 48], waxes [49, 50], ceramics [44, 45, 51-56], bioprinting applications [57, 58], and of course thermoset composites [6-10, 12, 14, 17, 39, 42, 43]. Epoxy inks with fillers like nanoclay, fumed silica, and carbon fiber (CF) have shown cured mechanical properties comparable to (and often better than) Acrylonitrile Butadiene Styrene (ABS) filled with CF [6-10, 22]. Additionally, the epoxy-based inks have shown greater temperature resistance, with T_g ranging from ~150-220°C [7, 13], than typical thermoplastic feedstocks (T_g of ABS ~ 105°C) [35]. Research has also demonstrated the printability of cyanate esters, which exhibit even greater temperature resistance with glassy, rigid behavior all the way up to 280°C [12]. Previous work also suggests that thermosets can provide more cohesive interlayer bonding than

thermoplastics. This finding indicates that thermosets may provide more isotropic behavior [17, 18].

1.6 Structural stability challenges in thermoset DIW

Although room temperature deposition is expected to solve many of the heat-related issues caused by thermoplastic printing, soft viscoelastic behavior limits the achievable height and scale of thermoset inks. Most of the current literature concerning thermoset printing is conducted at heights small enough to avoid collapse [6-12, 14, 16, 48, 49]. At larger scales, instabilities under self-weight can cause the material to lose geometric fidelity. In the uncured state, viscoelastic feedstocks are susceptible to slumping [18, 50, 52, 54, 59-61] and collapse under the weight of subsequent layers [37, 62-64]. Analysis of most solid, elastic engineering materials do not account for self-weight, but these materials are in a vastly different material property space than typical inks. Their specific stiffness ($E^{1/3}/\rho$) and strength (σ_y/ρ) are much higher than for DIW feedstocks. The low specific properties of DIW inks suggest that they may be susceptible to buckling and yielding under their own weight. Basic mechanical models that consider yielding [37, 62] and buckling [62, 65-69] under self-weight are expected to provide a link between rheological properties and the maximum stable height of thermoset inks. These models indicate that the structural stability of a slender wall subjected to its own weight depends on the thickness of the wall as well as the density, yield stress, and storage modulus of the material used to construct the wall. Increased yield stress, storage modulus, and thickness should enhance stability, whereas increased density should

diminish stability. With especially low yield stress and storage modulus with respect to density, thermoset inks tailored for 3D printing at room temperature without in-process curing are unlikely to successfully achieve heights demanded by large-scale additive manufacturing. Material systems that cure during the print may address self-weight instabilities, motivating research on in-process curing.

To adequately define structural stability, a structure must be chosen for analysis. Although AM can be used to print an infinite variety of structures, this work considers long, thin walls and unsupported, overhanging walls. Long thin walls provide great insight because they can be easily observed during printing and are the building blocks of more complex architectures.

Prismatic, sparse infill structures, also called “honeycombs,” are ubiquitous in material extrusion AM because they reduce the production time, material, and weight of printed objects. A honeycomb can be conceptually broken down to its simplest unit – a single wall. Long, thin, vertical walls that are unsupported on either end can be conveniently observed and analyzed with self-weight buckling [62, 65, 68-70] and yielding [37, 62] models. Therefore, this work analyzes this simple structure.

Out-of-plane printing has gained attention in recent years. Developments have been made to print overhanging features without supports [19, 21, 61, 71-73], structures on freeform surfaces [74-79], and nonplanar components using machines with more than 3 degrees of freedom [74, 80, 81], like robotic arms [82, 83]. Much like vertical walls, overhanging walls are convenient to observe and analyze using classical beam

mechanics. Therefore, this dissertation also focuses on the analysis of the structural stability of overhanging walls printed with thermoset inks.

Here, a key simplifying assumption is made about material behavior when examining these structures. At stresses below the yield stress, the ink is assumed to behave as an elastic solid with stiffness defined by the storage modulus, which is not necessarily true for all inks. As will be shown, this assumption provides remarkably accurate collapse height and deflection predictions for the inks studied here. This assumption applies to the inks chosen for this work because they have been developed over several iterations to provide good printability by behaving like elastic solids and maintaining their shape upon deposition. Although this analysis may not be universal across all inks, it is very useful for yield stress fluids that have been developed to maintain their shape after deposition.

1.7 In-process curing material systems

In-process curing of DIW inks provides an elegant solution to structural instability caused by self-weight loading [15-21, 39, 42, 43, 71, 84-88]. During extrusion, the material can exhibit low viscosity conducive to pumping. After deposition, the crosslinking reaction can be activated, causing the printed material to strengthen, stiffen, and resist self-weight collapse. An alternative solution to in-process curing would be to significantly increase the rheological properties of the uncured resin, so that it can resist collapse without any support provided by crosslinking. This approach would require high pumping pressures within pieces of equipment that have pressure limits (like hoses).

Extrusion rate, and consequently production rate, must be decreased to accommodate a resin with higher viscosity and avoid exceeding pressure limits [89]. Therefore, from a processing standpoint, in-process curing is favorable over more rigid ink formulations. Several concepts for in-process curing, other than chemical initiation, have emerged to cure the viscoelastic material during the print. A few are shown in Figure 4.

Ultraviolet (UV) light has been used to cure photopolymerizing materials [19, 20, 71, 85, 87]; an IR laser has been used to selectively heat and cure elastomers [15]; a heated bed has been used to initiate epoxy composite resins [16, 88]; and thermally activated frontal polymerization has been used to polymerize dicyclopentadiene (DCPD) [21]. These techniques allow for incredible flexibility, enabling free forms beyond those obtained through post-print curing. However, these rapid-cure approaches may sacrifice some of the value expected from thermoset printing. If used in a layer-by-layer fashion, rapid curing may impede the formation of a strong network of crosslinks across layer interfaces. Additionally, some of the toolpath flexibility is given up, since the hardened material will not be receptive to the nozzle returning to any location with previously deposited material. Finally, utilizing UV light, an IR laser, or a heated bed requires additional energy input. Chemical initiation using vinyl ester resin and an organic peroxide initiator is not expected to sacrifice any of these capabilities; therefore, its ability to suppress the previously described self-weight instabilities and reach the large scale is studied here.

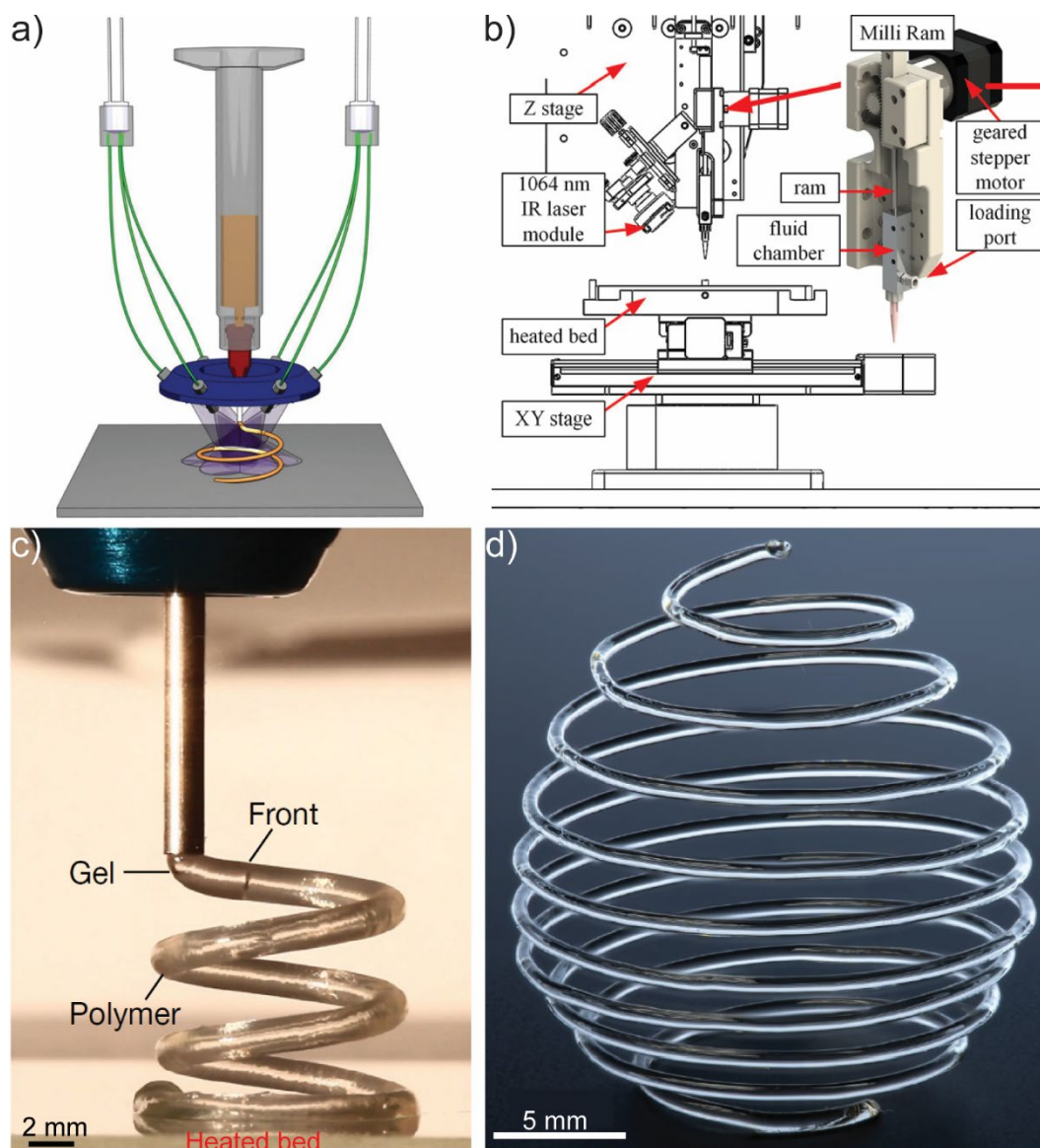


Figure 4: Examples of in-process curing. a) UV curing schematic [19]. b) Laser IR curing schematic [15]. c) Image showing the rapid curing of DCPD caused by the heated bed. d) Image showing the complex out-of-plane shapes offered by thermally activated frontal polymerization approach (adapted from [21]).

1.8 Chemical initiation of vinyl ester resin

Vinyl ester resins consist of vinyl prepolymer monomers and styrene. The styrene acts as a reactive diluent, lowering the viscosity and overall cost of the resin [90]. Vinyl ester resins cure when free radicals cause these two groups to react simultaneously, or “co-polymerize” [90-92]. The two vinyl end groups allow the vinyl ester to crosslink, whereas the styrene polymerizes linearly [90]. From a manufacturing perspective, these characteristics make vinyl ester highly applicable. These resins can be used in high temperature processes like pultrusion, resin transfer molding (RTM), compression molding of sheet-molding compound (SMC), and injection molding of bulk-molding compound (BMC) [92-94]. Vinyl esters are also processed at room temperature with manufacturing techniques like hand lay-up, spray-up, and vacuum-assisted resin transfer molding (VARTM) [90, 92, 93].

Expanding upon these applications, Polynt-Reichold has developed a vinyl ester resin specifically for large-scale chemically initiated printing called EX-1520 (Polynt-Reichold, NC). This dissertation uses EX-1520 to study this approach to printing. To enable the deposited vinyl ester to support itself before reaching full cure, fillers have been added to the resin. These fillers produce the Bingham plastic behavior that is so favorable for thermoset material extrusion. To protect their research, industrial partners have not communicated their exact material formulation, so the fillers used in this particular vinyl ester are unknown. However, several rheological modifiers, such as nanoclay or fumed silica [6-10, 12, 14], are known to impart shear-thinning and yield

stress behavior. Additionally, fibers, like glass and carbon fiber, are known to improve mechanical properties and help resist polymerization and thermal shrinkage that lead to residual stresses and warpage [93]. Since these fillers can alter material properties [6-10, 12, 14], properties of neat vinyl ester cannot be assumed. To understand the effects of the fillers, this work characterized the printed and cured properties to better understand the conditions that the final product can withstand. Since the shear imparted by the printing process is believed to induce filler alignment and cause anisotropy in printed components [7, 8, 22], directional properties were also examined.

Organic peroxides combined with promoters supply the free radicals required to initiate free radical polymerization and crosslinking of the vinyl ester at room temperature [3, 91, 92]. Again, to protect their research, industrial partners have not communicated their exact material formulation, so the promoter in this particular vinyl ester is unknown. However, common promoters are tertiary amines, like dimethyl aniline, and salts of metals, like cobalt octoate or cobalt naphthenate [90-92]. Methyl ethyl ketone peroxide (MEKP), dibenzoyl peroxide (BPO), and CHM-50 (a cumene hydroperoxide with phlegmatizer) are a few organic peroxides used to initiate reaction in vinyl ester resins. Only CHM-50 is considered here, because MEKP and BPO introduce safety and processing issues.

Since the initiator governs the gel time and heat generation, selection of the initiator is key to the printing process. The short gel time of CHM-50 enables rapid production rates, as previously deposited layers quickly gain resistance to self-weight

collapse. This behavior allows for deposition of subsequent layers earlier than a material with a longer gel time. In the context of chemically initiated thermoset printing at ambient conditions, the highly exothermic behavior of CHM-50 causes new layers to be deposited atop layers that are much warmer than room temperature. This behavior has implications on the properties of the cured resin, since both conversion and mechanical properties depend on the temperature of the reaction [90, 93, 94]. The highly exothermic behavior also presents some important disadvantages related to printability. Preliminary study has shown that the heat of previously deposited layers conducts up the wall and significantly reduces the rigidity of newly deposited material. This behavior can lead to print failure. Determining how to model thermal behavior and understanding how it affects printability must be understood to utilize this technology most effectively.

1.9 Research outline

This dissertation is organized in the following manner to address the issues of print stability described above. The first two studies address the gap in understanding of structural stability and collapse. The last study presents in-process chemical initiation to suppress collapse. Finally, preliminary modeling efforts are presented that motivate the future work required to better understand and utilize in-process chemical initiation.

1.9.1 Linking rheological properties of thermoset ink to stability of 3D-printed thin walls

This study aims to link basic rheological behavior to the limit of stability in 3D-printed thermoset inks. Long, thin, vertical walls of varying thickness are printed using a small-scale DIW setup and epoxy-based composite inks without a curing agent. Printed inks are assumed to exhibit elastic-plastic behavior; therefore, only the shear storage modulus and yield stress were taken from parallel plate rheometry. While the elastic-plastic assumption may seem severe, much of the prior effort in designing inks for material extrusion AM has focused on achieving elastic-plastic-like behavior in suspensions or polymer resins, precisely because this behavior imparts structural stability to the printed object prior to drying or curing. The measured shear storage modulus and yield stress are used in classical mechanics models to predict failure under self-weight. The model predictions are compared with the height of collapse observed during printing. These comparisons confirm that collapse can be predicted by using property values in analytical models. The link between rheological properties and structural stability can be used to tailor material systems to produce more stable printed structures. This link suggests that the collapse of other structures can be predicted using classical mechanics. Additionally, the limited structural stability of inks in the absence of curing provides a basis to investigate in-process curing mechanisms to suppress collapse and reach the large scale.

1.9.2 Structural stability of overhanging features during direct ink writing of thermosets

Building on the connection developed in the study of vertical walls and the apparent accuracy of the elastic-plastic assumption, this study aims to demonstrate that the collapse height and deflection of thin *overhanging* walls can be predicted given the rheological properties of the ink. An epoxy-based composite ink without curing agent is used to print and record walls at a range of overhanging angles. Yielding predictions based on an analytical model of beam bending agree with observed collapse height. A finite element simulation, designed to account for the deflection that occurs between the deposition of each layer, accurately predicts the deflected profile of the wall throughout the print. By demonstrating that the collapse height and deflected profile of overhanging features can be predicted, this work presents an additional tool to help design in-process curing systems that suppress collapse in thermoset AM and reach the large scale.

1.9.3 Large-scale reactive thermoset printing: Complex interactions between temperature evolution, viscosity, and cure shrinkage

The first two studies revealed the stability limits of uncured thermoset inks. This study investigates the feasibility of employing chemically initiated thermosets to suppress self-weight collapse. The RAM system is used to print and chemically initiate walls at different layer times and under different convective conditions. These experiments proved chemically initiated thermoset printing feasible on the large scale, but also revealed interactions between rheological, thermal, and chemical behavior that affect

printability. Viscoelastic collapse under self-weight remains possible at short layer times, whereas warpage is observed at very long layer times. Additionally, a new behavior was discovered in which the heat generated by the reaction of previous layers causes un-gelled layers to flow. Results and analysis indicate a path to selecting appropriate layer times and convective conditions to ensure successful printing of large-scale reactive thermoset materials. These findings suggest that developing less exothermic material formulations may enable more flexible printing. Evaluation of the mechanical and thermomechanical properties reveal properties comparable to vinyl ester resins processed in other ways.

1.9.4 Future directions of large-scale chemically initiated thermoset printing

Experimental results from the previous study revealed important failure modes in chemically initiated printing; however, the results only suggested qualitative measures to address these issues. In this chapter, results of a rudimentary 1D finite-difference thermal model are shown to qualitatively match the experiments, even though the model is based on approximate reaction kinetics and heat transfer properties measured at a single temperature. This provides powerful insight into the observed phenomena but could be more useful if the relationships between gelation, reaction kinetics, conversion, temperature, and temperature-dependent heat transfer properties were more well-defined. Future work on this process should focus on additional material characterization and modeling to increase the accuracy of this model and its utility in feedstock development.

2 CHAPTER 2: LINKING RHEOLOGICAL PROPERTIES OF THERMOSET INK TO STABILITY OF 3D-PRINTED THIN WALLS

A version of this chapter was originally published by Stian K. Romberg, Mohammad A. Islam, Christopher J. Hershey, Michael DeVinney, Chad E. Duty, Vlastimil Kunc, and Brett G. Compton [63]:

Stian K. Romberg, Mohammad A. Islam, Christopher J. Hershey, Michael DeVinney, Chad E. Duty, Vlastimil Kunc, and Brett G. Compton. “Linking thermoset ink rheology to the stability of 3D-printed structures.” *Additive Manufacturing* 37 (2021): 101621. <https://doi.org/10.1016/j.addma.2020.101621>.

This article was revised for reproduction in the current form. The introduction and conclusion were edited to relate this article to the other chapters. Figures were modified to fit within the margins and improve font visibility. Finally, the defined coordinate system was also changed. S.K. Romberg designed and conducted the rheological testing, designed and configured the experimental setup for printing walls, printed and captured data from printing experiments, analyzed the data, generated the figures, and wrote the article. M.A. Islam designed and created the software to analyze the data and assisted in writing the article. C.J. Hershey helped design the rheological testing and assisted in editing the article. M. DeVinney assisted in the conceptualization of the software. C.E. Duty helped to conceptualize the rheological and printing experiments, provided the equipment needed to conduct rheological experiments, and assisted in editing the article. V. Kunc helped obtain the funding for this work and assisted in editing the article. B.G.

Compton helped to conceptualize the rheological and printing experiments, provided the equipment needed to conduct experiments, and was the primary editor of this article.

2.1 Abstract

Thermoset composite inks expand the material palette and increase flexibility of polymer AM but suffer from structural instability under their own weight during printing. This instability has not impeded development and characterization of new thermoset feedstocks on the small scale but has hindered recent efforts to increase the scale of thermoset printing. This study addresses self-weight instability by investigating the mechanisms that cause collapse during printing of long, thin, vertical walls. Using nanoclay- and fumed silica-filled epoxy feedstocks, this work compares the collapse height for printed walls to stability models based on yielding and buckling mechanics. Inputs for these models – shear yield stress and storage modulus – were taken directly from parallel plate rheometry measurements. Model predictions based on these rheological properties after a shear excursion, were found to be in good agreement with experimental results, where both yielding and buckling behavior were observed. This work establishes a direct link between basic rheological properties of the feedstock, geometry of the printed object, and achievable height. The results presented highlight the importance of understanding recovery behavior in thermoset feedstocks and provide valuable guidance on the development of more effective direct-ink writing feedstock materials.

2.2 Introduction

To realize the benefits of large-scale thermoset printing, the fundamental behaviors causing self-weight instability must be understood. This work investigates the self-weight mechanisms that cause collapse of long, thin, vertical walls printed with DIW inks. This class of structure has been chosen because it is convenient to print and observe, is common in printed objects, and offers well-established mechanical models that can be used to investigate the link between rheological properties and collapse.

For a finite period after deposition, DIW inks must rely on rheological properties before they transition to an elastic state, which can occur during or completely after the printing process. Curing after printing is complete puts the most severe demands on the viscoelastic properties of the ink because the ink must resist deformation due to self-weight through the entire process. On the other hand, development of large-scale technologies for printing thermoset materials has focused on systems that mix resin with a chemical initiator just prior to deposition to activate curing during the print [17, 39, 42, 43], which will be discussed later in this dissertation. Regardless of which method is used to solidify the ink, the capacity of the uncured ink to maintain structural stability as print height increases is critically important. In post-print curing approaches, the structural stability of the uncured ink defines the maximum stable height of the printed structure. In systems that gain rigidity during the print, the structural stability of the uncured ink informs the curing kinetics required to maintain stability. Therefore, this study focuses on structural stability provided solely by uncured rheological properties. In comparison to

solid, elastic engineering materials which are commonly analyzed by neglecting self-weight [68], the viscoelastic materials used in DIW exhibit low mechanical properties with respect to density and are thus more susceptible to collapse under self-weight prior to and during curing [64]. Figure 5 illustrates the vast difference between specific material properties of inks and conventional solid materials. The disparity is more than a factor of four in the specific flexural modulus ($E^{1/3}/\rho$) and more than three orders of magnitude in the specific strength (σ_y/ρ). The low specific properties of the inks in the modulus versus density graph suggest that buckling under self-weight may initiate failure. Similarly, the low specific properties in the yield stress versus density plot indicate that yielding could cause collapse. Therefore, the presented work will focus on comparing self-weight buckling and yielding models to collapse observed in 3D printing experiments.

Predicting failure of self-loaded structures was investigated long before the advent of AM. Euler studied this type of problem in the late 1700's [95]. In 1881, inspired by the height capacity of trees, Greenhill extended Euler's work by studying the buckling stability of vertical columns under self-weight and proposed a numerical solution for maximum achievable height [65]. In the 1980's, Wang and Ang expanded on Greenhill's work by forming generalizations to account for a variety of boundary conditions and applied axial loading [69]. In the 2000's, Duan and Wang provided exact analytical solutions to Wang and Ang's work [68]. Recently, in 2018, two separate works by Duty et al. [37] and Suiker [62] applied similar self-weight stability analysis to AM. Both

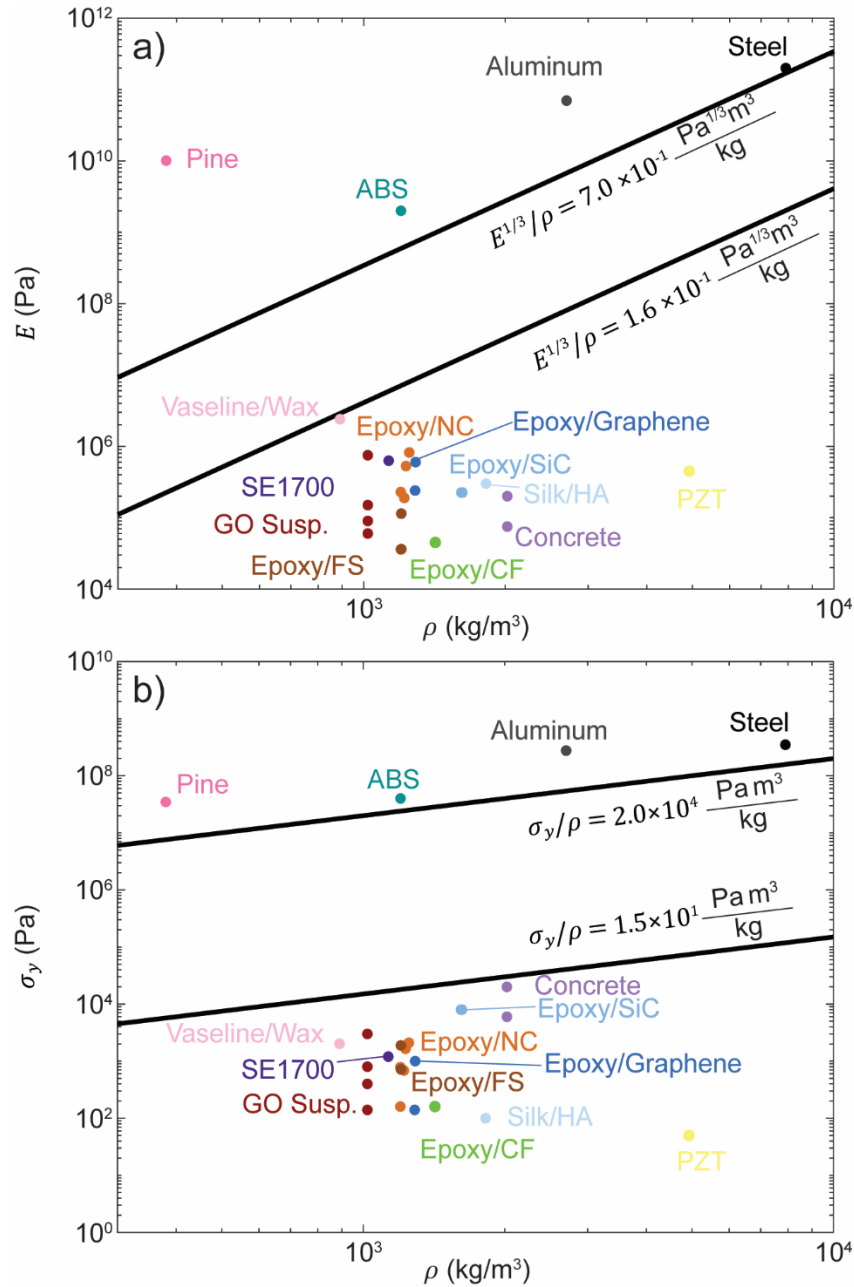


Figure 5: Property space maps comparing the properties of elastic engineering materials to DIW feedstocks [6, 7, 10, 11, 14, 50, 52, 57, 96-100]. a) Modulus vs. density and b) Yield stress vs. density. Modulus, yield stress, and density are based on estimates of available data provided in reference publications. Reported shear values were converted to uniaxial values assuming the Tresca yield criterion and isotropic behavior.

works included models for yielding under self-weight. In addition to considering both buckling and yielding failure modes, Suiker's work extended the self-weight models to include time-dependent material properties, particularly stiffening and strengthening, representative of concrete used in 3D printing [62].

The work presented by Duty et al. and Suiker establishes a framework to analyze stability of thin walls for a wide range of 3D printing processes. However, the Duty et al. study did not include buckling and Suiker's work focused solely on the time-dependent phenomena associated with concrete [37, 62]. This study expands on these efforts by examining buckling and yielding behavior observed in DIW of thermoset inks. Analytical links are formed between properties obtained through parallel plate rheometry and the stability of printed walls. Experiments designed to probe both yielding and buckling behavior allow for evaluation of the proposed models. The results of this work broaden the applicability of the models proposed by Duty et al. and Suiker [37, 62], deepen their links to material properties, and provide further verification of their utility.

Understanding the key parameters governing stability is essential to achieving thermoset printing on the large scale. Distinct from small-scale DIW printing of one-part, latent cure thermoset materials, printing in-process chemically initiated thermosets is a highly transient process. Much like the concrete in Suiker's research, the reactive polymer cures and stiffens after it is printed. Prior to full cure, the exothermic behavior caused by the crosslinking reaction can significantly affect the rigidity of the polymer. The material experiences a complex interplay between heating and curing as it transitions

from viscoelastic to elastic behavior [42]. Although enlightening and potentially mandatory to achieving large-scale thermoset material extrusion, using materials with multiple highly time-dependent properties obfuscates observation and evaluation of the fundamental behavior underpinning stability of printed walls.

To understand the rheological properties that govern structural stability of thin features in the absence of exothermic reactions, the present work utilizes epoxy inks without the addition of curing agent. Parallel plate rheometry is used to measure the shear yield stress as well as the shear storage modulus before and after shear. Then, this work links these rheological properties to the height at which printed walls collapse, which provides a basis for the subsequent study of overhanging walls and chemically initiated printing. Building on the mathematical work of previous investigators, models are proposed that consider geometry, density, storage modulus, and yield stress. These models assume elastic-plastic material behavior, and this work will do the same. This may seem like a severe assumption, but elastic-plastic-like inks typically used in DIW are chosen specifically because they impart stability to the printed object prior to drying or curing. Based on these models, thin walls are expected and shown to collapse due to buckling, which is predominantly governed by the storage modulus. The effect of shear history on storage modulus of the ink is characterized and demonstrated to play an important role in structural stability. Model predictions based on the storage modulus before and after a shear excursion are shown to approximately bound experimental observations. Yielding is expected and observed in thick walls. This behavior initiates

instability and leads to buckling. However, the yield stress, when measured before a shear excursion, appears to provide an overestimate of stable height. These behaviors highlight the value of considering both pre-shear and post-shear properties in inks designed for 3D printing.

2.3 Experimental methods

2.3.1 *Material formulation*

Before mixing, Epon 826 epoxy resin (Momentive Specialty Chemicals, Inc. Columbus, OH), was held at 60°C in an oven to melt any crystallized material. The resin was then allowed to cool to room temperature. Following Hmeidat et al. [7], 10 weight percent (wt.%) nanoclay (NC) (Garamite 7305, BYK-Chemie GmbH, Wesel, Germany) was added to the resin and mixed for 1.5 minutes at 1500 RPM under vacuum at 0.1 atm in a centrifugal planetary SpeedMixer (FlackTek, Inc. Landrum, SC). A second formulation was made using 10 wt.% fumed silica (FS) (Cab-o-sil TS-720, Cabot Corporation, Alpharetta, GA). In this case, half the FS was added and mixed for 1.5 minutes at 1500 rpm and 0.1 atm, then the remaining material was added and mixed under the same conditions. No curing agent was added to either formulation. Both inks showed favorable printing behavior, exhibiting an equilibrium shear storage modulus (G'_0), a shear yield stress (τ_y), and shear-thinning behavior. Each curve in Figure 56 of the appendix, which plots shear storage modulus (G') versus shear stress (τ) for both NC and FS inks, illustrates an initially constant G' , then a prominent shoulder at increased

stress. The constant G' is defined as G'_0 . The shoulder can be used to define τ_y . The G'_0 and τ_y values of printable inks, shown in Figure 5, range from ~12-800 kPa and ~25-4000 Pa, respectively. Below τ_y , these inks can be approximated as elastic-plastic solids with constant stiffness, since G' maintains a constant value. These characteristics enable shape retention upon deposition. At stresses beyond τ_y , the storage modulus of both inks monotonically decreased, revealing the shear thinning behavior that makes dispensing feasible. Further, these composites have been shown to exhibit desirable mechanical properties when cured [7]. These fillers also have different morphologies, which may lead to meaningful differences in recovery behavior. The nanoclay in this case is comprised of platelet-like Montmorillonite and fibrous Sepiolite [7], whereas fumed silica is comprised of spheroidal silica nanoparticles that agglomerate to form branched, chain-like secondary particles with extremely high surface area [8]. Both fillers are routinely used in thermoset DIW inks [7-9, 12, 14].

2.3.2 Material characterization

Rheological characterization was conducted on a Discovery Hybrid Rheometer-2 (DHR-2) (TA Instruments, New Castle, DE), outfitted with a 40-mm-diameter upper platen and a Peltier plate base, held at 22°C. Prior to all tests, the materials were subjected to a 2-minute conditioning step at a constant shear rate of 0.1/s, followed by 2 minutes of equilibration at no stress. This conditioning step was implemented to control the initial state across samples. In reality, the true initial state of the ink cannot be known, but this protocol was found to result in consistent rheological measurements within the linear

viscoelastic region (LVR) of the inks, providing confidence that variations in initial state are not significantly influencing interpretation of the measurements. Characterization of the NC ink was carried out with a 1.5-mm gap size. Stress-controlled dynamic oscillatory sweeps were conducted (at a frequency of 1 Hz) to compare the equilibrium shear storage modulus before a shear excursion and the recovered storage modulus after a shear excursion. All stress sweeps started at an initial oscillatory stress within the LVR, then increased to a maximum stress. Immediately after reaching the maximum value, the stress was relaxed to 50 Pa (within the LVR) and held for 15 minutes to probe the time-dependence of recovery. These tests will be referred to as the “structural recovery tests,” and the resulting post-shear data will be indicated by the subscript “SR” (i.e., G'_{SR} , the subscript “0” is not included here, because the *equilibrium* storage modulus cannot be measured from this test). Three different maximum stress values were tested to observe the recovery behavior as a function of maximum stress. The maximum stresses selected for the NC ink were 700, 1200, and 2000 Pa. 700 Pa was selected because it was found to be slightly greater than the yield stress of the NC ink, while 2000 Pa was determined to be an upper limit above which material began to flow out from underneath the upper platen. 1200 Pa was chosen as an intermediate value to examine behavior between these two limits. To observe the effects of time at maximum stress, each stress sweep was repeated with a hold at the maximum stress for 5 and 60 minutes. Characterization of the FS ink mirrored that of the NC formulation with a few minor differences. The lower storage modulus of the FS ink facilitated reliable data at a smaller gap size of 0.5 mm,

and the higher yield stress of FS ink increased the span of the LVR. Therefore, to ensure the material reached a flow state past the yield stress, the values of maximum stress were raised to 1200, 2000, and 3000 Pa.

Application of the hold times described above derives from a desire to completely break down the network structure in the inks prior to recovery. The present inks are based on those described by Hmeidat et al. [3], who fit a power law fluid model ($\tau = K\dot{\gamma}^n$) to rheological measurements to find K - and n -values of 3160 and 0.04, respectively, for a similar epoxy/nanoclay ink, where K is the consistency index and n is the shear-thinning exponent [3]. For typical DIW printing, characteristic shear rates range from 50 1/s to 1000 1/s [2, 3, 34], from which one would expect the shear stresses experienced by the ink during printing to fall between 3700 Pa and 4200 Pa. Since these values are higher than those that could be applied by parallel plate rheometry, extra time-at-stress was employed to attempt to mimic the additional stress experienced in the nozzle.

Additional oscillatory “ramp-down” tests were conducted to examine the LVR after a shear excursion. In these experiments, the material was ramped up to the maximum stress and held, as previously described. Then, instead of suddenly relaxing the stress, the stress was gradually ramped back down to the LVR. Results of these tests can be found in Figure 56 of the appendix. These tests confirmed that the 50 Pa stress, utilized in the structural recovery tests, would test the materials within their LVR. In the low stress region, rotational displacement data flagged by the DHR-2 software as “close to machine limits” have been omitted from the analysis. The equilibrium modulus

was calculated from the average values within the LVR, and shear yield stress was determined using the intersection power-law method [101]. This method fits behavior well past yield with a power-law function. Then, the intersection of the power-law fit with the equilibrium modulus is found. The oscillatory stress corresponding to the intersection is defined as the yield stress. The shear yield stress was only measured from the curves that spanned the broadest stress range (i.e., up to 2000 Pa for the NC ink and up to 3000 Pa for FS ink). Density was measured using the Archimedes method on a balance outfitted with a density kit (Mettler-Toledo, LLC, Columbus, OH).

2.3.3 3D printing

3D printing was conducted on a customized computer numerically controlled (CNC) 3-axis positioning stage (Shopbot Tools Inc., Durham, NC) configured with a gantry-mount for a syringe barrel and a voltage-regulated air pressure supply (Omega Engineering, Inc. Norwalk, CT) activated by g-code commands. NC and FS inks were loaded into 30-cc or 55-cc syringe barrels (Nordson EFD, Westlake, OH) using a spatula or a SpeedDisk (FlackTek, Inc. Landrum, SC), respectively. Full 30-cc syringe barrels were centrifuged in a Sorvall™ ST-8 Centrifuge (ThermoFisher Scientific, Waltham, MA) for 3.5 minutes at 3600 RPM to remove bubbles. This step was not necessary when using a SpeedDisk. The syringe barrels are equipped with a luer-lock fitting to accommodate several types of nozzles. Walls were printed onto a substrate consisting of a glass plate covered with PTFE-coated aluminum foil (Bytac, Saint-Gobain Performance Plastics, Worcester, MA). The substrate was secured to the build platform with masking tape.

Wall specimens were printed as shown in Figure 6a. Two tapered nozzles (with outlet diameters $d = 0.404$ and 0.872 mm) and several print paths were used to print walls with a range of thicknesses expected to exhibit both yielding and buckling behavior. The print paths, conceptually illustrated in Figure 6b,c, are “continuous,” meaning deposition does not stop and restart to transition to new layers. This design mitigates defects caused by transient flow during stopping and restarting. These custom g-codes were programmed in Scilab (Scilab Enterprises, France).

Walls expected to exhibit buckling ($w < \sim 10$ mm) were designed to be 60-mm long. This dimension was determined under two design requirements. Walls should be significantly longer than they are thick to ensure buckling occurs in the y -direction, and the syringe barrel should hold enough volume to print each wall to the height at which it will collapse. For thicker walls, length was decreased to 30 mm to enable greater wall height. All walls were observed to collapse in the desired direction.

The ratio between the layer height (Δh) and nozzle diameter, d , was set to 0.55, while the spacing between center points of adjacent beads on multi-bead prints was set at $1.375d$ to match the print parameters of the RAM system. The translation speed of the deposition head was set to 25 mm/s for all tests. When the nozzle or syringe barrel was changed, brief trials were conducted to identify the optimal extrusion pressure for the given nozzle and syringe barrel combination. The ideal pressure was determined by manually modulating the pressure regulator until adjacent printed beads coalesced. Print quality was monitored throughout the print. Minor adjustments to pressure were made to

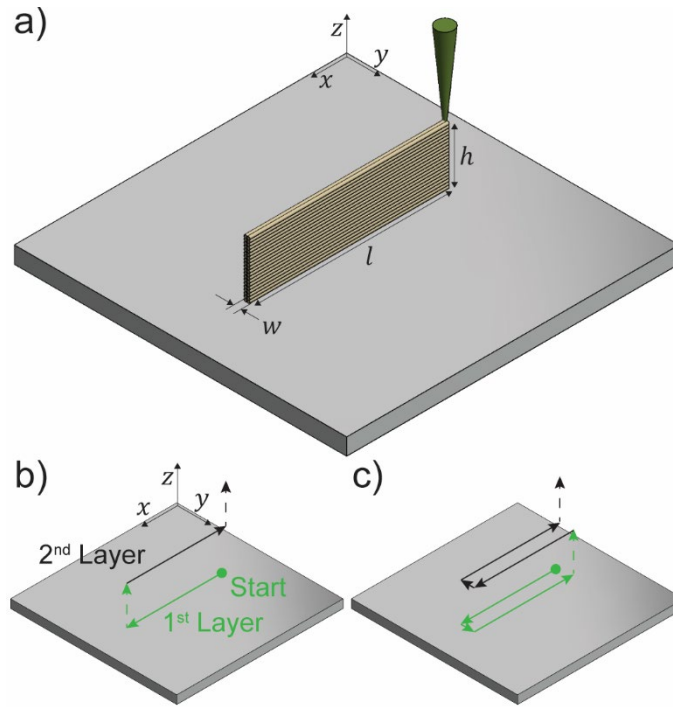


Figure 6: Depiction of printed walls. a) Conceptual diagram of a 2-bead printed wall, depicting thickness (w), height (h), and length (l). b,c) Print paths of the first two layers of the 1- and 2-bead walls. Walls printed with more beads per layer followed the pattern shown here.

ensure sufficient bonding of layers and avoid under-extrusion, which leads to destabilizing forces and torques as the filament is “pulled” across the top of the wall. Thicker walls ($w > \sim 10$ mm) required pressure adjustment during the print, whereas the thinner walls did not require adjustment to achieve desirable deposition. All walls collapsed as a monolithic structure without separating at layer boundaries, indicating that sufficient bonding between layers was achieved. The extrusion pressure ranged from ~ 275 -520 kPa for all printed walls.

2.3.4 Process monitoring

Figure 7 shows the experimental setup used to record data during print tests. Positioned to capture the y - z surface of the wall (the narrow vertical edge), an acA1920-155uc optical camera (Basler AG, Ahrensburg, Germany) outfitted with an LM16SC lens (Kowa, Düsseldorf, Germany) recorded the printing process. An input/output (I/O) cable running from the printer to the camera enabled the g-code to trigger the capture of an image, and the g-code was programmed to record a photo after deposition of each layer. The profile and thickness of the walls were determined from these images. A mirror, mounted on the gantry and positioned to capture the x - y surface, corroborated thickness measurements made from the y - z surface.

2.3.5 Image analysis

The compiled images of each test print were used to measure the thickness, identify the profile, and detect buckling of each wall. The key steps in the image analysis

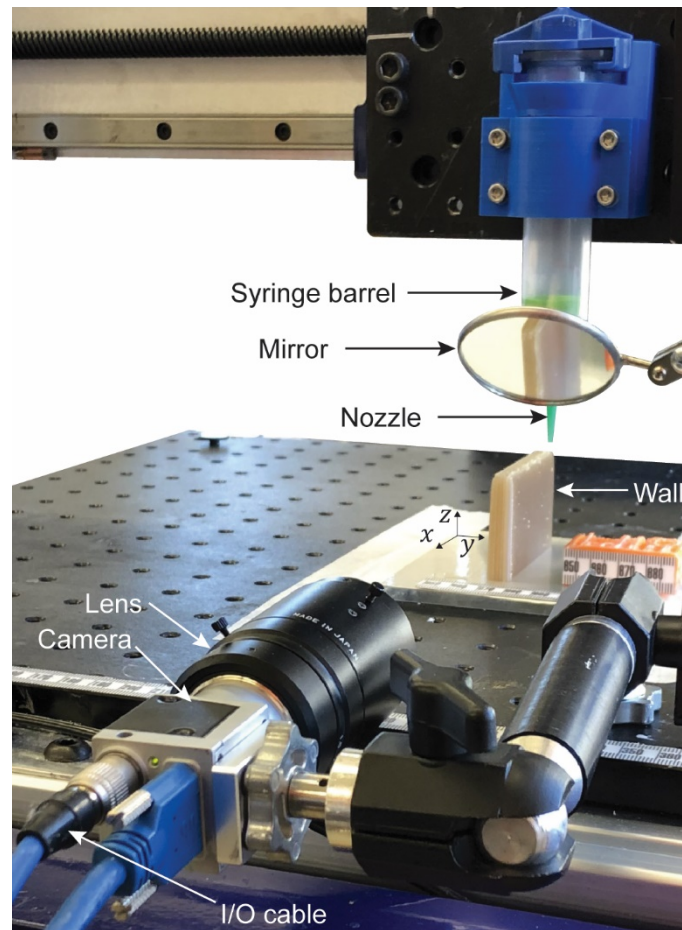


Figure 7: Process monitoring setup.

are depicted in Figure 8 and given a general description here. To identify the wall, a color threshold was used to distinguish between the light wall and the dark background. From this information, the average thickness of the wall was calculated by taking the average distance between the edges of the wall, which are indicated by the white lines in each image of Figure 8. To define the onset of buckling, a theoretical envelope for each wall had to be defined. This was accomplished by applying a linear regression to the edges of each wall and extrapolating vertically. The program waited to fix the linear regressions in place until the measurement of wall thickness became consistent for each layer. The green regression lines in Figure 8a indicate that the regression lines were not yet finalized, since they did not yet accurately represent the shape of the wall. Once the thickness measurement became consistent, the linear regressions were fixed in place (as indicated by the red regression lines in Figure 8b), and the thickness was defined. At this point, each line was offset from the wall by 5% of the thickness of that wall. Once either edge of the wall crossed its corresponding offset line, the program identified the height of the wall at the onset of buckling, h_b , as indicated in Figure 8c. Figure 8d shows the last layer to achieve successful deposition on top of the wall. The height of the wall at this point was defined as the ultimate collapse height, h_u . Finally, Figure 8e shows catastrophic collapse, which immediately followed h_u .

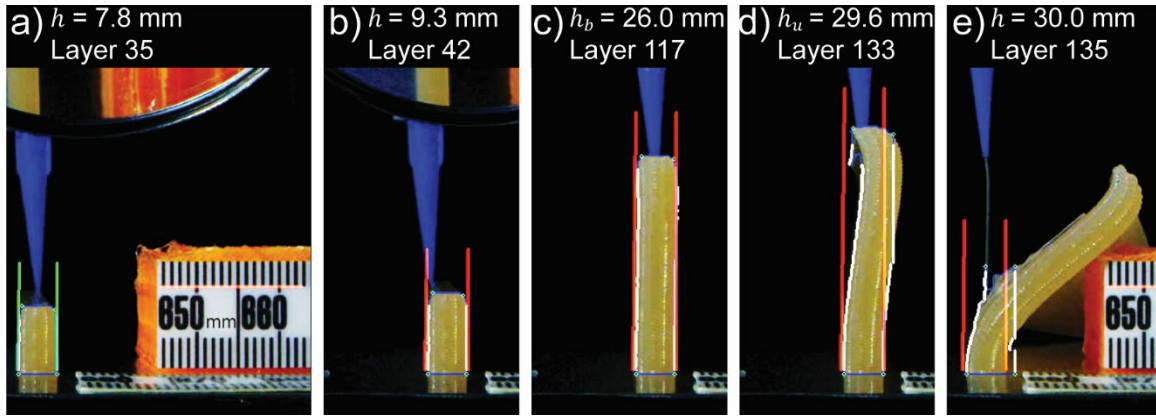


Figure 8: Visualization of image analysis using the 4.6-mm-thick, NC-ink wall printed with a 0.404-mm nozzle. These images depict the wall a) before thickness was defined and linear regressions were fixed in place; b) after thickness was defined and linear regressions were fixed in place; c) at h_b ; d) at h_u ; and e) upon full collapse. The light orange line, shown on the scale, was used to calibrate the pixel-to-distance factor. The scale is in mm.

2.4 Mechanical theory

2.4.1 *Effect of self-weight on stability*

Self-weight is often neglected in mechanical analysis, but as the specific strength and stiffness decrease, consideration of self-weight becomes more relevant to structural stability. Compared to structures made of an engineering material like steel ($E^{1/3}/\rho \sim 7.0 \times 10^{-1} \text{ Pa}^{1/3} \cdot \text{m}^3 \cdot \text{kg}^{-1}$; $\sigma_y/\rho \sim 2.0 \times 10^4 \text{ Pa} \cdot \text{m}^3 \cdot \text{kg}^{-1}$) [97], the uncured printable thermoset inks studied here have considerably lower modulus and strength relative to their density ($E^{1/3}/\rho \sim 1.6 \times 10^{-1} \text{ Pa}^{1/3} \cdot \text{m}^3 \cdot \text{kg}^{-1}$; $\sigma_y/\rho \sim 1.5 \times 10^1 \text{ Pa} \cdot \text{m}^3 \cdot \text{kg}^{-1}$), making self-weight a critical consideration in failure analysis of the printing process (see Figure 5). Although the inks studied here are known to exhibit complex viscoelastic behavior, the following models will assume elastic-plastic behavior. Much of the prior effort in designing printable inks has focused on achieving this behavior, because it imparts stability in the uncured state.

2.4.2 *Yielding due to self-weight*

The 1D stress distribution caused by stacking layers of material subject to gravitational force is given by

$$\sigma = \rho g(h - z) \quad (1)$$

where ρ is the density of the ink, g is gravity, h is the height of the wall, and z is the coordinate along the height of the wall (Figure 9). As implied by (1), the greatest stress is experienced at $z = 0$. The inks studied here exhibit a yield stress, above which they begin

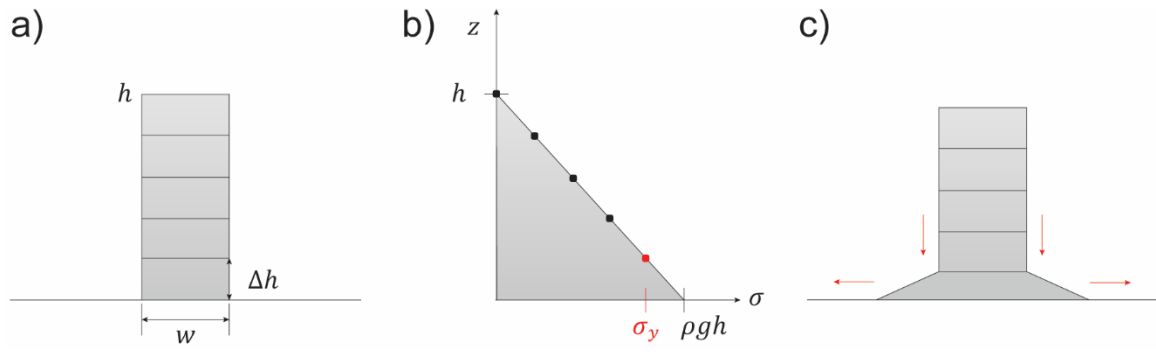


Figure 9: Conceptual diagram of yielding. a) Wall specimen. b) The corresponding stress distribution of the wall specimen under self-weight as it exceeds the yield stress. c) The expected yielding behavior if friction between the substrate and bottom layer is neglected.

to flow. By rearranging (1) and setting $z = 0$ and $\sigma = \sigma_y$, the height of material required to initiate yielding from self-weight can be expressed as follows

$$h_y = \frac{\sigma_y}{\rho g} \quad (2)$$

where σ_y is the uniaxial yield stress of the ink. Upon reaching h_y , the lowest layers yield and flow, losing height and increasing in thickness (Figure 9c).

The shear yield stress, τ_y , can be converted to σ_y by assuming the material yields according to the maximum shear stress criterion (Tresca yield criterion):

$$\sigma_y = 2\tau_y \quad (3)$$

Combining (2) and (3) produces the following height prediction.

$$h_y = \frac{2\tau_y}{\rho g} \quad (4)$$

Although (4) is a simple equation, the yield stress exhibits highly complex behavior and can be difficult to unambiguously define. As will be discussed, the yield stress can change when subjected to flow. Further, the yield stress can recover after flow, depending on the amount of time the material has been left undisturbed. However, as suggested by the straightforward relation in (4), this work disregards this complexity and approximates the material as elastic-perfectly plastic. Therefore, when the height reaches h_y , yielding failure is predicted. As will be seen in the results, this prediction is inexact but provides a reasonable framework with which to analyze the experimental observations. Refinement of (4), based on the observed behavior of τ_y , is warranted, but beyond the scope of the present effort.

2.4.3 Buckling due to self-weight

Before printed walls reach a height that causes yielding, the ink is assumed to behave elastically. Elastic buckling can occur within this regime, depending on the stiffness and geometry shown in Figure 10. The solution for the simplest boundary conditions (i.e. fixed at the bottom and free at the top) and loading scenario (i.e. only self-weight, with no additional axial force) is given by [68]

$$h_{b,column} = \left(7.8373 \frac{EI}{\rho g A} \right)^{1/3} \quad (5)$$

where $h_{b,column}$ is the height at which buckling occurs, g is gravity, E is Young's modulus, ρ is density, A is the cross-sectional area, and I is the second moment of area.

Referring to Figure 6, A and I are defined as follows:

$$A = lw \quad (6)$$

$$I = \frac{lw^3}{12} \quad (7)$$

Assuming a long plate geometry, the current study generalizes the column solution to walls.

To account for this geometrical difference, the plane-strain modulus, $\tilde{E}$, is used instead,

$$\tilde{E} = \frac{E}{1 - \nu^2} \quad (8)$$

where ν is Poisson's ratio, which was assumed to be 0.25. Figure 57 of the appendix shows the difference between predictions based on $\nu = 0$ and $\nu = 0.5$ was minimal compared to the scatter in experimental data. By assuming the ink behaves as an isotropic elastic solid prior to yielding, Young's modulus is given by

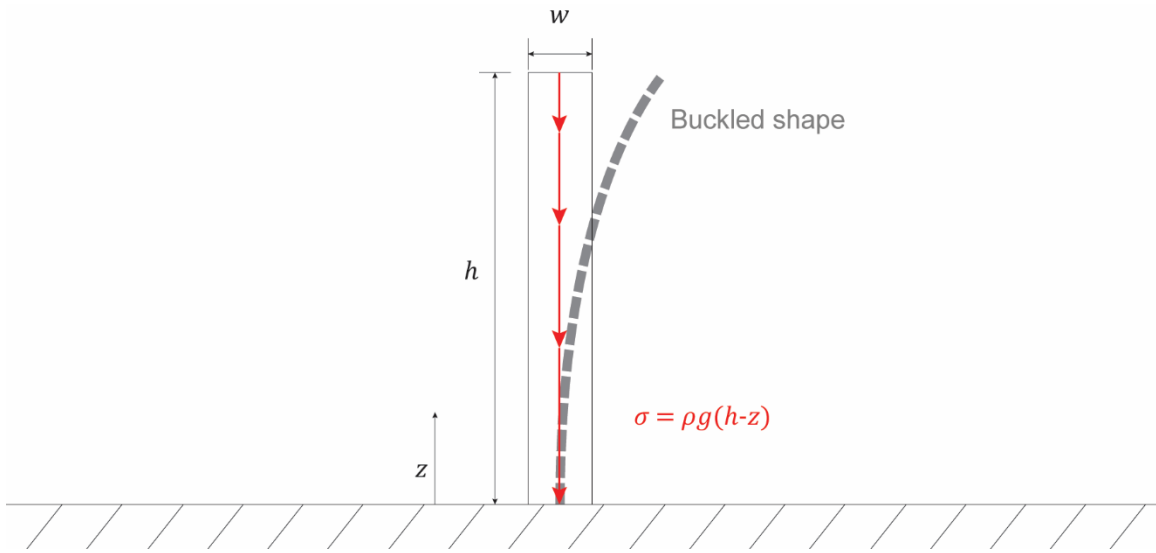


Figure 10: Conceptual diagram demonstrating the anticipated buckling behavior and relevant parameters.

$$E = 2G'(1 + \nu) \quad (9)$$

Rearranging (5) using the preceding relations, Equation 10 is obtained

$$h_b = \left(7.8373 \left(\frac{G'w^2}{6\rho g} \right) \left(\frac{1 + \nu}{1 - \nu^2} \right) \right)^{1/3} = \left(1.7416 \frac{G'w^2}{\rho g} \right)^{1/3} \quad (10)$$

for the height at which a printed wall is expected to buckle due to self-weight.

2.5 Results

2.5.1 Rheology

Both inks performed suitably for use in DIW, as shown by the dynamic oscillatory sweeps in Figure 56 of the appendix. The shear thinning behavior reduced the driving pressure needed at high shear, during extrusion, and increased resistance to deformation at low shear, after deposition. The yield stress provided sufficient resistance to flow to remain stable under the weight of multiple layers. Both behaviors are key to successful DIW printing [44, 45, 52, 55]. The equilibrium modulus and yield stress can be found in Table 1.

For both inks, the maximum stress and time at stress affected the post-shear properties, as shown by the structural recovery results in Figure 11a,c. Regardless of the maximum stress or hold time, all curves coincide in the ramp-up portion of the graph. Upon reaching the hold portion, the curves separate based on hold time. The family of 0-min hold tests begin structural recovery on the left of the graph; the 5-min tests recover in the middle; and the 60-min tests recover on the right. During recovery, all curves exhibit different storage moduli. The time-dependence of the structural recovery curves are

Table 1. Summary of ink properties.

	G'_0 (Pa)	Minimum $G'_{SR,15}$ (Pa)	Minimum $G'_{SR,0.1}$ (Pa)	τ_y (Pa)	ρ (kg/m ³)
NC	86,430	16,424	5,679	410	1,199
FS	38,511	21,090	17,084	928	1,202

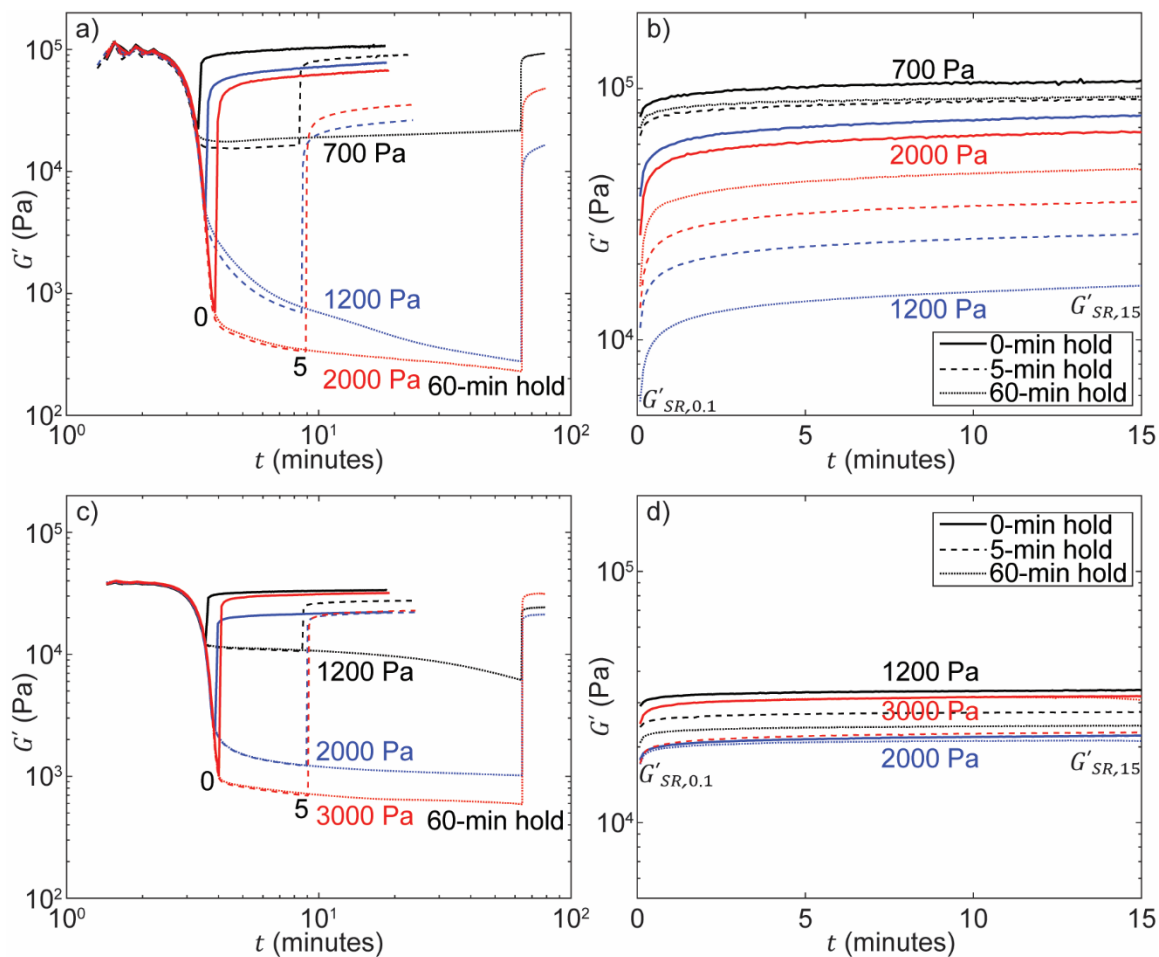


Figure 11: Stress-controlled dynamic oscillatory tests. a) Ramp up to maximum stress, hold, and structural recovery of NC ink. b) Structural recovery of NC ink (at 50 Pa). c) Ramp up to maximum stress, hold, and structural recovery of FS ink. d) structural recovery of FS ink (at 50 Pa).

detailed in Figure 11b,d. The first point on each curve, $G'_{SR,0.1}$, represents the earliest data point taken after the hold (which is 6 seconds, or 0.1 minutes, after the last data point of the hold). The last point on each curve, $G'_{SR,15}$, indicates the last data point taken during the structural recovery test. The behavior between these two points is non-linear. Immediately after returning to the LVR (50 Pa) following a shear excursion, the storage modulus recovers at a high rate. After ~ 90 s for the NC ink and ~ 30 s for the FS ink, the rate of recovery severely diminishes and appears to approach an asymptotic value. Measurements were stopped after 15 minutes.

Figure 12 summarizes the results of the structural recovery tests by showing the range of post-shear storage modulus as a graded bar for each maximum stress value and hold time. The nature of the relationship between these two variables and the post-shear storage modulus appears more complicated than a simple linear relation. G'_{SR} varies non-linearly with maximum stress and the hold time, with the intermediate stress level resulting in the lowest G'_{SR} . This behavior may be related to strain localization in the inks, but a satisfactory explanation warrants further study and is beyond the scope of the present effort. Since extrusion is expected to apply more shear stress than can be achieved on the DHR-2, the minimum range of G'_{SR} (resulting after the intermediate stress tests with a 60-min hold) will be used in the buckling model. The values are shown in Table 1.

The inks showed similarities in their density and rheological response to shear. However, differences in magnitude of rheological properties were observed, as

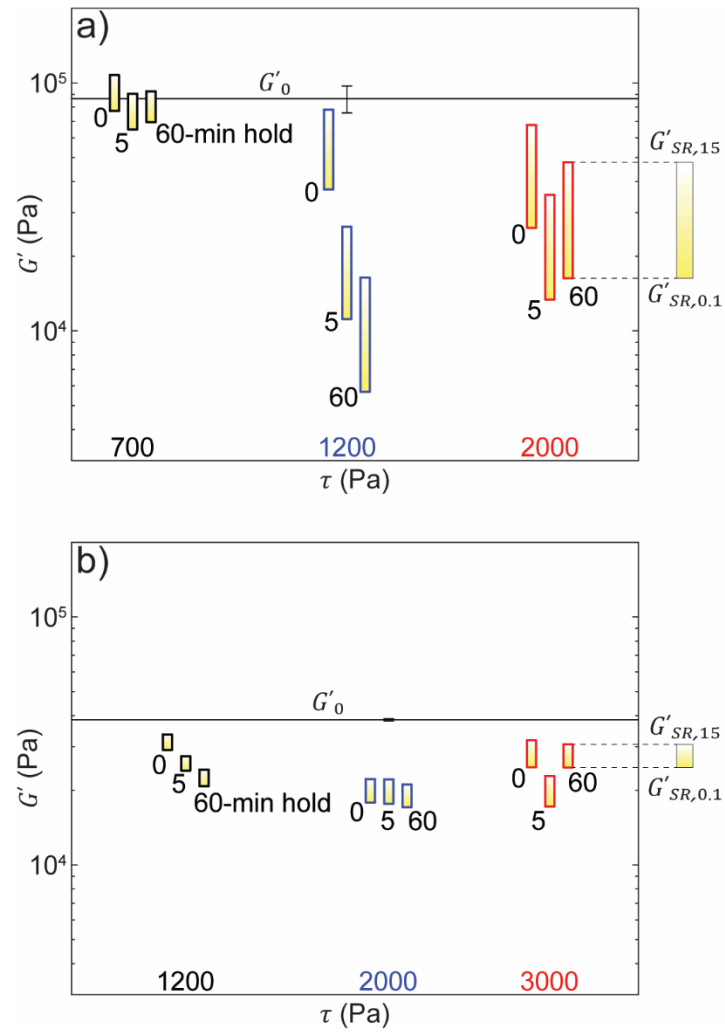


Figure 12: Summary of shear storage modulus after shear excursions to low, intermediate, and high stress with 0-, 5-, and 60-min holds. a) Nanoclay ink. b) Fumed silica ink.

summarized in Figure 12. In the initial state, the NC ink exhibited a higher pre-shear equilibrium storage modulus, but a lower yield stress than the FS ink. After shear, the NC ink exhibited a wider range of G'_{SR} values across all trials than the FS ink. Additionally, after the initial leap, the modulus of the NC ink continued to build, whereas the FS ink showed much more asymptotic behavior. These differences may be linked to filler morphology, but additional study is required to confirm this hypothesis.

Comparing the recovered storage modulus of each ink, using Figure 12, leads to some interesting observations. Within any given trial, the range between $G'_{SR,0.1}$ and $G'_{SR,15}$, was much larger for the NC ink. Further, the minimum values of $G'_{SR,0.1}$ and $G'_{SR,15}$ for the NC ink took a steep dive after shear, falling below that of the FS ink.

2.5.2 *Printed walls*

Representative images of a 4.6-mm-thick wall at various heights are shown in Figure 8 for the NC ink to illustrate the operation of the image analysis program. The first image, taken at $h = 7.8$ mm, shows the wall before the edge regression lines became fixed, as indicated by the green regression lines. At $h = 9.3$ mm, the wall was determined to have reached a steady-state thickness, and the regression lines were fixed and offset from the wall by 5% of the thickness. The wall crossed the fit line at $h = 26.0$ mm, triggering the identification of h_b . Layers continued to be deposited on top of the wall until just after $h = h_u = 29.6$ mm. All printed walls behaved similarly with several “successful” layers of deposition on top of a leaning wall. By the time layer 135 was

deposited (programmed $h = 30.0$ mm), the wall had completely fallen over. Buckling of thin walls generally followed this progression.

Image sequences for thicker walls are shown in Figure 13 (videos are shown in Attachments 1 and 2). The images in the top row illustrate the behavior of a 16.9-mm-thick wall printed with the NC ink. Early in the print at $h = 19.2$ mm, the vertical edges of the wall exhibited straight, parallel profiles. At $h = 48.0$ mm, well before the onset of buckling, lower layers began to visibly bulge under the weight of subsequent layers. This behavior suggests that the wall began to yield before it buckled. At the onset of buckling ($h = h_b = 58.5$ mm), the bulging had progressed further. After buckling, several layers were deposited before the bead no longer successfully landed on top of the wall. The last successful deposition is shown at $h = h_u = 61.9$ mm, where the thickness had continued to expand. Finally, the wall fell over just before the deposition of layer 138 (programmed $h = 66.2$ mm), after several layers had only partially landed on top of the wall.

The progression in the bottom row of Figure 13 does not show bulging in the 13.1-mm-thick FS wall. The lower layers of the wall did not visibly increase in thickness for the entire print. Instead, only buckling behavior was observed. The higher yield stress of the FS ink is believed to be responsible for the absence of bulging before collapse.

The results of the image analysis program allow h_b and h_u to be plotted in Figure 14. Within the range of thicknesses tested, buckling predictions based on the pre-shear equilibrium storage modulus overestimate failure height. On the other hand, predictions based on the range provided by the post-shear storage modulus (highlighted with a

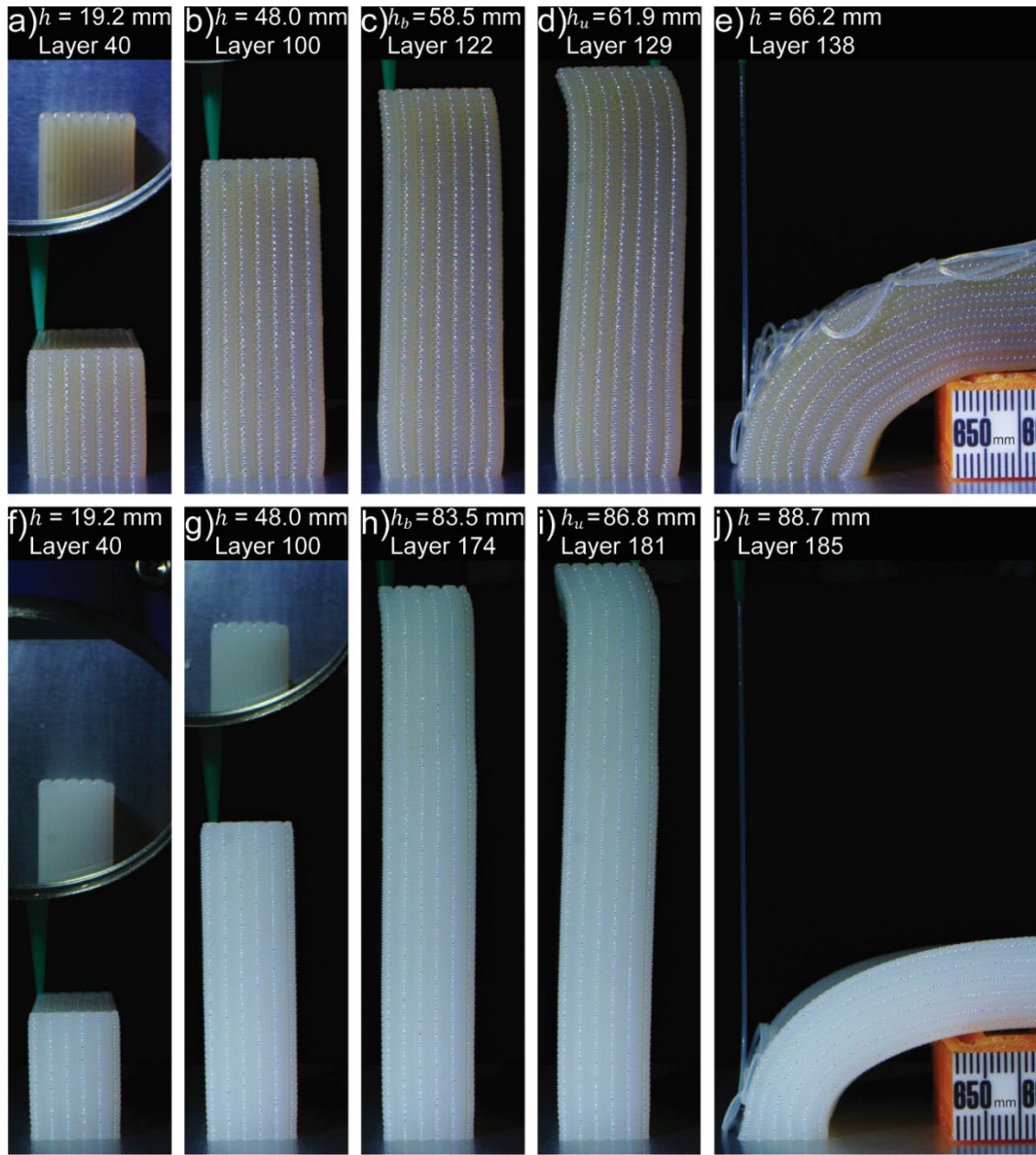


Figure 13: Image sequence for thick walls. a-e) Evolution of the wall printed 16.9-mm thick (14 beads wide) in NC ink using a 0.872-mm nozzle. a) At the deposition of layer 40. b) Upon visible yielding of lower layers (layer 100). c) At h_b (layer 122). d) At h_u (layer 129). e) Upon full collapse (layer 138). f-j) Evolution of the wall printed 13.1-mm thick (11 beads wide) in FS ink using a 0.872-mm nozzle. a) At the deposition of layer 40. b) At layer 100. c) At h_b (layer 174). d) At h_u (layer 181). e) Upon full collapse (layer 185).

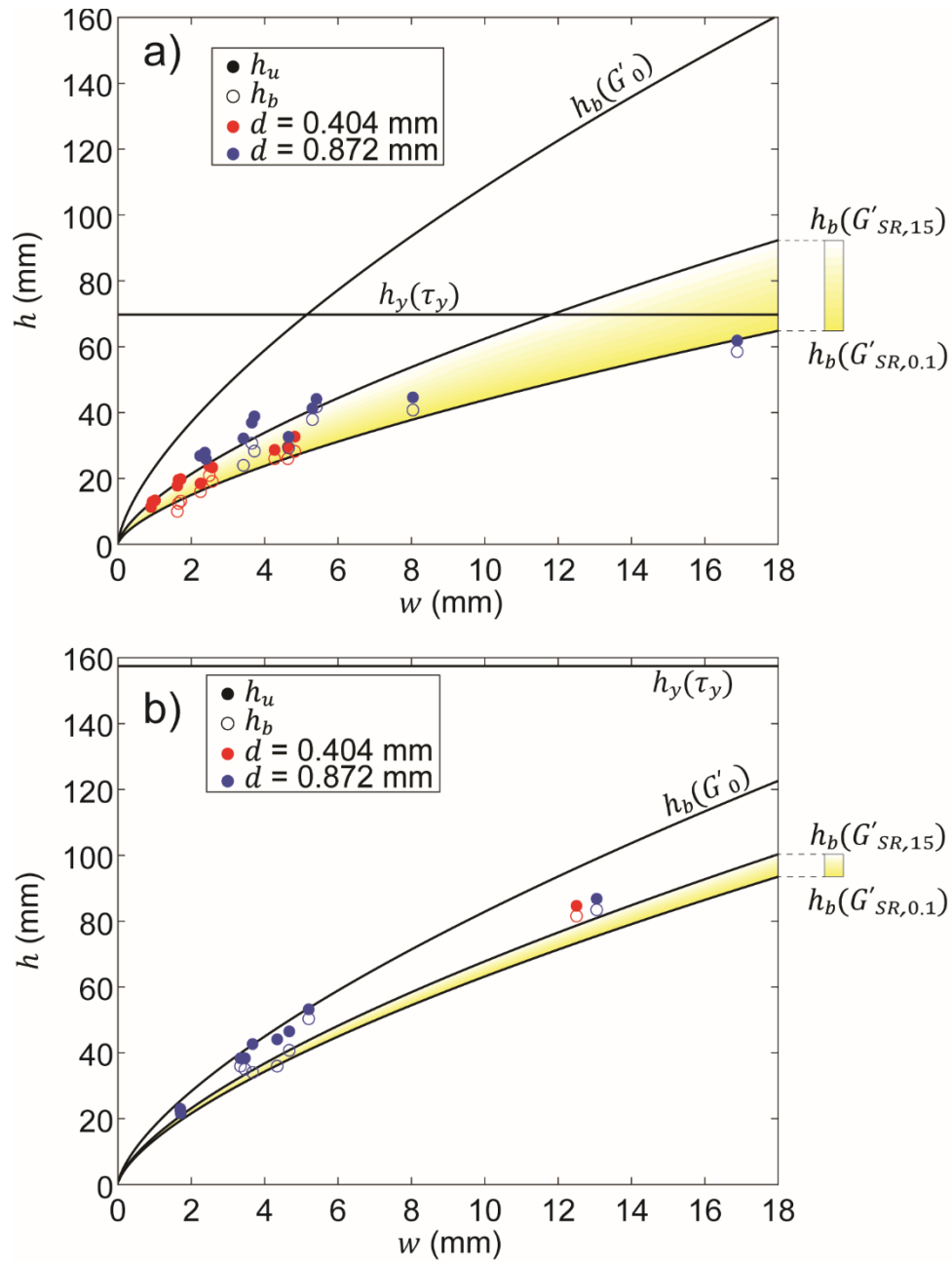


Figure 14: Failure height predictions with respect to initial thickness (prior to yielding) with experimental results overlaid. a) NC ink. b) FS ink.

yellow gradient) match experimental data reasonably well for both inks. However, for the two thickest NC walls, the data points fall close to or below the lowest prediction for elastic buckling height. Based on the proximity of this data to the yielding prediction, as well as the bulging seen in the top row of Figure 13, this behavioral change may be caused by activation of the yielding mechanism. In contrast, throughout the range tested, the collapse heights of the FS walls remain well within the pre-shear and post-shear predictions for elastic buckling.

2.6 Analysis and discussion

Reviewing the data presented in Figure 14, the experimental results suggest that stability of thin NC and FS walls can be reasonably well-modeled using buckling mechanics, provided the recovery behavior of the ink is considered. Predictions based on the pre-shear equilibrium storage modulus (G'_0) overestimate failure height, whereas models based on the post-shear storage moduli ($G'_{SR,0.1}$ and $G'_{SR,15}$) align more closely with observed behavior. The thicker 8.0-mm-thick and 16.9-mm-thick NC walls were able to reach greater heights that approached the yielding prediction, as shown in Figure 14a. Images shown in Figure 13a-e, suggest that the onset of yielding may begin to limit stability at greater heights. This behavior may explain why collapse of the thicker walls skews closer to the lower prediction provided by the recovered modulus. As suggested in the following section that discusses sources of error, a different definition of yield stress or yield criterion in the model may provide somewhat better agreement with the experimental data. Figure 57 of the appendix shows how the von Mises yield criterion

compares to the reported Tresca yield criterion. The following experimental analysis provides clearer understanding of the collapse behavior and active failure mechanisms.

2.6.1 Buckled shape

Figure 15 shows the profile of four different walls at three different points throughout the printing process. The first contour (at the deposition of layer 40) is straight, showing the wall profile well before any type of instability is identified. The second contour is slightly bowed, showing the wall profile as it begins to buckle (h_b). The third contour shows the heavily bowed shape of the profile as the last layer is successfully deposited on the top of the wall (h_u). The numerical approximation of a buckled profile for a column (based on analysis completed by Wang and Ang [69]) is also plotted in Figure 15 for comparison with the curves at h_b and h_u . The lower portion of the theoretical profile matches the observed profile, suggesting buckling led to collapse. However, the theoretical profile diverges from the experimental toward the top of the wall. As dictated by the CNC gantry, deposition occurred at the same x and y coordinates for each layer. The continuous deposition of filament stabilized the print after the onset of buckling. As the buckled wall moved away from the programmed deposition location, the newly extruded material acted as a partially pinned constraint that prevented the material from immediately collapsing after the onset of buckling. This behavior was a factor driving the difference between the onset of buckling and ultimate failure. This processing feature also explains why the buckled profile hooks back toward the nozzle rather than following the shape predicted by Figure 10. In the next chapter, a finite

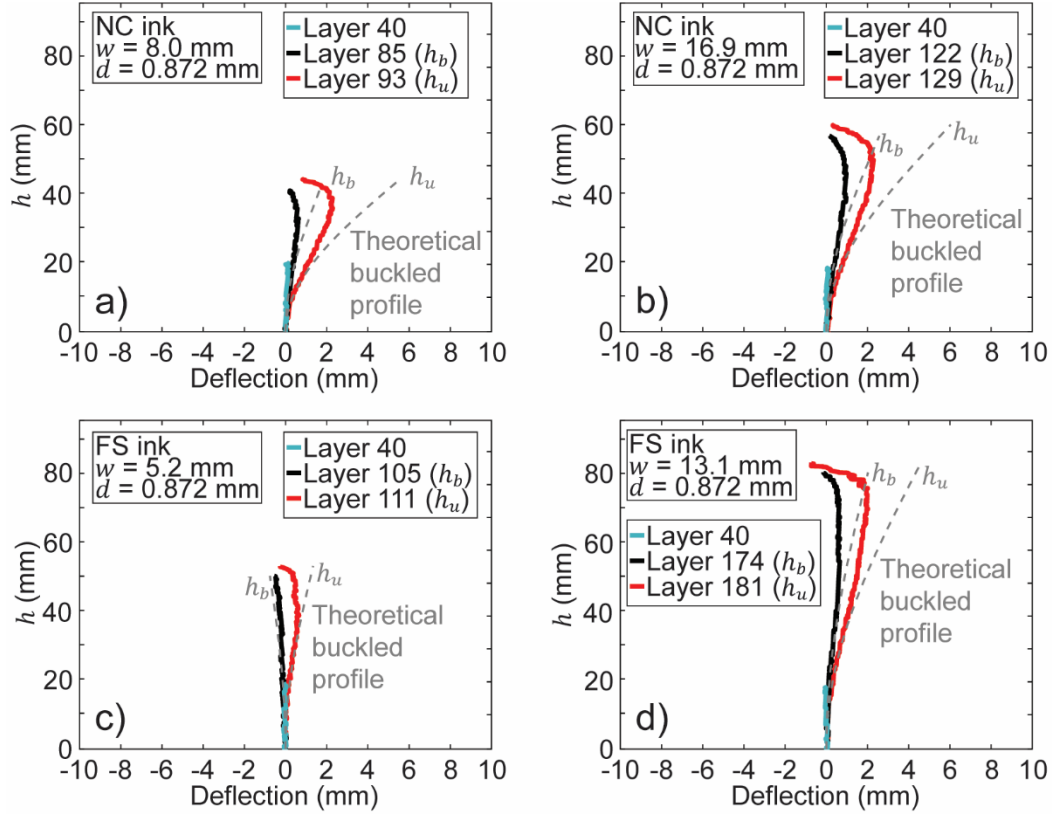


Figure 15: The deflection of selected profiles of walls before buckling at selected snapshots, including at the deposition of layer 40, at the onset of buckling (h_b), and upon ultimate failure (h_u), as well as the theoretical buckled profile at h_b and h_u . a,b) The 8.0-mm- and 16.9-mm-thick NC walls, respectively. c,d) The 5.2-mm- and 13.1-mm-thick FS walls, respectively.

element model is used to quantify a similar behavior observed while printing overhanging walls.

Comparison of the profiles of the NC walls (Figure 15a,b) to those of the FS walls (Figure 15c,d) reveals behavioral differences between the inks. Both selected NC-ink walls showed h_b and h_u occurring on the same side. However, the image analysis program detected h_b on the opposite side of h_u for the FS-ink wall depicted in Figure 15c. These two snapshots (at h_b and h_u) capture a unique behavior noted when printing with the FS ink. When the FS-ink walls started to become unstable, the walls would wobble back and forth, depending on where the print head was positioned relative to the centerline of the wall. A video of this oscillatory behavior can be found in Attachment 3. Attachment 4 shows the lack of oscillatory behavior in an NC wall. This difference in behavior may be due to the higher resiliency of the FS ink. Based on its rheological profile, the FS ink can experience greater deformation and stress without yielding. This behavior allows FS walls to survive oscillation. Additionally, the FS wall in Figure 15c reaches greater h_b and h_u than the wall printed with NC ink in Figure 15a, even though the NC wall was thicker. The same observation can be seen comparing the FS wall (Figure 15d) to the NC wall (Figure 15b). This behavior may be partially attributed to the superior post-shear storage modulus of the FS ink. The bulging observed in the thick NC wall, but not in the FS wall (as depicted in Figure 13), may also explain this observation. These behaviors indicate that, in addition to buckling, yielding played a role in the collapse of thick NC walls. Yielding will be discussed further in a later section.

2.6.2 *Time-dependent recovery of shear storage modulus*

Because the deposited material recovers over time, and because the printing process is continuous, one would expect that the actual storage modulus varies spatially throughout the wall during the printing process. Although the exact stress history and recovery behavior of the deposited ink is unknown, rheological experiments can be used to approximate the time-dependent recovery. By calculating the time elapsed after deposition and finding the corresponding storage modulus from the structural recovery tests (Figure 11b,d), spatial gradients of storage modulus can be constructed for specified snapshots. The expected storage modulus as a function of height within the wall is plotted at several snapshots in time in Figure 16a,b. For these plots, the most severely degraded post-shear behavior is assumed, which corresponds to the 1200 Pa, 60-min hold case for the NC ink, from Figure 11b. These graphs reveal how much variation in properties could exist within the printed walls. For a 60-mm-long, ~3.5-mm-thick NC wall (2-bead, 4.8-s layer time, $d = 0.872$ mm), a 95.92-mm tall wall (corresponding to 200 layers) is printed in 16 minutes, if the wall remains stable. At 16 minutes (t_{200}), Figure 16a shows only a few layers near the bottom of the wall have recovered to the upper value of storage modulus. Figure 16b, which represents a 60-mm-long, ~8.0-mm-thick NC wall (6-beads, 14.4-s layer time, $d = 0.872$ mm), shows similar behavior, but with increased storage modulus at each height. When compared to the shorter layer time, this figure demonstrates how increasing layer time can increase the storage modulus of the wall at each snapshot. In this case, many more layers achieve the upper value of storage modulus

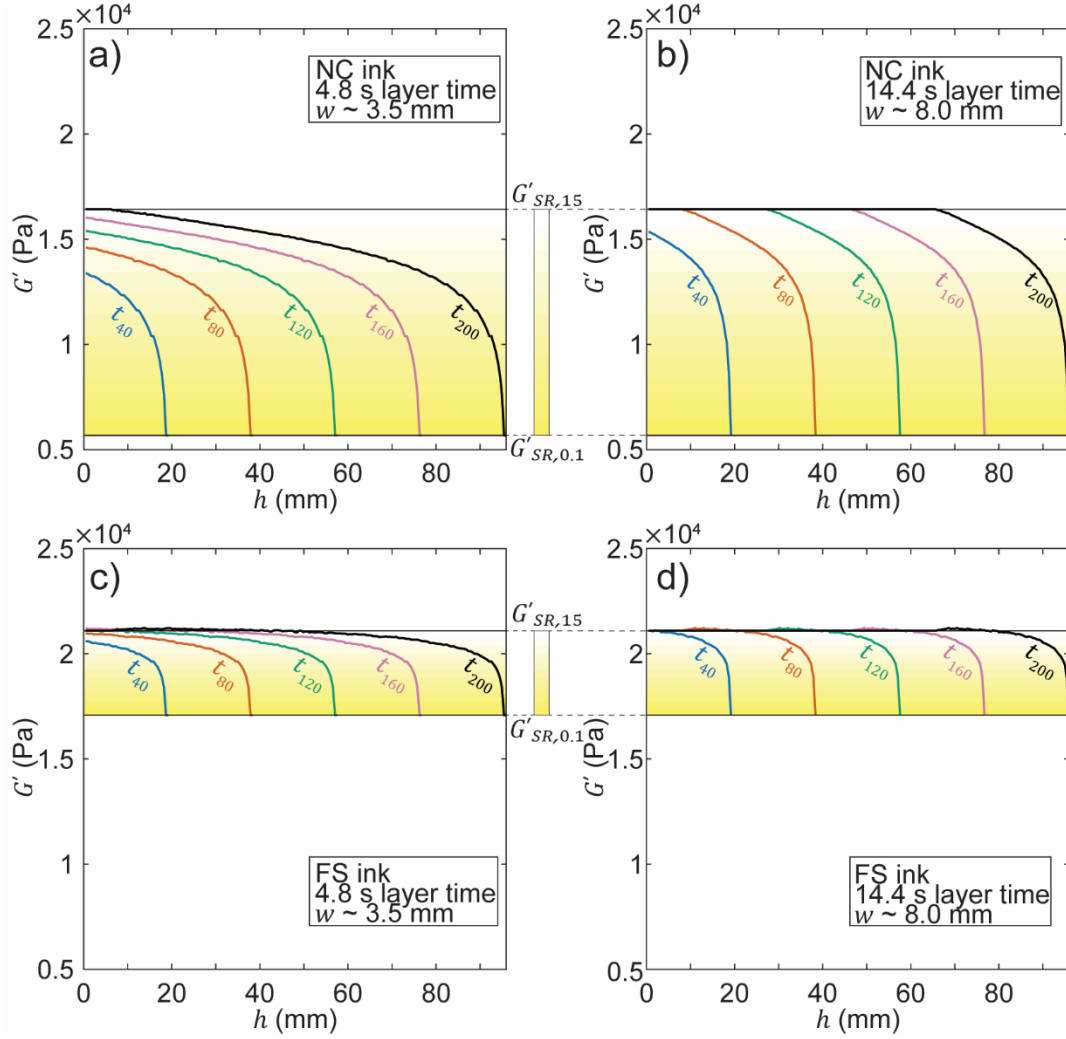


Figure 16: Shear storage modulus as a function of height at snapshots in time ($t_{\#}$). For instance, t_{40} refers to the storage modulus profile when the 40th layer is deposited. a) NC ink with a 4.8-s layer time ($l = 60$ mm, $w \sim 3.5$ mm, 2-bead, $d = 0.872$ mm). b) NC ink with a 14.4-s layer time ($l = 60$ mm, $w \sim 8.0$ mm, 6-bead, $d = 0.872$ mm). c) FS ink with a 4.8-s layer time ($l = 60$ mm, $w \sim 3.5$ mm, 2-bead, $d = 0.872$ mm). d) FS ink with a 14.4-s layer time ($l = 60$ mm, $w \sim 8.0$ mm, 6-bead, $d = 0.872$ mm).

starting between the deposition of layer 40 and 80, implying the wall should be more resistant to buckling at longer layer times. This behavior suggests that the NC ink should be able to form taller walls when layer times are longer. Even though thicker walls take longer to print than thin walls, the 8.0-mm-thick and 16.9-mm-thick NC walls were more unstable and collapsed near the curve representing the lower value of storage modulus rather than migrating toward the higher prediction in Figure 14a. Yielding behavior appears to be responsible for this unexpected behavior.

The height predictions in Figure 14b also agree with the experimental data for the FS ink. All the experimental results fall near the buckling predictions. This data is much closer to the curve representing the higher value of storage modulus than for the NC ink. The quicker recovery of the FS ink, compared to the NC ink (Figure 11b,d), may explain this behavior. Figure 16c,d support this hypothesis. In addition to having a much smaller range between the upper and lower value of storage modulus, the rapid recovery behavior of the FS ink suggests that a large portion of the layers have recovered to the higher value during printing of both thin (Figure 16c) and thick (Figure 16d) walls. Additionally, the FS-ink is more resistant to flow than the NC-ink, showing a higher yield stress (Table 1). A high yield stress may promote plug flow, which would protect inner regions of the bead from shear strain and the resulting breakdown in properties. Future work to quantify the flow profile in the nozzle may provide a more accurate representation of the amount of shear flow experienced during extrusion. This understanding may improve the

accuracy of the proposed model, which assumes a homogenous bead with constant properties throughout.

The majority of the walls took less than 15 minutes to print, so the 15-minute recovery measurements capture the expected range of behavior exhibited by the material during printing. Table 10 and Table 11 of the appendix list the parameters of the walls based on the number of beads, nozzle diameter, and ink. These tables show that all 1-, 2-, and 3-bead walls were printed in less than 15 minutes. Since these walls were thinner than prints with more beads per layer, they buckled and collapsed earlier. Plus, the layer time for these prints was shorter than for walls with more beads per layer.

2.6.3 *Yield behavior*

As the initial thickness (measured prior to yielding) increases in the NC walls in Figure 14a, failure height migrates toward the lower end of the buckling predictions as it approaches the height at which yielding is predicted. Although the exact interaction between yielding and buckling is not clear, the onset of yielding may simply seed the instability required to trigger buckling. It is also possible that the torque on the walls that arise from the shear forces between the moving print head and the stationary wall may lead to earlier onset of yielding than would be expected from self-weight alone. Finally, creep has been neglected entirely, but may also play a role. Further characterization and a different experimental setup would be required to definitively identify these behaviors.

To demonstrate that yielding occurred, this work quantifies the change in thickness of the wall. The 16.9-mm-thick wall visibly bulges as height increases in Figure

13a-e. Tracking the thickness of the printed walls at several locations over the duration of the printing process provides quantitative data to confirm yielding occurred in these thicker walls. Figure 17 plots Δw as a function of h . Δw is defined as the difference between the actual thickness, which changes as specimens begin to bulge, and the initial thickness measured by the image analysis program. The thickness data has been plotted in 5-layer increments. Figure 17a,b shows that the thickness of the bottom 30 layers of both the 8.0-mm-thick and 16.9-mm-thick walls began increasing before failure. This behavior confirms that yielding preceded collapse and may explain why these walls skew toward the lower end of the buckling height prediction. However, bulging and yielding begin at lower heights than predicted by the yield stress in Figure 14a. Experimental constraints make pinpointing the recovered yield stress of the material challenging. After flow, the yield stress appears to decrease, as suggested by Figure 56 of the appendix and [56]. Additionally, the method used to identify yield stress in this work requires the material to have reached an equilibrium state. This state cannot be achieved as the ink recovers to a static particle network. Although unavailable in the current setup, more rigorous characterization of the recovered yield stress could improve yielding predictions and strengthen understanding of the link between rheological properties and structural stability.

In the absence of data that characterizes the evolution of the yield stress during recovery, additional analysis in Figure 18 provides an alternative measurement of the yield stress using the yielded walls. These graphs use the *measured* (not average)

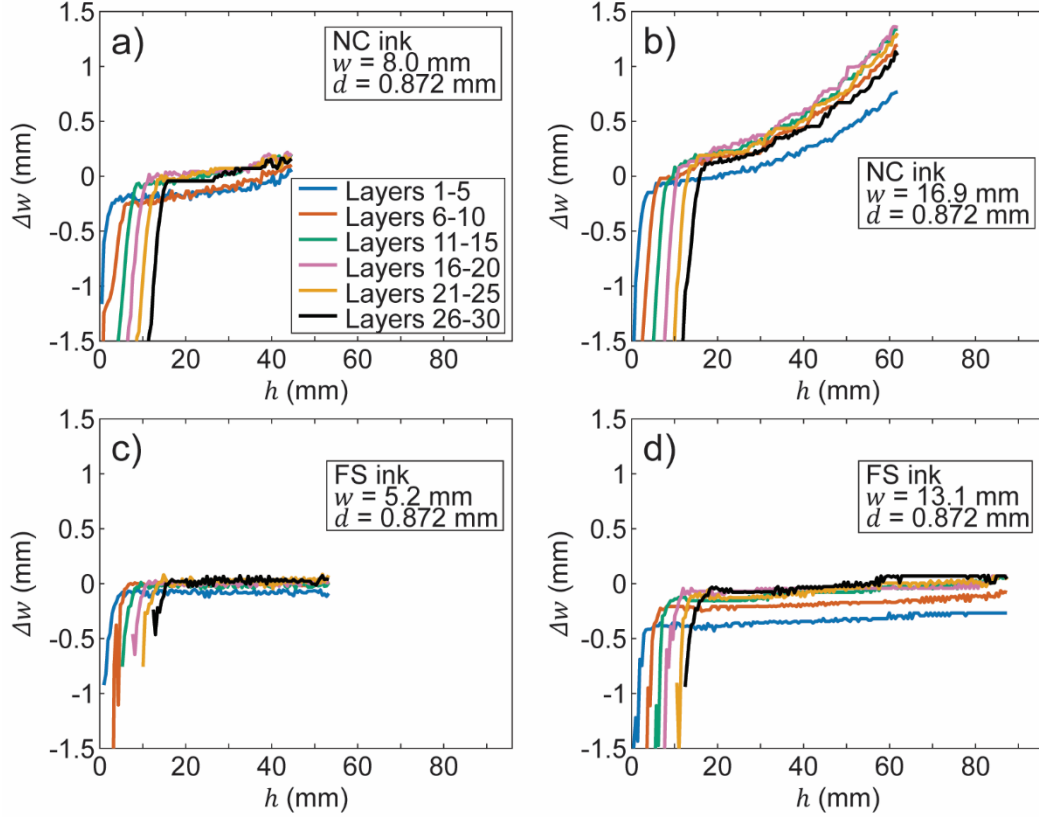


Figure 17: The change in thickness of the bottom 30 layers with respect to h of select prints, reported as the average of 5-layer increments. a,b) The 8.0-mm- and 16.9-mm-thick NC walls, respectively. c,d) The 5.2-mm- and 13.1-mm-thick FS walls, respectively.

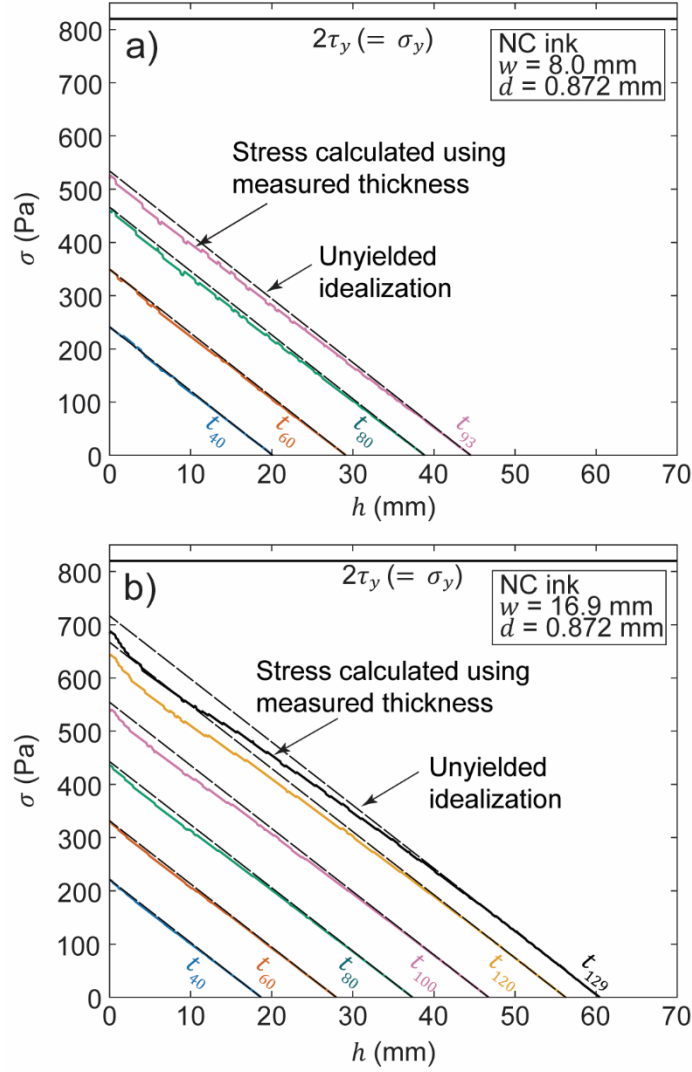


Figure 18: Axial stress along the height of the wall based on measured thickness at snapshots in time ($t_{\#}$). For instance, t_{40} refers to the stress when the 40th layer is deposited. a) the 8.0-mm-thick (6-bead), NC-ink wall and b) the 16.9-mm-thick (14-bead), NC-ink wall. Snapshots are defined by the layer being deposited at that time. For instance, t_{40} refers to the storage modulus profile when the 40th layer is deposited.

thickness to calculate the theoretical stress experienced within the wall at given snapshots. By looking for differences between the calculated curves and the “unyielded idealization,” the post-extrusion yield stress can be estimated. For both the 8.0-mm-thick and 16.9-mm-thick walls, deviation from the idealization begins when the walls experience $\sim 200\text{-}300$ Pa of axial stress, well below the prediction labelled “ $2\tau_y$.” This observation indicates that τ_y has decreased to $\sim 100\text{-}150$ Pa, suggesting that the material may also experience a decrease in yield stress after a shear excursion.

Neither of the FS walls exhibited the yielding behavior that was observed in the NC walls. Figure 17c,d illustrates almost no change in thickness throughout the entire print for both walls. These observations support the hypothesis that buckling was the dominant behavior causing failure in the FS walls. The lack of yielding also explains why the FS walls were able to reach greater heights than NC walls of equivalent thickness.

2.6.4 Importance of post-shear behavior and time dependence

The initial equilibrium storage modulus (before a shear excursion) is typically reported when characterizing DIW inks [6, 7, 11, 52]. This value provides a rough estimate of the stiffness of the material but, as explored in this work, fails to accurately describe the properties exhibited after extrusion. Recent work has considered the properties after a shear excursion to evaluate feedstocks for application in DIW [56-58, 102]. The findings presented here, summarized in Figure 14, confirm the importance of quantifying the post-shear storage modulus and yield stress in ascertaining DIW printability with respect to structural stability. Further, the analysis of the time-based

studies of recovery suggest that even more meaningful information can be gleaned from understanding the time dependence of rheological properties after shear. Much like the storage modulus, the yield stress is also anticipated to show time-dependent behavior as the material recovers. However, time-dependent characterization of the yield stress is less straightforward than that of the storage modulus and warrants a separate dedicated study. Therefore, this work is left to future research.

Shear flow has been hypothesized to disrupt the filler network and cause filler realignment, motivating the rheological tests described in this work. Stress applied beyond the yield stress has been shown to breakdown filler networks and reduce recovered properties [58]. Filler materials with non-unity aspect ratio are susceptible to realignment during shear, as shown by previous work which revealed a decrease in resistance to flow of materials with these types of filler [7, 103]. Due to the platelet morphology of its filler, the NC ink is expected to exhibit greater property reduction than the FS ink, which has more spherically shaped filler particles. This hypothesis is supported by recent work that has shown that printed and cured NC/epoxy composites display much more anisotropic strength and stiffness than similar printed epoxy composites that utilized FS instead of NC [7, 8]. The difference in recovery behavior between the NC and FS inks in Figure 11 provide further evidence to support this hypothesis.

2.6.5 Sources of error

Several sources of error could explain the discrepancies between the proposed models and the experimental data in Figure 14. A few of these sources are discussed below. These errors arise from limitations in the measurement of material properties as well as challenges in modeling time-dependent material behavior.

There are many ways to determine the yield stress of a yield stress fluid, making the measurement ambiguous, as discussed by [101]. This work implemented the “intersection power-law” method, which has been shown to give an intermediate yield stress between the values given by the “ G'/G'' crossover” and the “Herschel-Bulkley fit,” where G'' is the shear loss modulus. However, the method selected is likely to introduce some error into the predictive models. Determining the axial yield stress from the shear yield stress also presents some ambiguity. The Tresca yield criterion was chosen, as shown in (3), but the von Mises yield criterion is also an option. Under the assumption of the Tresca yield criterion, the uniaxial yield stress is double the shear yield stress, predicting h_y for the nanoclay to be 70 mm. On the other hand, the uniaxial yield stress and shear yield stress only differ by a factor of $\sqrt{3}$ under the assumption of the von Mises yield criterion, predicting h_y for the nanoclay to be 60 mm. The difference in these values can be seen in Figure 57 of the appendix. Clearly, some uncertainty is introduced when determining the axial yield stress. However, the discrepancy between the two criteria is likely negligible compared to lack of data describing the post-shear yield stress.

Future work to characterize the effects of shear on the yield stress will help to evaluate the error caused by the choice of yield measurement and yield criterion.

Without the capability to conduct accurate measurements of Poisson's ratio, its value was assumed to be 0.25. The difference between predictions of buckling height based on $\nu = 0$ and $\nu = 0.5$ was found to be minimal compared to the scatter in experimental data (Figure 57 of the appendix). Therefore, the midpoint between these two bounds was chosen.

The models assume fully elastic behavior below the yield stress; however, viscoelastic materials can experience time-dependent creep under loads less than the yield stress. Depending on the magnitude of creep, incorporation of this behavior is likely to decrease the achievable height predicted by the idealized stability models. Although incorporating creep behavior in the models would undoubtedly lead to relevant insight, this work is left to a more focused investigation than can be completed here.

Understanding the approximations made, it is remarkable to see the level of agreement between the predictions and experiments observed in this study. These highly accessible models appear to capture the main physical behaviors that govern structural stability of 3D-printed walls, providing a much-needed framework to approximate the height to which thermoset inks can be printed. Further work to address these approximations and improve accuracy of the models will certainly prove valuable, but it is encouraging that basic mechanistic models based on rheological properties can account for a significant portion of the behavior. This finding motivates study of more

complicated shapes, like overhanging walls, to determine if these approximate rheological properties can be used in other mechanical models and return valid predictions.

2.6.6 Conclusion

This study experimentally assessed the link between commonly measured rheological properties and structural stability of printed thin walls using DIW thermoset inks. Buckling and yielding appear to be key drivers of collapse behavior within the range of thicknesses tested, and models based on these failure mechanisms are in excellent agreement with experimental data. Thin walls collapsed in agreement with buckling predictions based on the post-shear storage modulus. Thicker walls collapsed below the bound proposed by yielding predictions. Yielding appears to be a much more persistent type of failure that will limit the height of printed structures regardless of thickness. However, buckling remains an important consideration because it limits the geometrical resolution of large-scale prints. Both of these failures can be addressed with an in-process curing mechanism.

This study also finds that post-shear properties are more relevant to modeling print stability than pre-shear properties. Predictions based on pre-shear properties match experimental data only behaviorally, and models become more accurate upon incorporation of the post-shear material behavior. The amount of time and level of stress experienced during the shear excursion, as well as the filler type were shown to significantly affect the post-shear properties, and hence, the stability of thin printed walls.

The apparent accuracy of the elastic-plastic assumption and the link between basic rheological properties, wall thickness, and achievable wall height provide a foundation for several important advancements in the field of additive manufacturing. The experiments and analysis presented can inform engineering design of printed components that incorporates stability limitations of the feedstock material itself during the printing process. More fundamentally, these results provide valuable guidance on the development of more effective DIW feedstock materials, while highlighting the need for reactive or dual-cure systems that begin to crosslink directly after deposition in cases where large components are desired. The agreement between the rheology-based collapse models and experimental data also motivates further study of the link between rheological properties and the stability of other structures, like the overhanging wall.

3 CHAPTER 3: STRUCTURAL STABILITY OF OVERHANGING FEATURES IN THERMOSET DIRECT INK WRITING

A version of this chapter has been submitted to *Additive Manufacturing* by Stian K. Romberg, Abrian Abir, Christopher J. Hershey, Vlastimil Kunc, and Brett G. Compton [104]:

Stian K. Romberg, Abrian Abir, Christopher J. Hershey, Vlastimil Kunc, and Brett G. Compton. “Structural stability of overhanging features during direct ink writing of thermosets.” *Additive Manufacturing* (In review).

This article was revised in two ways for reproduction in the current form. The introduction and conclusion were edited to relate the current article to the preceding and following chapters. Figures were modified to fit within the margins and improve font visibility. S.K. Romberg designed and configured the experimental setup for printing walls, printed and captured data from printing experiments, analyzed the data, generated the figures, and wrote the article. M.A. Islam designed and created the software to analyze the data. C.J. Hershey and V. Kunc helped obtain the funding for this work and assisted in editing the article. B.G. Compton helped to conceptualize the printing experiments, provided the equipment needed to conduct experiments, and was the primary editor of this article.

3.1 Abstract

Recent developments have enabled material extrusion additive manufacturing of thermoset-based composite inks on the large scale. In addition, printing out-of-plane

components is of broad interest to the polymer material extrusion community. This work addresses the challenges associated with both large-scale and out-of-plane thermoset material extrusion additive manufacturing by studying the height at which overhanging walls collapse. Walls at a range of overhanging angles were printed until they collapsed. An optical camera captured the profile of each wall throughout the print, allowing the collapse height to be identified and the geometric fidelity to the programmed angle to be evaluated. Using previously measured rheological properties, predictive models were generated to approximate the collapse height and profile of the deflected walls. First, an analytical model was created to predict the height at which the walls would yield. The analytical model assumes the walls exhibit a perfectly linear profile; however, experiments proved this assumption to be false. Therefore, a finite element simulation was developed to account for the elastic deflection that occurs during printing. The finite element simulation predicts both the yield height and the deflected profile after the deposition of each layer. For the properties of the thermoset ink used here, the yield height predicted by the analytical model and finite element simulation are virtually identical. These predictions match experimental data reasonably well, but minor errors are observed. Accounting for the fully plastic moment appears to explain the small mismatch between experimental data and predictions. Additionally, the finite element simulation provides an excellent prediction of the deflected profile before the wall begins to collapse. By demonstrating that the collapse height and deflected profile of

overhanging features can be predicted, this work provides a basis to tailor in-process curing systems to suppress these behaviors.

3.2 Introduction

The previous chapter used a simple geometry with well-established mechanical models that assumed elastic-plastic behavior to verify the link between rheological properties and self-weight stability [63]. Although that study improved understanding of the feasible scale of thermoset printing, additional study can broaden the applicability of this link. This chapter uses another simple geometry – an overhanging wall – to generalize the connection between stability and rheological properties to an out-of-plane geometry. Advancements in robotics [74, 80-83] and a general desire to expand manufacturing flexibility beyond “2-½D” [19, 21, 61, 71-79] make printing out-of-plane objects an exciting new topic for AM. Rigorous investigation of the deflection mechanisms in overhanging walls will enable design of in-process curing kinetics tailored to suppress deformation and collapse.

An epoxy-based composite ink without a curing agent is used to provide the limits of stability in the absence of crosslinking or in-process curing. Overhanging walls are printed at a range of angles and observed as they collapse. Predictions of the yield height based on classical beam mechanics and previously obtained rheological properties [63] are shown to be in good agreement with the collapse height observed in experiments. A finite element (FE) model designed to account for the elastic deflection that occurs between the deposition of each layer is shown to accurately predict the deflected profile of the

overhanging walls. These design tools strengthen the understanding of the relationship between rheological properties and stability while providing the information needed to tailor curing kinetics to suppress both collapse and elastic deflection of overhanging features printed with thermoset inks.

3.3 Experimental methods

3.3.1 *Material formulation*

A thermoset composite ink was formulated following Romberg et al. [63] by adding 10 wt.% fumed silica (Cab-o-sil TS-720, Cabot Corporation, Alpharetta, GA) to an epoxy resin (Epon 826, Momentive Specialty Chemicals, Inc. Columbus, OH) in several steps. 315 g of resin was added to a 750-cc mixing cup, then held in a 60°C oven for two hours to melt any crystallized material. The resin was then allowed to cool to room temperature. Next, 8.75 g of fumed silica was added to the resin and mixed for 1.5 min at 1500 RPM under vacuum at 100 mbar. This step was repeated 3 additional times until a total of 35 g of fumed silica was added to the resin. Finally, the material was scraped off the walls of the mixing cup, recombined and remixed to improve homogeneity of the formulation. No curing agent was added to the ink. This ink has exhibited favorable printability in previous research [7, 8, 63], displaying an equilibrium shear storage modulus (G'_0), shear yield stress (τ_y), and shear-thinning behavior. Previous rheological characterization [63] are listed in Table 2 and will be used in this work. This list includes the density of the ink (ρ), the shear yield stress, the shear equilibrium storage

Table 2. Rheological properties of the Epon 826 filled with 10 wt.% fumed silica [63].

ρ (kg/m ³)	τ_y (Pa)	G'_0 (before shear flow) (Pa)	G'_{rec} (after shear flow) (Pa)
1,202	928	38,511	17,084

modulus before shear flow, and the recovered shear storage modulus after shear flow (G'_{rec}).

3.3.2 3D printing

3D printing was performed using a customized computer numerically controlled (CNC) 3-axis positioning stage (Shopbot Tools Inc., Durham, NC) with a syringe mounted on the gantry and an air pressure controller (JB1113N, Fisnar, Germantown, WI). The ink was loaded into a 310-cc cartridge (EA110C-HD, Ellsworth Adhesives, Germantown, WI) using a SpeedDisk (FlackTek, In., Landrum, SC). The filled cartridge was placed into a fluid cartridge retainer (CR300, Fisnar, Germantown, WI) which deposits material under an applied pressure. The cartridge was equipped with a luer-lock adapter that accommodated an 18-gage tapered nozzle (Fisnar, Germantown, WI) with a measured inner diameter, d , of 0.872 mm. Walls were printed directly onto the stationary build platform, which was made of aluminum with a matte black anodized finish. Walls were cleared away after they collapsed.

Figure 19 describes the overhanging walls. Figure 19a defines the coordinate system and geometry that will be used in following sections. L is the length of the wall, w is the thickness of the layer, h is the height of the wall, and α is the angle between the centerline of the wall and the z -axis. Figure 19b illustrates the continuous toolpath used to print overhanging walls. Four adjacent beads were placed on each layer before the nozzle was moved vertically, then horizontally to print the next layer at the prescribed angle. These g-codes were programmed in Scilab (Scilab Enterprises, France). The layer

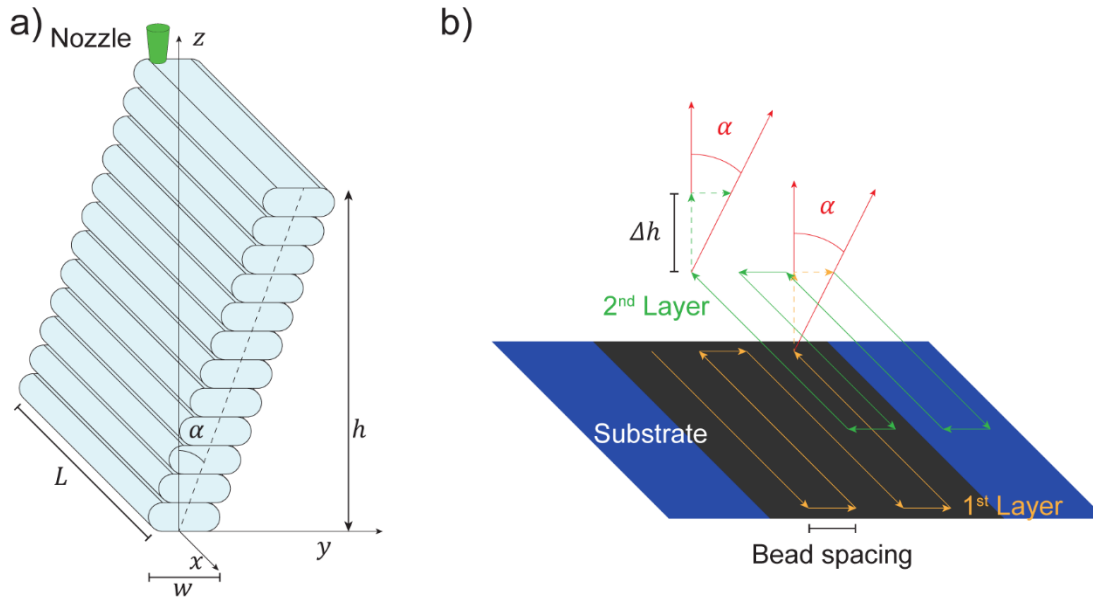


Figure 19: Geometry of overhanging walls. a) Conceptual diagram of overhanging walls showing the coordinate system and geometric definitions. b) Toolpath used to create overhanging walls (showing only the first and second layer).

height (Δh) was set to $0.55d = 0.4796$ mm. The spacing between center points of adjacent beads (i.e., “bead spacing”) was set to $1.375d = 1.199$ mm. These ratios match the print parameters used on the RAM system [42]. The translation speed, v , of the deposition head was set to 25 mm/s. Walls were programmed and printed at 5° increments for α between 0° and 50° . At least four samples were printed at each programmed α . At the beginning of each test, the extrusion pressure was adjusted until adjacent beads coalesced. Only small adjustments between 448 and 469 kPa were required to achieve the desired coalescence, and each wall collapsed without separating at layer or bead boundaries, indicating enough material was extruded to create a fully dense structure.

3.3.3 *Process monitoring and image analysis*

Figure 20 shows the experimental setup used to record data during printing. The thin edge of the wall was imaged with an acA1920-155uc optical camera (Basler AG, Ahrensburg, Germany) outfitted with an LM16SC lens (Kowa, Düsseldorf, Germany). The g-code was programmed to send a voltage signal through the input/output (I/O) cable to trigger the capture of an image after the deposition of each layer. The profile, angle, and thickness of the walls were determined from these images.

RGB color thresholding of each pixel was used to distinguish between the white wall and dark background. Then the locations of the left and right edges of the wall were identified. For a given image, the y-values of the left and right edges were averaged to find the centerline profile of the wall. α was measured by fitting the centerline with a

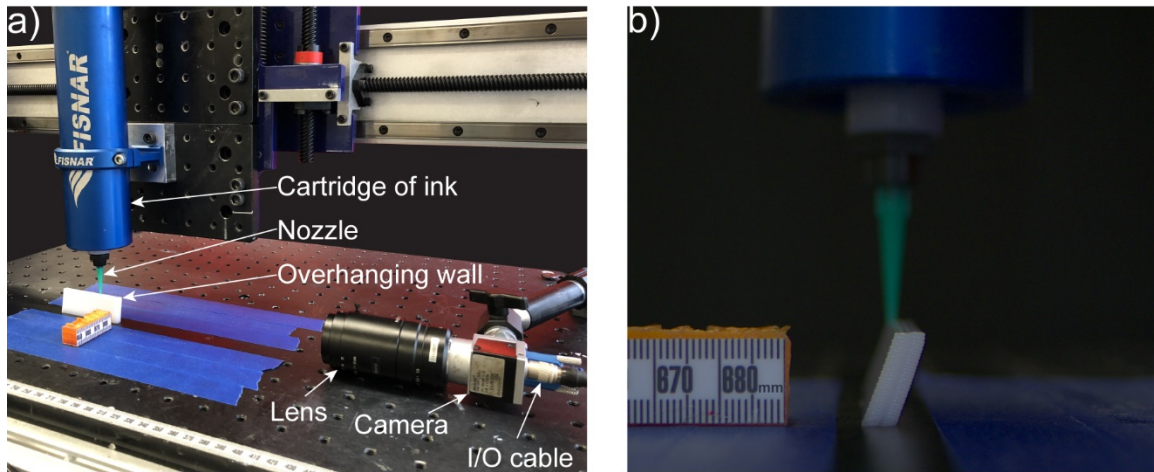


Figure 20: Experimental setup to observe the overhanging walls. a) Process monitoring. b) View from the camera.

linear regression, then taking the inverse tangent of the slope of the linear regression. The thickness was determined by calculating the difference between the y-values of the left and right edges. The measured thicknesses at all vertical points in the wall for each image were averaged to determine a single average thickness after the deposition of each layer. The experimental collapse height (h_f) was defined as the height at which the new layer did not land on top of the previous layer.

3.4 Mechanical theory and calculations

3.4.1 Analytical self-weight yielding model

As has been noted in previous work [62-64], self-weight is a key factor affecting the stability of printed thermoset inks because they exhibit such low specific strength and stiffness. Therefore, a mechanical model that assumes elastic-plastic behavior and considers beam bending under self-weight loading was generated to predict the height at which these overhanging features collapse. Additionally, a distributed load was included at the top of the wall to account for the force caused by deposition. This model assumes that yielding is the dominant failure mode when walls are built at an angle from the vertical. The maximum stress experienced by the wall is calculated then compared to the measured yield stress of the material.

Figure 21 illustrates the assumptions and analysis used to predict the height at which yielding would cause collapse. Figure 21a conceptually shows the difference between the printed wall and the idealized wall assumed in this analysis, where D is the

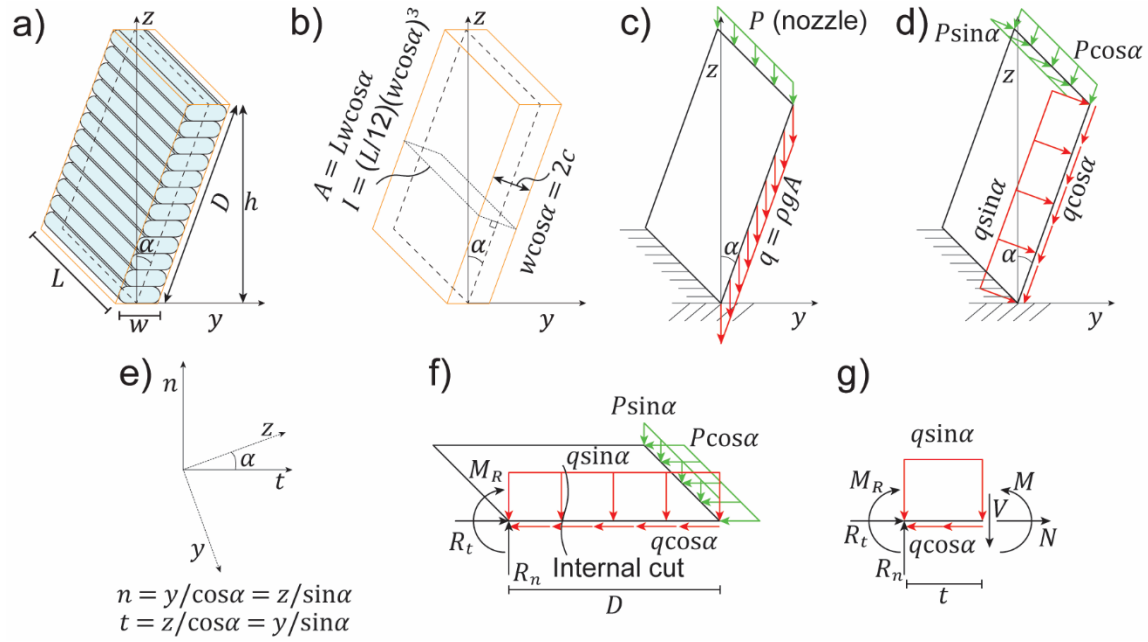


Figure 21: Analytical self-weight yielding model. a) Comparison of the printed wall and the idealized wall. b) Idealized geometry and centerline of the wall. c) Idealization of the printed wall as a beam under self-weight loading and a distributed deposition force due to the nozzle. d) Projection of the two loads into components normal and tangential to the diagonal length of the wall. e) Rotated axes. f) Rotated free body diagram. g) Free body diagram of the internal cut.

diagonal length of the wall. Figure 21b defines the idealized geometry, showing the centerline of the wall, the dimension perpendicular to the centerline ($2c$), the area perpendicular to the centerline (A), and the second moment of area perpendicular to the centerline (I). Figure 21c shows the idealization of the overhanging wall as a beam under self-weight loading ($q = \rho g A$) and a distributed deposition load from the nozzle (P), where g is gravity. Figure 21d resolves the two loads into components normal and tangential to the diagonal length of the wall. Figure 21e rotates the axes into a coordinate system that is normal (n) and tangential (t) to the diagonal length of the wall. Figure 21f shows the rotated free body diagram, which simplifies analysis of the global static equilibrium. The reaction forces and moments are found using the following equations.

$$\Sigma F_t = -PL \cos \alpha - qD \cos \alpha + R_t = 0 \quad (11)$$

$$R_t = PL \cos \alpha + qD \cos \alpha \quad (12)$$

$$\Sigma F_n = -PL \sin \alpha - qD \sin \alpha + R_n = 0 \quad (13)$$

$$R_n = PL \sin \alpha + qD \sin \alpha \quad (14)$$

$$\Sigma M_A = -PLD \sin \alpha - \frac{qD^2}{2} \sin \alpha - M_R = 0 \quad (15)$$

$$M_R = -D \sin \alpha \left(PL + \frac{qD}{2} \right) \quad (16)$$

where R_n is the reaction force normal to the wall, R_t is the reaction force tangential to the wall, and M_R is the reaction moment at the bottom of the wall. Figure 21g shows the free

body diagram of the internal cut within the wall, which allows the internal forces and moments to be calculated. Applying static equilibrium leads to the following equations.

$$\Sigma F_t = R_t - qt \cos \alpha + N = 0 \quad (17)$$

$$N = qt \cos \alpha - R_t \quad (18)$$

$$\Sigma F_n = R_n - qt \sin \alpha - V = 0 \quad (19)$$

$$V = R_n - qt \sin \alpha \quad (20)$$

$$\Sigma M_O = M - Vt - \frac{qt^2}{2} \sin \alpha - M_R = 0 \quad (21)$$

$$M = M_R + Vt + \frac{qt^2}{2} \sin \alpha \quad (22)$$

where N is the internal axial force, V is the internal shear force, and M is the internal moment. Inputting the reaction forces found from global static equilibrium and returning to the original y - z coordinate system gives the following equations for internal forces and moments.

$$N = -q(h - z) - PL \cos \alpha \quad (23)$$

$$V = PL \sin \alpha + q(h - z) \tan \alpha \quad (24)$$

$$M = \frac{-(h - z) \tan \alpha}{2 \cos \alpha} [q(h - z) + 2PL \cos \alpha] \quad (25)$$

The maximum internal axial force, internal shear force, and internal moment all occur at $z = 0$ (i.e., the bottom of the wall).

$$N_{max} = N(z = 0) = -qh - PL \cos \alpha \quad (26)$$

$$V_{max} = V(z = 0) = PL \sin \alpha + qh \tan \alpha \quad (27)$$

$$M_{max} = M(z = 0) = \frac{-h \tan \alpha}{2 \cos \alpha} (qh + 2PL \cos \alpha) \quad (28)$$

The stress experienced within the wall can be found by looking at the cross-sectional geometry of the rotated wall shown in Figure 21b. Approximating the geometry as constant along the diagonal length of each wall, the maximum internal stresses occur at the same location as the maximum internal forces and moments ($z = 0$), giving the following equations.

$$\sigma_{N,max} = \frac{N_{max}}{A} = \frac{-1}{LW} \left(PL + \frac{qh}{\cos \alpha} \right) \quad (29)$$

$$\tau_{max} = \frac{-V_{max}c^2}{2I} = \frac{-3 \tan \alpha}{2LW} \left(PL + \frac{qh}{\cos \alpha} \right) \quad (30)$$

$$\sigma_{M,max} = \frac{-M_{max}(-c)}{I} = \frac{-3h \tan \alpha}{LW^2 \cos^3 \alpha} (qh + 2PL \cos \alpha) \quad (31)$$

$\sigma_{N,max}$ is the average compressive stress that occurs over the entire cross-section of the wall that results from the axial forces caused by self-weight and deposition; τ_{max} occurs at the center of the wall; and $\sigma_{M,max}$ is a compressive stress that occurs at the bottom right corner of the wall in Figure 21a due to the moment supported in the wall. $\sigma_{M,max}$ is much greater than τ_{max} and occurs at a different location than τ_{max} . Therefore, the maximum compressive stress at the bottom right corner of the wall will be used to predict yielding collapse. Since $\sigma_{N,max}$ is also a compressive stress, it must be added to $\sigma_{M,max}$ to find the total compressive stress.

$$\sigma_{comp,max} = \sigma_{N,max} + \sigma_{M,max} \quad (32)$$

$$\sigma_{comp,max} = \left(\frac{-1}{LW^2} \right) \left[PLW + \frac{h}{\cos \alpha} \left(qw + \frac{3 \tan \alpha}{\cos \alpha} \left(2PL + \frac{qh}{\cos \alpha} \right) \right) \right] \quad (33)$$

As has been done in previous work [63], the measured shear yield stress of the material can be represented as an axial yield stress (σ_y) by assuming the material follows the Tresca yield criterion. Then the yield height can be predicted by equating the compressive yield stress to $\sigma_{comp,max}$.

$$-\sigma_y = -2\tau_y = \sigma_{comp,max} \quad (34)$$

Solving Equation 34 for h gives Equation 35.

$$h_{yield} = \frac{1}{6\rho g} \left(\frac{-6P}{w} - \frac{\rho g w \cos^2 \alpha}{\tan \alpha} + \frac{w \cos^2 \alpha}{\tan \alpha} \sqrt{\rho^2 g^2 + \frac{24\rho g \tau_y \tan \alpha}{w \cos^2 \alpha} + \frac{36P^2 \tan^2 \alpha}{w^4 \cos^4 \alpha}} \right) \quad (35)$$

For most of this work, it will be assumed that $P = 0$, which simplifies Equation 35:

$$h_{yield} = \frac{1}{6\rho g} \left(\frac{-\rho g w \cos^2 \alpha}{\tan \alpha} + \frac{w \cos^2 \alpha}{\tan \alpha} \sqrt{\rho^2 g^2 + \frac{24\rho g \tau_y \tan \alpha}{w \cos^2 \alpha}} \right) \quad (36)$$

3.4.2 Finite element model

The analytical yielding model neglects the elastic deflection of the wall that occurs during printing. However, this deflection may significantly affect the profile of the wall, since the ink exhibits such a low specific stiffness. The analytical model is not well-

suited to account for this deflection because the profile of the wall will begin to stray from a simple linear shape due to the serial printing of layers at prescribed locations, regardless of how the underlying layers have deformed. Therefore, a Python script was developed to run successive finite element (FE) analyses in ABAQUS (Dassault Systèmes, Waltham, MA) to more closely mimic the layer-by-layer printing process and more quickly and accurately predict the profile assumed by the overhanging wall.

Figure 22 conceptually illustrates the FE procedure. The deposition load is neglected for this analysis. For the first layer, a beam at angle α is loaded under self-weight, then the FE analysis is run to calculate the stress experienced by the beam and its deflected shape. Next, the FE analysis for the second layer is defined. The top node of the second layer is placed at the programmed location. The bottom node of the second layer is made coincident with the top node of the *deflected* first layer. Self-weight loading is applied only to the new layer. Again, the FE analysis is run to calculate the stress experienced by both layers of the wall and the deflected shape. The third layer follows the same routine, with the top node matching the programmed location and the bottom node merging with the top node of the *deflected* second layer. Self-weight loading is again applied to the new layer. Then, the analysis is run to calculate the deflected shape of all three layers. This procedure continues for the specified number of layers (i). This approach assumes that the rotation at each node is small, which means that the moment applied by the self-weight of each layer does not change as the wall deflects under the weight of subsequent layers. This allows the Principle of Linear Superposition to be used,

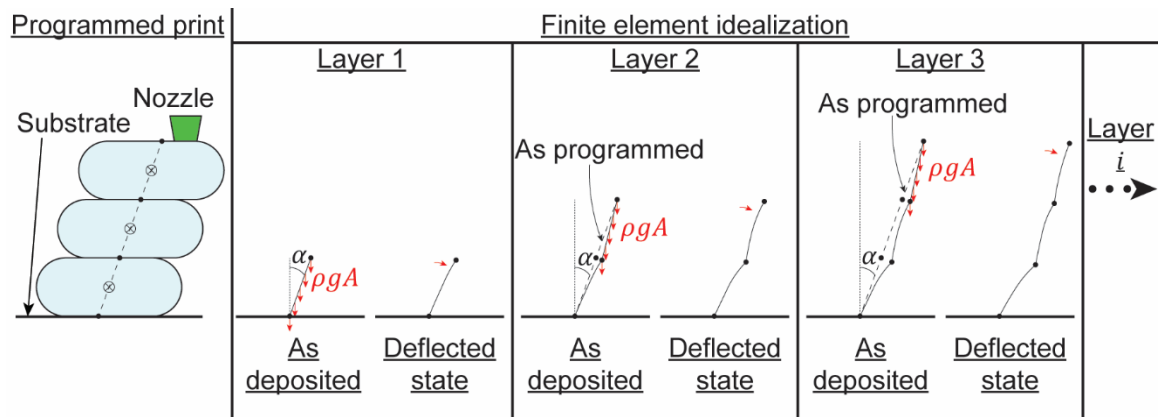


Figure 22: Finite element idealization and procedure to simulate the overhanging walls.

where the deflection caused by the self-weight of each new layer is summed to determine the total deflection experienced by the wall. Likewise, the stress caused by each new layer is summed to determine the total stress.

Each layer is discretized into ~ 10 Timoshenko beam elements, which account for the loading and deflection from both bending and shear. Timoshenko beam elements are suited for beams with a length-to-thickness ratio greater than 8/1. Of course, the length-to-thickness ratio of each wall is far below this value early in the print. However, as the print continues, the walls get closer to this ratio. The profile predicted by this simulation will be compared to experimental results to evaluate this choice of element.

This simulation was run for α between 5° and 85° at 5° increments. Table 3 lists the inputs used to run the FE analysis, where ν is Poisson's ratio. The recovered shear storage modulus (i.e., G'_{rec}) was used as the shear storage modulus (G') in the following equations because it provided the best agreement with the experimental profiles that will be shown in the Analysis and Discussion section. The compressive stiffness of the beam was approximated by assuming the plane strain modulus, then assuming isotropic behavior [50, 54, 63].

$$\tilde{E} = \frac{E}{1 - \nu^2} \quad (37)$$

$$E = 2G'(1 + \nu) \quad (38)$$

After each layer, the script outputs a text file listing all the node identification numbers, the starting position of each node, the deflection experienced by each node, all the element identification numbers, and the total stress experienced by each element, as

Table 3. Input parameters used for the FE simulations.

Layer height (mm)	Number of layers (<i>i</i>)	<i>w</i> (mm)	<i>L</i> (mm)	ρ (kg/m³)	τ_y (Pa)	G' (Pa)	ν
0.4796	130	5	60	1,202	928	17,084	0.25

well as the parameters used in the analysis. These files are read into MATLAB (The MathWorks Inc., Natick, Massachusetts) to plot the deflection of the wall. The deflected profile after each layer is determined by opening the corresponding text file, reading the original position and deflection for each node, then summing those values. The maximum stress in the wall is determined by extracting the stress accumulated in the bottom element of wall. Yielding initiation and wall collapse is assumed when the total stress in the bottom element of the wall exceeds $2\tau_y$ (the Tresca yield criterion).

3.4.3 *Analytical self-weight buckling model*

When $\alpha = 0$, self-weight buckling can cause collapse [62-64]. Equation 39, which was developed in the previous chapter [63], will be used to predict buckling of vertical walls ($\alpha = 0$) and provide context for the collapse height of walls with $\alpha \neq 0$.

$$h_b = \left(7.8373 \left(\frac{G'w^2}{6\rho g} \right) \left(\frac{1 + \nu}{1 - \nu^2} \right) \right)^{1/3} \quad (39)$$

The previous chapter showed that buckling occurs somewhere between the predictions based on the post-shear and pre-shear storage moduli. Therefore, the upcoming analysis shows a “Buckling range” between collapse height predictions based on the post-shear and pre-shear storage moduli (i.e., G'_{rec} and G'_0 , respectively).

3.4.4 *Theoretical maximum angle*

Physical limitations bound the maximum α that can be achieved with the presented approach to direct ink writing. This angle will be referred to as α_{max} .

depends on the deposited geometry of the bead and the nozzle. Figure 23 illustrates how this angle is determined. Figure 23a shows the geometry of the first layer, defining the nozzle diameter (d), bead spacing ($\psi_y d$), and layer height ($\psi_z d$). ψ_y is defined as the spreading factor, and ψ_z is the compression factor. Figure 23b shows the shallowest angle (i.e., α_{max}) that will cause the material extruded for the subsequent layer to miss the bead on the previous layer. Figure 23c shows a detail view of the geometry that defines α_{max} . In the described experiments, ψ_y was set to 1.375, and ψ_z was set to 0.55. Using these values in the trigonometric relation in Equation 40 gives $\alpha_{max} = 65.15^\circ$.

$$\alpha_{max} = \tan^{-1} \left(\frac{(d/2)(\psi_y + 1)}{\psi_z d} \right) = \tan^{-1} \left(\frac{\psi_y + 1}{2\psi_z} \right) \quad (40)$$

3.5 Results

3.5.1 Geometric fidelity

For each programmed α , Figure 24 shows how the measured value of α evolved as new layers were deposited. For clarity, only one print is shown for each value of α . Early in the print, the measured value of α was noisy for all the prints. After layer 10, all the prints stabilized to a plateau value of α . This plateau was longer and flatter for smaller values of α . This figure shows that the measured α did not match the programmed α , falling slightly below the intended value and creating a wall that was closer to vertical than expected. In fact, the discrepancy between the programmed and measured α increased as programmed α increased. The plateau regions ended with a large spike in the measured α ,

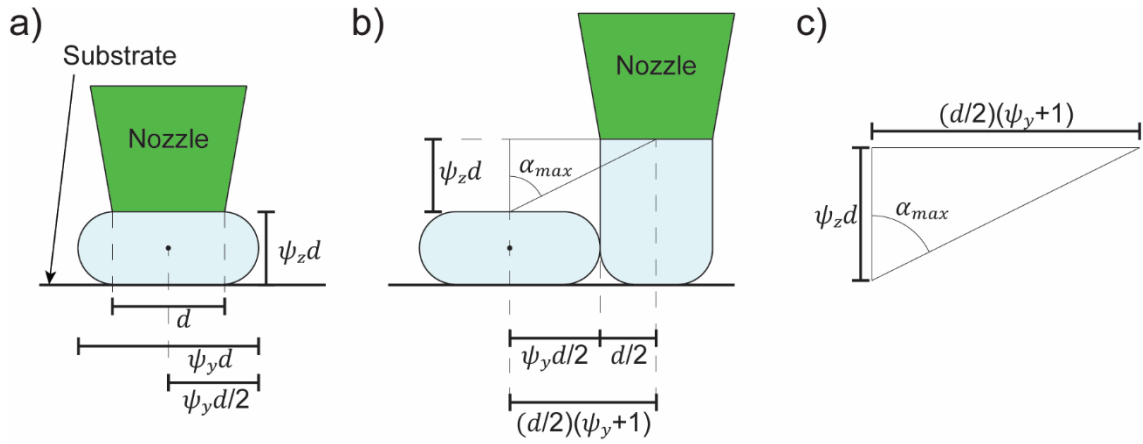


Figure 23: Conceptual diagram used to determine α_{max} . a) Deposited geometry of the bead and the diameter of the nozzle for the first layer. b) Geometry of the shallowest angle that causes a bead on the second layer to entirely miss the bead on first layer. c) Detail view of the geometry that defines α_{max} .

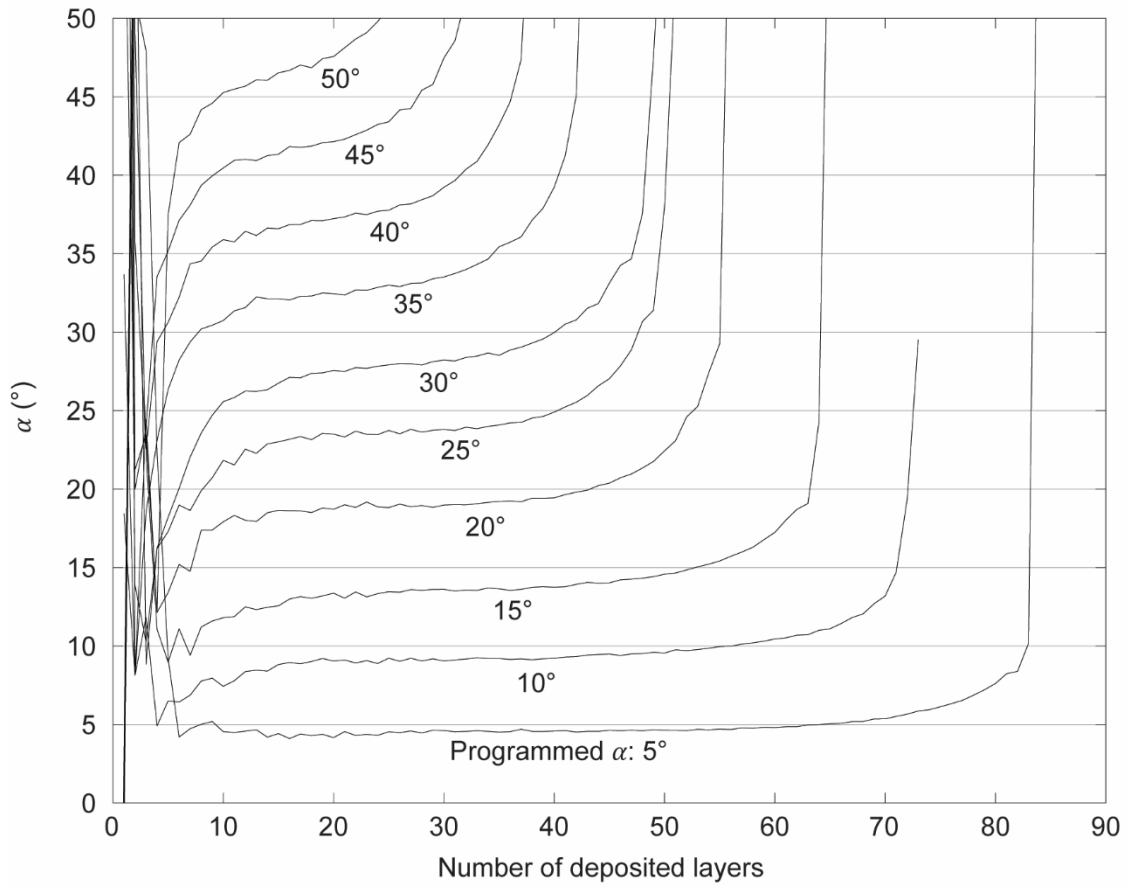


Figure 24: Evolution of measured α during printing.

corresponding to collapse of the wall. The values of α within the plateau region were averaged to calculate a single α value for each print that will be used to plot the collapse height versus α . The entire data set and the plateau region used to calculate an average value can be found in Figure 58 of the appendix. Although the theoretical maximum α that could be reached with the present setup is 65.15° , a programmed α of 50° was the greatest angle successfully printed here. When the programmed angle was increased to $\alpha = 55^\circ$, new layers contacted the previous layer, but rolled off and landed on the print bed.

A plot like the one shown in Figure 24 can be generated with w on the y -axis (Figure 59 of the appendix). Similarly, the values of w within the plateau region can be averaged to calculate a single w for each print. Figure 25 plots w for all the recorded prints. Bead spacing, layer height, and the translation speed of the nozzle were all held constant, and the pressure was kept as consistent as possible. However, the measured thickness of the walls appears to trend upwards as programmed α increases. The measured values of w fall between 4-6 mm. Therefore, w was set to 5 mm when generating predictions from the analytical model.

3.5.2 *Collapse height versus α*

Figure 26 plots collapse height predictions versus α . The analytical and FE yielding models are nearly identical and predict that yield height will decrease significantly as α increases. The buckling range intersects the yielding predictions between $\alpha \sim 5^\circ$ and 10° . A vertical line indicating α_{max} , the theoretical bound of α , is also shown.

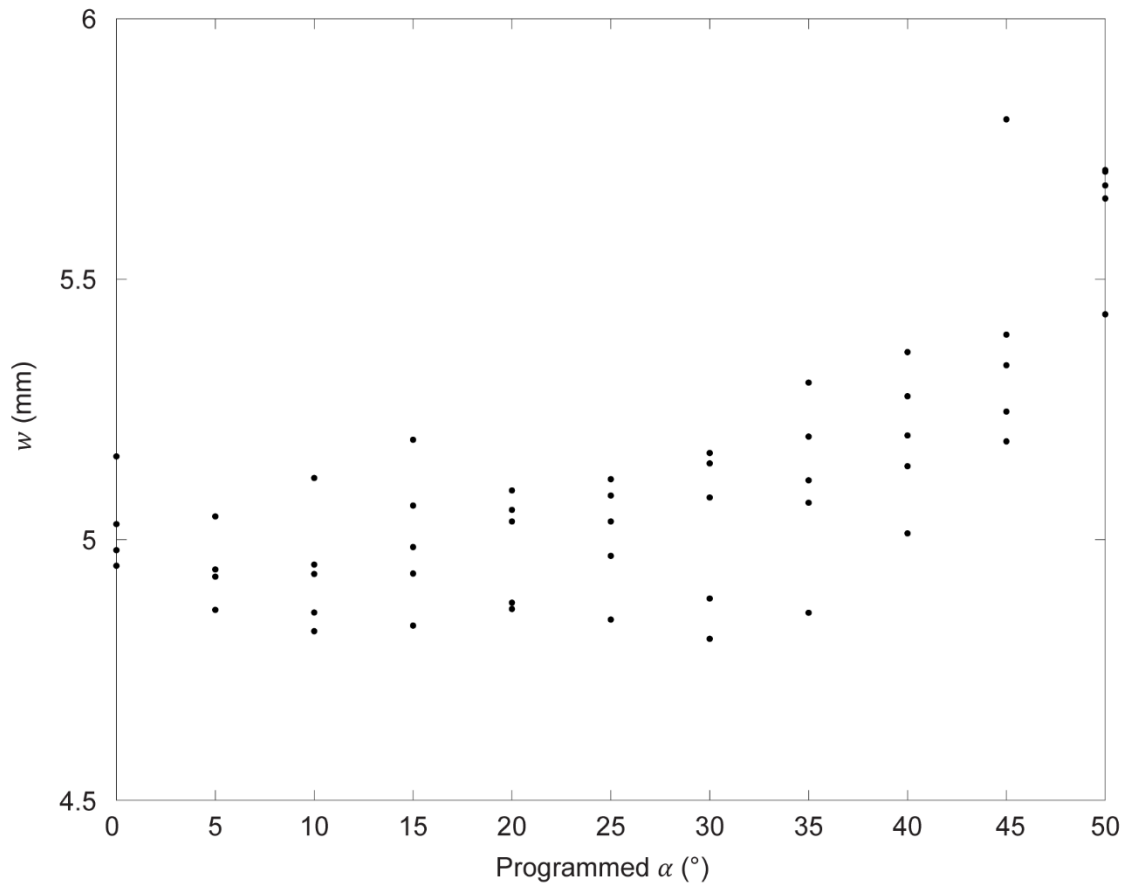


Figure 25: Measured thickness versus programmed α for all recorded prints.

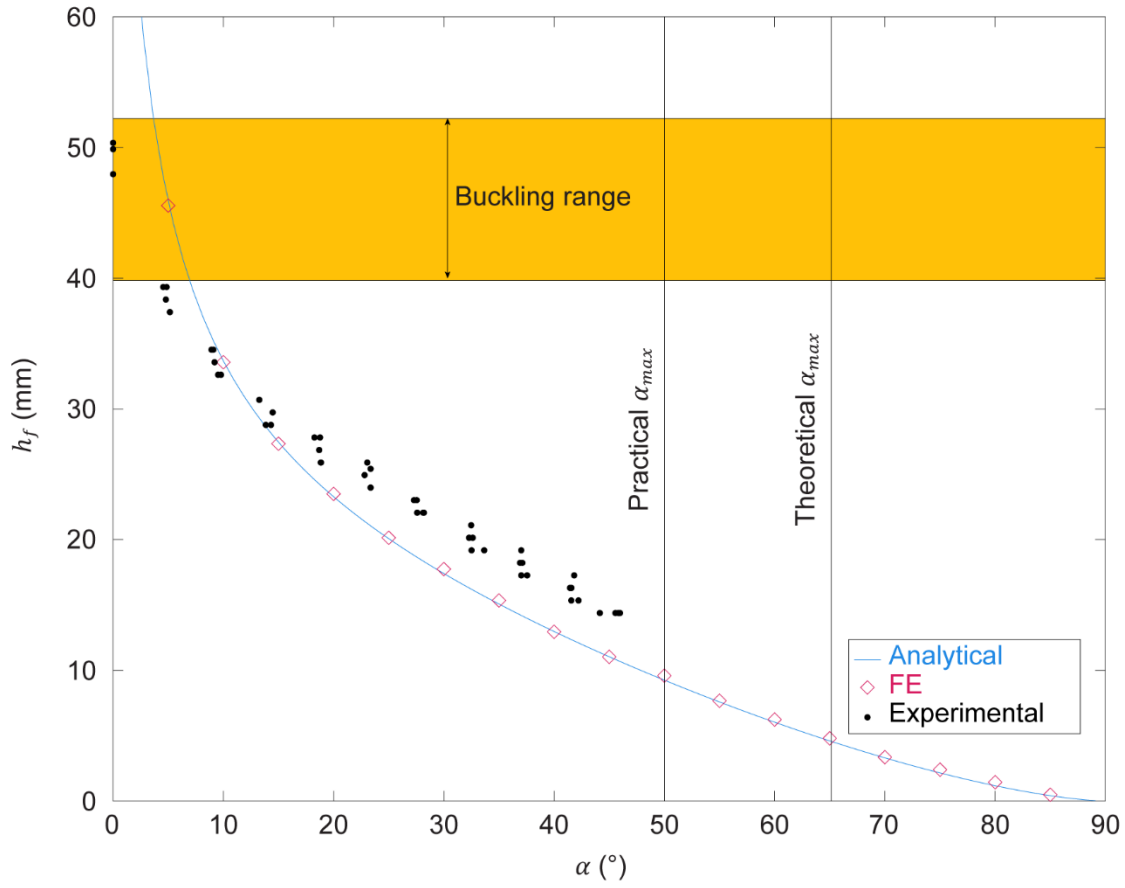


Figure 26: Collapse height versus α . The analytical yielding prediction, the FE model, the buckling range, the theoretical bound of α , the practical limit of α , and the experimental data are shown.

Figure 26 also plots the experimentally observed collapse height versus *measured* α . Overall, the predictions match the experimental data reasonably well, but some discrepancies are noted. The vertical walls ($\alpha = 0^\circ$) collapse within the range predicted by the buckling model. At $\alpha = 5^\circ$, the walls collapse at a height below both the yielding and buckling predictions. For α between 10° and 50° , the walls collapse at heights close to those predicted by the analytical and FE yielding models, with the yielding models generally underestimating collapse height. 50° was the largest *programmed* α that could be printed, which is 15.5° less than the theoretical bound. Figure 60 of the appendix shows the experimental data without the correcting for the *measured* α .

3.6 Analysis and discussion

3.6.1 Limitations on geometric fidelity

The results revealed limitations on the geometric fidelity of printed overhanging features. The measured α was generally less than the programmed α prior to collapse. Considering the way that beads compressed may explain these inconsistencies. Each layer of the walls consisted of four adjacent beads. Three of those beads landed directly on top of the previous layer, whereas the fourth bead made incomplete contact and was partially unsupported. This difference in boundary conditions caused the partially unsupported or “overhanging” bead to spread less than the other three, creating the mismatch between the programmed and measured α . This can be seen in Figure 27, which superimposes parallel lines at the programmed angle over three prints at $\alpha = 10^\circ$,

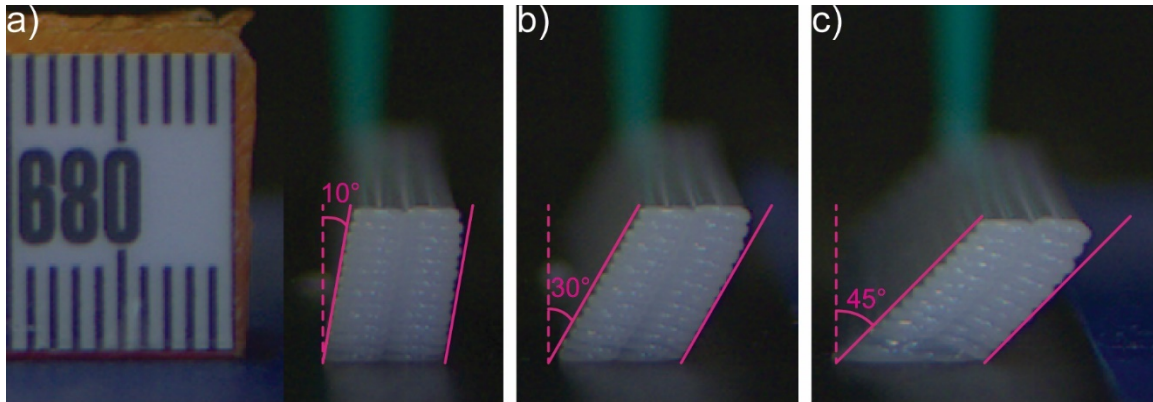


Figure 27: Images comparing the programmed α to the observed α . Walls after deposition of the fourteenth layer of a) $\alpha = 10^\circ$, b) $\alpha = 30^\circ$, and c) $\alpha = 45^\circ$ are shown. The dotted line is vertical. The solid lines are parallel to each other and are drawn at the programmed angle.

30°, and 45°. The left side of the wall, which consisted of beads that make full contact with previous layers, matched the programmed angle. However, the upper right corner of the walls, which are made up of overhanging beads, exhibited a smaller α than the programmed value. Since the centerline is calculated based on both sides of the wall, this behavior caused the mismatch between the programmed and measured angle. A more focused study linking the deformation of deposited layers to rheological properties, like that done by Mollah et al. [105], could provide a way to predict and correct for this discrepancy, but that subject warrants its own study and is left to future work.

The overhanging bead is also believed to have affected the measurement of w . w trended upward with increasing α , even though the print parameters were held constant. As α increased, the overhanging bead had less support and began to sag, adding to the observed thickness of the previous layer or layers. Figure 28, which shows four prints at different α , illustrates this behavior. The solid black line indicates a layer interface. The dotted pink line shows the corresponding measured thickness. At $\alpha = 0^\circ$, layer interfaces were parallel to the print bed. As α increased, layer interfaces became angled due to the described sagging behavior. Since the thickness was measured along the horizontal, the overhanging bead inflates the apparent thickness of lower layers. Extending the work done by Mollah et al. [105] to address the unique boundary conditions caused by printing at an angle may provide a way to predict and correct for this behavior.

The sagging behavior also limited the maximum value of α that could be achieved. Walls with programmed α values above 50° could not be printed because the

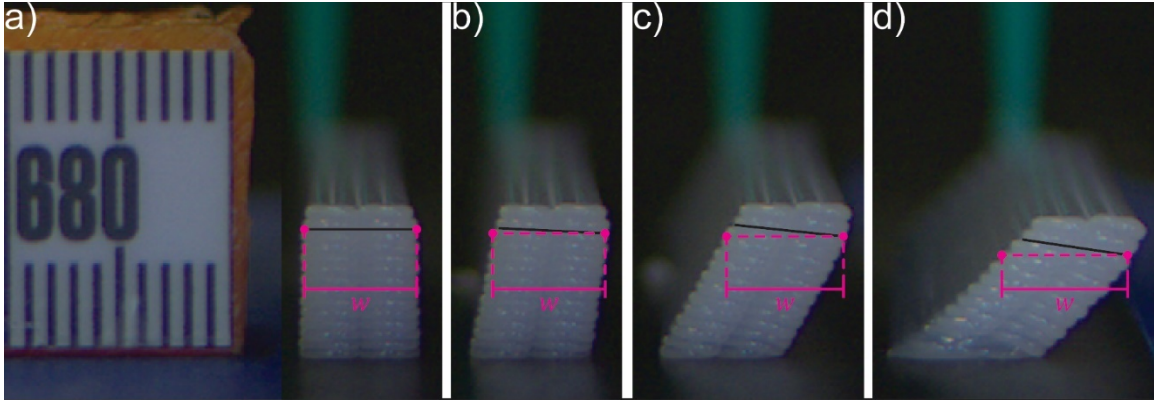


Figure 28: Illustration of the relationship between α and the measured thickness. Walls after deposition of the fourteenth layer of a) $\alpha = 0^\circ$, b) $\alpha = 10^\circ$, c) $\alpha = 30^\circ$, and d) $\alpha = 45^\circ$ are shown. The layer interface is indicated in black. The measured thickness is shown in pink.

overhanging layer sagged all the way to the print bed. Using a robotic arm or a machine with more than 3 degrees of freedom to control the approach angle of the nozzle [74, 79-83] could potentially help to mitigate this behavior and allow printing of greater angles by changing the geometric limits outlined in Figure 23.

3.6.2 Evaluation of the collapse height predictions

The FE model was based on the Principle of Linear Superposition. This convenient assumption enabled the stress and deflection caused by the self-weight of each layer to be calculated separately then summed together. In reality, the stress caused by the self-weight of previously deposited layers is magnified by the deflection caused by the deposition of new layers. If this non-linearity was incorporated in the FE model, then the predicted yield height would decrease.

Eccentric buckling is believed to have caused collapse of the 5° wall prior to reaching the predicted yield height. Tilting a wall by a small angle does not eliminate buckling behavior. Rather, small angles excite buckling at even lower heights, potentially explaining why the wall collapsed below the buckling range. This observation suggests that buckling, or a combination of buckling and yielding, is the limiting factor and will cause failure in this range.

Figure 26 shows that for α greater than 10°, the experimental collapse height of the walls exceeded the predicted yield height. The predicted yield height refers to the *initiation* of yielding within the wall, where the stress experienced at the outer edge of the wall exceeds the yield stress. More stress is required to cause the entire cross-section of

the wall to yield and develop a “fully plastic” zone, suggesting the wall can support deposition of layers even after it has begun to yield. For a beam with a rectangular cross-section in pure bending, this difference is often analyzed by comparing the moment that causes the initiation of yielding (M_{yield}) to the fully plastic moment (M_P) [106], which can also be represented in terms of stress:

$$\frac{M_P}{M_{yield}} = \frac{3}{2} \rightarrow \sigma_P = \frac{3}{2} \sigma_y \quad (41)$$

where σ_P is the stress created by the fully plastic moment and σ_y is the yield stress, as described previously. Since this relation is only valid for beams in pure bending, it is not directly applicable to the overhanging wall, which experiences combined axial loading and bending under self-weight. To determine the relative magnitudes of these stresses, Figure 29a plots the maximum axial and bending stresses at h_{yield} as a function of α . This plot shows that the magnitude of the axial stress becomes much smaller than the bending stress as α increases, enabling the stress state to be *approximated* as pure bending. This allows calculation of the fully plastic height (h_p) using the relationship in Equation 41 for σ_P . First, the equation for $\sigma_{comp,max}$ in Equation 33 must be truncated to include only the stresses caused by bending (i.e., pure bending). To do this, the axial loading caused by self-weight and stresses caused by P are removed from Equation 33 which simplifies to

$$\sigma_{bend} = \frac{-3qh^2 \tan \alpha}{Lw^2 \cos^3 \alpha} \quad (42)$$

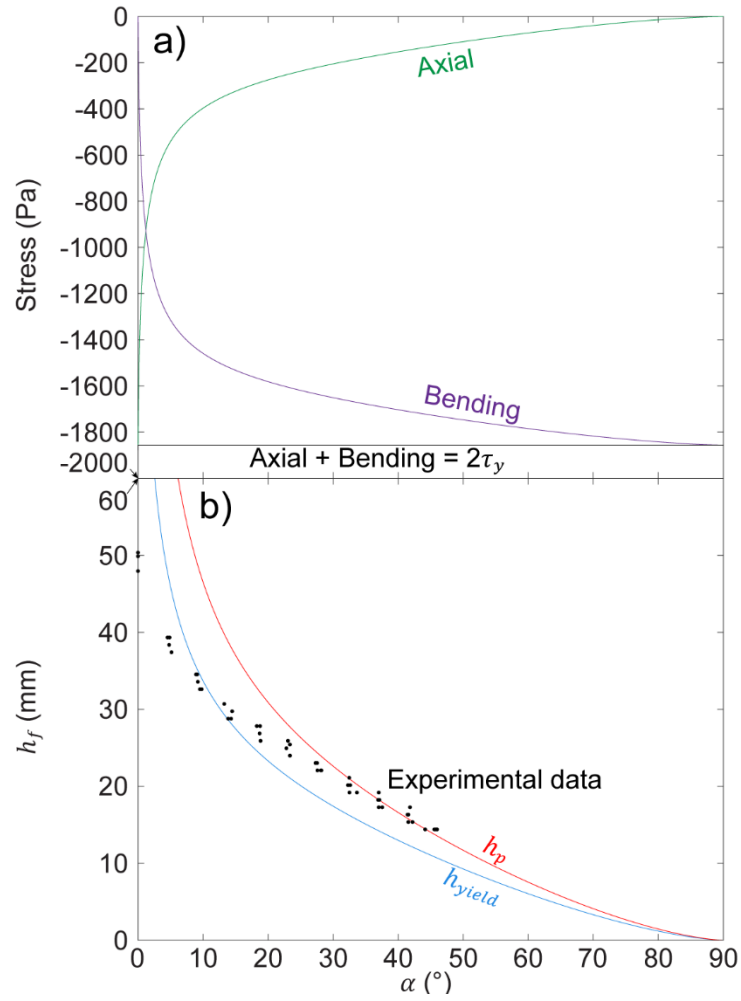


Figure 29: Fully plastic analysis. a) Comparison of the axial and bending stresses at the yield height. b) Comparison of the predicted fully plastic height to the predicted yield height and experimental data.

where σ_{bend} is the pure-bending stress caused by self-weight. Then the fully plastic height can be calculated by setting σ_{bend} equal to $-\sigma_P$ and solving for h .

$$\sigma_{bend} = -\sigma_P = -\frac{3}{2}\sigma_y = -\frac{3}{2}(2\tau_y) = -3\tau_y \quad (43)$$

Using the geometry and values for q , solving for h , and taking the positive value of the square root solution gives

$$h_P = \sqrt{\frac{w\tau_y \cos^2 \alpha}{\rho g \tan \alpha}} \quad (44)$$

Figure 29b compares h_P to h_{yield} and the collapse height data. The h_P prediction is much closer to the experimental data at large α than the h_{yield} prediction. This finding suggests that the discrepancy between the experimental data and the h_{yield} prediction is at least partially caused by the difference between the initiation of yielding and the development of the fully plastic stress.

Several variables in the model used to predict the yield height (Equation 35) are uncertain, including w , ρ , τ_y , and P . These variables may have also contributed to the mismatch between the predictions and experimental data. Rudimentary sensitivity studies help evaluate these potential causes of this error. Figure 30 shows how the predicted yield height varies with w , ρ , τ_y , and P .

Figure 25 shows that the walls are between 4 and 6 mm thick. Figure 30a shows that this level of uncertainty does not move the predictions significantly closer to the experimental data. The thickness would have to be approximately double the nominal thickness (i.e., $w = 10$ mm) to encompass all the data. Therefore, the variation in

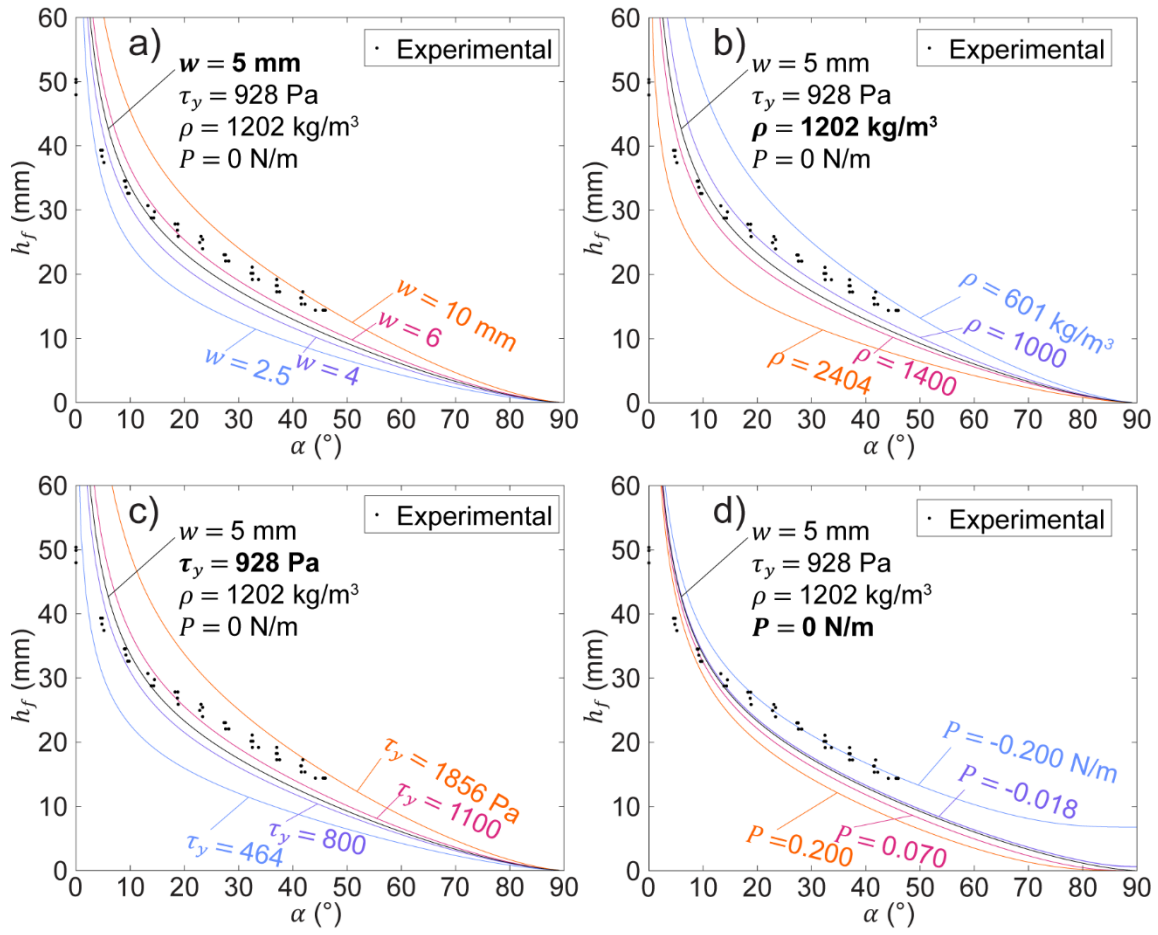


Figure 30: Sensitivity of the analytical model to uncertain variables. a) Sensitivity to w . b) Sensitivity to ρ . c) Sensitivity to τ_y . d) Sensitivity to P .

thickness is unlikely to be solely responsible for the difference between predictions and observations.

Ink formulation is another source of uncertainty. This could affect the density of the material. Figure 30b shows the sensitivity of the predictions to density. Small changes in the density between 1000 and 1400 kg/m³ do not account for the difference between predictions and data. The density would need to be half of the measured value (i.e., $\rho = 601 \text{ kg/m}^3$) to make the predictions match observations at the greatest overhang angle tested. At this density the material would float in water, which was not observed in Romberg et al. [63]. The uncertainty in the density measurement cannot be solely responsible for the gap between predictions and observations.

Variations in ink formulation, shear history, and recovery time can all affect the shear yield stress. Figure 30c shows the sensitivity of the predictions to τ_y . Small changes in the shear yield stress between 800 Pa and 1100 Pa do not significantly change the predictions. The shear yield stress would need to be doubled (i.e., $\tau_y = 1856 \text{ Pa}$) to encompass all the data. This explanation is stronger than the previous two. Dinkgreve et al. [101] noted and studied the many different ways to measure the yield stress of complex fluids. The “intersection power-law” method (used by Romberg et al. [63] to get the value of 928 Pa) is not the most conservative estimate of the shear yield stress, but there are other methods that result in higher values. It is plausible that the effective τ_y is double the value used to create the prediction shown in Figure 26. However, the data and model predictions show that the yield stress would have to vary systematically with

overhang angle in order for predictions to match experimental data. Clearly this is not realistic, and thus the uncertainty in the shear yield stress measurement is probably not the only cause for the mismatch between predictions and experiments.

The deposition force, P , has been set to 0 N/m for all the previous analyses. However, P can assume either a positive or negative value and its effect on predictions can be observed. Before addressing how the predictions react to changes in P , the physical meaning of P and the range of possible P values will be discussed.

As defined by Figure 21, a positive P value represents a downward force per unit length on the top edge of the wall. To achieve the bead geometry described in Figure 23a, the newly deposited bead must be compressed against previous layers, which results in a downward force on the wall. Duty et al. [37] proposed Equation 41 to estimate this compressive force.

$$F_{comp} = \frac{\pi}{\Delta h^2} \eta Q \left(\frac{Q}{vd} - \Delta h \right) \quad (45)$$

where η is the viscosity of the material and Q is the volumetric flow rate given by

$$Q = \pi \left(\frac{d}{2} \right)^2 v \quad (46)$$

The fumed silica ink is known to be shear thinning [8], meaning the viscosity depends on the shear rate. The shear rate can be approximated using the Rabinowitsch-corrected equation for shear rate [37, 107]:

$$\dot{\gamma} = \frac{4Q}{\pi \left(\frac{d}{2} \right)^3} \left(\frac{3n+1}{4n} \right) \quad (47)$$

where n is the shear-thinning exponent. Hmeidat et al. [8] reports n to be between 0.03 and 0.25. Choosing $n = 0.25$ provides the lowest estimate of shear rate, which gives the highest estimate of viscosity and leads to the highest estimate of F_{comp} . $n = 0.25$ gives a shear rate of 400 1/s, which is far above the range tested by Hmeidat et al. [8]; therefore, the closest data point, at $\dot{\gamma} = 100$ 1/s, is used to approximate η as 100 Pa.s. The viscosity versus strain rate curve of fumed silica ink is monotonically decreasing, meaning that 100 Pa.s is an overestimate of the viscosity experienced in the current experiments. Using these approximations in Equation 45, F_{comp} is calculated to be 0.004 N. Dividing this force by the length of the wall, L , P_{comp} is found to be 0.070 N/m. At early stages of the print, when the deflection is small and the wall is relatively stiff, this may be a reasonable estimation of the downward force on the wall as a result of the extrusion process.

As new layers are deposited and deflection grows, P would be expected to decrease. The top of the wall moves away from the nozzle as the wall deflects away from the programmed location, which can be seen in the video in Attachment 5. This means that the new layers towards the top of the wall experience less compression against previous layers than those near the bottom of the wall. At some point before collapse, the top of the wall deflects far enough away from the nozzle to completely eliminate the compression of the newly deposited material. Beyond this point, it is hypothesized that the material exiting the nozzle acts as a tensile member that pins the wall to the nozzle and provides a small amount of additional support. In this scenario, P assumes a negative value. The current experimental setup does not provide a way to measure the force

experienced by the material, so it is difficult to confirm whether the new material is indeed supporting a tensile load. However, insight is gained by calculating the maximum tensile force that an extruded cylindrical bead could support:

$$F_{tens} = -\sigma_y A_{bead} = -(2\tau_y) \left(\pi \left(\frac{d}{2} \right)^2 \right) \quad (48)$$

where A_{bead} is the cross-sectional area of the bead. For the given parameters, $F_{tens} = -0.001$ N. Dividing this force by L , $P_{tens} = -0.018$ N/m.

Now that the magnitude of P has been estimated, its effect on predictions can be addressed. Including a positive deposition force representative of the compression applied by the newly deposited bead ($P_{comp} = 0.070$ N/m) moves the predicted yield height even further below the experimental data. This force does not contribute to yielding because it only occurs early in the print, before the wall begins to deflect away from the nozzle. Additionally, at these early layers, the internal stress experienced by the wall is not close to reaching the yield stress.

A null or upward deposition force is much more appropriate based on how the shape of the bead evolves in the video in Attachment 5. A P value representative of the tension that can be statically supported by the newly deposited bead ($P_{tens} = -0.018$ N/m) moves the predictions slightly closer to reality, but a large gap still remains. The deposition force would need to reach -0.200 N/m (more than 10 times the force that can be sustained by the cylindrical bead) to match the data. Therefore, it is unlikely that this is the sole reason for the mismatch between predictions and experiments.

Individually, none of these uncertainties fully explain the observed behavior. However, they are all active simultaneously. When all the uncertainties are combined, it is possible that they could have caused the small difference between the predictions and the observed behavior, but the difference between the initiation of yielding and the fully plastic stress offers a much more convincing argument.

3.6.3 *Deflected shape*

The profile predicted by the FE model is compared to the results for programmed α values of 5°, 25°, and 45° in Figure 31. The FE model was adjusted to simulate a wall printed at the measured α rather than the programmed value. These images reveal excellent agreement between the FE model and the observed profile, while illustrating the difference between the programmed α and the measured angle. The first column shows the walls before any deflection is detectable. As α increases the difference between the measured and programmed α can be seen. The second column shows the profiles in a deflected state, with excellent agreement between the FE model and experimental profile. The third column shows the profiles at the last layer that the FE model matches the experimental profile. The fourth column shows the experimental profile moving away from the FE model, and the last column shows the collapsed wall. The FE model assumed elastic conditions and did not incorporate any yielding behavior. Between the layers shown in the third and fourth columns, the wall is believed to have begun yielding, causing the migration away from the calculated profile. This finding supports the argument that the walls can accommodate deposition for several layers after yielding and

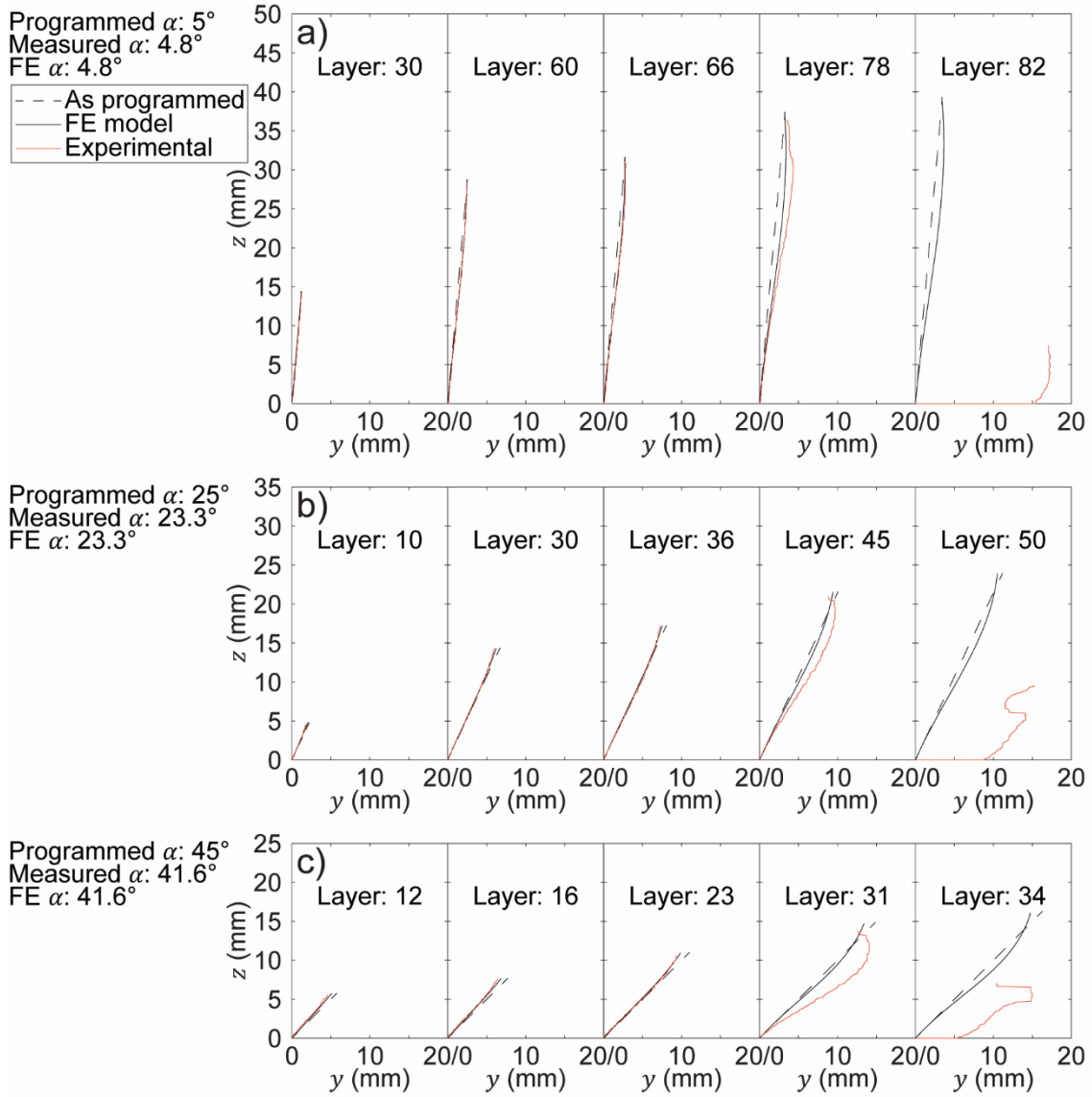


Figure 31: FE model compared to the experimental and as-programmed profiles. a) As-programmed $\alpha = 5^\circ$, b) 25° , and c) 45° .

before reaching the fully plastic stress, helping to understand the discrepancies between predicted yield height and the actual collapse height. Attachments 6-15 are videos that show the profile evolution for every non-zero α . Attachments 16-26 compile the raw images for one sample at each α . In addition, the results shown in Figure 31 are reproduced in Figure 61 of the appendix with the y-axis scaled to highlight the lateral deflection.

The FE model used Timoshenko beam elements, which assume a length-to-thickness ratio greater than 8/1. Most of the walls printed here do not reach that ratio before collapsing. Therefore, the Timoshenko beam elements underestimate the amount of deflection that occurs between each layer. This model also assumes that the Principle of Linear Superposition applies. This approach neglects additional moments caused by previously deposited layers as the wall rotates under the self-weight loading of the new layer. However, the excellent agreement between the FE profile and experimental profile suggests that the error caused by these underestimates is not significant.

Regardless of the inherent errors, the FE model is a significant improvement upon an analytical deflection model that does not account for the nonlinear profile that is caused by layer-by-layer deposition. This simple FE model provides a new design approach that allows the profile of the wall to be compared to geometric tolerances prior to printing. Several modifications would make this tool even more useful, but significantly more material characterization would be required. The accuracy of the model could be improved by accounting for the nonlinear stresses induced by the

deflection of the wall rather than approximating using the Principle of Linear Superposition. Yielding and post-yielding behavior could be added to better understand the behavior between initial yielding and collapse. To improve understanding of printing with an in-process curing mechanism, adding the ability to incorporate time-dependent material properties would help tailor curing kinetics to suppress unacceptable levels of deflection.

3.7 Conclusion

This work has focused on expanding the understanding of the link between rheological properties and the structural stability of thermoset inks by modeling and printing overhanging structures with a direct ink writing system. Thermoset inks were successfully printed at prescribed overhang angles up to 50° , and yield height predictions were generated with analytical and FE models that assumed elastic-plastic material behavior and used the shear yield stress and storage modulus as inputs. The analytical model assumed that the wall maintained a linear profile until yielding, whereas the FE model updated the profile of the wall based on the elastic deformation experienced between layers. Even though they assumed different profiles, both models predicted nearly identical yield heights.

For overhanging angles between 10° and 50° , the yield height predictions were shown to agree reasonably well with the collapse height observed in experiments. Smaller overhanging angles appear to be governed by eccentric buckling, falling near the buckling prediction developed in previous work. Overhang angles larger than 50° are

impossible simply due to geometric constraints of the 3-axis print platform and the reduced ability of this ink to maintain its deposited shape with partial support. These findings demonstrate that the collapse height and printability of overhanging walls can be predicted using rheological properties and rudimentary beam mechanics under the assumption of elastic-plastic material behavior.

Small differences between the predicted yield height and collapse height were observed. Analysis of the fully plastic moment showed that the wall can resist a small but significant amount of weight after the outer edges of the wall started yielding. Additionally, sensitivity studies were conducted on the variables input into the analytical yield height prediction. The variables included the thickness of the wall, the density of the ink, the yield stress of the ink, and the force between the deposition nozzle and the wall. Analysis showed that it is unlikely that any one of these variables is the sole cause of the discrepancies, but when combined may contribute to the mismatch.

Along with predicting the yield height, the FE model was used to predict the profile of the wall. Before yielding, the FE model accurately predicted the profile of the wall by calculating and enforcing the elastic deformation of the wall prior to depositing the next layer. This approach can be used as a design tool to compare the deflected shape with geometric tolerances. This information is critical for tailoring in-process reaction mechanisms that suppress levels of deflection that fall outside required geometric tolerances (which, for example, may be dictated by a target through-thickness compressive strength for a printed honeycomb).

The results and analysis presented here will form the basis for the design of new materials and process controls to enable large-scale, out-of-plane, and conformal printing of low-density cellular structures with high geometric fidelity by guiding rheological targets for inks as well as the design of in-process curing mechanisms. Chemical initiation is one promising in-process curing technique and will be the focus of the following chapters.

**4 CHAPTER 4: LARGE-SCALE REACTIVE THERMOSET
PRINTING: COMPLEX INTERACTIONS BETWEEN
TEMPERATURE EVOLUTION, VISCOSITY, AND CURE
SHRINKAGE**

A version of this chapter was originally published by Stian K. Romberg, Christopher J. Hershey, John M. Lindahl, William Carter, Brett G. Compton, and Vlastimil Kunc [42]:

Stian K. Romberg, Christopher J. Hershey, John M. Lindahl, William Carter, Brett G. Compton, and Vlastimil Kunc. “Large-scale additive manufacturing of highly exothermic reactive polymer systems.” *SAMPE Journal* 55 (2019): 8-13.
<https://doi.org/10.33599/nasampe/s.19.1616>.

This article was revised in several ways for reproduction in the current form. This dissertation reports an array of wall printing experiments, whereas the original article presented only one. Additional mechanical and thermomechanical characterization is reported here. The main text was reorganized to include this new experimentation. Figures were modified to fit within the margins and improve font visibility. The introduction and conclusion were edited to relate the current article to the previous and subsequent chapters. S.K. Romberg designed the experimental setup for printing walls; conducted the printing, data capture, and analysis; fabricated the mechanical and thermomechanical samples; conducted the mechanical and thermomechanical experiments; generated the figures; and wrote the article. C.J. Hershey designed and conducted the rheological and adiabatic experiments. He also contributed to writing the article. J.M. Lindahl acquired the machine, taught S.K. Romberg how to use the machine,

and helped edit the article. William Carter setup the infrared and optical vision systems. B.G. Compton helped to conceptualize the wall printing experiments, how to analyze these experiments, and was the primary editor of this article. V. Kunc helped obtain the funding for this work and assisted in editing the article.

4.1 Abstract

Thermoset feedstocks show promise for AM applications to address some of the limitations of the more widely used thermoplastic materials. Thermosets offer attractive mechanical properties while providing excellent interlayer bonding, high thermal and chemical stability, and reduced energy consumption as a result of deposition at room temperature. However, at the heights demanded by large-scale AM, thermosets have been shown to be unstable against their own weight. A large-scale printer, called the RAM system, has been developed which chemically initiates the crosslinking reaction of the thermoset just before deposition. This approach is intended to address stability issues by strengthening and stiffening previously deposited layers against the weight of newly deposited layers. In this work, thin, vertical walls with varying layer time and convective conditions were printed on the RAM system with a peroxide-initiated vinyl ester resin. Infrared (IR) and optical cameras were used to observe the thermal evolution and stability of these walls. These studies proved chemically initiated thermoset printing feasible on the large scale, but also revealed interactions between rheological, thermal, and chemical behavior that affect printability. Self-weight collapse remains possible at short layer times, whereas warpage is observed at very long layer times. Additionally, a new

behavior was discovered in which the heat generated by the reaction of previous layers causes un-gelled layers to flow. By describing and categorizing these phenomena in the context of large-scale thermoset AM with in-process curing for the first time, this work provides a foundation for more rigorous studies of the complex interplay between rheological, thermal, and chemical behavior. Further, results and analysis indicate a path to selecting appropriate layer times and convective conditions to ensure successful printing of large-scale chemically initiated thermoset materials. These findings suggest that developing less exothermic material formulations may enable more flexible printing. Evaluation of the tensile modulus of a printed wall reveals anisotropy between the longitudinal (3.79 GPa) and transverse (2.95 GPa) directions. The tensile strength follows the same pattern with longitudinal strength of 36.11 MPa and transverse strength of 18.83 MPa. The glass transition temperature of the printed material is found to be 93.13°C. These mechanical and thermomechanical properties are comparable to vinyl ester resins processed in other ways.

4.2 Introduction

Thermosets may address some of the issues that have been observed while printing thermoplastics on the large scale. However, the previous chapters demonstrated the instability in thermoset printing that has hindered its realization on the large scale. In the present work, through collaborations between ORNL, Magnum Venus Products, and Polynt-Reichold, the RAM was used to characterize the large-scale printability of thermoset feedstocks that are chemically initiated during printing. The RAM platform

mixes composite vinyl ester resin with a chemical initiator (organic peroxide) to begin the curing process just before deposition. Gelation, designed to commence shortly after deposition, counteracts the self-weight instability that limits the stable height of uncured thermoset inks. However, successful printing may be hindered by a large mismatch between curing rates and layer times, as well as the heat generation and shrinkage associated with curing. Seeking to understand these fundamental challenges, we have developed a simple experimental setup which varies layer time and convective conditions while monitoring print stability, thermal history, and layer height of thin printed walls. This work proves the feasibility of chemically initiated thermoset printing on the large scale, identifies key phenomena governing print success, and presents techniques to improve printability. Categorizing the relevant failure modes and ways to address them is a critical first step in modeling these behaviors and understanding the parameters that affect this new approach to large-scale printing. This research also presents preliminary evaluation of the glass transition temperature and the anisotropy in the mechanical properties of large-scale printed thermosets to provide context for the applicability of this processing approach.

4.3 Experimental methods

4.3.1 Printing platform and material system

ORNL and Magnum Venus Products have led development of the world's first large-scale thermoset printer, called the RAM system (Figure 32a) [39, 42, 43]. The RAM system houses a 2.4 m x 4.9 m print bed that can accommodate printed structures

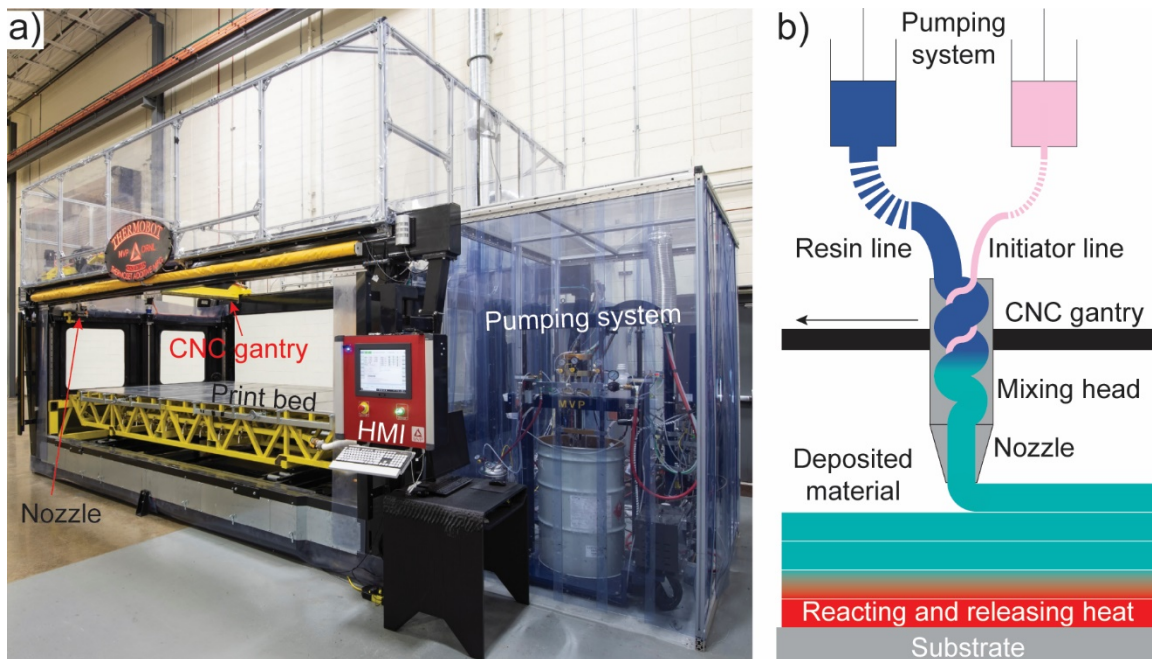


Figure 32: The RAM printer. a) Picture of the RAM system showing the print bed, human machine interface (HMI), and pumping system. b) Conceptual diagram of the RAM system illustrating pumping, chemical initiation, and deposition.

up to 1 m in height. The gantry can translate in the horizontal x - and y -directions up to 1,270 mm/s while the print bed can translate in the vertical z -direction up to 13 mm/s. The nozzle diameter currently ranges from 1.27 to 7.62 mm. As illustrated in the conceptual diagram in Figure 32b, the resin and initiator are pumped separately from a remote location through feedlines (~20 m long) into the mixing head. At the mixing head, the materials meet and mix, initiating the crosslinking reaction. Immediately after mixing, the material flows through the nozzle and is deposited as a bead onto the print bed. Then, the initiated material proceeds to crosslink, generating heat as the exothermic reaction progresses.

In this study, the RAM printing system was used to print a glass-fiber-filled vinyl ester resin, called EX-1520 (Polynt-Reichold, NC), initiated with NOROX CHM-50 (United Initiators, Pullach, Germany). NOROX CHM-50 is a solution of cumene hydroperoxide in an accelerating phlegmatizer [108]. The resin-to-initiator mixing ratio was set at 50:1 (by volume). Table 4 displays the print parameters used in this study.

EX-1520 is the developmental predecessor to the commercially available PRD-1520 resin (Polynt-Reichold, NC). The findings presented here motivated changes to the resin and initiator to improve printability of the commercial material.

4.3.2 Chemical and rheological characterization of the material system

A dynamic temperature sweep of uninitiated resin was conducted on a Discovery Hybrid Rheometer-2 (DHR-2) (TA Instruments, New Castle, DE) with 25 mm disposable aluminum parallel plates. Adhesive-backed, 600-grit sandpaper (Saint Gobain Abrasives,

Table 4. Selected print parameters.

Nozzle diameter (mm)	<i>x-y</i> speed (mm/s)	<i>z</i> speed (mm/s)	Flow rate (kg/h)	Bead spacing (mm)	Layer height (mm)
5.08	68.58	13.00	6.70	6.99	2.79

Worcester, MA) was sized, cut, and adhered onto the parallel plates to promote surface adhesion and prevent slip between the resin and parallel plates. A very small amount of initiator is required for reaction; therefore, the pre-gel rheology is expected to be closely approximated by the uninitiated resin. In addition, strain-controlled, dynamic, isothermal curing measurements of the initiated resin were conducted at room temperature and 60°C on the DHR-2. The room temperature measurement was used to corroborate the manufacturer-reported room temperature gel time, $t_{g,RT}$. The 60°C measurement was used to approximate the gel time at 60°C, $t_{g,60}$.

The adiabatic curing temperature was measured following a procedure called the adiabatic temperature rise described by Pannone and Macosko [109, 110] (Figure 33). Initiated material was extruded from the RAM system into an insulated 500-mL polystyrene cup for 4 minutes (which amounts to ~0.45 kg of material). A J-type thermocouple was placed at the center of the inner cup to record the temperature. The insulation provided by the extruded material, the two cups, and the insulative packing between the cups was expected to produce approximately adiabatic conditions at the thermocouple. The time and corresponding temperature of the thermocouple were recorded using an SD-947 SD Card Data Logger Thermometer (Reed Instruments, Wilmington, NC).

Volumetric shrinkage of the EX-1520 was determined by measuring the specific gravity before and after crosslinking. Specific gravity was measured on an XS204 analytical balance (Mettler-Toledo, LLC, Columbus, OH) using the Archimedes method

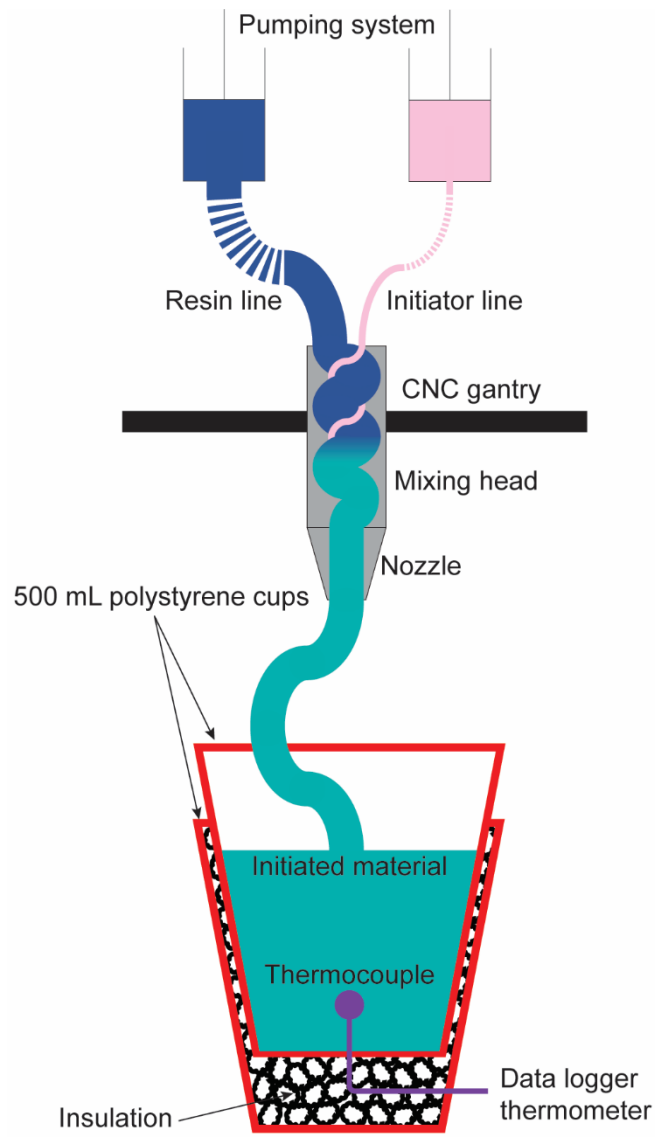


Figure 33: Adiabatic curing temperature experimental setup.

and ASTM D792 for reference [111]. To eliminate voids, the uncured material was spun in a dual asymmetric centrifugal mixer (Flacktek Inc., Landrum, SC). The hydrophobic nature of the resin allowed the Archimedes method to be used to measure the specific gravity of the uncured resin.

4.3.3 *Stability experiment*

Thin-wall specimens with end supports were built two beads wide and 914.4 mm in length (Figure 34). Walls of varying layer time (LT) with identical geometry were printed under constant translation speed and volumetric flow (Table 4). 0.68-, 2.25-, 4.50-, and 6.50-minute layer times (LT_{0.68}, LT_{2.25}, LT_{4.50}, and LT_{6.50}, respectively) were tested. The LT_{0.68} wall was printed continuously, whereas the LT_{2.25}, LT_{4.50}, and LT_{6.50} walls required pauses between deposition of layers to produce the target layer time. The nozzle was purged at the end of these pauses to ensure the material experienced the same amount of time in the mixing head before deposition onto the specimens. These tests were repeated under forced convection using the desktop fans shown in Figure 35a.

Positioned to observe the broad side of the wall, an A65 infrared temperature sensor (FLIR, Wilsonville, OR) captured the thermal history of each printed wall (Figure 35a). The sensor has a resolution of 640 x 512 pixels and a field of view of 45° x 37°. The sensor was placed 381 mm from the wall, centered 20 mm above the print bed, and situated to monitor the middle of the wall with a viewing window 255 mm tall. This setup resulted in a spatial resolution 2.0 pixels/mm, meaning that there are 5.6 vertical pixels on each layer. Presented IR images have been cropped to show only the top 160 mm that

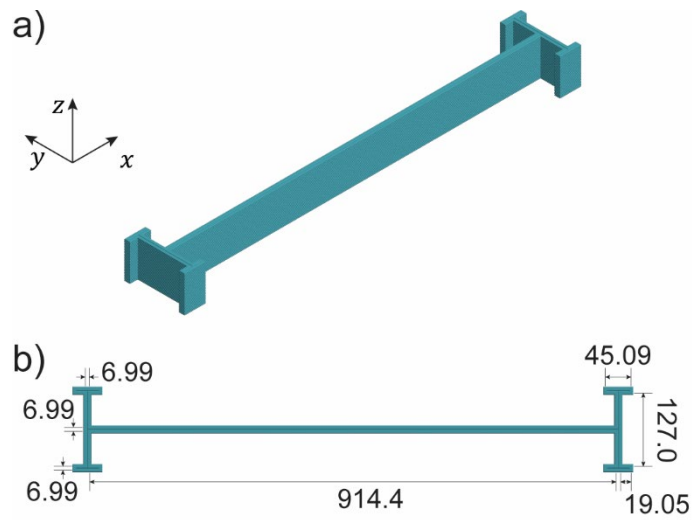


Figure 34: Thin-wall specimen geometry. a) Isometric view of the thin-wall specimen. b) Thin-wall specimen schematic with dimensions (mm).

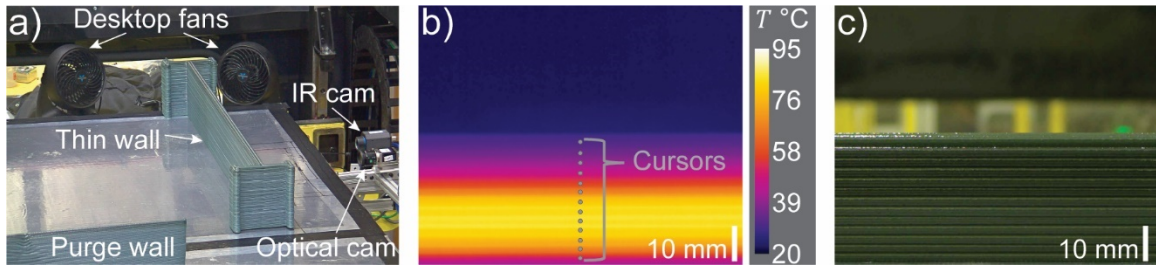


Figure 35: Thin-wall stability experiment. a) Experimental setup (LT_{2.25} with desktop fans engaged). b) Cropped infrared image showing data extraction using cursors (Layer 13 of LT_{2.25} without fans). c) Cropped optical image (Layer 13 of LT_{2.25} without fans).

contain the wall. Figure 35b shows the perspective from the IR sensor. The sensor captured IR video at a rate of 1 frame/s. Using ResearchIR software (FLIR, Wilsonville, OR), cursors were placed at the center pixel of each layer to extract temperature data for each layer (Figure 35b). The temperature data was smoothed using a three-point centered moving average function in MATLAB (The MathWorks, Inc., Natick, MA). The emissivity of the material was found to be 0.84 after deposition. ResearchIR used this value to determine the temperature of the material.

As shown in Figure 35a, an acA4112-8gc optical camera (Basler, Ahrensburg, Germany) was placed next to the IR camera to monitor layer height. Figure 35c shows the perspective from the optical camera. The data acquisition rate was 12 images/layer. The optical images were used to determine the difference between the programmed wall height and the wall height before deposition of the next layer, providing a measure of flow and deformation for the given layer. For each layer, the last image before subsequent deposition was manually measured using Fiji is Just ImageJ (FIJI) [112].

4.3.4 Characterization of the mechanical and thermal properties of printed material

Mechanical specimens were fabricated from the LT_{4.50} wall that was printed under forced convection. After the end supports were removed, the remaining wall was machined with a milling bit on a computer numerically controlled (CNC) router. A plaque was produced that isolated a vertical column of beads on one side of the wall. The plaque did not include the porosity between adjacent beads in the x - y plane. Additionally, the scalloped edge on the external face of the wall (created by the round

edges of the bead) was removed. This approach was designed to minimize the porosity and stress concentrators associated with the geometry of the bead. After milling, the plaque was sanded with 400 grit sandpaper to minimize surface defects. The thickness of the plaque ranged from 1.50-2.75 mm. Cusps and sudden changes in thickness were eliminated in the milling and sanding processes.

Waterjet cutting test specimens from printed plaques is an alternative to testing as-printed specimens [113]. Waterjet cutting eliminates the stress concentrators associated with discretization of as-printed specimens [114] and allows for specimens that are non-integer multiples of the layer or bead size. Further, vinyl esters are known to withstand environments with high moisture content, like swimming pools and sewer pipes [91]. Therefore, a waterjet cutter was used to extract mechanical specimens from the plaque. ASTM standard D638 [115] served as a guide for the design of tensile specimens. The selected geometry was based on Type V specimens but incorporated a longer gage section (17.15 mm rather than 7.62 mm) to improve accuracy of the strain measured by the laser extensometer (MTS Systems Corporation, Eden Prairie, MN). As shown in Figure 36a,b, several specimens were tested in the x -direction (along the bead or “longitudinal”) and in the z -direction (across the bead or “transverse”). The figure illustrates that specimens were extracted at different heights along the wall. ASTM D5279 [116] was used as a guide to design the specimens for torsional dynamic mechanical analysis (DMA). The specimens in Figure 36c were tested in torsion about

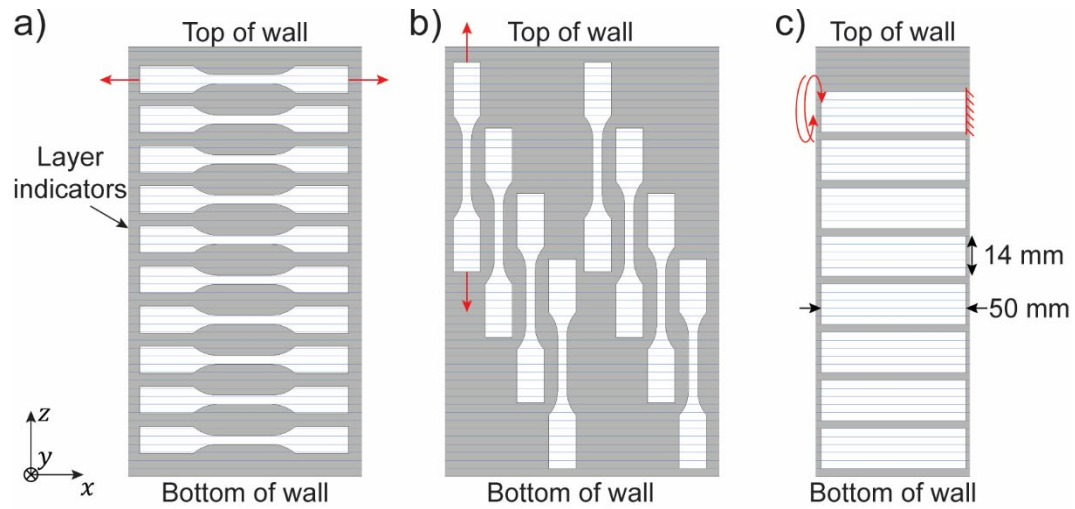


Figure 36: Extracted test specimens. a) Tensile specimens in the x -direction (longitudinal). b) Tensile specimens in the z -direction (transverse). c) DMA specimens tested in torsion about the x -axis (x - y shear).

the x -axis (x - y shear). These specimens were also extracted at different heights along the wall.

Tensile testing was conducted on a Criterion C45 electromechanical load frame (MTS Systems Corporation, Eden Prairie, MN) at an extension rate of 1 mm/min. Results of these tests provided the Young's modulus and the ultimate tensile strength (UTS) of each specimen. Torsional DMA was conducted on the DHR-2. The DHR-2 was set to apply 0.1% shear strain at an angular frequency of 10.0 rad/s. The machine was set to ramp at a rate of 2°C/min between 40°C and 140°C, while maintaining 2 N of tensile force. T_g was defined as the temperature corresponding to the peak value of the loss tangent ($\tan \delta$).

4.4 Theory

Many thermoset feedstocks can be tailored to be stable against collapse under the weight of a relatively small amount of subsequently deposited material [9, 11, 12, 16, 37, 48, 49, 64]. Formulating a thermoset resin with properties that can withstand greater self-weight imparted by taller, large-scale parts becomes challenging. Increasing the rigidity (i.e. yield stress, storage modulus, and viscosity) of the material leads to improved print stability [63]. However, this approach requires high extrusion pressures, as greater viscosity increases resistance to flow. Chemically initiated polymers provide an elegant solution to this limitation. Initiating the reaction just before deposition activates the crosslinking process during printing, enabling low resistance to flow during extrusion, but high rigidity after deposition.

In-process chemical initiation cures the material “on-the-fly,” increasing the yield stress, viscosity, modulus, and consequently, overall stability of the material. A gel time designed to keep pace with the layer time allows the previously deposited layers to stiffen and resist the weight of subsequent layers. However, the crosslinking process for vinyl ester is exothermic, which can significantly increase the temperature of the deposited material. After deposition, the resin remains un-gelled for a finite period, making the deposited material susceptible to flow due to the temperature rise caused by the warmer lower layers. Understanding the interaction of gel time, heat of reaction, and temperature dependence of rheological properties is key to determining the large-scale stability and printability of this material.

Material expansion and contraction play a role in large-scale printability. In thermoplastic printing, the coefficient of thermal expansion coupled with the significant drop in temperature after deposition drives warpage [32, 34, 36, 37]. Much like thermoplastics, thermosets experience thermal expansion, but it is driven by the exothermic reaction rather than heated extrusion. Additionally, thermosets shrink as a result of polymerization [93]. The layer-by-layer nature of material extrusion AM [2] creates a time offset between the initiation of cure between layers. This offset leads to differential shrinkage, which manifests as residual stress within the printed part. Residual stress is exacerbated by the thermal gradients caused by the energy generation during the crosslinking reaction. Depending on the magnitudes of the coefficient of thermal expansion, shrinkage, and time offset between layers (i.e., layer time), the induced

residual stress can lead to excessive warpage that causes the print to collide with the nozzle. Typically, the print is terminated at this point to avoid damaging the deposition head. Since warpage is proportional to print size, this behavior becomes more problematic at larger scales [36].

4.5 Results

4.5.1 Chemical and rheological characterization of the material system

The oscillatory temperature sweep of the uninitiated resin indicates that the complex viscosity (η^*) of the material begins to plateau to a minimum at 60°C, which will be defined as the “characteristic temperature,” or T_c (Figure 37a). At this temperature and above, the un-gelled material is least resistant to deformation and flow. The heat generated by the adiabatic reaction with CHM-50 produces temperatures greater than the characteristic temperature (Figure 37b). After 15 minutes, the temperature stabilizes at ~90°C for ~15 minutes then increases again to ~100°C. The manufacturer reports the room temperature gel time for the reaction with CHM-50 as 8 minutes, and Figure 37c corroborates this measurement. Figure 37c also shows the curing behavior at 60°C. The material starts at a lower storage modulus (G') but gels more quickly than at room temperature, revealing a gel time at 60°C ($t_{g,60}$) around 0.6 minutes. Isothermal cures at higher temperatures were attempted, but the material cured immediately upon contact with the platens. Since the temperature reaches 100°C in the adiabatic case, the apparent gel time may range from 0 to 8 minutes. This understanding guides the selected layer

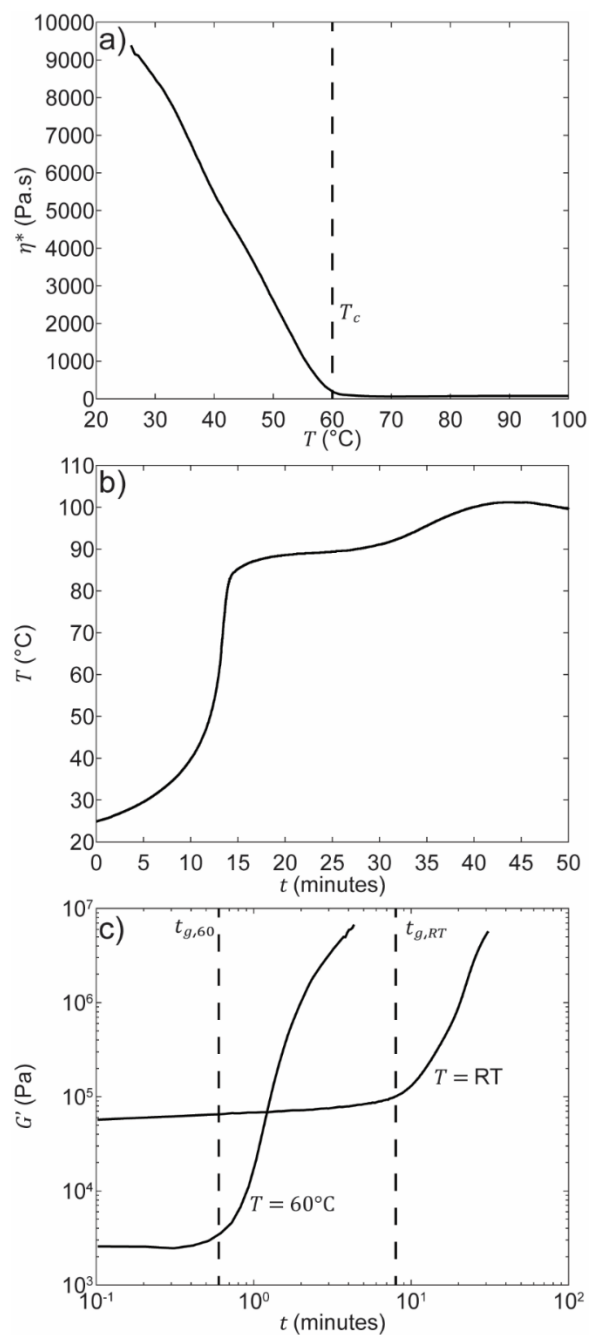


Figure 37: Thermal and rheological behavior of the EX-1520. a) The complex viscosity of the resin without initiator during a temperature sweep. b) Temperature evolution of the resin after chemical initiation under adiabatic conditions. c) Evolution of the storage modulus of the resin after initiation at room temperature and 60 $^{\circ}\text{C}$.

times, which fall between these two limits. Volumetric shrinkage associated with the crosslinking process was measured to be 8.3%.

4.5.2 Stability experiment without forced convection

The wall with the shortest layer time, $LT_{0.68}$, fell over at Layer 22 ($z = 61$ mm) (Figure 38a). The temperature in the wall was $\sim 35^{\circ}\text{C}$ when collapse occurred, well below the peak temperature in the adiabatic test (Figure 39a). The collapsed shape, which mirrored the shape presented in previous chapters, and the low temperature suggest that the layer time outpaced the gel time, allowing the wall to reach a self-weight viscoelastic instability. This behavior will be referred to as “pre-gel collapse.”

The wall with the longest layer time, $LT_{6.50}$, was terminated at Layer 25 ($z = 75$ mm) because excessive warpage caused collision with the nozzle. At the ends of the wall, upper layers were compressed and exhibited more defects than lower layers (Figure 38d). This behavior is an artifact of the part warping and moving closer to the nozzle. The print was terminated when the warpage exceeded the height of a layer, causing collision with the nozzle.

All prints that survived pre-gel collapse experienced an initial temperature spike that reached between 70 and 90°C . Before termination, the $LT_{6.50}$ wall demonstrated behavior characteristic of these chemically initiated prints that survived past the initial temperature spike (Figure 39d). Initial layers experience a delay before their temperature begins to rise. Then, in unison, all deposited layers experience an abrupt temperature

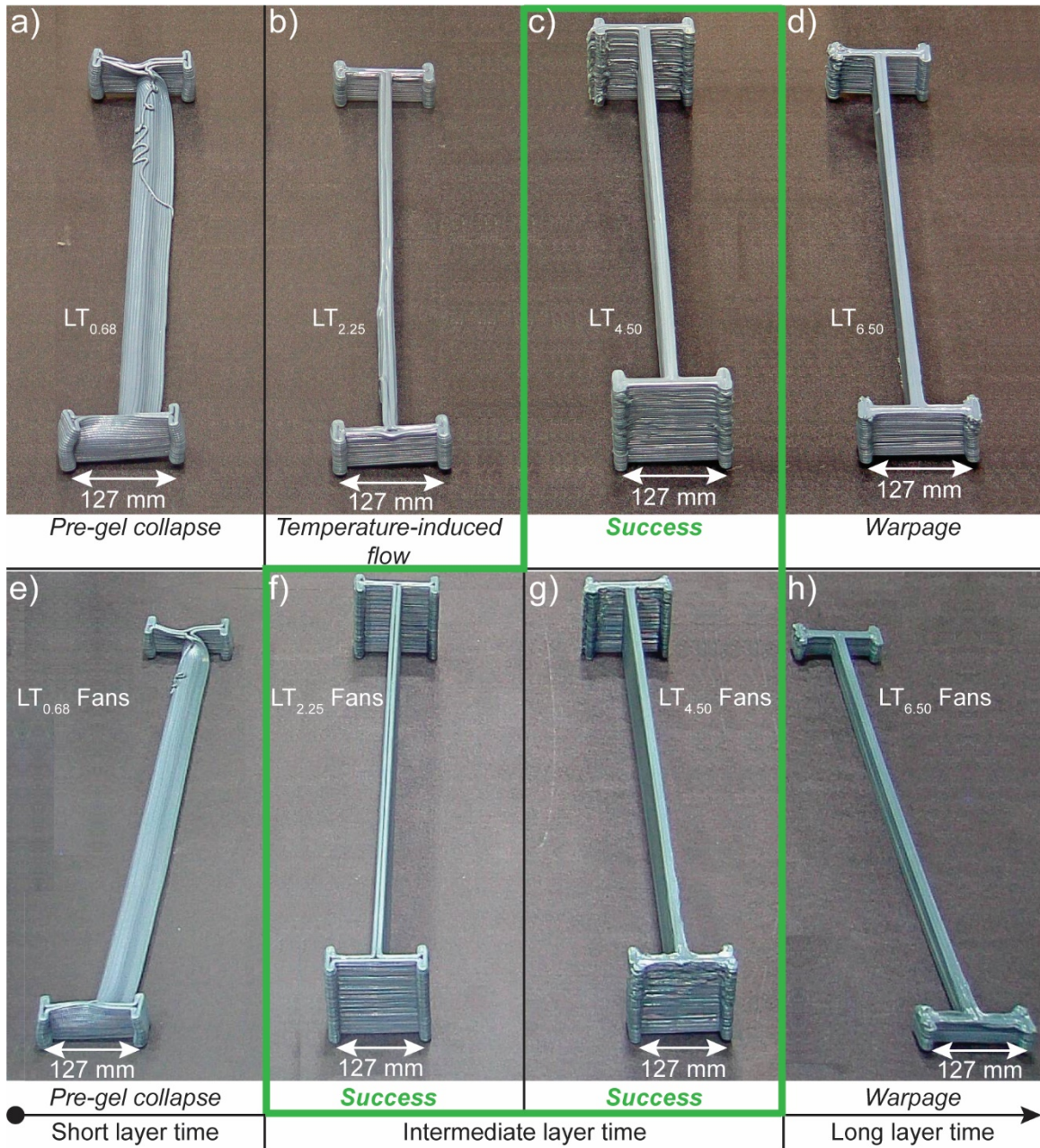


Figure 38: Results of the stability experiment. a) LT_{0.68}, b) LT_{2.25}, c) LT_{4.50}, and d) LT_{6.50} without fans. e) LT_{0.68}, f) LT_{2.25}, g) LT_{4.50}, and h) LT_{6.50} with fans.

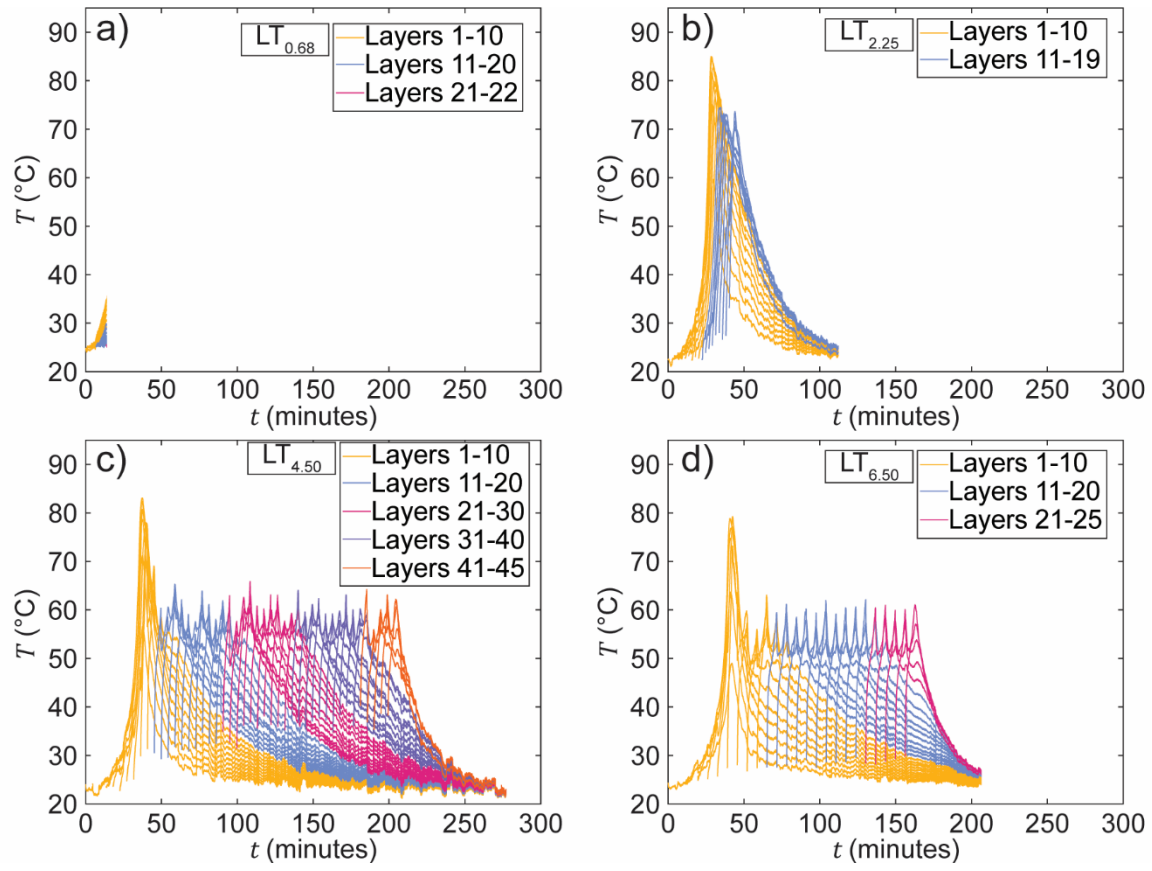


Figure 39: Temperature history without forced convection. a) $LT_{0.68}$ b) $LT_{2.25}$ c) $LT_{4.50}$ d) $LT_{6.50}$.

spike. Immediately following the spike, the temperature drops to a steady state in which all layers have nearly identical temperature histories. At this steady state, all layers experience a maximum temperature lower than the initial temperature spike. $LT_{6.50}$ mitigated viscoelastic collapse and allowed the wall to reach a thermal steady state without collapse. However, warpage caused this print to be terminated.

At the intermediate layer time, $LT_{2.25}$ (Figure 38b), the print was terminated at Layer 19 ($z = 53$ mm) when material flowed off the top surface of the print. The temperature spike, shown in Figure 39b, reached $\sim 85^{\circ}\text{C}$, which is not much greater than that observed in the $LT_{6.50}$ wall. However, the shorter layer time resulted in less time for the wall to cool before deposition of new material. The glossy finish of the top layer of the wall specimen, and the fact that the maximum observed temperature exceeded the characteristic temperature, suggest that the heat released by lower layers caused a critical loss in viscosity leading to flow. This type of behavior will be referred to as “temperature-induced flow.”

Increasing the layer time within the intermediate region to $LT_{4.50}$ alleviated temperature-induced flow, resulting in the print shown in Figure 38c. The print survived the initial temperature spike of $\sim 82^{\circ}\text{C}$ without exhibiting excessive flow. Figure 39c shows that after the initial spike the maximum temperature of each layer leveled off to a steady state around 60°C . This layer time was long enough to avoid temperature-induced flow, but short enough to avoid excessive warpage. No other failure modes were

observed as the wall reached a final height of 126 mm, indicating that a 4.5-minute layer time results in successful printing.

4.5.3 Stability experiment with forced convection

Adding forced convection did not eliminate pre-gel collapse at short layer times or warpage at long layer times. The $LT_{0.68}$ print with fans collapsed at Layer 21 ($z = 59$ mm), nearly the same height as the case without fans. The $LT_{6.50}$ print with fans collided with the nozzle at Layer 16 (45 mm), significantly earlier than the case without fans. These behaviors persisted regardless of cooling conditions, as shown in Figure 38e,h. However, the addition of forced convection eliminated the temperature-induced flow in the 2.25-minute layer time, resulting in stable printing conditions (Figure 38f). Figure 40b shows that under forced convection $LT_{2.25}$ experienced a less severe initial temperature spike ($\sim 80^{\circ}\text{C}$). Steady state was reached with the maximum temperature of each layer remaining just below 60°C . No other unstable behaviors were observed as the print reached a final height of 154 mm. With fans, printing a layer every 2.25 minutes proved slow enough to avoid self-weight collapse, fast enough to mitigate warpage, and cool enough to survive temperature-induced flow. $LT_{4.50}$ remained printable with the addition of forced convection as shown by Figure 38g and Figure 40c. Applying forced convection expanded the range of successful layer times to include both $LT_{2.25}$ and $LT_{4.50}$. IR videos of all eight walls can be found in Attachments 27-34.

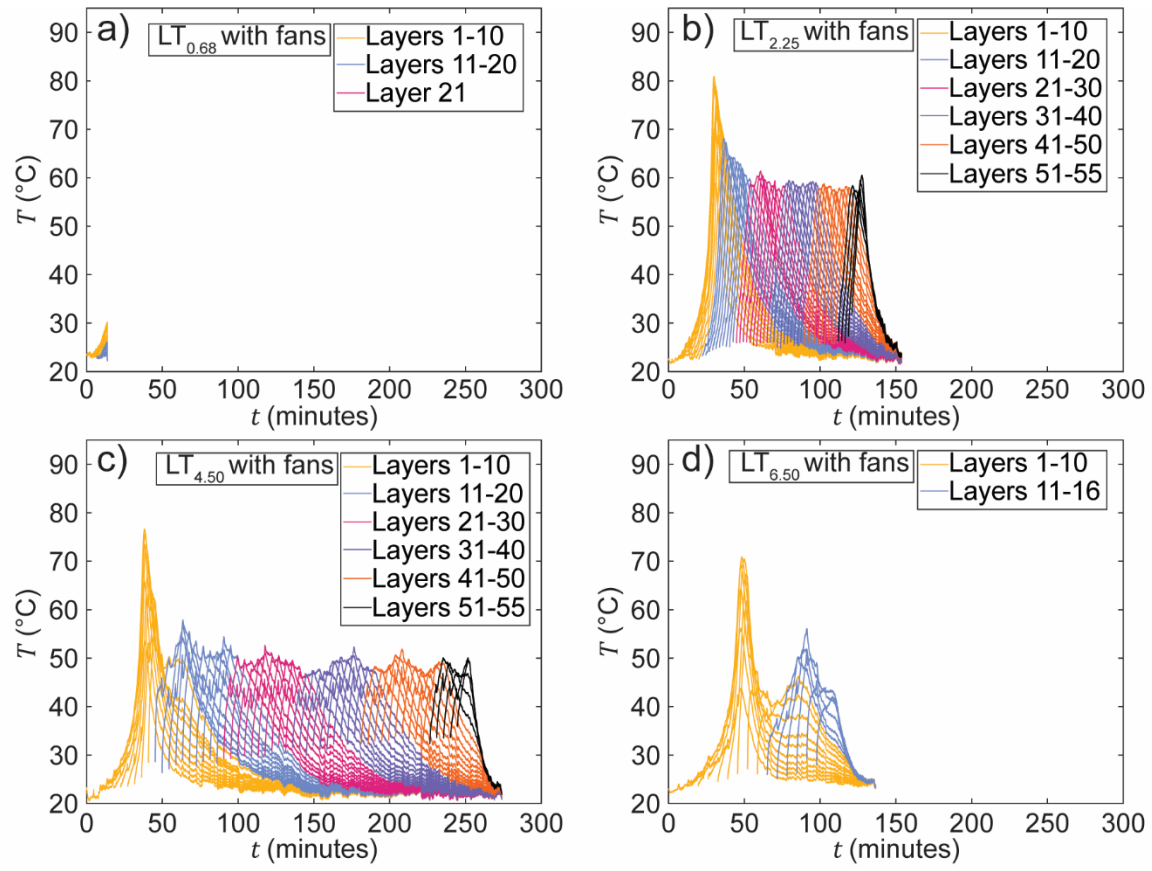


Figure 40: Temperature history with forced convection. a) $LT_{0.68}$ b) $LT_{2.25}$ c) $LT_{4.50}$ d) $LT_{6.50}$.

4.5.4 Properties of printed material

Table 5 summarizes the results from the tensile and DMA testing on the samples extracted from the $LT_{4.50}$ wall printed with forced convection. The tensile results showed notable anisotropy. The longitudinal specimens were 28% stiffer than the transverse specimens. The material was more anisotropic with respect to strength. The longitudinal specimens were 92% stronger than the transverse specimens. The torsional DMA testing revealed a glass transition temperature of 93.13°C and a shear storage modulus of 1.47 GPa at 40°C . Representative results of the tensile and DMA testing are shown in Figure 41.

4.6 Analysis and discussion

4.6.1 Viscoelastic collapse at short layer time ($LT_{0.68}$)

Walls printed with thermoset inks that do not cure during the printing process collapse under self-weight [63, 64]. The $LT_{0.68}$ wall collapsed in a similar manner. This behavior and the low maximum temperature shown in Figure 39a suggest that the deposition rate of this print outpaced the stiffening and strengthening imparted by the crosslinking reaction. Viscoelastic instability likely caused collapse of the $LT_{0.68}$ wall, indicating that this layer time is too short for crosslinking to stabilize the material against its own weight.

As expected, adding forced convection did not mitigate self-weight collapse. To avoid this failure mode, the material system must cure faster. Rather than accelerating the

Table 5: Properties of printed material.

$E - x\text{-direction}$ (GPa)	$E - z\text{-direction}$ (GPa)	UTS – $x\text{-direction}$ (MPa)	UTS – $z\text{-direction}$ (MPa)	G'_{xy} at 40 °C (GPa)	T_g (°C)
3.79 ± 0.39	2.95 ± 0.17	36.11 ± 2.24	18.83 ± 2.39	1.47 ± 0.03	93.13 ± 2.06

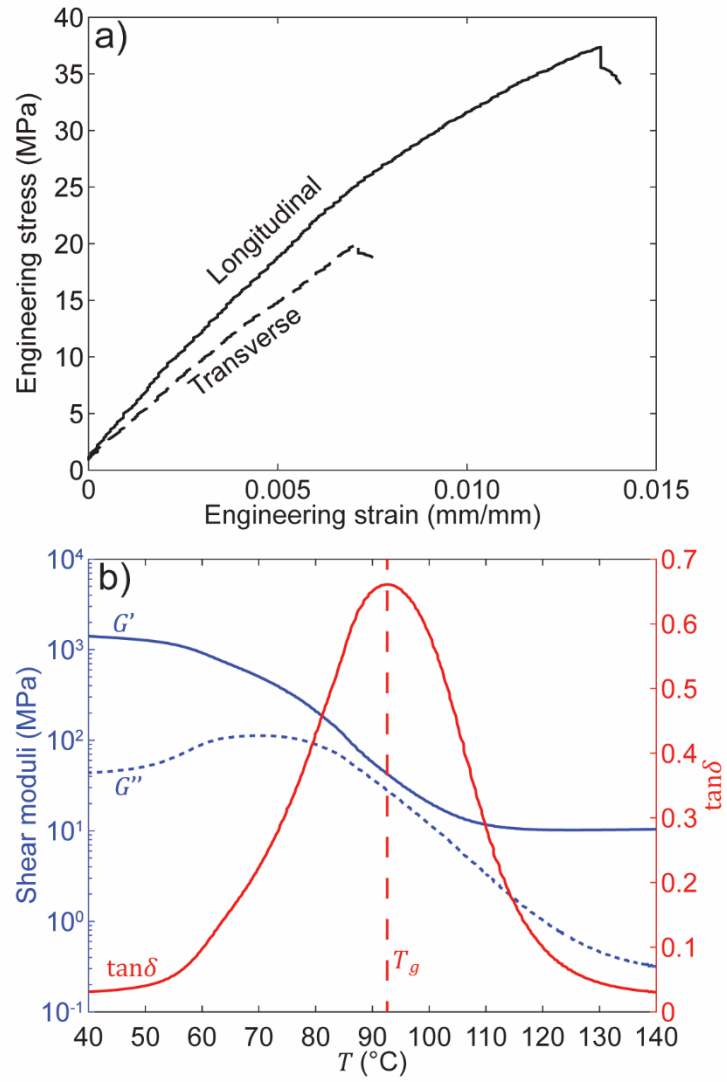


Figure 41: Representative results from the specimens extracted from the LT_{4.50} wall printed with forced convection. a) Tensile. b) DMA.

cure, forced convection decreases the temperature of the reaction (Figure 40a), slowing the reaction kinetics. This behavior places a lower limit on the layer time, restricting production rate. Material alterations may address this challenge. A different initiator could be used to induce faster gel times, which should provide support more quickly and allow faster printing. Another approach would be to reformulate the material with the goal of increasing the rigidity of the uncured material. However, a balance must be found between stability and pumpability. Although the lower limit on layer time decreases the flexibility of this system, it is unlikely to affect the applications targeted by the RAM printer, which are large objects with long layer times. In most cases, the amount of time required to deposit all the desired material is expected to exceed the lower limit on layer time.

4.6.2 Warpage at long layer time ($LT_{6.50}$)

As illustrated in Figure 39d, the $LT_{6.50}$ wall reached a steady state after the initial temperature peak, suggesting a successful print from a thermal perspective. This behavior indicates that increasing the layer time beyond the intermediate range suppressed viscoelastic collapse and temperature-induced flow. However, increasing layer time exacerbated warpage and caused termination of this print. The longer layer time allowed more curing, shrinkage, and heat release before subsequent deposition. The mismatch in shrinkage and temperature between layers led to residual stresses and warpage, which compressed the upper layers of the print (Figure 38c). After Layer 25, the warpage caused the wall to collide with the nozzle.

Applying forced convection intensified residual stresses, causing collision with the nozzle much earlier than the case without fans. Although the fans reduced peak temperature, their cooling created larger differences in temperature between layers. Figure 40d reveals a second temperature spike at 91 minutes. It is hypothesized that the additional cooling decreased the temperature enough to decelerate the reaction after the initial spike. The low temperature may have created conditions akin to the beginning of deposition where several layers react in unison, thereby causing a second temperature spike. The second temperature spike intensified thermal gradients. Between ~70-95 minutes, the LT_{6.50} print with fans (Figure 40d) exhibited larger temperature differences between adjacent layers than the LT_{6.50} print without fans (Figure 39d). Models indicate that greater temperature differences lead to greater warpage [36]. This temperature difference may have also exacerbated the warpage caused by polymerization shrinkage, as indicated by the accelerated kinetics at elevated temperature (Figure 37c).

Warpage imposes an upper limit on the layer time, restricting the scale of the print. Much like thermoplastic printing, preventing residual stress is key to overcoming scaling limitations in thermoset printing. Flexibility in resin formulation presents several potential solutions unavailable to thermoplastics. Using low-shrinkage additives to minimize shrinkage associated with crosslinking [93] is a direct remedy to warpage, but may not be feasible, depending on the chemistry and formulation of the resin. The choice of organic peroxide initiator significantly affects reaction kinetics and exothermic behavior, providing other ways to mitigate warpage. Decelerating the curing process may

reduce differential shrinkage between layers. Less exothermic material may also help to reduce thermally induced residual stress. This approach is analogous to decreasing deposition temperature or increasing ambient temperature in thermoplastic printing, which reduces residual stress and tendency to warp [34, 36, 37].

4.6.3 Intermediate layer times ($LT_{2.25}$ and $LT_{4.50}$)

4.6.3.1 Thermal profiles

The walls printed at intermediate layer times ($LT_{2.25}$ and $LT_{4.50}$) experienced unique behavior caused by the temperature-sensitivity of the resin and the heat released by the crosslinking reaction. The resin reaches a minimum viscosity at the characteristic temperature of 60°C. The reaction reaches an adiabatic temperature above the characteristic temperature (Figure 37). In the context of layer-by-layer deposition, the coexistence of these behaviors makes this material system susceptible to temperature-induced flow.

Figure 42 and Figure 43 show the thermal profile of the intermediate-layer-time walls at several snapshots in time. These figures demonstrate how temperature-induced flow occurs. The graphs on the left of each figure show the temperature as a function of height at each snapshot. These snapshots are taken after the deposition of each layer and are defined by the last layer that was deposited. For example, a curve labeled t_{13} refers to the temperature profile between deposition of Layers 13 and 14. Important snapshots are highlighted by a thicker line and a label. IR images corresponding to each highlighted curve are shown in the images on the right.

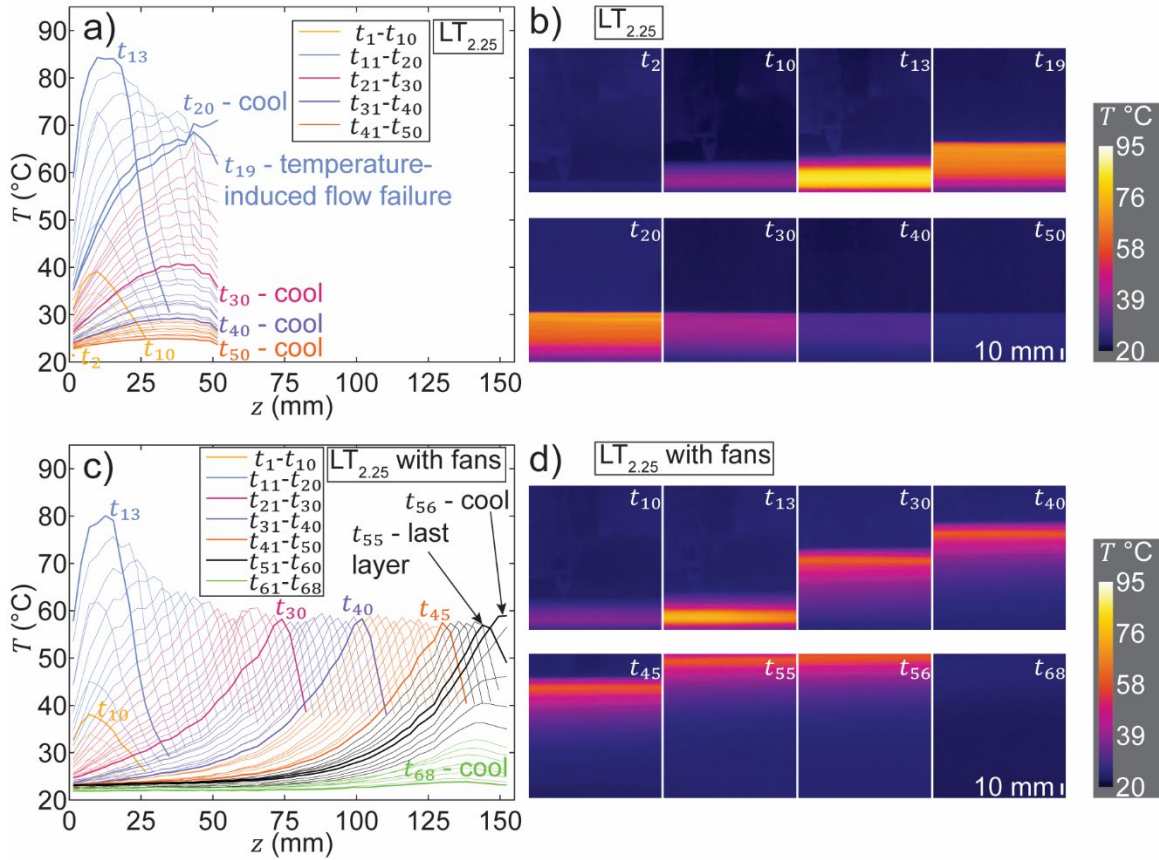


Figure 42: Spatial profile of the LT_{2.25} prints. a,c) Temperature as a function of height at snapshots in time for the LT_{2.25} prints without and with fans, respectively. Important snapshots are indicated by the bold lines. b,d) Infrared images showing the thermal gradient obtained by the infrared sensor corresponding to the important snapshots.

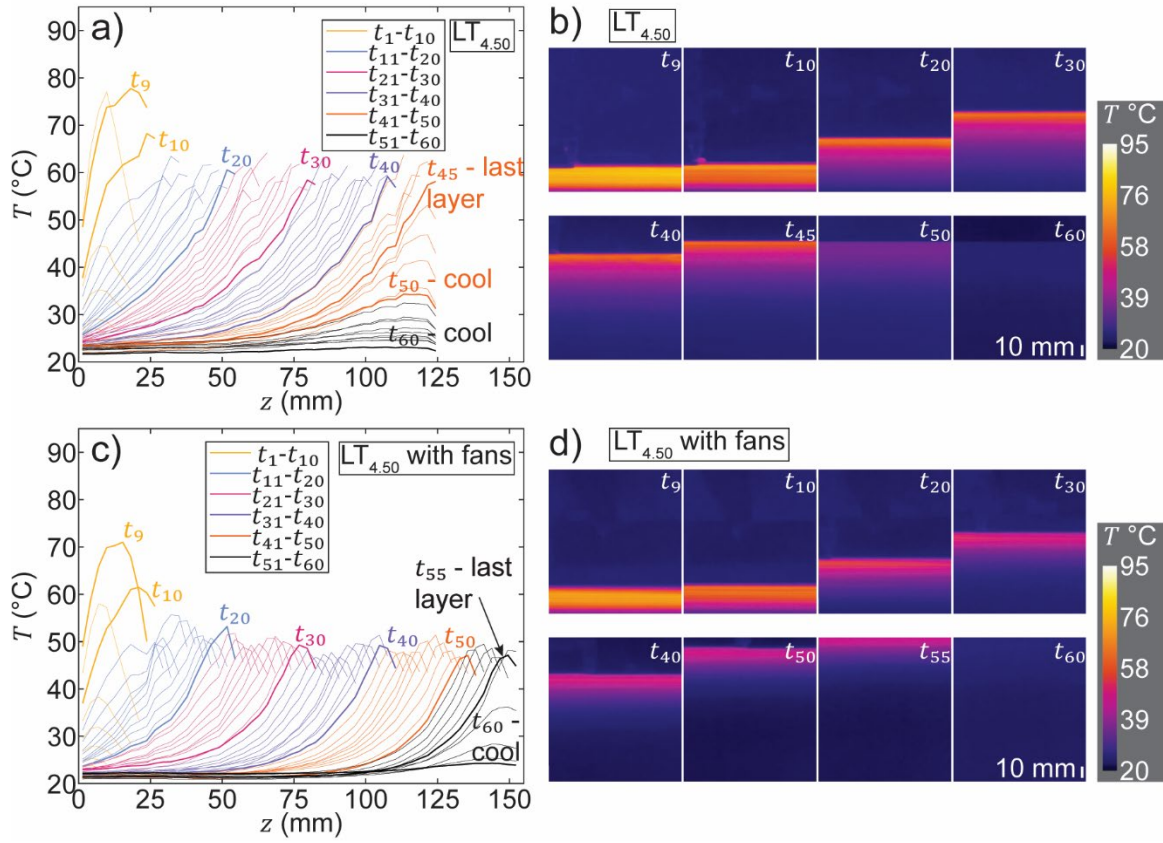


Figure 43: Spatial profile of the LT_{4.50} prints. a,c) Temperature as a function of height at snapshots in time for the LT_{4.50} prints without and with fans, respectively. Important snapshots are indicated by the bold lines. b,d) IR images showing the thermal gradient obtained by the IR sensor corresponding to the important snapshots.

The LT_{2.25} wall without fans exhibited the most extreme example of temperature-induced flow and resulted in failure. Figure 42a,b explain how this flow happened. At t_2 , heating had not yet begun. t_{10} shows the temperature of the wall increasing. The exothermic behavior created a temperature spike, causing the highest measured temperature at t_{13} . The peak temperature of t_{13} remained several layers below the top of the wall. By t_{19} the location of peak temperature had migrated up the wall, causing newly deposited, flow-susceptible layers to experience temperatures above the characteristic temperature shortly after deposition. In turn, the top layer lost rigidity and flowed off the top of the wall before it had time to gel, as demonstrated in Figure 38b. The first temperature profile after printing was halted, “ t_{20} ,” shows that the terminal layer (Layer 19, in this case) experienced a higher peak temperature than the previous layers. Newly deposited layers at room-temperature act as a heat sink for lower layers. Since Layer 20 was not deposited, the peak temperature was experienced at the top of the wall at t_{20} . Snapshots at t_{30} , t_{40} , and t_{50} show the behavior of the wall as it cools to room temperature after deposition was terminated.

Adding forced convection to the LT_{2.25} print removed heat and allowed for successful printing. Comparing Figure 42c,d to Figure 42a,b explains how this approach mitigated temperature-induced flow. Adding forced convection lowered the peak temperature at each snapshot. Additionally, the temperature at each snapshot peaked several layers below the top of the wall. With this processing change, all layers had sufficient time to crosslink before reaching the characteristic temperature. The extended

period below the characteristic temperature protected the newly deposited layers from flow, which allowed the print to reach a stable thermal steady state and enabled successful printing to arbitrary height.

Increasing the layer time to 4.50 minutes without adding fans also enabled successful printing. However, Figure 43a,b suggest that the $LT_{4.50}$ wall nearly experienced the same failure as the $LT_{2.25}$ wall. It is key to note that there is more time between each snapshot in Figure 43 than in Figure 42. The additional time between layers is responsible for several differences in behavior when compared to the $LT_{2.25}$ wall. First, the temperature spike of the $LT_{4.50}$ wall happened at a lower layer snapshot, t_9 . Further, the peak temperature was closer to the top of the wall in each snapshot. In this case, there was more time to conduct heat from lower layers to the new layer before deposition of the next layer. This plot shows several times where the top layer reached above the characteristic temperature, including t_9 and t_{10} . Even after reaching a thermal steady state, a handful of snapshots show top layers reaching just above the characteristic temperature. This behavior suggests temperature-induced flow should have caused the print to fail. However, the time between layers, which is not explicitly shown in this graph, explains how this print survived. Although the longer layer time allowed more heat to be conducted into the new layer before each snapshot, it also meant that the new layer was given more time to crosslink. The additional crosslinking is responsible for the survival of $LT_{4.50}$, despite the high temperature of the newly deposited layers. This

unintuitive behavior motivates the graphs and criterion for temperature-induced flow introduced in the next section.

Figure 43c,d shows that adding forced convection to the $LT_{4.50}$ print resulted in a more stable thermal history. Like the previously discussed prints, the $LT_{4.50}$ print with fans had an initial temperature spike followed by a steady state. However, the temperature in this case was significantly lower, and none of the top layers reached above the characteristic temperature at the chosen snapshots. The increased layer time and the addition of forced convection made this print less prone to temperature-induced flow than the other three intermediate-layer-time prints.

4.6.3.2 *Criterion for temperature-induced flow*

Figure 42 and Figure 43 provide a good sense of where the peak temperature occurs. However, they neither show the maximum temperature (T_{max}) experienced by each layer, nor the time to reach the maximum temperature (t_{max}). These two measurements are critical to predict temperature-induced flow. A simple criterion for temperature-induced flow can be created using the characteristic temperature and the gel time. T_{max} and t_{max} can fall into three categories with respect to the “ T_c -gel time” criterion:

1. T_{max} is below T_c ($T_{max} < T_c$).
 - Temperature-induced flow IS NOT expected.
2. T_{max} is above T_c , but it takes longer than the gel time to reach T_{max} ($T_{max} > T_c$ and $t_{max} > \text{gel time}$).

- Temperature-induced flow IS NOT expected.
3. T_{max} is above T_c , and T_{max} is attained faster than the gel time ($T_{max} > T_c$ and $t_{max} < \text{gel time}$).
- Temperature-induced flow IS expected.

Figure 44 uses Layer 12 of the LT_{2.25} wall to illustrate the extraction of T_{max} and t_{max} for a single layer. Figure 45 plots T_{max} and t_{max} of every layer for the intermediate-layer-time prints along with the characteristic temperature and gel time. Gel time is temperature dependent as shown by Figure 37; therefore, the gel time at room temperature and 60°C are both shown for reference. It should be noted that temperature-induced flow does not always cause failure. The next section measures the change in height of the wall caused by temperature-induced flow and shows that varying levels of temperature-induced flow occur. Extreme cases lead to failure, but the print can survive small amounts of height loss caused by high temperatures.

Figure 45a shows T_{max} and t_{max} for each layer of the LT_{2.25} wall that failed due to temperature-induced flow. Many of the layers in this print reached maximum temperatures far above the characteristic temperature. As proposed by the T_c -gel time criterion, these layers are susceptible to flow if t_{max} falls below the room-temperature gel time, which happened for the first time at Layer 15 and again at Layers 18 and 19. This new criterion agrees with behavior observed in experiments, where failure due to temperature-induced flow occurred at Layer 19.

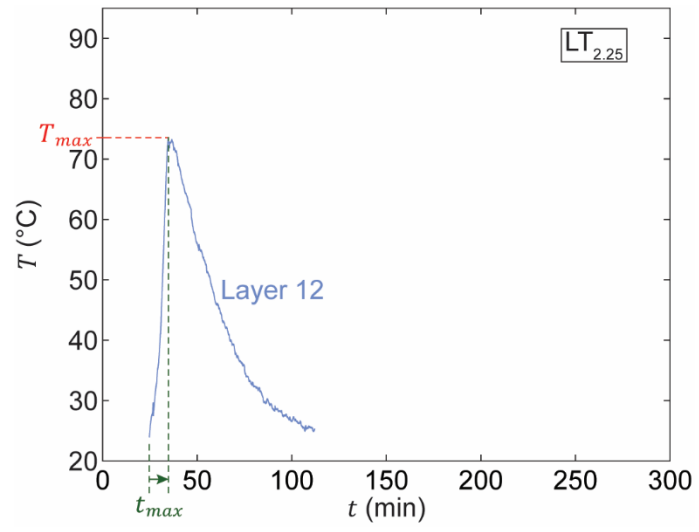


Figure 44: Example of the extraction of T_{max} and t_{max} for Layer 12 of the LT_{2.25} wall.

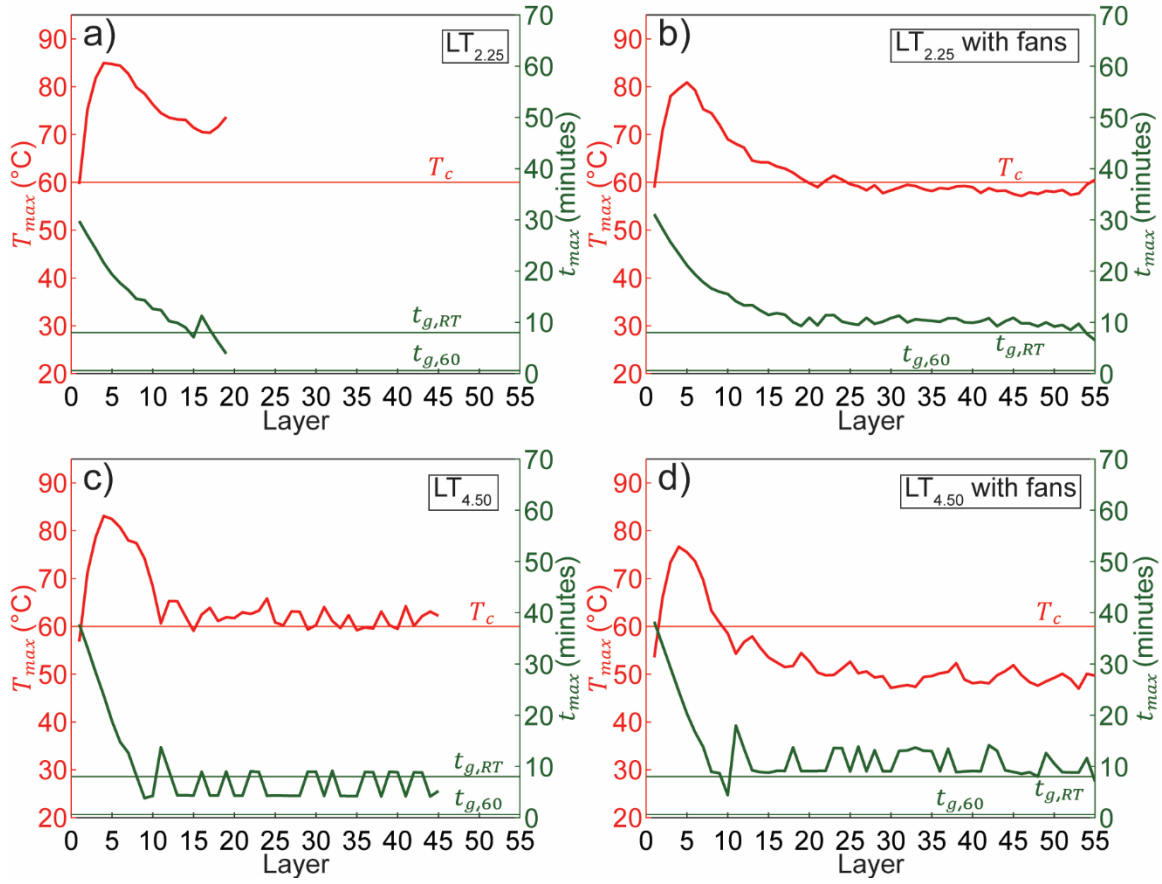


Figure 45: T_{max} and t_{max} plotted for each layer of the intermediate-layer-time prints. a) LT_{2.25} b) LT_{2.25} with fans c) LT_{4.50} d) LT_{4.50} with fans.

Figure 45b shows T_{max} and t_{max} for each layer of the successful LT_{2.25} wall with forced convection. Much like the wall without forced convection, many of the layers in this print reached maximum temperatures far above the characteristic temperature. However, t_{max} was greater than the gel time at room temperature for every layer of the print, except the last layer (which did not benefit from the cooling imparted by an additional layer). The proposed criterion agrees with the observed success.

Figure 45c shows T_{max} and t_{max} of the successful LT_{4.50} wall without forced convection. Again, T_{max} of many layers exceeded the characteristic temperature. Starting at Layer 9, t_{max} was less than the gel time at room temperature, suggesting temperature-induced flow was expected. This criterion was met several additional times throughout the thermal steady state. However, the wall remained stable. The success of this wall highlights the importance of the temperature dependence of the gel time. In the steady state, T_{max} hovers around 60°C. The gel time at 60°C is much shorter than at room temperature. Therefore, stable walls can still be printed when t_{max} is shorter than the room-temperature gel time. This finding warrants further investigation and will be addressed in the following section, which discusses the geometric evolution of each layer.

Figure 45d shows T_{max} and t_{max} of the successful LT_{4.50} wall with forced convection. Here, T_{max} of only a few layers (2-9) during the initial temperature spike exceeded the characteristic temperature. In the thermal steady state, the fans cooled the layers below the characteristic temperature. Additionally, all layers, except 10 and 55, exhibited t_{max} values lower than the room-temperature gel time. In other words, none of

the layers met the criterion for temperature-induced flow. This finding matches the success observed in the experiment.

The presented criterion is approximate and could benefit from refinement. However, it provides excellent understanding of temperature-induced flow, guidance to avoid this phenomenon, and a framework for further study. Exothermic behavior, the characteristic temperature, and gel time are key factors governing temperature-induced flow. Lower temperatures and slower heating rates can help avoid this behavior and improve printability.

The information conveyed in Figure 45 provides useful guidelines to reformulate the material system to improve printability. Starting with thermal solutions, reducing exothermic behavior such that the peak adiabatic temperature does not reach the characteristic temperature may circumvent the issues associated with temperature-induced flow. This could be done by using a different initiator that decreases the amount of energy released during reaction or simply reduces the rate of reaction. The success of the walls shown in Figure 45b-d suggests that a less exothermic material system is likely to mitigate temperature-induced flow and promote printability. Based on this simple guidance, a less exothermic initiator, cumene hydroperoxide (CHP) (United Initiators, Pullach, Germany) was tested and observed to eliminate temperature-induced flow. CHP is now recommended for use with the commercially available PRD-1520. This less exothermic material system has enabled large, commercially relevant parts to be printed with the RAM system, as demonstrated by the mold of a kayak paddle in [117].

Several alternatives exist that do not require a less exothermic reaction.

Decreasing the gel time should enable layers to gel before reaching flow-susceptible temperatures. Increasing the characteristic temperature is another approach to mitigate temperature-induced flow. Finally, increasing material rigidity at the characteristic temperature may also decrease flow susceptibility. Discussion of how to achieve these material properties warrants its own study and is left to further research.

4.6.3.3 Measurement of temperature-induced flow

The successful LT_{4.50} wall, which should have experienced flow based on Figure 45c, motivates examination of the evolution of the layer height. Figure 46 shows the difference between the programmed wall height and the wall height just before deposition of the next layer for all the intermediate-layer-time prints. This figure provides evidence for the existence of temperature-induced flow. If the wall gets shorter between successive layers, then the wall experienced flow. It also shows varying degrees of height loss.

As predicted by Figure 45a, Figure 46 shows that the LT_{2.25} wall experienced flow. Starting at Layer 12, the measured height drifted below the programmed height until Layer 19. At Layer 19, the wall lost more than one layer of height, causing failure. Although both Figure 45a and Figure 46 predict the same outcome, these graphs are not in perfect agreement. Figure 45a first predicts flow at Layer 15, yet flow is observed at Layer 12 in Figure 46. Examination of the viscosity in Figure 37a explains this discrepancy. The viscosity monotonically decreases until it begins to plateau to a minimum at the characteristic temperature. This behavior creates the opportunity for

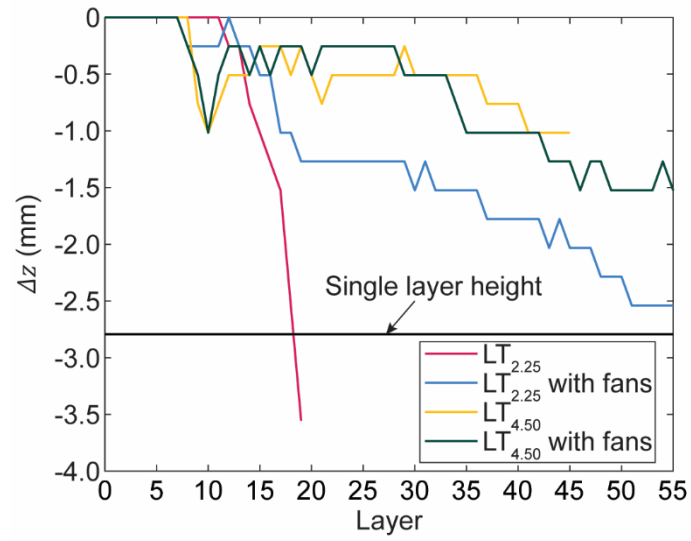


Figure 46: Change in height of the intermediate-layer-time prints between deposition of layers.

temperature-induced flow even below the characteristic temperature. All the time spent above room temperature, but below the characteristic temperature may have caused flow. A significantly more advanced study of the time-dependent interaction among temperature, reaction rate, and rigidity would be required to eliminate this discrepancy. In the absence of that information, the simple proposed criterion is remarkably useful. Although some error exists, it predicts flow near the time that the layers flow and the print fails.

The curve for the LT_{2.25} wall with fans in Figure 46 shows that many layers decreased in height. Figure 45b does not predict flow for any layers (except Layer 55). Again, the temperature-dependent rigidity is believed responsible for the unexpected flow. However, failure was avoided because none of the layers lost more than a full layer height. This modest loss in height allowed the print to survive flow. Interestingly, even after the print had reached a thermal steady state (after ~Layer 25), Figure 46 indicates that layers continued to lose height. Rather than being physically representative, the physical constraints of the optical camera are believed to have caused artifacts that were interpreted as apparent loss in height. Since the camera was placed close to the bed (with its line of sight aimed near Layer 8), measurements of the higher layers were slightly underestimated, causing the apparent height loss.

The curve for the LT_{4.50} wall without fans in Figure 46 shows height loss starting at Layer 9. This behavior matches the prediction in Figure 45c. From that point on, height loss continued to fluctuate, again matching Figure 45c. Failure was avoided because none

of the layers lost more than a full layer height. Again, higher layers erroneously appear to lose height due to the placement of the camera.

The curve for the LT_{4.50} wall with fans in Figure 46 parallels the results for the LT_{4.50} without fans. Height loss started at Layer 8 and continued to fluctuate till the end of the print. This behavior does not match Figure 45c, which predicts that none of the layers will flow. As has been discussed, this is not surprising due to the temperature sensitivity of the rigidity. T_{max} was close to the characteristic temperature, especially early in the print. These elevated temperatures combined with the resin's temperature-dependence could have caused flow. Failure was avoided because none of the layers lost more than a full layer height. Again, higher layers erroneously appear to lose height due to the placement of the camera.

4.6.4 Mechanical and thermomechanical behavior of printed material

Table 5 and Figure 41a show that the printed material exhibits mechanical properties comparable to other vinyl esters in literature [94, 118]. Table 5 and Figure 41a also reveal anisotropic tensile properties of EX-1520. Given the nature of the fiber-filled resin, evaluation of the improved isotropy promised by thermosets remains challenging. As observed in previous works concerning fiber-filled polymers [6, 9, 10, 22], the shear stresses in the nozzle align fibers in the direction of flow, resulting in greater properties along the bead in the x -direction (i.e., longitudinal). This phenomenon obfuscates whether the present material system and printing method offers greater isotropy than large-scale printed thermoplastics. Inks with low aspect ratio (~ 1) fillers may provide

means to more conclusively evaluate the degree of isotropy provided by the stronger interlayer bonding associated with thermosets. Alternatively, mechanical tests that isolate interlayer properties could help assess the enhancements provided by thermoset feedstocks [33].

The glass transition temperature of the cured EX-1520 is 93.13°C, which is comparable to vinyl esters processed in other ways [90, 91, 119]. 93.13°C significantly exceeds the extrusion temperature. This behavior demonstrates that the glass transition temperature of printed material can be decoupled from the extrusion temperature, validating one major benefit of thermoset printing.

The transient temperature spike observed in these samples subjects lower layers in the wall to higher temperatures. This fact combined with the knowledge that degree of conversion in vinyl ester systems depends on temperature suggests that the lower layers may exhibit different stiffness, strength, and T_g than upper layers [90-94, 118-120]. However, no such trend was observed. This observation may mean that this particular resin/initiator system is insensitive to the temperature differences experienced during curing, or it may be that any differences in properties due to thermal history are smaller than the experimental scatter in measurements. Additional, focused studies on the effects of spatially varying temperature evolution within printed thermoset materials is clearly warranted.

4.7 Conclusion

This work proved in-process chemically initiated thermoset printing can successfully eliminate self-weight collapse on the large scale. However, this success was only observed over a limited range of processing conditions. Layer time is a key factor governing the feasibility of chemically initiated thermoset printing. Three challenges were observed at three different layer times, providing a general understanding of the behavior expected to impede successful printing. Walls with short layer times stack layers too quickly to resist self-weight collapse. Shrinkage and exothermic behavior trigger residual stresses and warpage at long layer times. Between these two limits, a behavior unique to large-scale, chemically initiated thermoset printing was discovered. The heat released from the previously deposited material can cause flow of newly deposited material prior to gelation. The addition of forced convection was shown to mitigate temperature-induced flow and allow for a wider range of printable layer times. However, this technique was shown to increase thermal gradients, residual stresses, and warpage.

The discovery of temperature-induced flow motivated development of a simple criterion to predict this phenomenon. The criterion compares the maximum temperature of each layer and the time taken to reach that temperature to the characteristic temperature and the gel time of the material. This criterion provides simple but useful guidance. Temperatures below the characteristic temperature are desirable. If this is not possible, then slower heating rates are preferable. These goals can be accomplished by

tuning processing parameters, as shown here, or by tailoring new material systems. Material systems with reduced exothermic behavior should reduce the likelihood of temperature-induced flow. Preliminary research with a less exothermic initiator has confirmed this hypothesis and enabled more flexible production of large-scale thermoset prints. The next chapter discusses how a thermal model that incorporates reaction kinetics can provide even more insight than the simple criterion presented in this chapter.

This research also provided an estimate of the mechanical properties and glass transition temperature that can be expected from chemically initiated vinyl ester printing. The properties are comparable to vinyl ester processed in molding applications. However, mechanical anisotropy is apparent, but shows promise to be decreased with appropriate ink formulation.

5 CHAPTER 5: FUTURE DIRECTIONS OF LARGE-SCALE CHEMICALLY INITIATED THERMOSET PRINTING

5.1 Abstract

Previous analysis highlighted several failure modes that can occur during chemically initiated thermoset printing. Viscoelastic collapse can happen when layers are stacked too quickly. The energy released during the reaction can cause newly deposited layers to flow. Finally, warpage can occur if layers are stacked too slowly. Here, a rudimentary model is presented that compares the gelled layers to the total number of layers printed to determine stability. Additionally, a 1D finite-difference thermal model of a thin wall is developed to learn more about each of these behaviors and determine the next research tasks that should be addressed to improve control of chemically initiated printing. Results of rudimentary material characterization and curve-fitting are used in this model and shown to provide good agreement with experimental results. However, much more accurate thermal histories are expected with more precise kinetic models and temperature-dependent material characterization efforts. These objectives should be targeted for future work. Additionally, the model provides an estimate of the conversion experienced by every layer of the printed material. This result could be used to estimate warpage, but better understanding of how conversion affects gelation and shrinkage would be required. Future work should also focus on relating conversion to gelation and shrinkage, so that warpage can be predicted.

5.2 Introduction

The previous chapter indicated that in-process chemical initiation is one of the most practical ways to achieve large-scale thermoset printing. This work highlighted

three behaviors that must be researched to fully understand how to implement this technology most effectively. First, the relationship between gel time and the rate at which layers are stacked on top of the print is critical to determining the stable height that can be reached with this approach [42, 62, 117]. Second, understanding how the energy released by the chemically initiated reaction affects thermal behavior during the printing process is also important [17, 18, 42] because this transience affects the gel time, apparent properties [94, 118], warpage, and ultimately, printability. Third, the effect of shrinkage during the crosslinking process must be investigated because it creates differential shrinkage between layers that can lead to significant warpage. The following work presents preliminary experiments and analysis on the chemically initiated vinyl ester resin that begin to shed light on these complicated and interrelated behaviors.

To comply with generally accepted notation in the fields of heat transfer and chemical reaction kinetics, the definitions of some of the symbols have been changed in this chapter of the dissertation. The symbols that have new definitions are listed below.

- α is the chemical conversion of a reaction, with $\alpha = 0$ representing a reaction that has not begun and $\alpha = 1$ representing a reaction that is complete.
- h is the convective heat transfer coefficient.
- L_{wall} is the height of the wall.
- σ is the Boltzmann constant.
- ν is the kinematic viscosity.
- n is the order of the reaction.

- t is time.
- q is the rate of heat transfer.

These definitions will be reiterated at their first appearance in this chapter.

5.3 Materials and methods

5.3.1 *Material*

The same peroxide-initiated vinyl ester resin system from the previous chapter was studied in this work.

5.3.2 *Thermal characterization*

The thermal conductivity of the vinyl ester resin was measured on the TPS 2500 (Hot Disk AB, Göteborg, Sweden) using two cured disks of material with the minimum dimensions recommended by Hot Disk [121] (i.e., 10 mm in diameter and 2.5 mm thick). This test was repeated nine times. An intermediate value that generated reasonable agreement between the thermal model and experimental data and fell within the range measured in the nine tests was used here. Differential scanning calorimetry (DSC) was used to determine the heat capacity of the material. Three scans were conducted on the initiated resin between 25°C to 200°C at 10°C/min. After the initial spike caused by equilibration of the system, the heat capacity reaches a plateau between ~30°C and 40°C. An intermediate value that generated reasonable agreement between the thermal model and experimental data and fell within the range measured in the three scans was used here.

5.3.3 *Chemical and rheological characterization*

The methods used to determine the gel time at different temperatures, the adiabatic curing temperature, and the shrinkage are all described in the previous chapter.

5.3.4 *Thermal evolution of the print*

The methods used to measure the thermal evolution of the thin printed walls are described in the previous chapter.

5.4 Theory

5.4.1 *Stability as a function of gel time and layer time*

The wall specimens addressed in the previous chapter are large and take a long time to print relative to the gel time. This means that some of the layers gel during the print, while others remain in a viscoelastic state. Given the gel time and layer time, the “gel front” (i.e., the height of layers that have gelled) can be compared to the “print front” (i.e., the total height of material that has been deposited) to predict the stability of the print. The print front is defined as follows:

$$H_{print} = \Delta H * m \quad (49)$$

where ΔH is the layer height and m is the number of layers that have been deposited.

t_{print} is the elapsed time since the start of the print. Assuming the layer time is constant,

t_{print} can be defined as follows:

$$t_{print} = \text{layer time} * m \quad (50)$$

Assuming steady-state conditions where the gel time, t_g , is constant, the gel front is defined as follows:

$$H_{gel} = \Delta H \left[\frac{t_{print}}{t_g} \right] \quad (51)$$

The height difference between the gel front and the print front describes the portion of the wall that remains viscoelastic and will be referred to as δ_{visc} .

$$\delta_{visc} = H_{print} - H_{gel} \quad (52)$$

The stability of the wall at any point during the print can be predicted by comparing δ_{visc} to the collapse height of the un-gelled printed structure. In the previous chapter, the LT_{0.68} print experienced pre-gel collapse at Layer 22 ($z = 61$ mm), because the gel front did not keep pace with the print front. This result allows us to approximate the δ_{visc} value that will lead to collapse. At layer 22, $t_{print} = 15$ minutes. Assuming the material exhibits the room temperature, manufacturer reported gel time of 8 minutes under these conditions, then only one layer gelled in this print before it collapsed. Therefore, $\delta_{visc} \approx \Delta H(22-1) \approx 59$ mm. This will be approximated as the maximum stable value for δ_{visc} .

5.4.2 Kinetic modeling

This work aims to predict the temperature evolution of thin walls in large-scale chemically initiated thermoset printing. To achieve this goal, a kinetic model of the material must be generated to approximate the thermal behavior of the reaction. Pannone and Macosko [109, 110] used the adiabatic temperature rise experiment (Figure 37b from previous chapter) to model the kinetics of materials that react at room temperature. These

materials make rigorous DSC measurement difficult. Before DSC can be conducted, the material must be weighed and loaded into the test chamber. During this time, the material is reacting, meaning that the DSC will not measure the full amount of heat generated by the material. The adiabatic temperature rise, on the other hand, is much more practical, allowing measurement of the reaction immediately after mixing to capture all of the heat generation. The adiabatic data will be used to determine the parameters of the kinetic model.

Several types of reactions exist to model kinetic behavior [90-92, 109, 110, 119, 122-130]. However, only the n^{th} order will be considered here. The n^{th} order reaction has fewer parameters than other options, simplifying the fitting process. It will also be shown that the n^{th} order model provides a reasonably good fit to the data from the adiabatic experiment. ASTM E2070 and ASTM E2041 [122, 123] define the n^{th} order reaction as:

$$\frac{d\alpha}{dt} = k_{rxn}(T)(1 - \alpha)^n \quad (53)$$

$$k_{rxn}(T) = Ze^{-E/RT} \quad (54)$$

where $\frac{d\alpha}{dt}$ is the reaction rate, t is time, T is temperature, k_{rxn} is the rate constant that depends on temperature through and Arrhenius relationship, α is conversion, n is the unitless reaction order, E is the activation energy, Z is the Arrhenius pre-exponential factor, and R is the gas constant (8.3145 J/(mol.K)).

5.4.3 Thermal model

To predict the temperature evolution of the reactive deposition process, this work presents a 1D finite-difference thermal model of a thin wall that builds upon the analysis of thermoplastic printing introduced by Compton et al. [34]. The following description will mirror that of Compton et al. with a few modifications to account for energy generation ($\dot{E}_g$) created during the exothermic crosslinking reaction of the chemically initiated vinyl ester. Figure 47 shows an idealized schematic of the model geometry, printing process, boundary conditions, heat transfer terms, and energy generation.

5.4.3.1 Processing parameters

In the physical printing process, the deposition of each layer requires a finite amount of time, called the layer time. The layer time can be approximated by dividing the length of the print path for a layer by the translational speed of the deposition head. The 1D nature of this model does not allow for explicit incorporation of the deposition head speed. Rather, each new layer is assumed to be deposited instantaneously at increments defined by the layer time. In this way, the layer time can be thought of as a proxy for the speed of the deposition head. Longer layer times in the model represent larger layers or slower deposition head speeds. The layer time, deposition temperature (T_{dep}), bed temperature (T_b), ambient temperature (T_∞), wall thickness, layer height, total number of layers (m_{total}), and cool-down period (t_{cool}) are used as inputs to the model. These processing parameters are shown in Table 6.

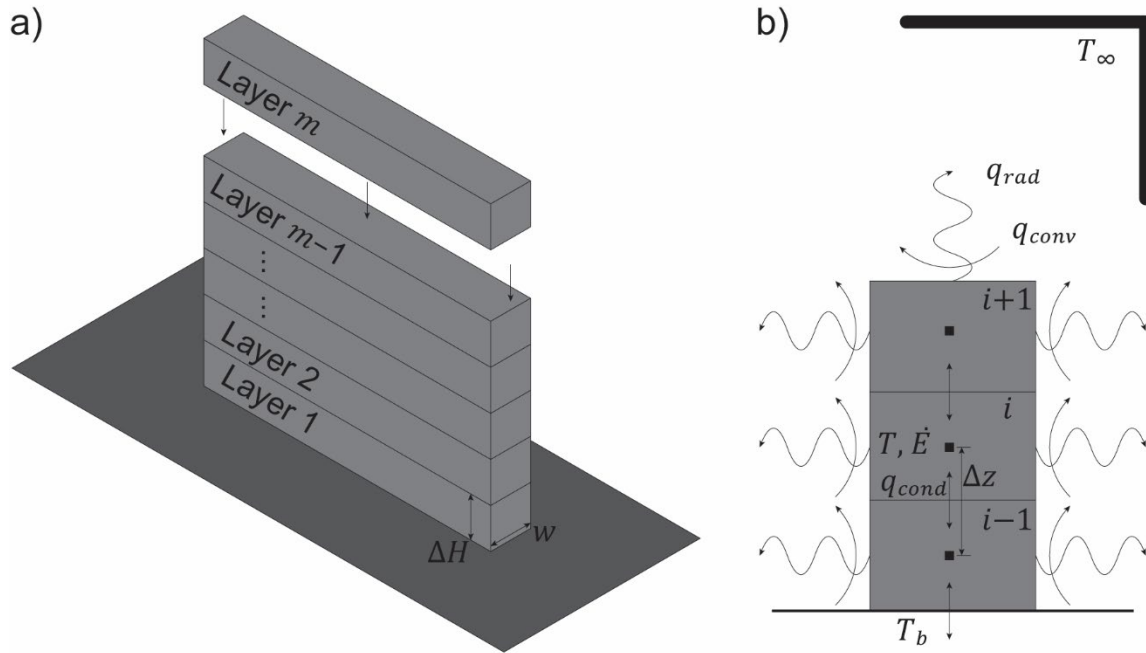


Figure 47: Conceptual schematic of the thermal model. a) Geometry and printing process. b) 3-node mesh showing the temperature, nodal spacing, boundary conditions, and energy generation.

Table 6: Thermal model input parameters.

LT (min)	T_{dep} (°C)	T_b (°C)	T_{∞} (°C)	w (mm)	Δh (mm)	m_{total}	t_{cool} (min)
4.5	21	21	21	17.5	2.8	40	67.5

5.4.3.2 Geometry and mesh

The length of each layer is assumed to be infinite, whereas the thickness and layer height are modeled as finite values. The mesh was generated with three nodes per layer as shown in Figure 47b. In the future, these conditions should be repeated with more nodes to assess the sensitivity of the model to the number of nodes.

5.4.3.3 Energy balance

The model is built by writing an energy balance for the control volume around each node. Equation 55 shows the most general form of the energy balance.

$$\dot{E}_{in} + \dot{E}_g = \dot{E}_{st} \quad (55)$$

where $\dot{E}_{in}$ is the rate of energy coming into the control volume, $\dot{E}_g$ is the rate of energy generation within the control volume, and $\dot{E}_{st}$ is the rate of change of energy stored in the control volume. Unlike the thermoplastic version presented by Compton et al. [34], $\dot{E}_g$ is left in the equation to account for the heat generated during the crosslinking reaction. The rate of energy input into the system from the environment can be divided into contributions from conduction, convection, and radiation. This allows for a more explicit representation of the energy input into the control volume.

$$\dot{E}_{in} = q_{cond} + q_{conv} + q_{rad} \quad (56)$$

where q represents the rate of heat transfer, and the subscripts *cond*, *conv*, and *rad* refer to conduction, convection, and radiation, respectively. The energy generation term comes from the heat released by the crosslinking reaction, which can be defined as follows

$$\dot{E}_g = \rho C_p V * \Delta T_{ad} \frac{d\alpha}{dt} \quad (57)$$

$$\Delta T_{ad} = (T_{max,ad} - T_{\infty,ad}) \quad (58)$$

where ρ is density, C_p is the specific heat capacity, V is the volume of the material, ΔT_{ad} is the total temperature change observed in the adiabatic test, $T_{max,ad}$ is the maximum temperature observed in the adiabatic test, and $T_{\infty,ad}$ is the ambient temperature used in the adiabatic test. As stated before, this work will utilize the n^{th} order kinetic model to fit the reaction.

Now, the heat transfer terms in the energy balance can be written for each node, as shown in Equations 59-62. Since each layer is infinitely long, it is convenient to express all terms per unit length, as indicated by the prime symbol. The mesh has three types of nodes – the bottom node, middle nodes, and top node.

- The bottom node conducts heat to the print bed and to the node above, while convecting and radiating heat from the two side surfaces.
- The middle nodes conduct heat to the nodes above and below, while convecting and radiating heat from the two side surfaces.
- The top node conducts heat to the node below it, while convecting and radiating heat from the two side surfaces and top surface. After the deposition of each new layer, the original top node becomes a middle node, and the new top node is the highest node in the new layer.

The bottom and top nodes describe half the volume of the middle nodes. This conceptual difference causes a factor of ½ or 2 to appear in the equations for the bottom and top nodes that is not seen in the equations for the middle nodes.

$$q'_{cond} = \begin{cases} \frac{2kw}{\Delta Z}(T_b - T_i^p) + \frac{kw}{\Delta Z}(T_{i+1}^p - T_i^p), \text{bottom node} \\ \frac{kw}{\Delta Z}(T_{i-1}^p - T_i^p) + \frac{kw}{\Delta Z}(T_{i+1}^p - T_i^p), \text{middle nodes} \\ \frac{kw}{\Delta Z}(T_{i-1}^p - T_i^p), \text{top node} \end{cases} \quad (59)$$

$$q'_{conv} + q'_{rad} = \begin{cases} \Delta z(h^p + h_{rad_i}^p)(T_\infty - T_i^p), \text{bottom node} \\ 2\Delta z(h^p + h_{rad_i}^p)(T_\infty - T_i^p), \text{middle nodes} \\ \Delta z(h^p + h_{rad_i}^p)(T_\infty - T_i^p) + w(h^p + h_{rad_i}^p)(T_\infty - T_i^p), \text{top node} \end{cases} \quad (60)$$

$$\dot{E}'_g = \begin{cases} \rho C_p w \frac{\Delta z}{2} (T_{max,ad} - T_{\infty,ad}) Z e^{-E/RT_i^p} (1 - \alpha_i^p)^n, \text{bottom/top nodes} \\ \rho C_p w \Delta z (T_{max,ad} - T_{\infty,ad}) Z e^{-E/RT_i^p} (1 - \alpha_i^p)^n, \text{middle nodes} \end{cases} \quad (61)$$

$$\dot{E}'_{st} = \begin{cases} \frac{\rho C_p w \Delta z}{\Delta t} (T_i^{p+1} - T_i^p), \text{bottom/top nodes} \\ \frac{\rho C_p w}{\Delta t} \Delta z (T_i^{p+1} - T_i^p), \text{middle nodes} \end{cases} \quad (62)$$

where Δt is the time increment chosen for the model, i indicates the current node, p indicates the current time increment, h is the convective heat transfer coefficient, and h_{rad} is the radiative heat transfer coefficient, Δz is the distance between nodes, and k is the thermal conductivity. The relationships in Equations 59-62 can be substituted into the

energy balance (Equation 55) to solve for the temperature of each node at the next time step, T_i^{p+1} .

The program starts by setting the nodes of the first layer equal to T_{dep} . It then proceeds by calculating the temperature for all deposited nodes at the next time step (T_i^{p+1}) using the current temperature (T_i^p), heat transfer coefficients (h^p and $h_{rad_i}^p$), and conversion (α_i^p) of each node. This calculation is repeated for each time increment required to reach a full layer time, after which a new set of nodes with temperature T_{dep} is added on top of the original nodes to represent a newly deposited layer. Again, the temperature of each node in the current model is calculated for each time increment for another layer time. The solution continues in this manner until the specified number of layers and the specified cool-down period has been calculated.

5.4.3.4 Heat transfer coefficients

h , the convective heat transfer coefficient, can come from forced convection or can be caused by natural convection. Natural convection is expected to occur in the absence of forced convection. For this demonstration, the model will assume no forced convection is present. The convective heat transfer coefficient caused by natural convection can be calculated using the following equations [34, 131]:

$$h = \frac{Nu * k_f}{H_{print}} \quad (63)$$

$$Nu = \left(0.825 + \frac{0.387Ra^{1/6}}{\left(1 + \left(\frac{0.492}{Pr} \right)^{9/16} \right)^{8/27}} \right)^2 \quad (64)$$

$$Ra = Gr * Pr \quad (65)$$

$$Gr = \frac{g\beta_{\infty}(T_s - T_{\infty})L_{wall}^3}{\nu} \quad (66)$$

$$Pr = \frac{\nu_f}{\kappa_f} \quad (67)$$

where k_f is the thermal conductivity of the surrounding air, κ_f is the thermal diffusivity of the air, ν_f is the kinematic viscosity of the air, $\beta_{\infty} \approx 1/T_{\infty}$ (the volumetric expansion coefficient), T_s is the surface temperature of the wall (approximated by taking the average temperature of all the nodes in the wall at each time step), Nu is the Nusselt number, Ra is the Rayleigh number, Pr is the Prandtl number, and Gr is the Grashof number. The relevant parameters are listed in Table 7. In this model, h is updated at every time step using the preceding equations. All nodes are assumed to experience the same convective heat transfer coefficient at a given time. Equation 64 is only valid for $Ra > 10,000$.

Therefore, h is only activated when $Ra > 10,000$.

h_{rad} is calculated for each node at every time step using the following equation.

$$h_{rad_i}^p = \varepsilon\sigma(T_i^p + T_{\infty})(T_i^{p^2} + T_{\infty}^2) \quad (68)$$

where $\sigma = 5.670 \times 10^{-8} W/(m^2K^4)$ is the Boltzmann constant, and ε is the emissivity of the material. The emissivity was found to be 0.84 after deposition.

Table 7: Parameters of air for calculating the natural convective heat transfer coefficient.

Parameter	Value
Air density, ρ_f (kg/m ³)	1.214
Air kinematic viscosity, ν_f (m ² /s)	1.493×10^{-5}
Air specific heat, $C_{p,f}$ (J/(kg.K))	1005
Air thermal conductivity, k_f (W/(m.K))	0.0256
Air thermal diffusivity, κ_f (m ² /s)	$k_f / (\rho_f C_{p,f})$

5.5 Results and discussion

5.5.1 Effect of gel time and layer time on stability

Figure 48 plots how δ_{visc} evolves at different combinations of gel time and layer time and compares it to the height at which viscoelastic collapse is expected. The dotted curves represent δ_{visc} . The solid line represents the δ_{visc} value that is expected to cause collapse. The collapse prediction is based on the height at which the LT_{0.68} print fell over (Figure 38a) and the number of layers that had gelled at that point.

Figure 48a shows how varying the layer time at a constant gel time of 8 minutes affects δ_{visc} . Figure 48a demonstrates three cases for the relationship between gel time and layer time. The first case is when the layer time is less than the gel time. Collapse is inevitable for this family of layer times, with collapse occurring at an earlier layer for shorter layer times. The second case is when the layer time is equal to the gel time. In this case, δ_{visc} remains at zero, and collapse is not expected. The third case happens when the layer time is greater than the gel time. The curve showing a 10-minute layer time suggests that δ_{visc} becomes negative. This is impossible unless δ_{visc} started out as a positive value. In this case the negative value corresponds to δ_{visc} shrinking.

Previous experiments showed that the gel time was not stagnant when printing at constant layer time. Instead, the energy generated by the reaction heated the wall. As shown by Figure 37c, an increase in temperature accelerates the gelation. To address this behavior, Figure 48b shows how varying gel time at a constant layer time of 4.5 minutes affects δ_{visc} . This graph presents the same three cases as Figure 48a, but in a manner

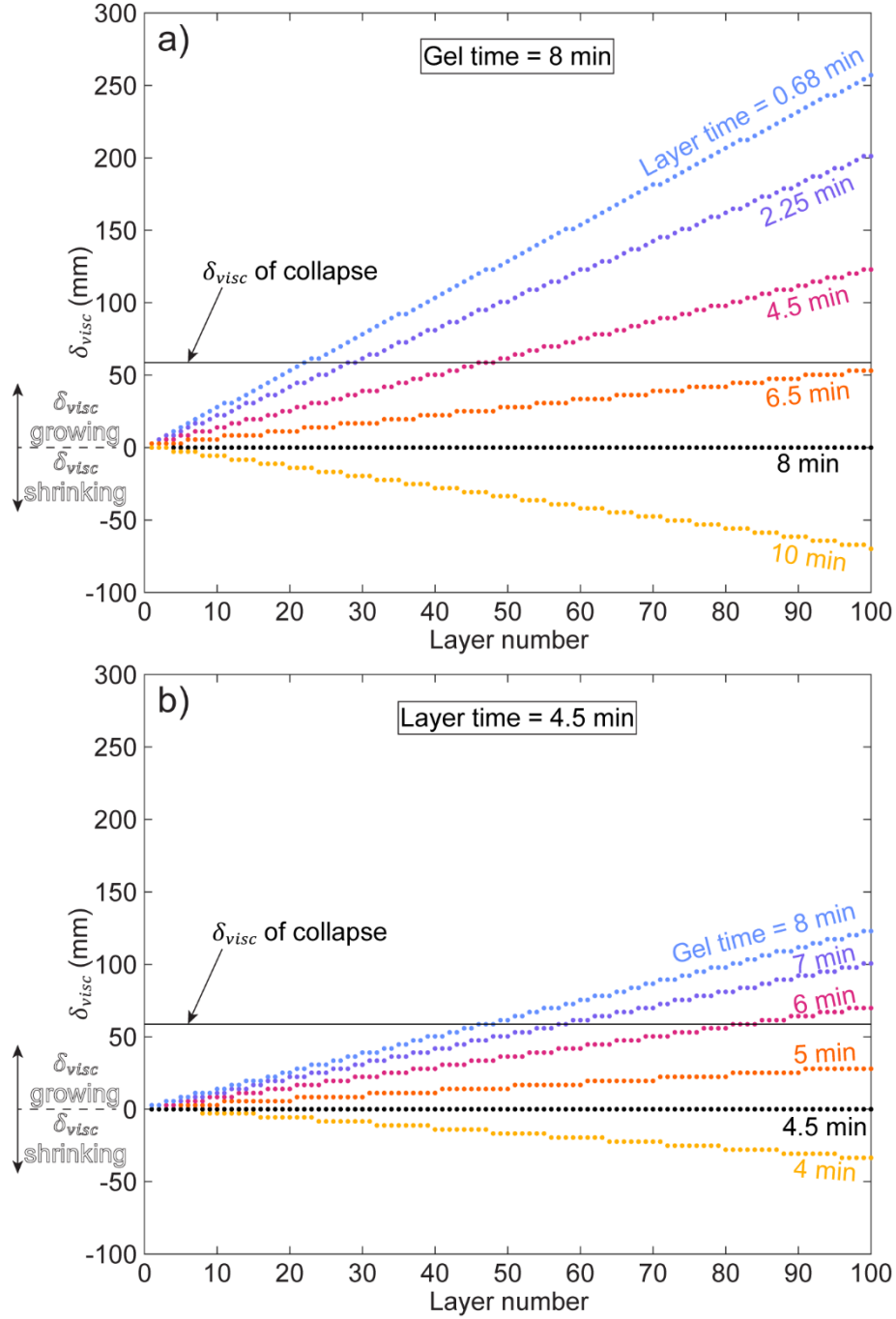


Figure 48: Evolution of δ_{visc} at each layer given different combinations of gel time and layer time. a) δ_{visc} when the gel time is held constant at 8 minutes while varying layer time between 0.68 and 10 minutes. b) δ_{visc} when the layer time is held constant at 4.5 minutes while varying gel time between 4 and 8 minutes.

more practical for the experiments conducted in the previous chapter. δ_{visc} grows when the gel time is greater than the layer time. δ_{visc} remains at zero when the gel time and layer time are equal. δ_{visc} shrinks if the gel time is less than the layer time and δ_{visc} started at a positive value.

The gelation information in Figure 37c can be used to generate another plot based on the LT_{4.50} print without fans. First, it is assumed that the relationship between the gel time and temperature is linear between the room temperature and 60°C. This relationship is shown in Figure 49a. Then, the temperature experienced by each layer one minute after it was deposited is extracted in Figure 49b. This temperature is plotted for each layer in Figure 50a and is used to approximate the reaction temperature of that layer. These approximations and assumptions allow the gel time to be estimated for each layer in Figure 50b. This plot shows that the estimated gel time started out far greater than the layer time, meaning that δ_{visc} was growing and approaching an unstable state (as indicated by Figure 48b). Then the deposited material began to react and release heat, causing the temperature experienced by each layer to increase and the gel time to drop. At Layer 9 (25 mm), the estimated gel time fell below the layer time of 4.5 minutes, meaning that δ_{visc} began to shrink (as indicated by Figure 48b) before reaching the unstable value of 59 mm. The gel time appeared to stay below 4.5 minutes for the rest of the experiment suggesting that this print could have remained stable for an indefinite number of layers.

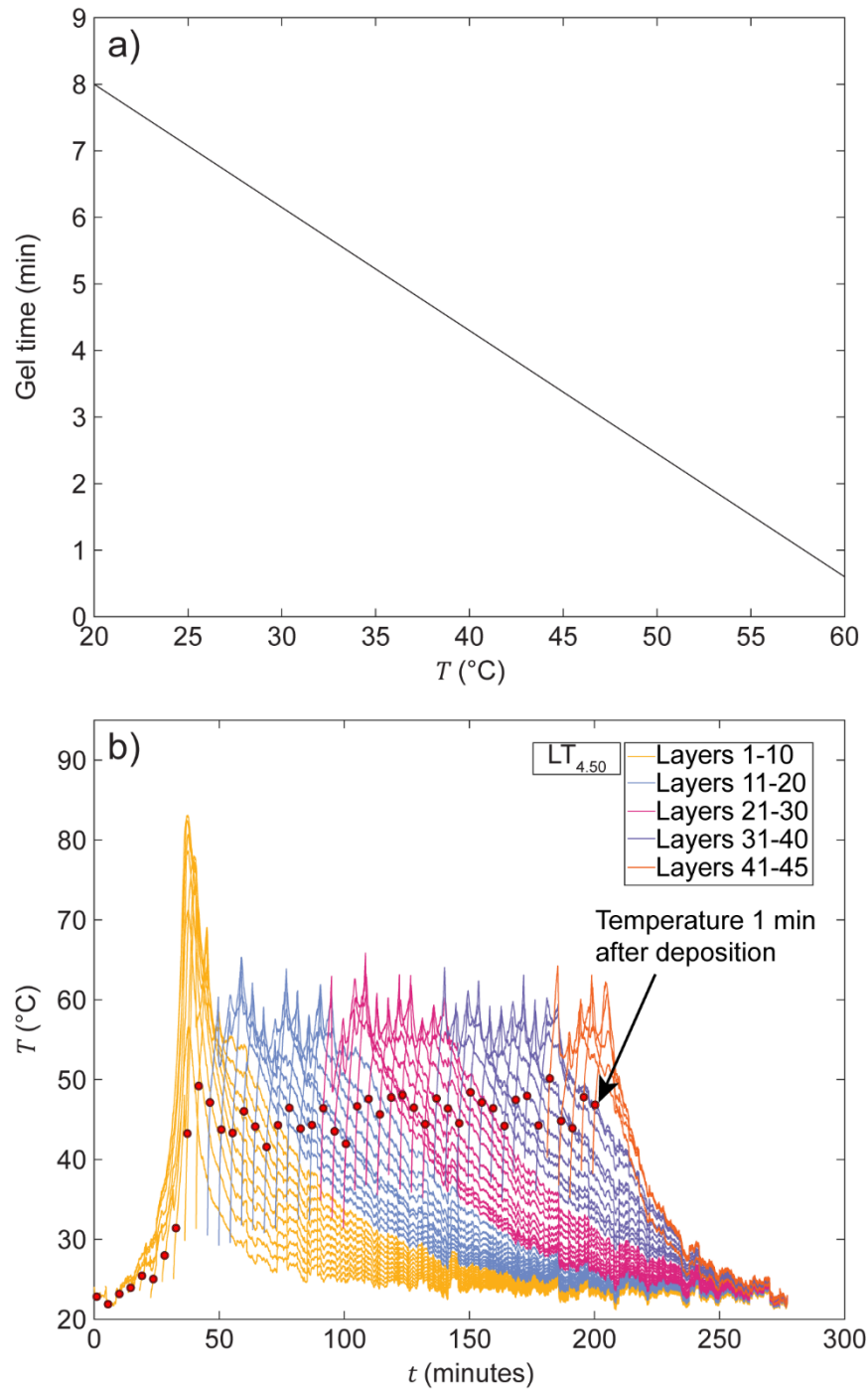


Figure 49: Data required to approximate the gel time of each layer of the $\text{LT}_{4.50}$ print. a) Linear approximation of the gel time as a function of temperature. b) Temperature of each layer one minute after deposition.

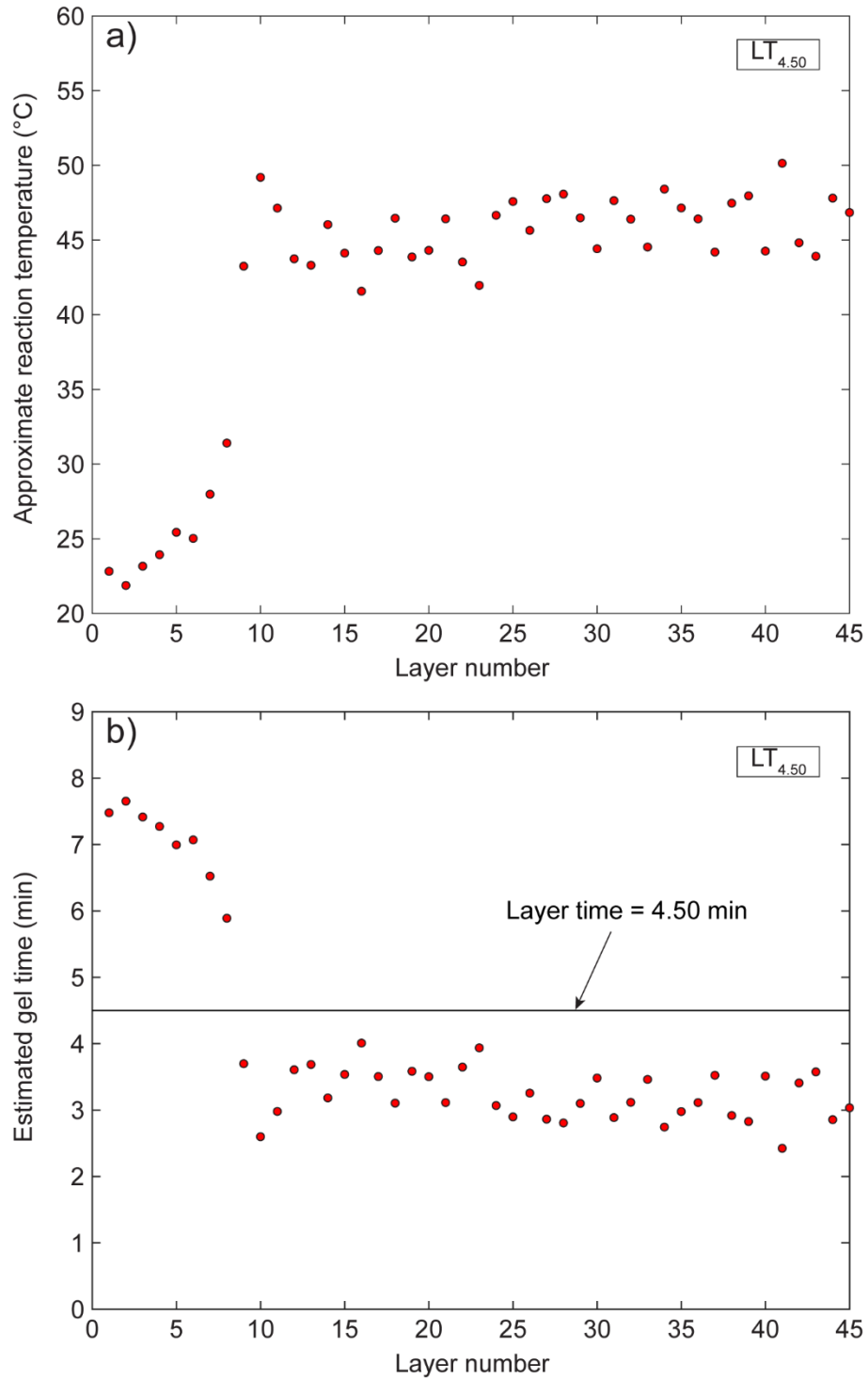


Figure 50: Analysis of the gel time of the LT_{4.50} print. a) Approximate reaction temperature. b) Estimated gel time for each layer.

Clearly, the exothermic behavior of the chemically initiated reaction severely complicates analysis. Several approximations and assumptions were required to develop these figures and draw these imprecise conclusions, highlighting the need for more rigorous understanding of the relationships between temperature, gel time, and the thermal evolution of the print. A thermal model that incorporates the reaction kinetics of the material will provide key insight to address these issues with more certainty.

5.5.2 *Thermal model*

Results of the thermal characterization are listed in Table 8. The parameters that resulted in a reasonable fit of the adiabatic temperature rise are shown in Table 9. The fit is compared to the experimental data in Figure 51. These values were used as inputs in the thermal model.

Figure 52 uses the $LT_{4.50}$ (without fans) to compare the thermal history of each layer observed in the experiment and predicted by the model. The temperature experienced by each layer is plotted as a function of time. The model agrees with experimental behavior remarkably well, given that the reaction was assumed to be second order and several material properties were approximated as constants. The model in Figure 52b recreates many of the behaviors observed in the experiment (Figure 52a), including, in order:

- an initial induction time, where very little heat was generated in each layer;
- a spike in the temperature of each layer;

Table 8: Material properties assumed for the vinyl ester resin.

Material property	Value
Thermal conductivity, k (W/(m.K))	0.39
Heat capacity, C_p (J/(kg.K))	2750
Emissivity, ε	0.84
Density, ρ (kg/m ³)	1070

Table 9: Kinetic parameters of the vinyl ester reaction.

Kinetic parameter	Value
Arrhenius pre-exponential factor, Z (1/s)	1×10^{14}
Activation energy, E (J/mol)	1.01×10^5
Reaction order, n (unitless)	2

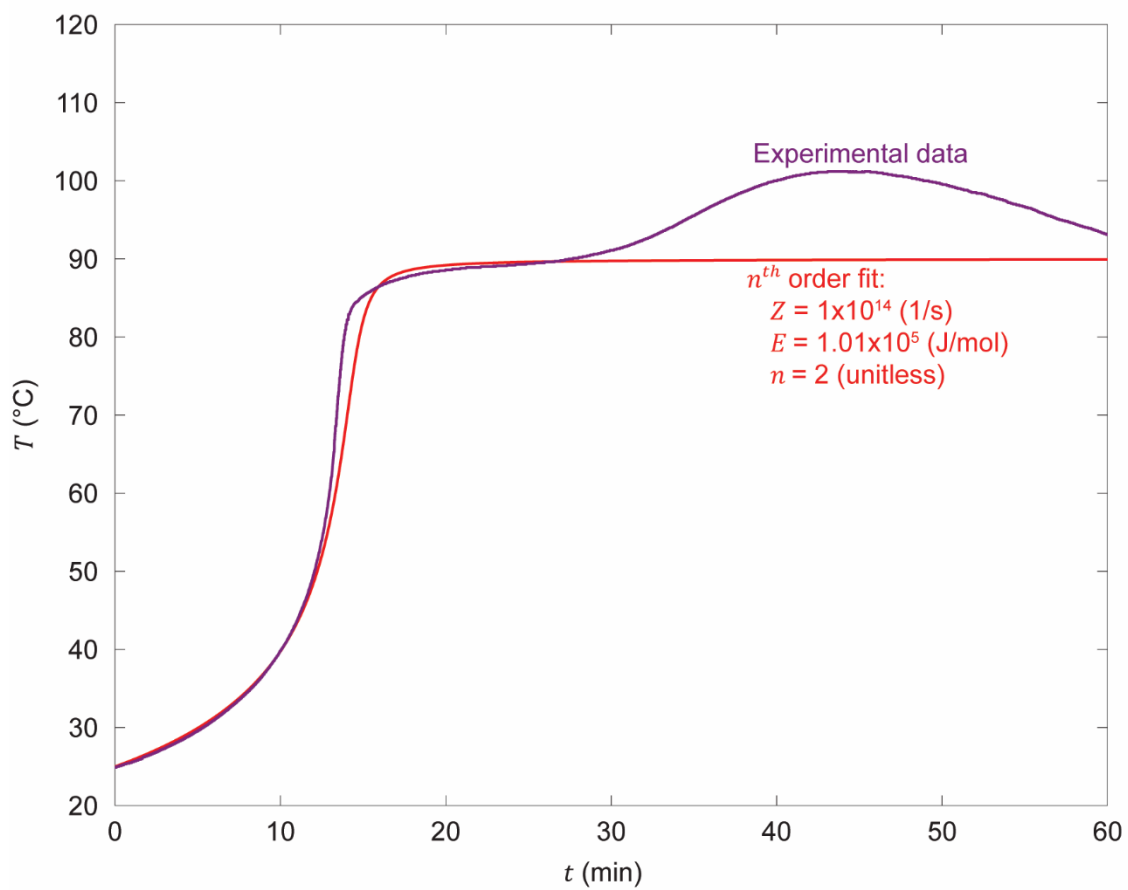


Figure 51: Adiabatic temperature rise and second order fit.

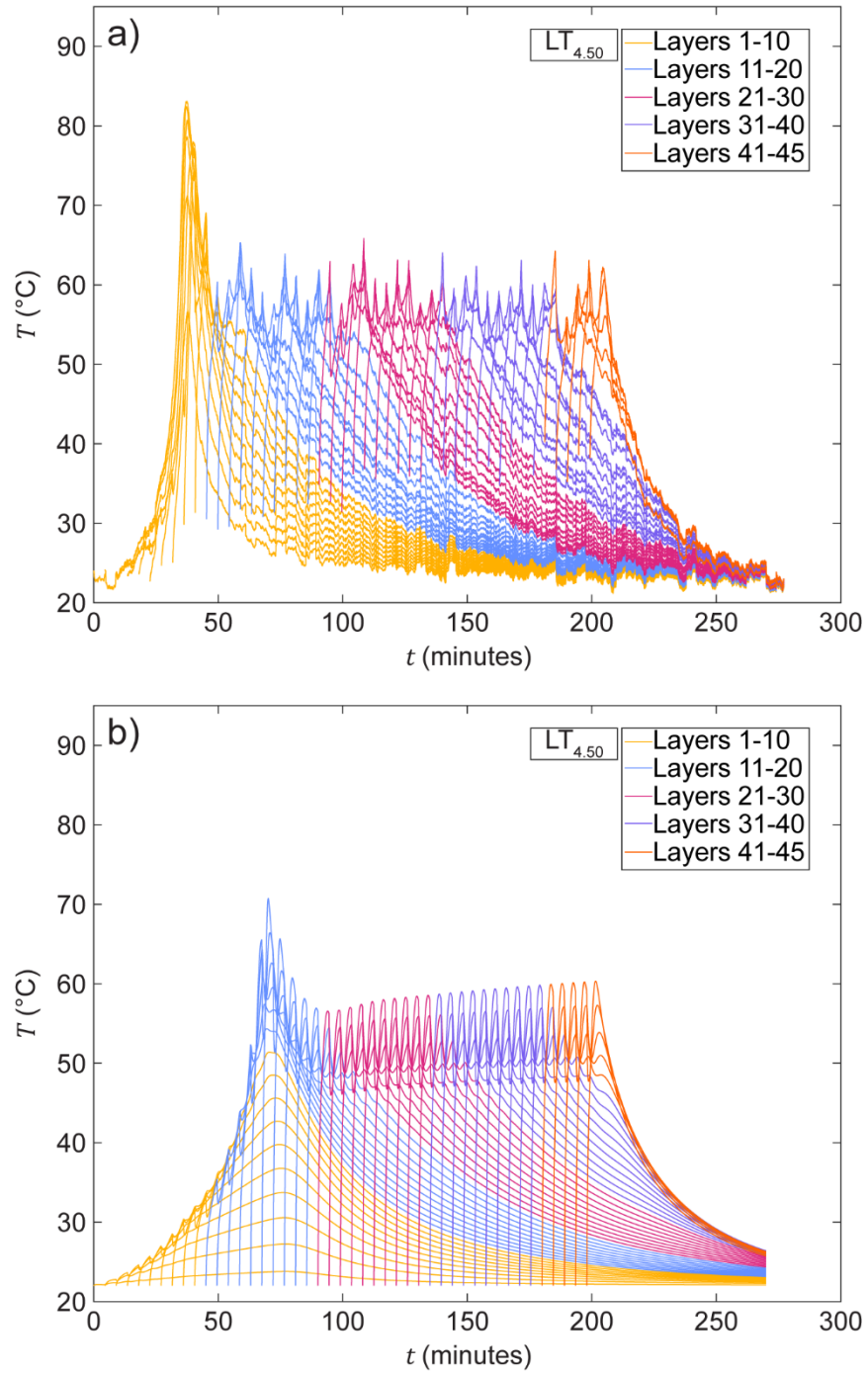


Figure 52: Temperature history of each layer of the LT_{4.50} print. a) Experimental results. b) Thermal model results.

- a rapid decline in the maximum temperature of each layer; and
- a steady state where the maximum temperature of each layer is nearly constant.

However, several differences are noted. The temperature spike occurs later in the model than it does in the experiment. The peak temperature of the spike is lower in the model. The steady state in the model is much more consistent than the experimental data, which oscillates up and down. The steady state appears to be slowly building in the model, whereas the experimental data oscillates around 60°C. Finally, the thermal history for each layer is much smoother in the model.

Figure 53 compares evolution of the thermal gradient of the experiment to the model. “Snapshots” of the thermal gradient are captured at integer multiples of the layer time. For example, t_1 refers to the thermal gradient between deposition of the first and second layer, and t_2 refers to the thermal gradient between deposition of the second and third layer, etc. Again, good behavioral agreement is observed between the experiment and the model in Figure 53a and Figure 53b. Both show that early in the print, a concave thermal gradient builds from room temperature up to the previously mentioned spike. After the temperature spike, the gradient assumes a mostly convex shape, with the maximum temperature near the top of the wall. However, the shape at the top of the wall remains concave. Finally, the shape of the gradient and magnitude of temperature during the cool-down period are very similar. Key differences can also be observed. The time taken to reach the temperature spike and the time to transition to a mostly convex shape

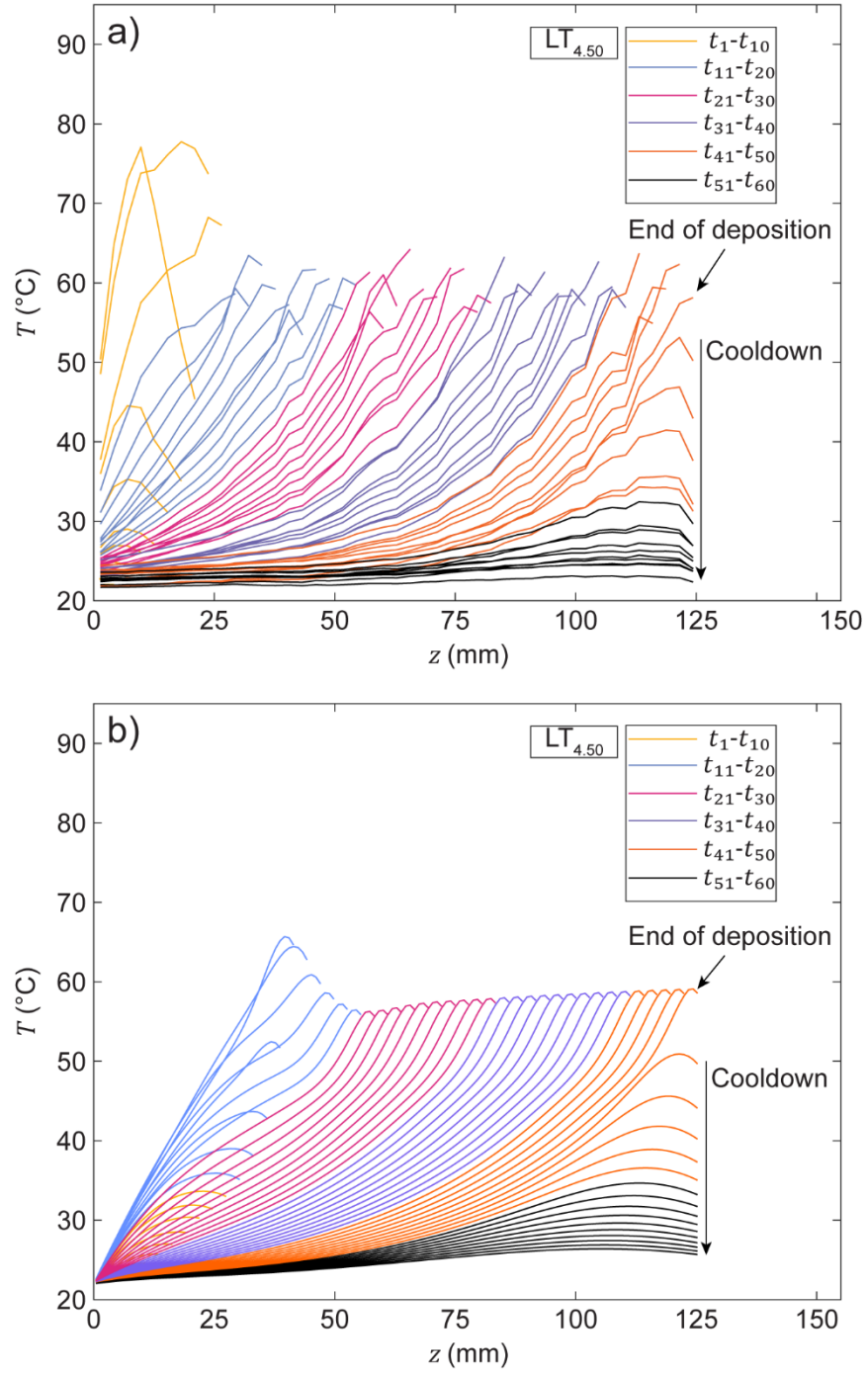


Figure 53: Thermal gradient at snapshots in time of the $LT_{4.50}$ print. a) Experimental results. b) Thermal model results.

are much longer in the model. Additionally, the shape of the gradient is much more consistent in the model than the experiment.

It is not presented here, but the differences between the model and experimental data become larger when the layer time is changed. This fact combined with the previously mentioned differences motivates future work to improve agreement between the model and experiments. Given the rough approximation of the curing kinetics given by the second order reaction and the multitude of kinetic models available in literature [90-92, 109, 110, 119, 122-130], more accurately characterizing the reaction kinetics is certainly feasible and could provide even better modeling capabilities. A more challenging, but certainly important, task is characterizing the temperature dependence of the material properties throughout the print. The model is setup so that more complicated reaction kinetics and material properties can easily be incorporated.

The flexibility to change the model makes it an excellent tool for material design. If the kinetics and temperature-dependent properties of a material can be measured, then they can be used in this model to get a benchmark of the printability of that material. Additionally, this tool can evaluate the large-scale printability of standard, commercial material systems that have already been well-characterized.

Along with this capability, the model provides insight to the fundamental behavior driving the unique thermal evolution that has been observed. Isolating the heat transfer and generation terms explains what is causing these behaviors. Figure 54 takes each layer and plots the total energy generated, heat lost due to conduction to the bed,

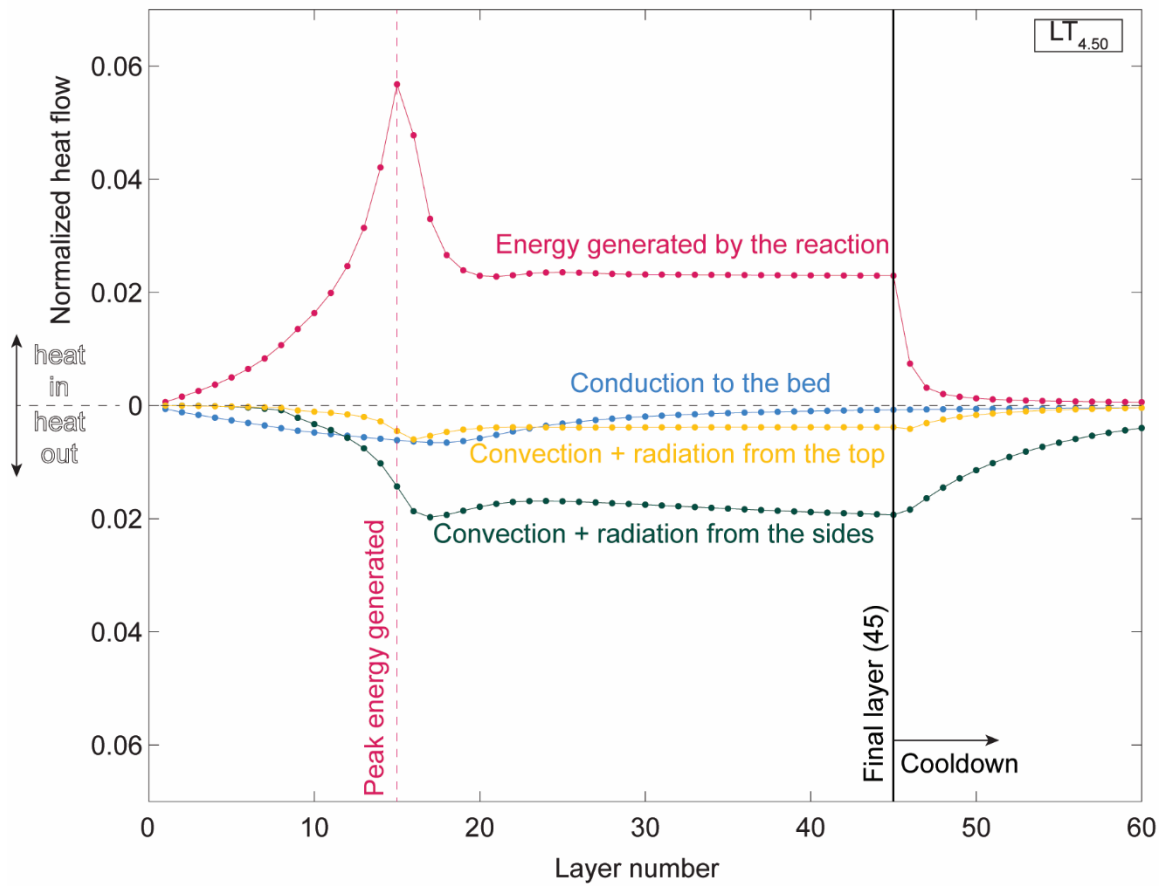


Figure 54: Normalized heat generated and released at each layer of the LT_{4.50} print, as predicted by the thermal model.

heat lost due to convection and radiation from the top of the wall, and heat lost due to convection and radiation from the sides of the wall. All of these values are normalized by the total energy generated in the 60 layer times shown on the graph. As expected, the energy generation is driving the thermal evolution. The heat lost through conduction, convection, and radiation lags behind the spike in energy generation. This behavior explains the buildup in energy that caused the initial temperature spike. When the heat loss terms do increase, their sum does not fully offset the energy spike. This behavior explains why the temperature of the wall remains elevated above room temperature throughout the print. Once deposition is terminated, the energy generation rapidly drops to zero, allowing the heat loss terms to cool the wall back to room temperature.

This analysis suggests that a material with decelerated reaction kinetics could eliminate the rapid release of energy, the corresponding temperature spike, and the temperature-induced flow that causes some prints to fail. This would allow more time for the heat transfer terms to cool the wall. ORNL's partner, Polynt-Reichold, has used this guidance to develop a less exothermic material system. This new material system avoids the large temperature spike and the temperature-induced flow it can cause. However, printing with this material requires a longer layer time because the gel time is greater. To tailor printing parameters to this new system, future work should focus on recreating the modeling discussed here.

5.5.3 *Warpage and conversion*

Finally, the previous chapter identified warpage as a key challenge in in-process chemically initiated printing. Residual stresses caused by thermal gradients and curing shrinkage can contribute to this behavior. Although these deleterious behaviors have been identified, they require more study to be fully understood. Studying the conversion could help understand these behaviors. As a byproduct of tracking energy generation, the thermal model estimates the conversion experienced by all the material within the wall, which cannot be easily observed by experimental methods during printing. Figure 55 shows snapshots of the modeled conversion gradient at integer multiples of the layer time, similar to Figure 53.

Much like in thermoplastic printing [32, 34, 36], the thermal gradients measured and modeled in Figure 53 can cause warpage. However, the magnitude of this behavior cannot be estimated without knowing when the residual stresses become active. In thermoplastic printing, residual stresses are only considered after the material has cooled below the glass transition temperature [36, 132]. At this point the polymer becomes solid-like and rigid enough to resist the thermal deformation of surrounding layers and create residual stress. The analog to this assumption for thermoset printing is that residual stresses are not created until the material gels. To predict when the material gels, and thus the magnitude of warpage, gelation behavior must be more well-defined than the linear approximation between gel time and temperature made in Figure 49a. Since the conversion experienced by the printed material can be predicted with high resolution

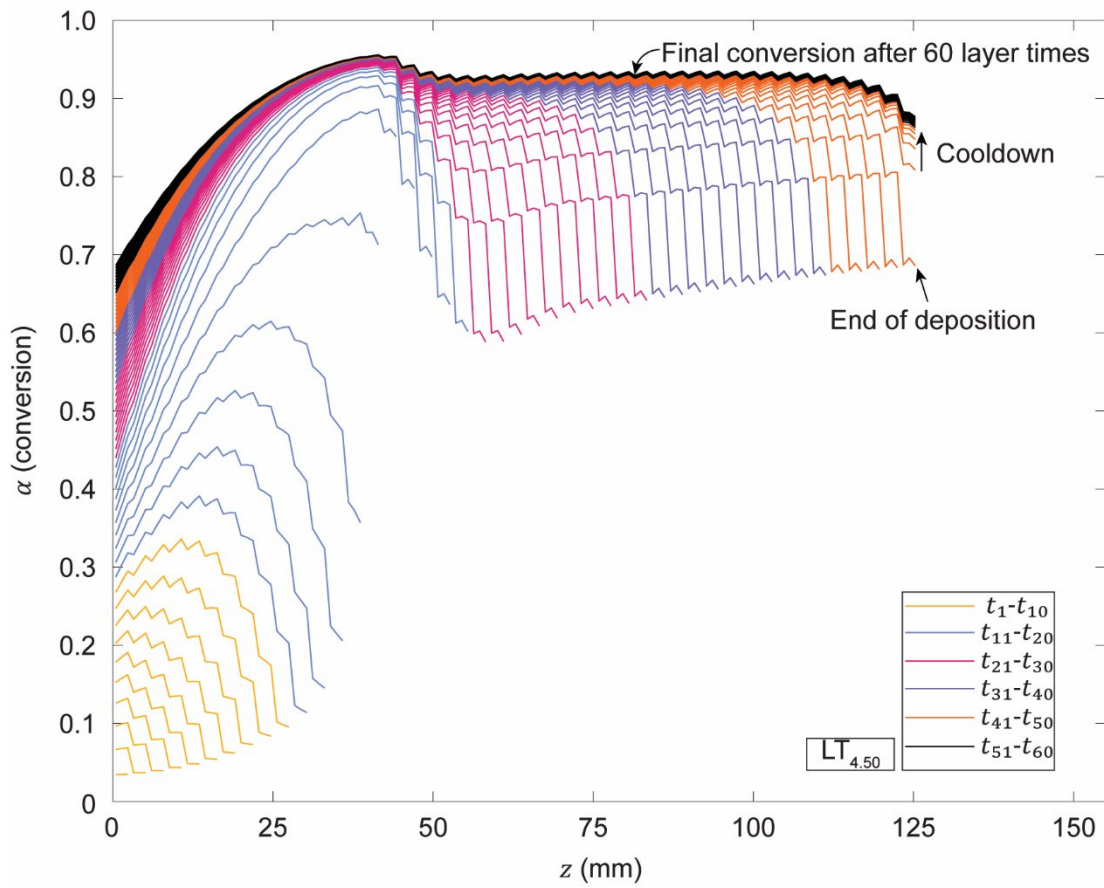


Figure 55: Conversion gradient predicted by the model at snapshots in time of the LT_{4.50} print.

(Figure 55), the relationship between conversion and gelation would be very helpful in understanding thermally induced warpage. Understanding this relationship would also make calculation of δ_{visc} much more accurate than the analysis presented in Figure 48- Figure 50. Future work should focus on modeling and characterizing the relationship between conversion and gelation.

Unlike thermoplastic printing, chemically initiated printing experiences shrinkage related to curing. This shrinkage is believed to scale with conversion. Under this assumption, the conversion gradients in Figure 55 suggest that each layer will experience a different amount of shrinkage than its neighbors. This differential shrinkage drives warpage. Again, to estimate the magnitude of this effect the relationship between conversion and gelation must be defined. Further, the relationship between conversion and shrinkage must also be determined. Future research should focus on modeling and characterizing both of these conversion-dependent behaviors.

5.6 Conclusion

First, this chapter presented a way to determine the un-gelled portion of the wall in thermoset printing with in-process curing, which provided an approximate way to predict pre-gel collapse. Additionally, this work presented a 1D finite-difference thermal model that incorporated the energy generation caused by the reaction of chemically initiated material. Results were shown to qualitatively agree with experimental data for the LT_{4.50} print without fans. These findings provide insight to the viscoelastic collapse, temperature-induced flow, and warpage observed in the previous chapter. Despite the

good agreement between the model and experiment, some key differences were observed in the thermal history. To address these differences, future work should focus on modeling and characterizing the temperature-dependence of the thermal properties of the material as well as more rigorously modeling the reaction kinetics. Additionally, characterizing the relationships between conversion, gelation, and shrinkage can make this model much more powerful. This understanding will allow the warpage to be predicted and improve the accuracy of pre-gel collapse predictions. However, the new capabilities promised by this 1D model are restricted to the thin wall. A model that considers the thickness dimension will be required to generalize this type of analysis to thicker features. Therefore, future research should also focus on extending this approach to 2D and 3D numerical analysis.

6 CONCLUSION

The goal of this work was to determine the feasibility of using material extrusion AM to print thermosets on the large scale. Structural instability became the clearest impediment to this goal. To address this challenge, the fundamental behavior governing instability and collapse had to be understood. Instability was studied by printing vertical walls, overhanging walls, and chemically initiated thermosets.

In the second chapter, the resistance to self-weight collapse was studied using a simple shape that is often found in the sparse infill structures used in AM – a long, thin, vertical wall. This work demonstrated that measurable rheological properties can be used in basic analytical mechanical models that assume elastic-plastic material behavior to accurately predict collapse height. This finding motivated the following two studies focused on the stability of a more complex shape and a system that cures during printing to suppress collapse on the large scale.

The third chapter extended the previously discovered link between rheological properties and structural instability by printing overhanging walls. These features are of broad interest because their successful implementation will enable even greater manufacturing flexibility. This work showed that analytical and finite element models of yielding and deflection agree remarkably well with experimentally observed collapse and deflection. Like the first chapter, this study motivates investigation of an in-process curing mechanism to suppress collapse and unacceptable levels of deflection.

The second and third chapter showed that higher storage modulus and yield stress result in prints that reach greater heights before collapsing. However, the increased

viscosity that comes along with greater storage modulus and yield stress make extrusion more difficult. In-process curing provides a solution to these competing behaviors, allowing low viscosity during extrusion and high storage modulus and yield stress after deposition. The fourth chapter used thin, vertical walls to evaluate in-process chemical initiation as a way to suppress collapse. This process was shown to increase structural stability, allowing for much taller walls to be printed. However, this success is not universal. Since curing is a time-dependent, exothermic process that can cause shrinkage, the level of success that was observed depended on the rate at which layers were stacked on top of the print and the thermal history of each layer. Adding layers too quickly resulted in the pre-gel collapse, which is similar to the phenomena observed in the second chapter. Adding layers too slowly magnified differential shrinkage and thermal stresses between successive layers and caused warpage. A window of successful printing was identified between these two bounds but was narrowed by the highly exothermic reaction of layers that affected the rigidity of the newly deposited layers. This study showed promise for the future of in-process curing, but the many variables affecting success need to be studied more rigorously.

The fifth chapter extended the study of chemically initiated printing. It presented a model to predict pre-gel collapse. This model motivates much more focused study of how the gel time of each layer evolves as temperature changes. Additionally, a 1D finite difference thermal model was created to predict the thermal and conversion history of chemically initiated, thin-wall prints. With only rudimentary characterization and

modeling of reaction kinetics and heat transfer properties, this model showed remarkable agreement with experimental results. However, the minor differences motivate future work to model the reaction kinetics and temperature-dependent heat transfer properties more accurately. These modeling efforts lay a strong foundation to design experiments that address these gaps in knowledge.

This dissertation identified and rigorously characterized the cause of collapse that is often observed in thermoset material extrusion AM. The study of two structures demonstrated the link between rheological properties and deflection mechanisms. In-process chemical initiation was shown to suppress instability, but also showed that its success depends on how quickly layers are stacked on top of the print. The presented modeling efforts motivate targeted material characterization studies that will help to implement thermoset printing with in-process curing more effectively. Overall, this work provides a foundation for studying how in-process curing systems can be tailored to suppress collapse of different thermoset inks and structures during material extrusion additive manufacturing.

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APPENDIX

7.1 Chapter 2

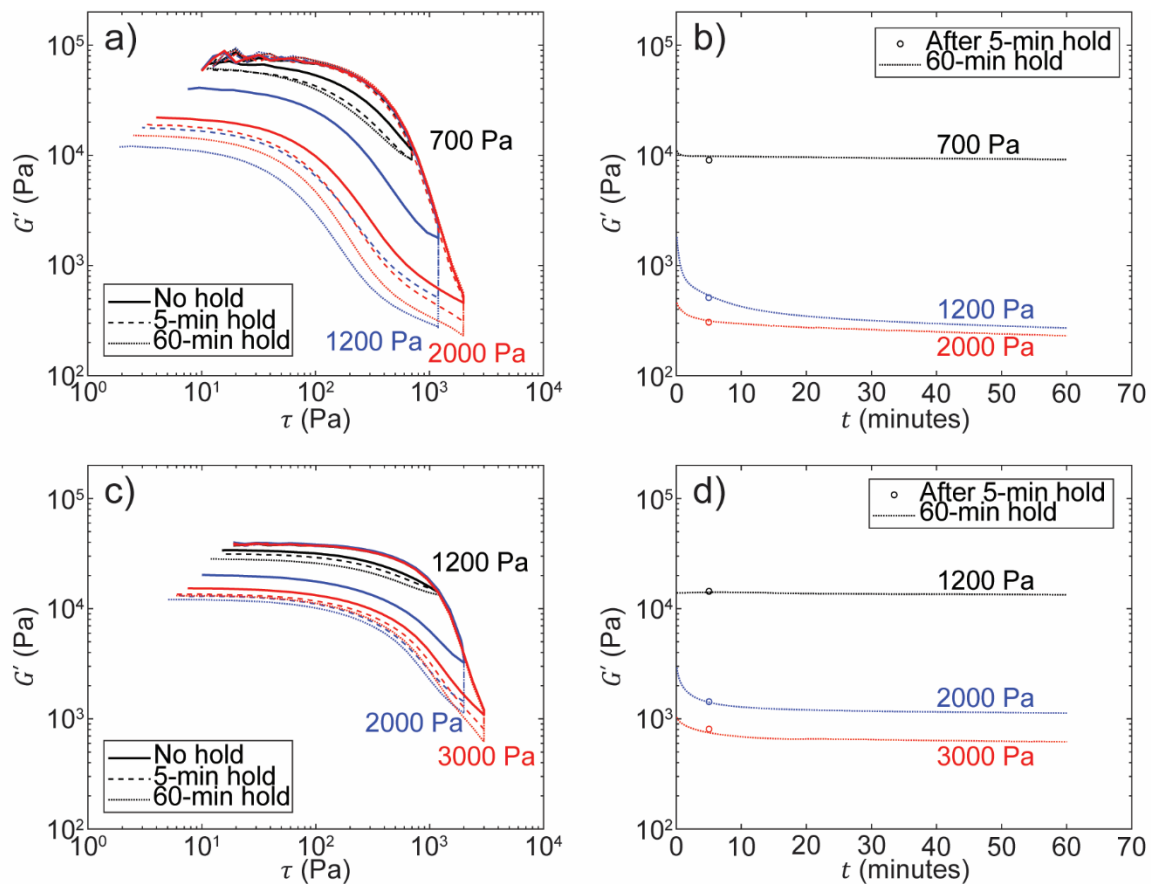


Figure 56: Ramp-up and ramp-down oscillatory tests of the NC and FS inks. a) NC oscillatory response in the initial (ramp-up) and post-shear (ramp-down) conditions. b) Shear storage modulus of NC during the holds. c) FS oscillatory response in the initial (ramp-up) and post-shear (ramp-down) conditions. d) Shear storage modulus of FS during the holds.

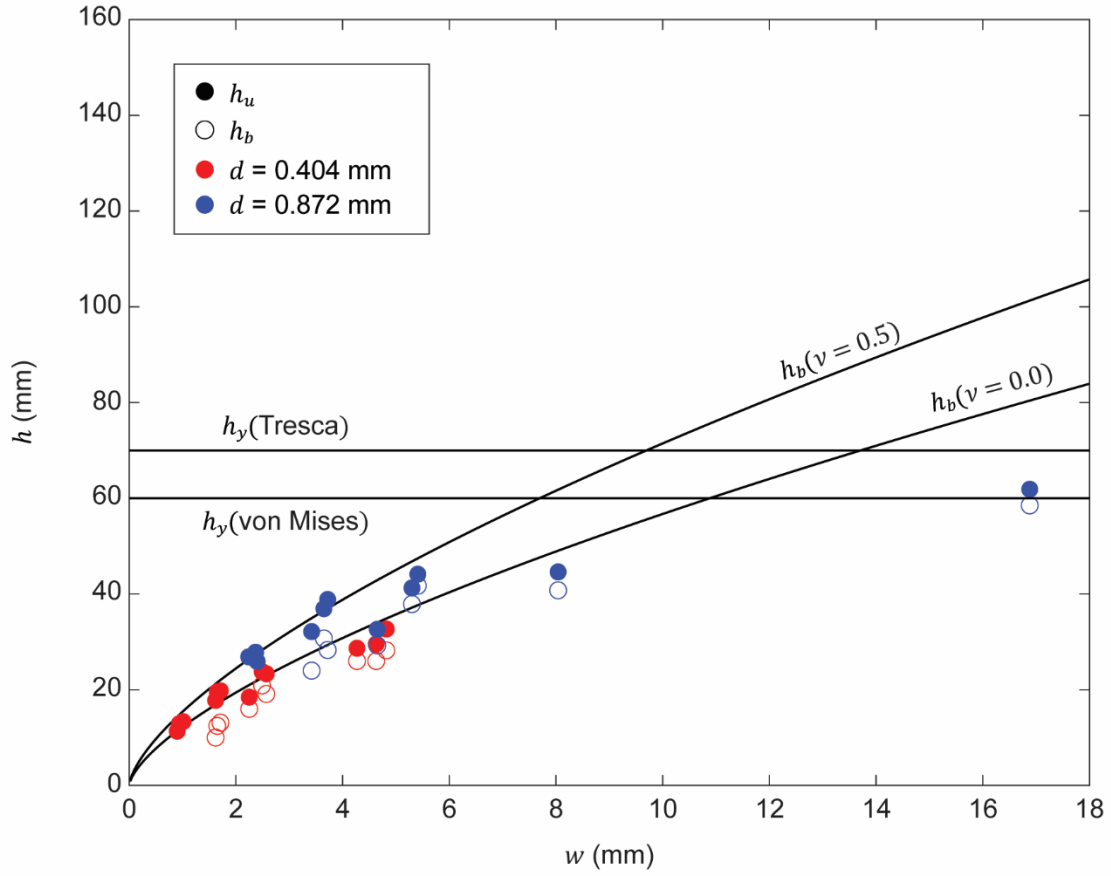


Figure 57: Comparison of the buckling and yielding height predictions under different assumptions. The NC ink is used to compare yielding height predictions based Tresca and von Mises yield criterion as well as the buckling height predictions assuming $\nu = 0$ and 0.5.

Table 10: Processing details of the printed NC ink walls.

	No. of beads	1	2	3	6	11	14	23
	Speed (mm/s)	25.0	25.0	25.0	25.0	25.0	25.0	25.0
	l (mm)	60.0	60.0	60.0	60.0	30.0	30.0	30.0
	Layer time (s)	2.4	4.8	7.2	14.4	13.2	16.8	27.6
NC 0.404-mm nozzle	w (mm)	0.9	1.6	2.3	4.3	-	-	-
	Total no. of layers	51	80	83	129	-	-	-
	h_u (mm)	11.3	17.8	18.4	28.7	-	-	-
	Print time (min)	2.0	6.4	10.0	31.0	-	-	-
	w (mm)	1.0	1.7	2.6	4.8	-	-	-
	Total no. of layers	60	89	105	147	-	-	-
	h_u (mm)	13.3	19.8	23.3	32.7	-	-	-
	Print time (min)	2.4	7.1	12.6	35.3	-	-	-
	w (mm)	0.9	1.7	2.5	4.6	-	-	-
	Total no. of layers	58	88	107	133	-	-	-
	h_u (mm)	12.9	19.6	23.8	29.6	-	-	-
	Print time (min)	2.3	7.0	12.8	31.9	-	-	-
NC 0.872-mm nozzle	w (mm)	2.2	3.7	4.7	8.0	-	16.9	-
	Total no. of layers	56	81	68	93	-	129	-
	h_u (mm)	26.9	38.8	32.6	44.6	-	61.9	-
	Print time (min)	2.2	6.5	8.2	22.3	-	36.1	-
	w (mm)	2.4	3.7	5.4	-	-	-	-
	Total no. of layers	54	77	92	-	-	-	-
	h_u (mm)	25.9	36.9	44.1	-	-	-	-
	Print time (min)	2.2	6.2	11.0	-	-	-	-
	w (mm)	2.4	3.4	5.3	-	-	-	-
	Total no. of layers	58	67	86	-	-	-	-
	h_u (mm)	27.8	32.1	41.2	-	-	-	-
	Print time (min)	2.3	5.4	10.3	-	-	-	-

Table 11: Processing details of the printed FS ink walls.

	No. of beads	1	2	3	6	11	14	23
	Speed (mm/s)	25.0	25.0	25.0	25.0	25.0	25.0	25.0
	l (mm)	60.0	60.0	60.0	60.0	30.0	30.0	30.0
	Layer time (s)	2.4	4.8	7.2	14.4	13.2	16.8	27.6
NC 0.404-mm nozzle	w (mm)	-	-	-	-	-	-	12.5
	Total no. of layers	-	-	-	-	-	-	381
	h_u (mm)	-	-	-	-	-	-	84.7
	Print time (min)	-	-	-	-	-	-	175.3
	w (mm)	-	-	-	-	-	-	-
	Total no. of layers	-	-	-	-	-	-	-
	h_u (mm)	-	-	-	-	-	-	-
	Print time (min)	-	-	-	-	-	-	-
	w (mm)	-	-	-	-	-	-	-
	Total no. of layers	-	-	-	-	-	-	-
	h_u (mm)	-	-	-	-	-	-	-
	Print time (min)	-	-	-	-	-	-	-
NC 0.872-mm nozzle	w (mm)	1.7	3.7	4.3	-	13.1	-	-
	Total no. of layers	45	89	92	-	181	-	-
	h_u (mm)	21.6	42.7	44.1	-	86.8	-	-
	Print time (min)	1.8	7.1	11.0	-	39.8	-	-
	w (mm)	1.7	3.3	4.7	-	-	-	-
	Total no. of layers	47	80	97	-	-	-	-
	h_u (mm)	22.5	38.4	46.5	-	-	-	-
	Print time (min)	1.9	6.4	11.6	-	-	-	-
	w (mm)	1.7	3.5	5.2	-	-	-	-
	Total no. of layers	48	80	111	-	-	-	-
	h_u (mm)	23.0	38.4	53.2	-	-	-	-
	Print time (min)	1.9	6.4	13.3	-	-	-	-

7.2 Chapter 3

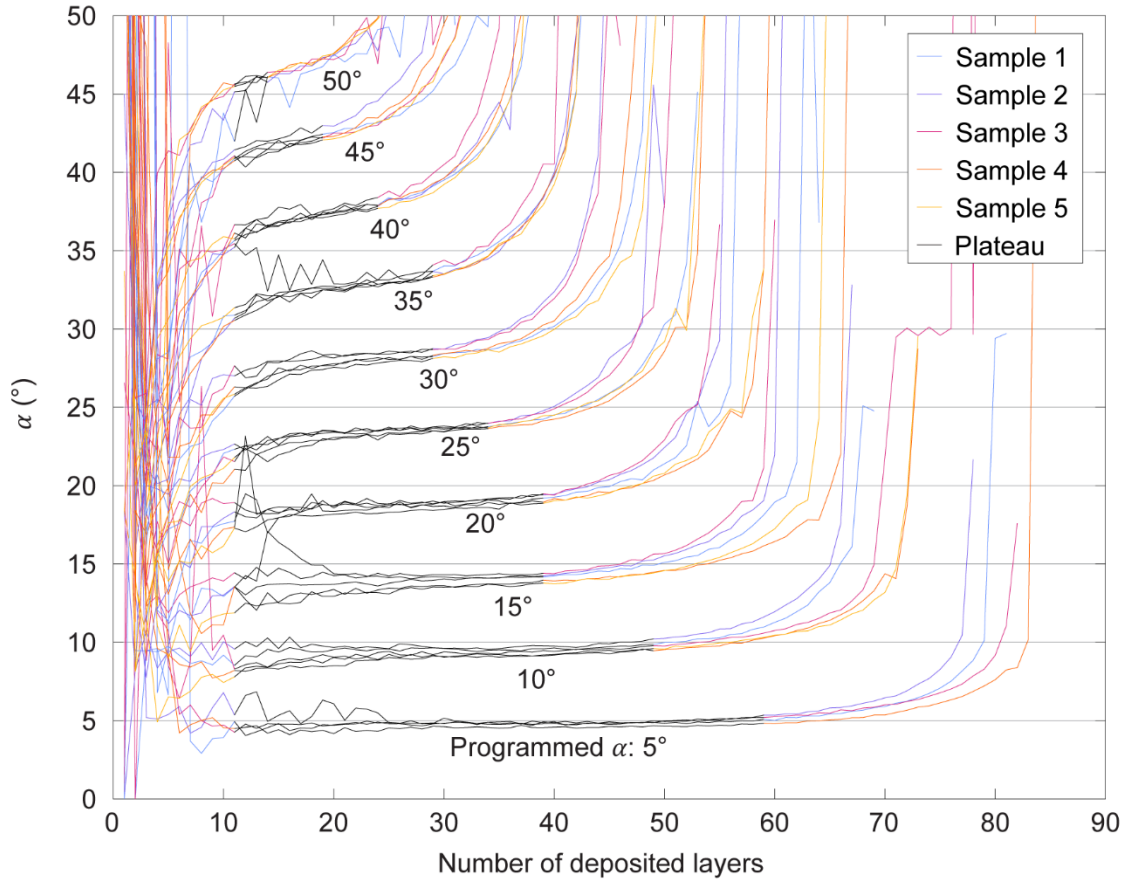


Figure 58: Evolution of α during printing, showing all of the prints (color) and the plateau region (black) used to find the average α .

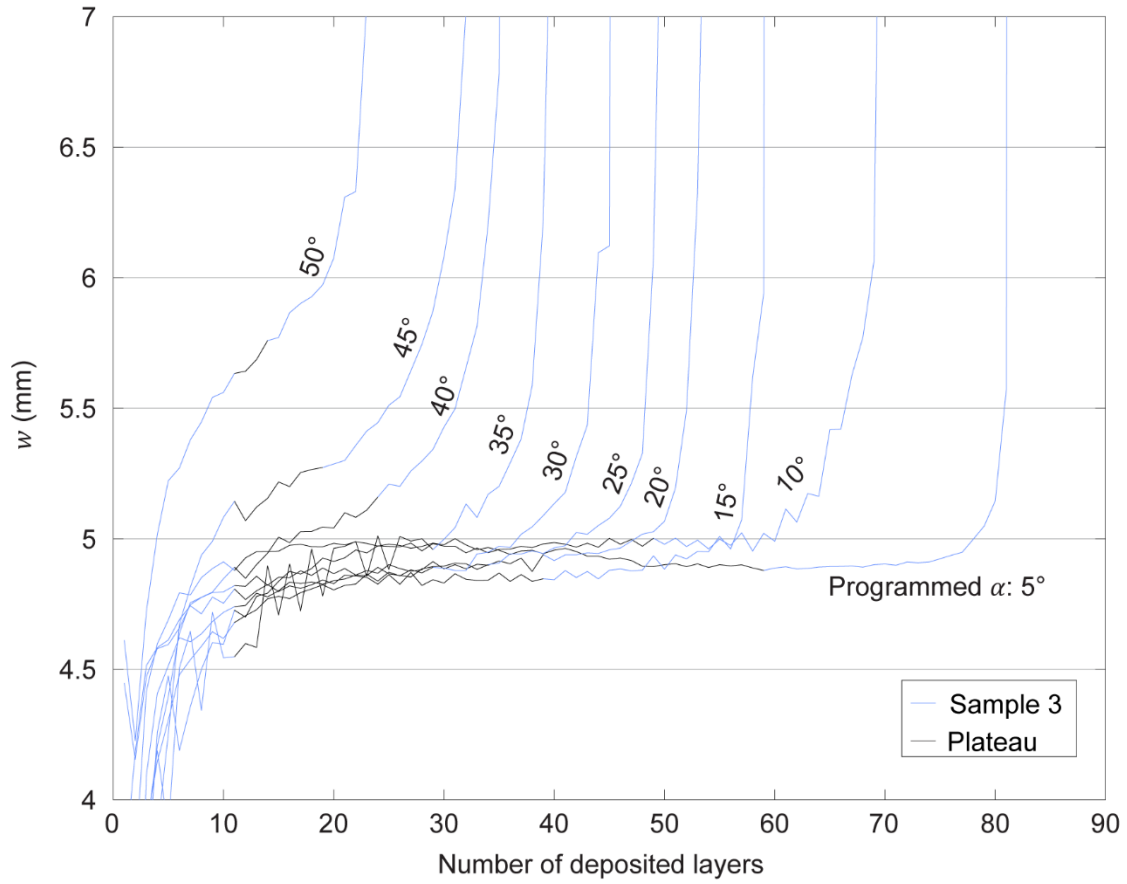


Figure 59: Evolution of w for “Sample 3” at each programmed α value, showing the plateau region (black) used to find the average w . For clarity, samples 1, 2, 4, and 5 are not shown.

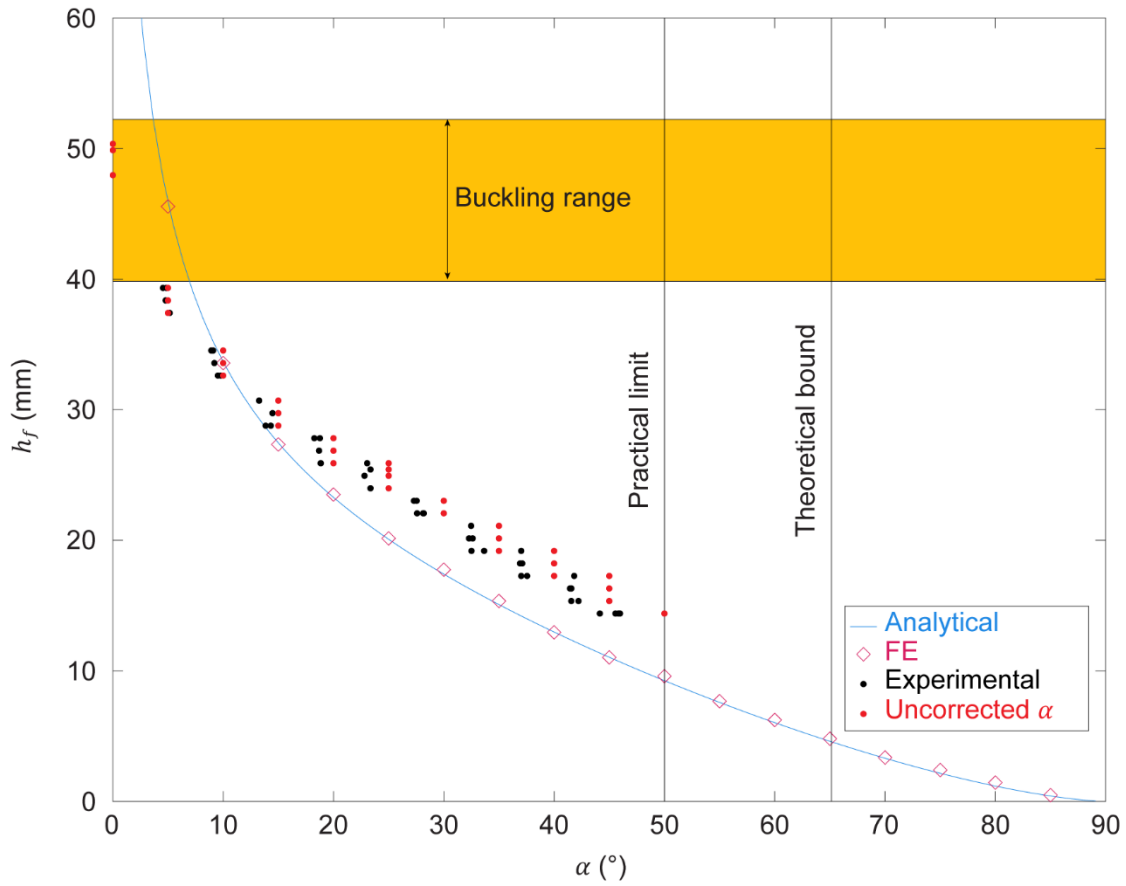


Figure 60: Collapse height versus α , showing the analytical yielding prediction, the FE model, the buckling range, the theoretical bound of α , the practical limit of α , the experimental data, and the experimental data before it was corrected for the measured value of α .

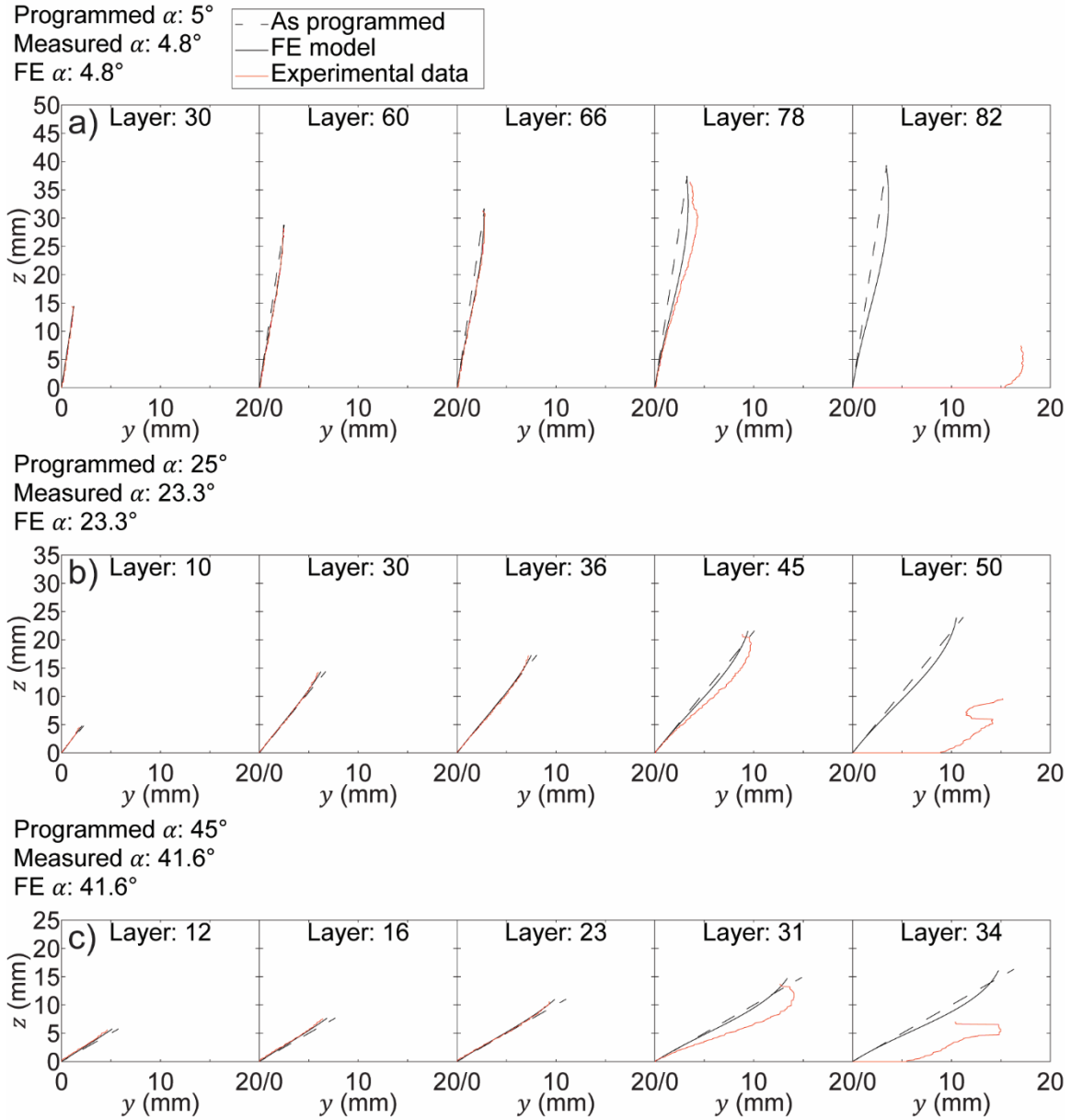


Figure 61: FE model compared to the experimental and as-programmed profiles. As-programmed α = a) 5°, b) 25°, and c) 45°. The y-axes are scaled to be double the z-axes.

VITA

Stian Kristov Romberg was raised in Maryville, Tennessee. In 2011, he enrolled at Brown University where he was elected to Tau Beta Pi in 2013 and earned a Bachelor of Science degree in Mechanical Engineering in 2015. After completing his undergraduate study, Stian worked at Y-12 National Security Complex as a Mechanical Engineer till 2017. Then, he joined Dr. Brett G. Compton's research group at the University of Tennessee, Knoxville and began studying thermoset additive manufacturing with the goal of obtaining both Master of Science and Doctor of Philosophy degrees in Mechanical Engineering. In 2018, Stian began collaboration with Dr. Vlastimil Kunc, John M. Lindahl, and Dr. Christopher J. Hershey at the Manufacturing Demonstration Facility of Oak Ridge National Laboratory. At ORNL, he helped research and develop a large-scale thermoset printing machine and the corresponding material feedstock. In 2019, he earned a Master of Science degree in Mechanical Engineering. During his time at the University of Tennessee, Stian has been thrilled to receive the Tickle Graduate Fellowship.

Stian's primary research aims to understand the structural stability challenges impeding the development of large-scale thermoset printing and develop methods to address those challenges. He sees this type of additive manufacturing as a way to mitigate the environmental impact of manufacturing by saving material, reducing energy consumption, and creating lighter components that are suited to reduce energy costs associated with transportation. Stian has accepted a position at the National Institute of

Standards and Technology (NIST) in the NIST NRC Postdoctoral Research

Associateship Program, where he plans to continue his study of structural stability and scalability of thermoset printing.