

Physics Based Modeling and Characterization of Filament Extrusion Additive Manufacturing

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Eric Gilmer

Abstract

Additive manufacturing (AM) is a rapidly growing and evolving form of product development that has the potential to revolutionize both the industrial and academic spheres. For example, AM offers much greater freedom of design while producing significantly less waste than most traditional manufacturing techniques such as injection and blow molding. Filament-based material extrusion AM, commonly referred to as fused filament fabrication (FFF), is one of the most well-known AM modalities using a polymeric feedstock; however, several obstacles currently prohibit widespread use of this manufacturing technique to produce end-use products, which will be discussed in this dissertation. Specifically, a severely limited material catalog restricts tailored product development and the variety of applications. Additionally, poor interlayer adhesion results in anisotropic mechanical properties which can lead to failure, an issue not often observed in traditional manufacturing techniques. A review of the current state of the art research in the field of FFF, focusing on the multiphysics-based modeling of the system and exploring some empirically determined relationships, is presented herein to provide a more thorough understanding of FFF and its complexities. This review further guides the work discussed in this dissertation.

The primary focus of this dissertation is to expand the fundamental understanding of the FFF process, which has proven difficult to measure directly. On this size scale, introduction of measurement devices such as thermocouples and pressure transducers can significantly alter the

behavior of the process or require major changes to the geometry of the system, leading to spurious measurements, incorrect outcomes, and/or conclusions. Therefore, the research presented in this dissertation focuses on the development and validation of predictive models based on first principles approaches that can provide information leading to the optimization of printing parameters and exploration of novel and/or modified materials without an exhaustive and inefficient trial-and-error process.

The first potential issue a novel material may experience in FFF is an inability to extrude from the heated nozzle. Prior to this work, no efforts were focused on the molten material inside the liquefier and its propensity to flow in the reverse direction through the annular region between the filament and the nozzle wall, referred to as annular backflow. The study presented in this dissertation explores this phenomenon, determining its cause and sensitivity to processing parameters and material properties. A dimensionless number, named the “Flow Identification Number” or FIN, is defined that can predict the propensity to backflow based on the material’s shear thinning behavior, the filament diameter, the nozzle diameter, and the filament feed rate and subsequent pressure inside the nozzle. An analysis of the FIN suggested that the backflow potential of a given material is most sensitive to the filament diameter and its shear thinning behavior (power law index). The predictive model and FIN were explored using three materials with significantly different onsets of shear thinning. The experiments validated both the backflow model and a previously derived buckling model, leading to the development of a rapid screening technique to efficiently estimate the extrudability of a material in FFF.

Following extrusion from the nozzle, the temperature profile of the deposited filament will determine nearly all of the mechanical properties of the printed part as well as the geometry of the individual roads and layers because of its temperature dependent viscoelastic behavior. Therefore,

to better understand the influence of the temperature profile on the evolution of the road geometry and subsequent interlayer bonding, a three-dimensional finite element heat transfer analysis was developed. The focus of this study is the high use temperature engineering thermoplastic polymer polyetherimide, specifically Ultem™ 1010, which had not been studied in prior modeling analyses but presents significant challenges in terms of large thermal gradients and challenging AM machine requirements. Through this analysis, it was discovered that convective cooling dominated the heat transfer (on the desktop FFF scale) producing a significant cross-sectional temperature gradient, whereas the gradient along the axis was observed to be significantly smaller. However, these results highlighted a primary limitation in computer modeling based on computational time requirements. This study, utilizing a well-defined three-dimensional model based on a geometry measured empirically, produced results describing 0.5 s of printing time in the printing process and elucidated great details in the road shape and thermal profile, but required more than a week of computation time, suggesting a need for to modify the modeling approach while still accurately capturing the physics of the FFF layer deposition process.

The determination of the extensive time required to converge the three-dimensional model, as well as the identification of a relative lack of axial thermal transfer, led to the development of a two-dimensional, cross-sectional heat transfer analysis based on a finite difference approach. This analysis was coupled with a diffusion model and a stress development model to estimate the recovery of the bulk strength and warping potential of a printed part, respectively. Through this analysis, it was determined that a deposited road may remain above T_g for 2-10 s, depending on the layer time, or time required for the nozzle to pass a specific point in the x-y plane between each layer. The predicted strength recovery was significantly overestimated, leading to the discovery of the extreme sensitivity of the predictive models to the relaxation time of a material, particularly at

long layer times. When the deposited filament has enough time to attain an equilibrium temperature, small changes in the relaxation time of the material resulted in significant changes in the predicted healing results. These results highlight the need for exact estimations of the material parameters to accurately predict the properties of the final print.

Physics Based Modeling and Characterization of Filament Extrusion Additive Manufacturing

Eric Gilmer

General Audiences Abstract

Additive manufacturing (AM), particularly filament-based material extrusion additive manufacturing, commonly known as fused filament fabrication (FFF), has recently become the subject of much study with the goal of utilizing it to produce parts tailored to specific purposes quickly and cheaply. AM is especially suited to this purpose due to its ability to produce highly complex parts with the ability to change design very easily. Furthermore, AM typically produces less waste than many traditional manufacturing techniques due to the process building a part layer by layer rather than removing unneeded material from a larger piece, resulting in a cheaper process. These freedoms make AM, and FFF in particular, highly prized among industrial producers.

However, numerous challenges prevent the adoption of FFF by these companies. Particularly, a lack of available material options and anisotropic material properties lead to issues when attempting to produce a part targeted for use in a specific field. FFF is primarily commercially limited to two materials: polylactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS) with a few other materials available in more specialized fields. However, essentially all these materials are limited to low use temperatures (less than 300 °C) and are primarily amorphous or with nearly negligible amounts of crystallinity. This severely limits the ability to tailor a printed part to a specific purpose and restricts the use of printed parts to applications requiring very low strengths. This is one reason why FFF, and most types of AM, is limited to the prototyping field rather than end-use applications. The other reason, anisotropic mechanical properties, is caused by

the building methodology of AM. Creating a part layer by layer naturally introduces potential areas of weakness at the joining of the layers. If bulk properties are not recovered, the interlayer bond acts as a stress concentrator under load and will break before the bulk material.

The work presented in this dissertation proposes methods to better understand the FFF system in order to address these two issues, leading to the optimization of the printing process and ability to expand the material catalog, particularly in the direction of high use temperature materials. The research discussed herein attempts to develop predictive models that may allow exploration into the FFF system which can be difficult to do experimentally, and by predicting the properties of a printed part, the models can guide future experimentation in FFF without the need for an extensive trial-and-error process. The work presented in this dissertation includes exploring the flow phenomena inside the FFF nozzle to determine extrudability as well as two-dimension and three-dimension heat transfer models with the goal of describing the viscoelastic, flow, diffusion, and stress development phenomena present in FFF.

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Format of Dissertation

A number of the chapters in this dissertation are self-contained manuscripts that are either published (Chapter 3 and 4) or in preparation for submission (Chapter 5). As such, these chapters are presented in their manuscript format and copied with permission from the relevant journal. Each of these chapters present their own background, motivation, experimental techniques, results, and discussions.

Table of Contents

Abstract.....	i
General Audiences Abstract.....	v
Acknowledgements.....	vii
Format of Dissertation	ix
1. Introduction	1
1.1 Overview of Additive Manufacturing Technologies and Market.....	1
1.2 Research Objectives	3
References	6
2. Literature Review	8
2.1 Defining Printability in FFF	9
2.2 Printability and Liquefaction: Determining Extrusion Failure.....	10
2.2.1 Identification of Common Failure Modes Inside the Heated Nozzle	10
2.2.2 Buckling Analysis of Filament Feedstock	11
2.2.3 Fluid Flow Analysis Inside the Heated Nozzle	13
2.3 Modeling Heat Transfer: From Liquefaction to Deposition	15
2.3.1 Methodologies for Developing Heat Transfer Analyses	16
2.3.2 Estimation of the Temperature, Pressure, and Flow Inside a Heated Nozzle	19
2.3.3 Exploring the Thermal Profiles of Deposited Filaments.....	22
2.3.3.1 Experimental Measurement of Temperature of Deposited Filaments.....	23
2.3.3.2 Biot Number and Its Use in Simplifying Heat Transfer Analyses	24

2.3.3.3	Examples of One-Dimensional Heat Transfer Analysis	25
2.3.3.4	Examples of Two-Dimensional Heat Transfer Analysis	29
2.3.3.5	Examples of Three-Dimensional Heat Transfer Analysis	30
2.4	Interlayer Bonding and Recovery of Bulk Properties in FFF.....	31
2.4.1	Polymer Welding as an Analog to FFF Printing	32
2.4.2	Exploration of Bond Development and Healing in FFF	35
2.4.2.1	Stages of Bond Development.....	35
2.4.2.2	Impact of Process Parameters on Interlayer Bonding	37
2.4.3	Modification of the Interface or Material to Increase Bonding in FFF	41
2.4.4	Application of Reptation Theory in Interlayer Bonding	45
2.4.5	Influences Other than Diffusion on Recovery of Bond Strength	49
2.4.6	Influence of Crystallization on Interlayer Bonding.....	50
2.4.6.1	Crystallization Effect on Welding	51
2.4.6.2	Effect of Crystallinity on Strength of Bond	53
2.4.6.3	Application of Crystallization in Fused Filament Fabrication.....	55
2.5	Development of Residual Strain and Stress in FFF.....	56
	References	59
3.	Model Analysis of Feedstock Behavior in Fused Filament Fabrication: Enabling Rapid Materials Screening.....	71
3.1	Abstract.....	71
3.2	Introduction	72

3.3	Numerical Methods	77
3.3.1	Governing Equations.....	77
3.3.2	Boundary Conditions.....	79
3.3.3	Constitutive Equations	79
3.3.4	Pressure Drop Estimation	80
3.4	Experimental	80
3.4.1	Materials	80
3.4.2	Elastic Modulus	81
3.4.3	Shear Rate Dependent Viscosity Measurements.....	82
3.5	Results and Discussion	83
3.5.1	Model Development to Predict Backflow	83
3.5.2	Analysis of FIN on Propensity to Backflow.....	87
3.5.3	Shear Rheology	93
3.5.4	FIN Backflow Model Predictions	95
3.5.5	Buckling Model Predictions.....	99
3.5.6	Experimental Validation of Models and Practical Impact on Extrudability	102
3.6	Conclusions	105
	References	106
4.	Characterization and Analysis of Polyetherimide: Realizing Practical Challenges of Modeling the Extrusion-Based Additive Manufacturing Process.....	110
4.1	Abstract.....	110

4.2	Introduction	111
4.3	Experimental	113
4.3.1	Materials and Printer System.....	113
4.3.2	Rheology Measurements	114
4.3.3	Scanning Electron Microscopy (SEM).....	115
4.4	Modeling	115
4.4.1	Governing Equations.....	116
4.4.2	Model Analysis of IR Temperature Measurements	117
4.5	Results and Discussion	117
4.5.1	Analysis of IR Temperature Data	117
4.5.2	Shear Rheology	118
4.5.3	Complete Re-Entanglement Time	120
4.5.4	SEM	123
4.5.5	Development of Representative Mesh Geometry from SEM Cross-Section Data.....	126
4.5.6	Thermal Model.....	129
4.6	Conclusions	131
4.7	Acknowledgments.....	132
	References	133
5.	Temperature, Diffusion, and Stress Modeling in Filament Extrusion Additive Manufacturing of Polyetherimide: An Examination of the Influence of Processing Parameters and Importance of Modeling Assumptions.....	136
5.1	Abstract.....	137

5.2	Introduction	138
5.3	Modeling.....	141
5.3.1	Heat Transfer	141
5.3.2	Degree of Healing.....	144
5.3.3	Shear Stress Development.....	146
5.4	Experimental	147
5.4.1	Sample Preparation.....	147
5.4.2	Degree of Healing Measurement.....	147
5.4.3	Reptation Times	148
5.4.4	Determination of Printing Conditions.....	149
5.5	Results and Discussion	150
5.5.1	Heat Transfer Model Results.....	150
5.5.2	Tear Strength: Measurement and Predictive Analysis.....	152
5.5.3	Warpage measurements: Comparison to Stress Predictions	158
5.6	Summary and Conclusions	162
	References	165
6.	Conclusions and Recommendations for Future Work.....	168
6.1	Conclusions	168
6.2	Scientific Contributions.....	170
6.3	Recommendations for Future Work	171
	Publications.....	173

Peer Reviewed Journal Manuscripts.....	173
Articles in Preparation for Peer Review.....	173
Conference Presentations.....	174
Appendix A – Supplementary Information	176
A.1 Supplementary Information for Chapter 5	176
A.1.1 References	184

Table of Figures

Figure 1.1. Image depicting FFF process ¹⁴	2
Figure 2.1. Schematic detailing the three common failure modes inside the FFF nozzle ⁸	11
Figure 2.2. Schematic showing boundary conditions used for modeling heat transfer in FFF nozzle ¹⁶ . Reprinted with permission from Ramanath, H. S.; Chua, C. K.; Leong, K. F.; Shah, K. D., Melt flow behaviour of poly-ε-caprolactone in fused deposition modelling. Journal of Materials Science: Materials in Medicine 2008 , 19 (7), 2541-2550. Copyright 2008 Springer.....	20
Figure 2.3. FFF nozzle heat transfer results produced by Nikzad, et al. ¹⁴ Reprinted with permission from Nikzad, M.; Masood, S. H.; Sbarski, I.; Groth, A., A Study of Melt Flow Analysis of an ABS-Iron Composite in Fused Deposition Modelling Process. Tsinghua Science and Technology 2009 , 14 (June), 29-37. Copyright 2009 Elsevier.	21
Figure 2.4. IR temperature measurements of three layers of an FFF print. Solid lines denote the measured temperature of the layer, and the dotted lines denote the estimated temperature of the weld between layers ⁵⁴ . Reprinted with permission from Seppala, J. E.; Migler, K. D., Infrared thermography of welding zones produced by polymer extrusion additive manufacturing. Additive Manufacturing 2016 , 12, 71-76. Copyright 2016 Elsevier.	24
Figure 2.5. Series of images displaying the temperature profile of a printed part during the printing process and the subsequent cooling. The lightest color corresponds to a temperature of about 180 °C, and the darkest color corresponds to a temperature of approximately 20 °C ²⁰ . Reprinted with permission from Compton, B. G.; Post, B. K.; Duty, C. E.; Love, L.; Kunc, V., Thermal analysis of additive manufacturing of large-scale thermoplastic polymer composites. Additive Manufacturing 2017 , 17, 77-86. Copyright 2017 Elsevier.	27
Figure 2.6. Experimental (hollow circles) and predicted (solid line) temperature of an extruded filament showing good agreement of the surface temperature between the two methods ²³ . Reprinted with	

permission from Costa, S. F.; Duarte, F. M.; Covas, J. A., Estimation of filament temperature and adhesion development in fused deposition techniques. <i>Journal of Materials Processing Technology</i> 2017 , 245, 167-179. Copyright 2017 Elsevier.	28
Figure 2.7. Representative results of an interrupted shear test showing the overshoot due to inception of shear, the attaining of a steady state stress value, the cessation of shear, and the subsequent inception of shear producing a smaller overshoot ⁹⁴ . Reprinted with permission from Pisipati, R.; Baird, D. G., Correlation of Non-Linear Rheological Properties of Polymer Melts with Weld-Line Strength. 1 ed.; Astarita, G.; Nicolais, L., Eds. Plenum Press: New York, 1984; pp 215-228. Copyright 1984 Springer.	34
Figure 2.8. Actual representation of the bond formation process ¹⁹ . Reprinted with permission from Bellehumeur, C.; Li, L.; Sun, Q.; Gu, P., Modeling of bond formation between polymer filaments in the fused deposition modeling process. <i>Journal of Manufacturing Processes</i> 2004 , 6 (2), 170-178. Copyright 2004 Elsevier.	36
Figure 2.9. Image depicting traditional FFF printing style (left) and the staggered printing style (right) proposed by Romeijn ¹¹⁴ . Reprinted with permission from Romeijn, T.; Wells, B.; Wei, D.; Paul, G., Investigation into the shear property of thin-walled additively manufactured structures using staggered fused filament fabrication. <i>Additive Manufacturing</i> 2020 , 35, 101259. Copyright 2020 Elsevier.	43
Figure 2.10. Figure adapted from Boiko, et al. displaying the growth of the interfacial shear strength as a function of $t^{1/4}$, proving that bond healing at amorphous-amorphous and amorphous-crystalline interfaces is diffusion controlled ⁹¹ . Reprinted with permission from Boiko, Y. M.; Guérin, G.; Marikhin, V. A.; Prud'homme, R. E., Healing of interfaces of amorphous and semi-crystalline poly (ethylene terephthalate) in the vicinity of the glass transition temperature. <i>Polymer</i> 2001 , 42 (21), 8695-8702. Copyright 2001 Elsevier.	53
Figure 2.11. DSC plots adapted from Schuman, et al. displaying the melting (a) and crystallization (b) peaks associated with HDPE/LLDPE melt blends of different compositions ¹³³ . Reprinted with permission from	

Schuman, T.; Stepanov, E. V.; Nazarenko, S.; Capaccio, G.; Hiltner, A.; Baer, E., Interdiffusion of Linear and Branched Polyethylene in Microlayers Studied via Melting Behavior. <i>Macromolecules</i> 1998 , 31 (14), 4551-4561. Copyright 1998 American Chemical Society.	55
Figure 3.1. Material extrusion failure modes, from left to right: inconsistent filament diameter that exceeds the nozzle diameter, annular backflow, filament buckling.....	75
Figure 3.2. Schematic of transition of solid filament to viscous fluid in FFF nozzle. Inset image illustrates representative velocity profile in the annulus between the solid filament and nozzle wall, as would be observed during annular backflow. Note the chosen coordinate system and direction. Geometry of nozzle is based on schematic diagram provided by E3D.	77
Figure 3.3. Graphical representation of velocity profile of a fluid that is not backflowing (red circles), a fluid in the transition region (blue diamonds), and a fluid that is backflowing (green triangles). Left and right y-axes represent filament (0.825mm) and nozzle (1.00mm) boundaries, respectively. Negative velocity is towards nozzle exit.	87
Figure 3.4. A parabolic relationship is observed between FIN and the normalized net flow magnitude. At a normalized net flow magnitude of zero, all material is flowing towards the nozzle exit. Below a FIN of 153, the material is expected to extrude assuming buckling does not occur. Above a FIN of 185, backflow is expected to always occur. A transition region occurs within which inconsistent extrusion may be observed. Open circles are modeled experimental conditions, solid line is a parabolic fit of the data.....	90
Figure 3.5. Sensitivity Analysis of FIN Parameters on normalized net flow magnitude. Blue represents a nominal case; red and green represent the lower and upper limits of analysis, respectively.	91
Figure 3.6. Overlay of SAOS (hollow shapes) and capillary steady shear (filled shapes) rheometry to determine correlation between the two measurement techniques for the materials analyzed in this study and to analyze the onset of shear thinning at their respective printing temperatures for ABS (O), LDPE (◇), and NaSPEG (Δ)	94

Figure 3.7. Results of backflow model analysis of ABS (O), LDPE (◊), and NaSPEG (Δ). From left to right, diameter: 1.65 mm, 1.75 mm, 1.85 mm. From top to bottom, feed rate: 5 mm/min, 5 mm/s, 10 mm/s. Zero z-direction velocity is represented by the solid line.	97
Figure 3.8. Results of buckling analysis. Vertical dotted lines represent range of shear rates that should be experienced inside the liquefier geometry. Data points above the horizontal dotted line should not buckle, and below the dotted line should buckle.	102
Figure 3.9. Image of NaSPEG backflow (left) and LDPE buckling (right) following attempt for FFF extrusion.	104
Figure 4.1. Image from IR video processed with the use of custom software demonstrating the cooling rate of the deposited filament. Lighter colored areas represent changing temperature, and dark colored areas represent material with a constant temperature.	118
Figure 4.2. Overlay of small amplitude oscillatory shear (hollow shapes) and steady torsional shear (filled shapes) rheometry of Ultem 1010 at 345 (●), 360 (▲), and 375 °C (■).	120
Figure 4.3. Relationship between the complete re-entanglement time of Ultem 1010 and isothermal temperature.	123
Figure 4.4. Cross-section image of a single road width wall (SRWW) displaying ovular shape. (a) The bottom layer of a 10-layer SRWW. (b) The top layer of the SRWW, illustrating differences in shape and weld width as a function of distance from the print bed.	124
Figure 4.5. Distribution of weld width as a function of layer height. Bond number corresponds to the bottom layer creating the weld.	125
Figure 4.6. Measurements required to develop geometry for meshing that represents the shape of the SRWW.	126

Figure 4.7. Measurements used to describe the representative shape of the individual layers in a single road width wall. (a) Corresponds to dimension A, (b) corresponds to dimension B, and (c) corresponds to dimension E from Figure 5.	128
Figure 4.8. Three-dimensional image describing the shape of the individual roads of a single road width wall. The curved top surface allows the analysis of the roads in sequence or isolation.	129
Figure 4.9. Image depicting node density used in the heat transfer finite element analysis of a single road width wall based on the parametric model.	129
Figure 4.10. Image displaying the thermal profile of an extruded filament at the end of 0.43 s.	131
Figure 5.1. Example of finite difference mesh used to predict heat transfer in FFF, not representative of mesh size used in analysis but simplified to highlight node matrix geometry. Top image depicts the full layer geometry, showing all axes. Bottom image depicts the cross-section of the layers, indicating the x- and z-axes.	143
Figure 5.2. Depiction of the locations used to determine the localized behavior during layer deposition. The image shows a radial cross-section of a deposited layer with the deposition direction going into the page.	151
Figure 5.3. Predicted temperature of layer 1 (a) and layer 22 (b) at different locations (described in Figure 5.2) in the layer as a function of time after deposition. A limited, coarse time step is represented in the plot for ease of visualization; however, a time step of approximately 0.007 s was utilized in the analysis.	152
Figure 5.4. a) Predicted degree of healing as a function of time after deposition for layer 1 and layer 22 and b) the predicted degree of healing as a function of the layer number	154
Figure 5.5. Analysis performed using method introduced by McIlroy and Olmstead demonstrating delay in entanglement recovery and sensitivity to minor changes in relaxation spectrum.	158

Figure 5.6. a) Stress developed in layer 1 as a function of time and b) final stress developed in each layer as a function of the layer number.....	160
Figure 5.7. Average warpage at the corners of each part as a function of the predicted stress developed in the final layer. Error bars represent a single standard deviation. A linear fit of the data is included. Deposition temperatures included 345 °C (●) and 375 °C (■). Bed temperatures included 175 °C (solid shapes) and 200 °C (hollow shapes). Print speeds included 15 mm/s (blue shapes) and 60 mm/s (red shapes).....	162
Figure 8.1. Tear test results of sample printed with $T_{dep} = 375$ °C, $T_{env} = 164$ °C, and $t_{layer} = 15$ s	176
Figure 8.2. Tear test results of compression molded PEI sample compared to the thickness of the film	177
Figure 8.3. Sensitivity analysis of the degree of healing examining the effect of varying bed temperature (a), environment temperature (b), heat transfer coefficient (c), nozzle temperature (d), and layer time (e).	180
Figure 8.4. Sensitivity analysis of the shear stress present in layer 1 and layer 24 examining the effect of varying bed temperature (a), environment temperature (b), heat transfer coefficient (c), nozzle temperature (d), and layer time (e).....	183

Table of Tables

Table 2.1. Measured and predicted adhesion strength (B_p) of various geometries based on a one-dimensional heat transfer prediction of the cooling rate. Recreated from Costa, et al. ²³ A, B, and C refer to three different deposition patterns used to relate the deposition parameters to adhesion. Reprinted with permission from Costa, S. F.; Duarte, F. M.; Covas, J. A., Estimation of filament temperature and adhesion development in fused deposition techniques. Journal of Materials Processing Technology 2017 , 245, 167-179. Copyright 2017 Elsevier.	29
Table 3.1. Range of parameters used in FIN analysis and expected to be observed in currently implemented filament AM systems with similar nozzle geometry.	89
Table 3.2. FIN values from modeled velocity profiles for ABS, LDPE and NaSPEG.	97
Table 3.3. Modulus measurements of ABS, LDPE, and NaSPEG at 20°C.	100
Table 5.1. List of parameters used to estimate the reptation time based on different approaches	149
Table 5.2. Comparison of final degrees of healing using different methods of approximating reptation time as a function of specified process parameters. Reptation time approximation techniques are specified in Table 5.1.	155
Table 8.1. Ranges of variables used in the sensitivity analysis	178

1. Introduction

1.1 Overview of Additive Manufacturing Technologies and Market

Additive manufacturing (AM) has roots extending as far back as 1890 with topographical and photosculpture technologies¹⁻⁴. These early, primitive techniques set the groundwork for further advancements which took the form of stereolithographic and direct deposition methodologies⁵⁻⁷. AM as we know it today was first introduced in 1981 by Hideo Kodama as a method of creating a physical part in an additive, rather than subtractive, manner⁸. The first methods of AM were crude, but they paved the way for the various modalities of AM to develop. Today, additive manufacturing has grown exponentially in both the research and industrial fields. From 1990 to 2018, the number of research articles published about AM increased exponentially⁹. The commercial market is similarly growing at a very fast rate with a compound annual growth rate (CAGR) of 25.9% from 2014 to 2015 resulting in a market value of \$5.165 billion worldwide¹⁰.

Currently, seven modalities of AM exist: material extrusion, material jetting, binder jetting, vat polymerization, powder bed fusion, directed energy deposition, and sheet lamination¹¹⁻¹². Of these, material extrusion (ME) is one of the most prevalent^{10, 13}. According to the 2016 Wohler's Report, ME comprises about 15% of the AM market at that time, just behind photopolymerization and laser sintering at 45% and 25%, respectively. ME benefits from a cheap and easy to use feedstock material as well as low energy costs, especially compared to its vat polymerization and powder bed counterparts. In material extrusion additive manufacturing, a polymer feedstock, generally a filament or pellets, is fed into a heated nozzle. Inside the nozzle, the polymer is heated to a fluidic state. The solid material above this molten pool pushes out the fluidic material and is in turn heated to a fluidic state. The extruded material is then selectively placed in a two-dimensional layer dictated by a computer aided design (CAD) model that has been converted into

individual layers by a slicing software. After the first layer of the design is completed, either the print bed is lowered or the print head is raised, and another layer is placed on top of the first. This pattern is repeated until the part is completed. Figure 1.1 displays the steps of this process.

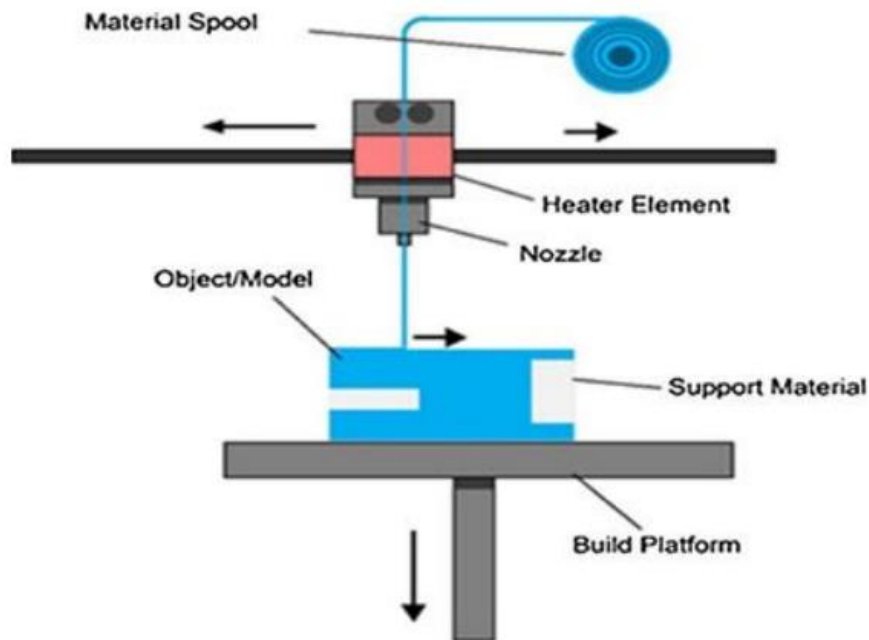


Figure 1.1. Image depicting FFF process¹⁴

Additive manufacturing provides multiple benefits not available in traditional manufacturing. The process of building through the addition of layers allows the production of parts with highly complex geometries such as internal voids¹⁵. Because of this, AM has been used in areas ranging from jewelry¹⁶ to cellular structures¹⁷ to construction¹⁸ and many others¹⁹. With greater freedom of design, researchers are able to create parts with different structures and materials that allow for optimized mechanical properties such as strength and flexibility while using less material. Along

with geometric freedom, AM provides the ability to immediately alter materials during the manufacturing process. Multi-material printing, especially without seams or joints, can produce parts with tailored mechanical properties. To produce a similar product, traditional manufacturing must produce multiple pieces of a whole and join them in a post-production step, increasing time, cost, and potential for error.

Furthermore, the ability to print any design straight from a CAD model allows for quick turnaround and short waiting times. Instead of building a part at a factory and shipping it to its final destination, companies are able to print on location, thus saving in excessive shipping costs. Also, because AM does not require new, complex molds for each part, manufacturers using AM are able to save the time and money inherent in designing and making the molds²⁰.

Overall, additive manufacturing stands to offer many beneficial changes to the current market once it achieves widespread implementation. Lowering of costs, time, and environmental hazards are but a few of the potential areas where AM can improve on the current manufacturing technologies. However, to realize this potential AM must first address the few challenges inherent to the process, particularly low mechanical properties stemming from a limited material catalog and lack of adhesion between layers.

1.2 Research Objectives

The research objectives proposed in this dissertation revolve around modeling the extrusion based additive manufacturing process and validating those models with thorough experimentation. This work will advance AM by providing insight into a system that is difficult to explore in-situ and lead to the optimization of the process parameters, development of new processes or machine designs to enhance printed part properties, and expansion of the limited material catalog. The proposed research objectives are as follows:

1. Investigate the applicability of first principles flow models to describe the complex flow field inside the fused filament fabrication (FFF) nozzle. Pair the flow model with previously reported buckling analysis to enable rapid screening of novel and/or modified materials for FFF printing.
2. Determine whether a three-dimensional heat transfer analysis based on first principles and representative geometries could be coupled with viscoelastic models to predict the evolution of the road geometry and interlayer bonding, particularly in high temperature amorphous polymers.
3. Explore a two-dimensional heat transfer model in conjunction with degree of healing and stress development models to predict the ultimate properties of a printed part to guide future experimental optimization of printing parameters and efficiently identify the printability of novel materials. Validate the accuracy and sensitivity of the models through experimental measurements of the bond strength and warpage.

Currently, most of the methods for determining optimal parameters and exploring novel materials have been highly inexact and inefficient. These techniques typically include general “rules of thumb” and exhaustive trial-and-error sets of experiments. The research objectives proposed in this dissertation should provide work toward removing the need for these inefficient methodologies by providing a much more detailed understanding of the FFF process that is currently lacking. The objectives should provide a framework for predicting the outcome of the an FFF experiment, thus guiding experimental design and removing the expensive and time-consuming trial-and-error approach. Likewise, novel materials can be further explored by anticipating their behavior to rapidly determine which materials are inherently impossible to print and which materials require specific printing parameters. The results of the research objectives

also have the opportunity to suggest approaches that can be used to modify the printers themselves to improve the process at its core.

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2. Literature Review

Seven types of additive manufacturing are currently in use: material extrusion, material jetting, binder jetting, vat polymerization, powder bed fusion, directed energy deposition, and sheet lamination¹⁻². Of these seven modalities, one of the most recognizable is filament based material extrusion, also known as fused filament fabrication (FFF) or its trademarked name, fused deposition modeling. This type of AM typically uses polymer filament feedstock to build a part by extruding molten material in layers.

The FFF process begins by feeding a solid polymer filament into a nozzle which has been heated to a temperature at which the material becomes fluidic. The heat from the nozzle causes the end of the filament to become molten, but the filament above the heated region remains solid. This solid filament acts as a piston as it is forced into the nozzle, extruding the molten material and continuing to feed fresh polymer into the nozzle. A gantry system moves the extrusion nozzle and places the extrudate in an exacting pattern dictated by a computer aided design (CAD) model, creating a single thin layer, typically less than 0.5 mm thick. Once the layer is completed, the distance between the nozzle and bed is increased, and the sequence repeats until the CAD model has been fully reproduced. A schematic of this process is shown in Figure 1.1.

FFF currently experiences multiple problems that prevent its adoption to create end use products. One of the most pressing issues is the material catalog for FFF. Compared to traditional manufacturing, FFF has an extremely limited number of options available for applicable materials due to extrusion issues such as filament buckling, annular backflow, excessive warping, and unoptimized printing parameters. Further, the lack of strong interlayer bonding, which is a function of the molecular mobility of the polymer, prevents the printed parts from matching the mechanical properties of their traditional manufacturing counterparts. This reduction in interlayer bonding, as

well as warping and residual stress buildup, is further exacerbated by crystallization in semi-crystalline materials and road geometry which leads to void formation and lack of interlayer contact.

Currently, understanding of FFF is limited because exploring it experimentally can be challenging and no accurate models exist to describe the entire process in detail. This review presents the current state of the literature regarding the process modeling and experimental analysis of FFF including the failure modes during the extrusion process, the heat transfer both in the nozzle and following deposition, the growth and development of the bond between layers of a printed part, the influence of crystallinity on the interlayer bonding, and the residual buildup of stresses during printing. All these issues are hindering the advancement of AM, including FFF. The goal of this research is to advance the fundamental understanding of the filament extrusion AM process.

2.1 Defining Printability in FFF

The question of “What material is printable?” has long been a concern of researchers. The field of traditional manufacturing possesses an extensive material catalog, but AM is severely limited because of a lack of answers to this question. Duty, *et al.* recently stated that a material is printable if it meets four criteria: i) must be able to be extruded out of a nozzle, ii) extruded material must hold its shape, iii) extruded material must be able to bridge a gap of a specific length, and iv) the extruded material must remain geometrically stable as the material cools to room temperature³. Zawaski, *et al.* and Chatham, *et al.* suggested similar requirements for “printability,” although these researchers focused on deposition of the material, i.e. maintaining geometric accuracy, ability to produce small features, and gap bridging, with the assumption that any printable material will also be extrudable⁴⁻⁵. Researchers have examined the process of FFF in numerous ways, which will be discussed in this dissertation, but not many have examined it from the perspective of

developing techniques to guide material selection efficiently. This is the approach that has been adopted for much of the work presented in Chapters 3, 4, and 5. The following sections explore the current research beginning with examining the behavior of the polymer inside the FFF nozzle, the first aspect of printability, and then leading to layer deposition and interlayer adhesion.

2.2 Printability and Liquefaction: Determining Extrusion Failure

The extrusion process, while seemingly simple in practice, can be very complex⁶. Extrusion from the heated nozzle has been compared to a flow through a pipe due to the fluidic nature of the polymer in this region, but this does not account for the inclusion of, and transition from, the solid filament feedstock. This comparison has often led to inaccurate assumptions and, by extension, inaccurate models. To facilitate an increase in accuracy, the common failure modes inside the nozzle must be addressed.

2.2.1 Identification of Common Failure Modes Inside the Heated Nozzle

Valkenaers, *et al.* examined the various failure modes during the extrusion process and narrowed the potential modes to the three most probable, shown in Figure 2.1 from left to right: inconsistent filament diameter, annular backflow, and filament buckling⁷. Inconsistent filament diameter often results in filaments that are too wide to fit into the nozzle. Because the filament is unable to go into the nozzle, the extrusion fails. When the filament is too thin, it cannot withstand the forces required to expel the molten material, and it buckles or breaks. Therefore, the diametric tolerance of the filament needs to be very narrow. However, this failure mode can be eliminated by refining the filament fabrication methods. Due to this reason, researchers have not studied this failure mode and account for it in models by specifying that the filament diameter remains constant with minor, if any, variation.

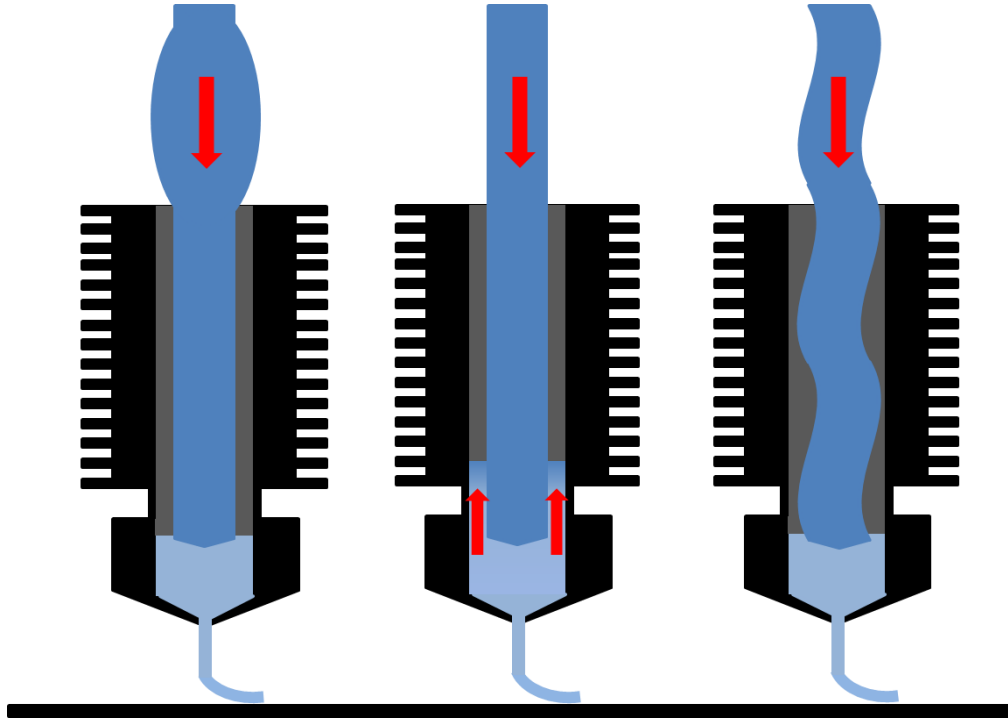


Figure 2.1. Schematic detailing the three common failure modes inside the FFF nozzle⁸.

2.2.2 Buckling Analysis of Filament Feedstock

Filament buckling becomes an issue when the filament is not thick enough or stiff enough to withstand the forces required to expel the molten polymer through the nozzle⁹. A method was developed to predict the potential for a polymer to buckle by calculating the critical buckling stress with Euler's analysis for pin ended boundary condition and comparing this to the pressure required to extrude the molten material, Equations (2.1) and (2.2), respectively¹⁰⁻¹¹.

$$\sigma_{cr} = \frac{\pi^2 E}{4(L/R)^2} \quad (2.1)$$

$$\Delta P = \frac{8\eta_a Q l}{\pi r^4} \quad (2.2)$$

In these equations, σ_{cr} is the critical buckling stress, E is the elastic modulus, L is the length of the column from the top of the liquefier to the rollers, R is the radius of the filament, ΔP is the pressure difference measured in a capillary rheometer, η_a is the apparent viscosity, Q is the volumetric flow rate, l is the length of the capillary, and r is the radius of the capillary.

The pressure required to extrude the material, which is a function of the viscosity, should not exceed the critical buckling stress. Because it is difficult to measure the pressure in-situ, Venkataraman, *et al.* developed a method to relate the pressure measured in a capillary rheometer to the pressure inside the FFF nozzle¹¹. A material that requires a higher pressure to extrude in the capillary rheometer should exhibit similar behavior in the heated nozzle, for a fixed nozzle and liquefier geometry and volumetric flow rate. Since the systems are not perfectly identical, i.e. the capillary and nozzle possess different L/D values, and the liquefier and barrel are not the same diameter, the pressures and viscosities will not be equal at equivalent volumetric flow rates. To account for this, a scaling factor, k , was identified to relate the pressure measured in the capillary rheometer, ΔP , to that which the material would experience in the FFF nozzle, $\Delta P'$, shown in Equation (2.3)¹¹.

$$\Delta P = k\Delta P' \quad (2.3)$$

The filament should buckle when the extrusion pressure exceeds the critical buckling stress, Equation (2.4), leading to the final relationship, shown in Equation (2.5).

$$\Delta P' > \sigma_{cr} \text{ or } \Delta P/k > \sigma_{cr} \quad (2.4)$$

$$\frac{E}{\eta_a} < \frac{8Q \left(\frac{L}{R}\right)^2}{\pi^3 r^4 k} \quad (2.5)$$

in this equation, k is a scaling factor that allows the pressure measured in the capillary rheometer to apply in the FFF liquefier. Recent studies performed by Coogan and Kazmer and Anderegg, *et al.* have shown that it is possible to measure the pressure inside the FFF nozzle with modified designs, although the two studies do not completely agree with each other regarding the potential accuracy of utilizing this method to calculate the viscosity of the material during printing¹²⁻¹³.

Venkataraman, *et al.* tested multiple materials in a 508 μm nozzle and discovered that the critical value for most polymers lies in the E/η_a range of 3×10^5 to $5 \times 10^5 \text{ s}^{-1}$ ¹¹. The materials they tested that exceeded this range printed without buckling, while materials that fell short of this range buckled during the extrusion process. This work was performed without changing nozzle geometry, nozzle temperature, or other system parameters, but proved that the buckling potential of the materials could be predicted with a mathematical model with minimal measurements performed outside the printer.

2.2.3 Fluid Flow Analysis Inside the Heated Nozzle

No one has examined annular backflow in any detail to the knowledge of this author. Most work considered the filament diameter to be equal to the nozzle diameter and immediately transitions from solid filament to molten polymer. This allowed researchers to model the thermal, velocity, and pressure profiles based on purely fluid flow inside the nozzle, similar to the flow

within a cylindrical pipe¹⁴⁻¹⁵. Ramanath, *et al.* showed a slow transition to an isothermal state, which would greatly affect the viscosity and, by extension, the fluid flow¹⁶. Nikzad, *et al.* showed a system that reached the isothermal state very quickly, most likely due to different material properties such as heat capacity¹⁴. However, these two groups focused primarily on the nozzle exit (i.e. not the nozzle entrance) and did not consider backflow to be a possibility.

When considering the fluid flow inside the heated nozzle, one of the most vital parameters is the pressure exerted on the molten polymer to extrude it. Because the nozzle walls are stationary, this pressure provides the driving force for extrusion in a Hagen-Poiseuille style flow. Michaeli modeled this flow for die geometries, and Bellini *et al.* adopted the equations, Equation (2.6) to (2.9), to describe the flow for a polymer in a nozzle with a conventional cylindrical shape with a converging zone between the liquefier and nozzle tip¹⁷⁻¹⁸. These equations take into account the non-isothermal behavior inside the liquefier by introducing an Arrhenius style relationship incorporating activation energy to flow.

$$\Delta P_1 = 2L_1 \left(\frac{v}{\phi} \right)^{\frac{1}{m}} \left(\frac{m+3}{(D_1/2)^{m+1}} \right) e^{[\alpha(1/T-1/T_\alpha)]} \quad (2.6)$$

$$\Delta P_2 = \left(\frac{2m}{3 \tan(\beta/2)} \right) \left(\frac{1}{D_2^{\frac{3}{m}}} - \frac{1}{D_1^{\frac{3}{m}}} \right) \left(\left(\frac{D_1}{2} \right)^2 (m+3) * 2^{m+3} \right)^{\frac{1}{m}} e^{[\alpha(1/T-1/T_\alpha)]} \quad (2.7)$$

$$\Delta P_3 = 2L_2 \left(\frac{v}{\phi} \right)^{\frac{1}{m}} \frac{(m+3)(D_1/2)^2}{(D_2/2)^{m+3}} e^{[\alpha(1/T-1/T_\alpha)]} \quad (2.8)$$

$$\Delta P = \Delta P_1 + \Delta P_2 + \Delta P_3 \quad (2.9)$$

where ΔP is the calculated pressure gradient, ΔP_i is the calculated pressure gradient for section i , L is the length of the liquefier, v is the solid filament feed rate, m and ϕ are material constants, D is the diameter of the liquefier, β is the convergence angle of the narrowing section of the nozzle, α is activation energy to flow, T is the temperature and T_α is the reference temperature at which the activation energy was measured.

Ramanath compared these calculations to values produced through ANSYS finite element simulation modeling¹⁵. The results were found to be comparable which suggests the calculations accurately predict the pressure drop produced during the AM process. The pressure calculation will be vital to understanding the backflow potential of novel materials and will greatly help when determining the optimal parameters for printing.

2.3 Modeling Heat Transfer: From Liquefaction to Deposition

To better understand the printability and potential to fail, more information regarding the temperature inside the nozzle and deposited filament is required. However, since the inception of the FFF process, empirically measuring temperature profiles has been a challenge, leading to a drive for the development of heat transfer models to describe the system. These heat transfer models have primarily focused on two areas: inside the nozzle and throughout the extrudate¹⁴⁻¹⁵. Because viscosity is a function of temperature, modeling the heat transfer inside the nozzle provides more information on the flow behavior and may offer a better understanding of how the material will behave as it is extruded. Being able to accurately map the temperature of the material inside the nozzle and as it exits the nozzle is important to being able to accurately model the cooling rate of the deposited filament. This can, in turn, lead to understanding the viscoelastic state following extrusion and during the deposition and subsequent interlayer bonding processes.

The majority of current AM heat transfer models focus on the material following extrusion. The cooling rate of the material determines the interlayer diffusion and bond between layers which, in turn, determines the overall mechanical properties of the printed part. The cooling rate will also heavily influence the viscoelastic properties, as mentioned previously, which will determine polymer chain orientation, stress state of the layers, and the actual cross-sectional shape of the layer. To better understand the cooling rate and its relationship to the printing process, many researchers have worked to identify which printing parameters most strongly affect the cooling rate as well as connecting the cooling rate prediction to bond strength development¹⁹⁻²³. Ideally, both areas of the heat transfer models, nozzle and deposited filament, would be modeled concurrently. However, doing so introduces a great deal of complexity, primarily in accounting for both convective and conductive heat transfer in multiple directions for extended periods of time, and requires a high level of computing power. The following sections discuss the general methodologies for developing heat transfer analyses and the current research into modeling heat transfer in the FFF process from nozzle to deposited and solidified road.

2.3.1 Methodologies for Developing Heat Transfer Analyses

The temperature profile inside the heated nozzle and liquefier provides the initial state of a material prior to its deposition. However, because it is difficult to directly measure the thermal profile inside the nozzle without significant changes to its design, a modeling approach can allow exploration into this system. This section will explore some of the aspects of the development of the heat transfer models. These aspects include the boundary conditions applicable to the heated nozzle and the viscosity of the material inside the nozzle and its dependence on the temperature.

Boundary conditions play a vital role in all aspects of modeling. In FFF nozzles, these often take the form of either a constant temperature boundary or a constant heat flux boundary^{16, 24-25}.

Most liquefiers are heated using a single cartridge heater controlled by a PID controller using a single thermocouple to measure the temperature. Both the cartridge heater and thermocouple are often a distance away from the liquefier and filament, which can cause incorrect temperature readings. However, knowing the amount of heat supplied by the cartridge heater should allow the constant heat flux boundary to be the more accurate choice. This can be calculated using Equation (2.10).

$$q = \dot{m}C_p(T - T_i) = \left(\frac{\rho v A}{2\pi \left(\frac{D}{2}\right) L} \right) C_p(T - T_i) \quad (2.10)$$

where q is the heat flux, $\dot{m}$ is the mass flow rate of the molten polymer, C_p is the specific heat capacity of the polymer, T is the temperature of the polymer at the exit of the liquefier, T_i is the temperature of the polymer at the entrance of the liquefier, ρ is the density of the polymer, v is the velocity of the molten polymer inside the liquefier, A is the cross sectional area of the liquefier, and D and L are the diameter and length of the liquefier, respectively. The constant temperature boundary condition is simpler to implement, but it requires the assumption that the liquefier has a thermal conductance great enough to evenly spread the heat from the cartridge heater without creating any temperature gradients. Since most liquefiers are constructed of aluminum, brass, or copper²⁵⁻²⁶, this is often a valid assumption to make. The heat generated by shearing the polymer must also be assumed to be negligible, which can be verified through in-situ measurements²⁷. Efforts to directly measure the temperature of the polymer melt inside the nozzle have produced some results, but it requires significant change to the nozzle, so there is some concern that it is not perfectly representative¹²⁻¹³.

Another consideration that must be accounted for is the flow behavior of the polymer, specifically the viscosity, and how it changes based on the parameters of the process. Since viscosity is a function of temperature, it can be written as Equations (2.11) and (2.12)²⁸

$$\eta(T, \dot{\gamma}) = H(T)\eta(\dot{\gamma}) \quad (2.11)$$

$$H(T) = \exp \left[\alpha \left(\frac{1}{T - T_0} - \frac{1}{T_\alpha - T_0} \right) \right] \quad (2.12)$$

where $H(T)$ is an Arrhenius relationship accounting for the temperature dependence of the viscosity, α is the activation energy to flow, T_α is a reference temperature at which $H(T)$ is 1, T_0 is 0 °C, and T is the temperature of interest. Therefore, any time when T is not equal to the reference temperature, the temperature dependence becomes potentially important. This issue is not a concern when the system is operating at a quasi-steady state, where the heat supplied by the cartridge heater is sufficient to maintain a nearly isothermal temperature of the molten pool. However, with any change in the polymer flow, primarily due to lack of controlled filament feed rate, the conditions will change. An increase in the filament velocity will prevent the pool from attaining the isothermal behavior and will cause the local temperature of the polymer to decrease which, in turn, will cause the local viscosity to increase. This could cause a buckling failure in the system due to a sudden increase of the pressure required to extrude the molten polymer or a backflow failure due to a change in the shear thinning behavior.

Measurement of the viscosity of polymeric materials is often performed on a capillary rheometer²⁹⁻³². This instrument is particularly useful to examine materials for AM because it closely mimics the FFF system, i.e., a solid piston extrudes a molten pool of polymer through a

narrow opening. Furthermore, this instrument can measure the apparent viscosity of polymers at similar shear rates to those observed in FFF printing, $\dot{\gamma} \geq 100 \text{ s}^{-1}$. If shear rates less than 100 s^{-1} are required, rotational steady and dynamic shear rheometry may be performed with parallel plate or cone-and-plate geometries and related to the viscosity measured in the capillary rheometer through the Cox-Merz rule³³⁻³⁴.

2.3.2 Estimation of the Temperature, Pressure, and Flow Inside a Heated Nozzle

Some researchers have developed models, particularly finite element models, that utilize the details discussed in the previous section to describe a material's thermal, velocity, and pressure profiles inside the FFF nozzle. Ramanath, *et al.* modeled poly- ϵ -caprolactone (PCL) in an FFF nozzle with a very long liquefier¹⁶. This allowed the polymer plenty of time to reach an isothermal state, which, in turn, provided the polymer the opportunity to achieve a consistent velocity and pressure until the nozzle diameter changed. Ramanath, *et al.* studied this system to gain a better understanding of the melt flow behavior of the polymer, which aids in developing a better final print. Some of the boundary conditions this group used include an inlet velocity of 0.0011 m/s, determined by the filament feed rate, velocities of 0 m/s at the wall due to the no slip boundary condition, and temperatures at the wall of the liquefier and entrance of the liquefier of 60 °C and 40 °C, respectively, shown in Figure 2.2.

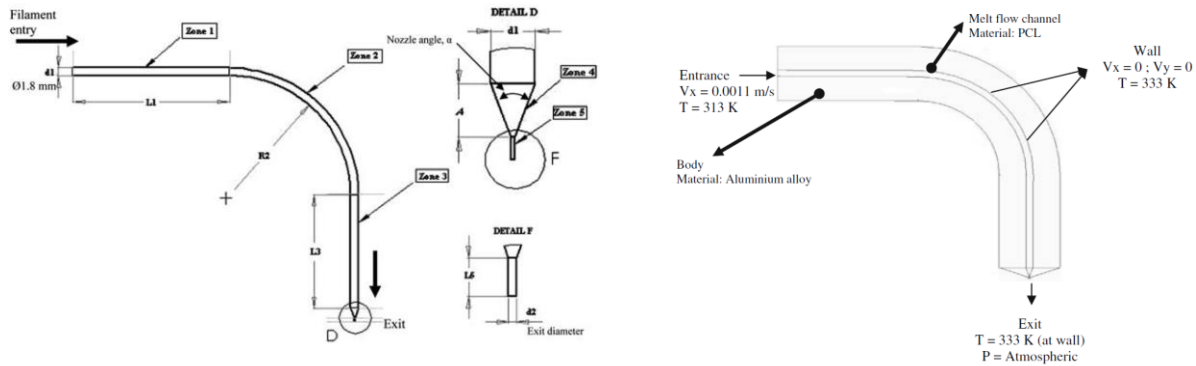


Figure 2.2. Schematic showing boundary conditions used for modeling heat transfer in FFF nozzle¹⁶. Reprinted with permission from Ramanath, H. S.; Chua, C. K.; Leong, K. F.; Shah, K. D., Melt flow behaviour of poly-ε-caprolactone in fused deposition modelling. *Journal of Materials Science: Materials in Medicine* **2008**, 19 (7), 2541-2550. Copyright 2008 Springer.

Ramanath's model predicted the PCL required about 42 mm inside the nozzle to reach an isothermal state. This is approximately 35% of the length of the liquefier they were using in the study. They also suggest that common AM polymers such as ABS would require even longer times to reach the isothermal state. This highlights the importance of material properties and nozzle design in the application of AM. The researchers further calculated the maximum pressure of the system to be $1.64 \times 10^6 \text{ N/m}^2$ at the entrance of the liquefier. At the same time, the group performed the pressure calculations developed by Michaeli and Bellini¹⁷⁻¹⁸ and compared them to their finite element modeling (FEM) results. They saw similar trends between the Bellini calculations and the ANSYS FEM results, although the magnitude was slightly different, which they attributed to the FEM methodology, including causes such as the number and placement of nodes as well as the shape of the elements.

Nikzad *et al.* performed a similar FEM analysis on the same style of liquefier with the goal of accelerating the identification of novel materials by modeling their behavior inside the liquefier¹⁴. This group used an ABS-iron composite system as their subject and used similar boundary conditions as Ramanath¹⁶ except that the entrance and liquefier temperatures were 60

°C and 270 °C, respectively. This group demonstrated a rapid, nearly immediate, transition to isothermal behavior, Figure 2.3. This further demonstrates the effect that different materials and different material properties may have on the behavior inside the liquefier. Nikzad *et al.* also showed that along with the temperature, the velocity and pressure both reach a steady value almost immediately at the entrance of the liquefier for the material in their study, and it only changes upon contraction of the liquefier at the nozzle exit.

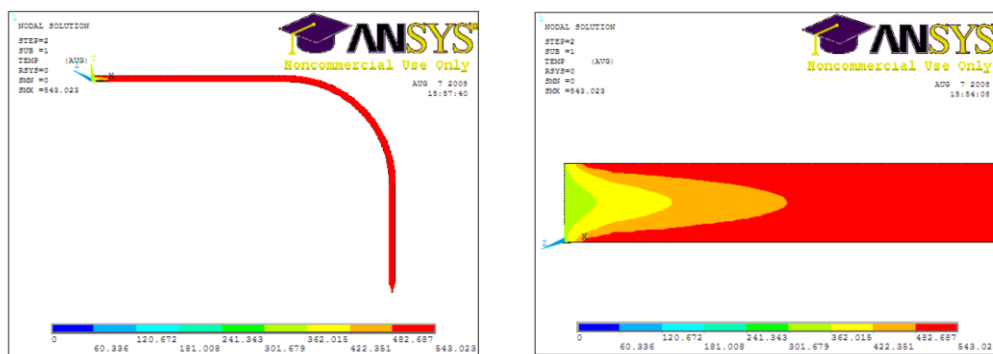


Figure 2.3. FFF nozzle heat transfer results produced by Nikzad, *et al.*¹⁴ Reprinted with permission from Nikzad, M.; Masood, S. H.; Sbarski, I.; Groth, A., *A Study of Melt Flow Analysis of an ABS-Iron Composite in Fused Deposition Modelling Process*. *Tsinghua Science and Technology* **2009**, 14 (June), 29-37. Copyright 2009 Elsevier.

Considering a more conventional nozzle design, Osswald, *et al.* suggested a significantly smaller melt pool than Ramanath and Nikzad³⁵. This group still assumed a nearly instantaneous transition from solid to molten material and perfect contact between the filament and the liquefier wall, but they developed a model for melting with pressure flow removal. Their results, which they validated empirically, indicated that the melting rate would be significantly influenced by the liquefier temperature, the temperature of the filament as it enters the liquefier, and the angle of the tip of the nozzle.

Recently, Serdeczny, *et al.* demonstrated the effectiveness of modeling the behavior of the material inside the nozzle using computational fluid dynamic (CFD) simulations³⁶. This group

simulated the localized temperature inside the nozzle to better understand the fluid flow behavior of the molten polymer. Through this approach, Serdeczny, *et al.* identified a backflow region similar to what is discussed in Section 2.2.3, although they suggest that it should never cause failure. This group's results also corroborate data presented by Phan, *et al.* who had previously demonstrated that the temperature of the material exiting the nozzle does not always match the temperature of the nozzle, which is a common assumption in the modeling of the extrudate³⁷⁻³⁸. Models similar to these can be further utilized to estimate the limits of filament feed rates based on the flow behavior of the material and nozzle geometry as well as understand the influence of the process parameters on the temperature of the material as it is deposited³⁹⁻⁴¹.

Mackay, *et al.* examined the pressure drop inside the nozzle. Using this pressure, the group identified the maximum feed rate and minimum temperature that can be used during the FFF process. By examining three different materials, they were able to observe that their predictions can be made to follow a mastercurve by utilizing dimensionless numbers to describe the system⁴².

2.3.3 Exploring the Thermal Profiles of Deposited Filaments

Following extrusion from the heated nozzle, the material will experience rapid shifts in temperature due to the new environmental conditions. Measurement of the temperature in the extrudate can be difficult as will be discussed in this section, so most researchers have resorted to computationally modeling the thermal profile. To simplify the modeling of the system, many researchers have made assumptions that reduce the system to one-^{19-20, 43-44} or two dimensions⁴⁵ as well as assuming unrealistic cross-sectional shapes such as rectangles⁴⁵, circles¹⁹, and ellipses⁴⁶. It has been shown that these idealized shapes are not accurate, and the true cross-sectional shape of the deposited filament is a function of the print speed, although they are useful for initial explorations into the system⁴⁷.

2.3.3.1 Experimental Measurement of Temperature of Deposited Filaments

Experimentally verifying the temperature of the filaments during the printing process poses many challenges. Introducing thermocouples, even extremely thin thermocouples, has the potential to add a large amount of error due to a potential conducting away of the heat or reflecting heat from an external source, similar to that seen in automated tape placement⁴⁸⁻⁴⁹. There is a further issue regarding a potential lack of contact on the lower or upper layer⁵⁰. Although some analyses have been performed using the thermocouple approach⁵¹⁻⁵², most employ an infrared camera to capture the temperature change in real time^{44, 53-54}.

The research conducted using infrared cameras to monitor the temperature of the printed filaments suggests that the polymer only remains above its glass transition temperature (T_g) for less than two to three seconds, Figure 2.4. The results indicate that previous layers absorb some heat from the new layer and the nozzle itself as it passes over, but this does not greatly increase the time at which the polymer is above T_g . While this method appears to be a useful, non-interference option to measure the temperature, it possesses its own disadvantages. A primary limitation of this method is the lack of temperature data at the weld interface. Because this interface is so small, the infrared camera does not have the resolution necessary to capture the small-scale gradients. Seppala *et al.* accounted for this by assuming the temperature at the interface was an average value of the bulk temperature of the two adjacent filaments, although this is not necessarily an accurate assumption, especially at short time scales⁵⁴. A further drawback, which is prevalent in all current temperature measurement techniques, is the lack of information regarding the internal temperature of the extruded filaments. All current methods of measuring the temperature of the filaments, including infrared thermography, can only measure the temperature of the surface. This

dearth of information increases the difficulty of ascertaining if a one- or two-dimensional heat transfer assumption is valid.

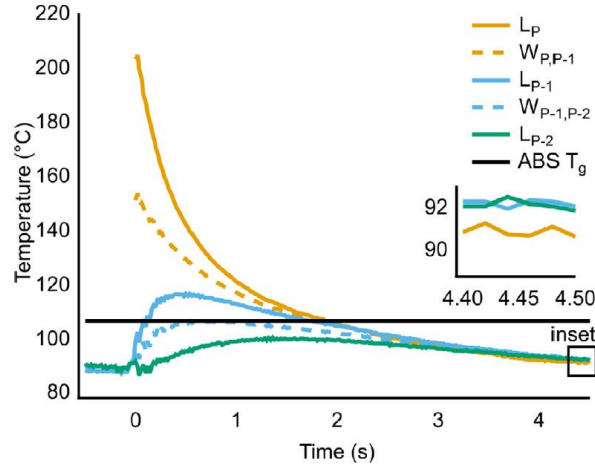


Figure 2.4. IR temperature measurements of three layers of an FFF print. Solid lines denote the measured temperature of the layer, and the dotted lines denote the estimated temperature of the weld between layers⁵⁴. Reprinted with permission from Seppala, J. E.; Migler, K. D., *Infrared thermography of welding zones produced by polymer extrusion additive manufacturing*. *Additive Manufacturing* **2016**, 12, 71-76. Copyright 2016 Elsevier.

2.3.3.2 Biot Number and Its Use in Simplifying Heat Transfer Analyses

Some researchers have attempted to simplify the FFF system to a one-dimensional heat transfer problem through the lumped capacitance method^{19, 55-56}. The lumped capacitance method assumes that the conduction along the length of the deposited filament would be much greater than the convection at the air-polymer interface. If this is the case, the temperature profile of the cross-section of a single extruded fiber should be uniform. To determine if this assumption is valid, the Biot number may be calculated using Equations (2.13) or (2.14)^{44, 55}. The Biot number must be less than 0.1 to indicate that the heat will conduct along the length of the deposited filament more easily than it will convey away from the polymer-air interface, allowing for the reduction to a one-dimensional heat transfer problem.

$$Bi = \frac{h(V/A_p)}{k} \quad (2.13)$$

$$Bi = \frac{hL}{k} \quad (2.14)$$

where Bi is the Biot number, h is the convective heat transfer coefficient of the air, V is the volume of the solid, A_p is the surface area of the solid, L is the characteristic length of the material, and k is the thermal conductivity of the polymer.

Li calculated the Biot number of an FFF system based on a cross-section of an ellipse with axis lengths of 2a = 0.5105 mm and 2b = 0.254 mm, convection coefficient of 50 – 100 W m² °C⁻¹, and thermal conductivity of 0.15 – 0.19 W m⁻¹ °C⁻¹, and estimated that the Biot number should be in the range of 0.021 – 0.054, suggesting a one-dimensional assumption is valid⁵⁵. Compton *et al.* performed a similar analysis using a characteristic length of 0.0055 m, a convective heat transfer coefficient of 8.5 W m⁻² °C⁻¹, and a thermal conductivity of 0.17 W m⁻¹ °C⁻¹, resulting in a Biot number of 0.275⁴⁴. Even though this value is larger than 0.1, Compton *et al.* argued that the conductive term is large enough compared to the convective term that any cross-sectional temperature gradient would be minimal and can be neglected.

2.3.3.3 Examples of One-Dimensional Heat Transfer Analysis

Compton *et al.* analyzed a basic heat transfer model using a one-dimensional assumption and rectangular cross-section on a scale similar to that found in big area additive manufacturing (BAAM)²⁰. The researchers compared the results of their model to a set of infrared images detailing the surface temperature of the material during the printing process, Figure 2.5. The group discovered that the temperature of each layer, immediately upon deposition, is approximately

equal to that of the nozzle orifice, in this case, 180 – 200 °C. The layer below, being cooler than the one placed atop it, quenches the new road to approximately 170 °C, immediately. The layer then quickly cools to ambient temperature. When comparing the results of the model to the experimental measurements, some agreement is observed, but several discrepancies are also apparent, especially during the cooling stage.

This group further examined the temperature of the top layer of the print immediately before a new layer is laid down, which they called the characteristic temperature. This temperature should influence the bonding ability of the two layers the most strongly. Unsurprisingly, the researchers discovered that a shorter layer time, or faster print speed, resulted in a higher characteristic temperature before a new layer is deposited. When the layer time was set to larger values, such as 300 seconds, the characteristic temperature decreased to values much too low to allow significant bonding to occur²⁰.

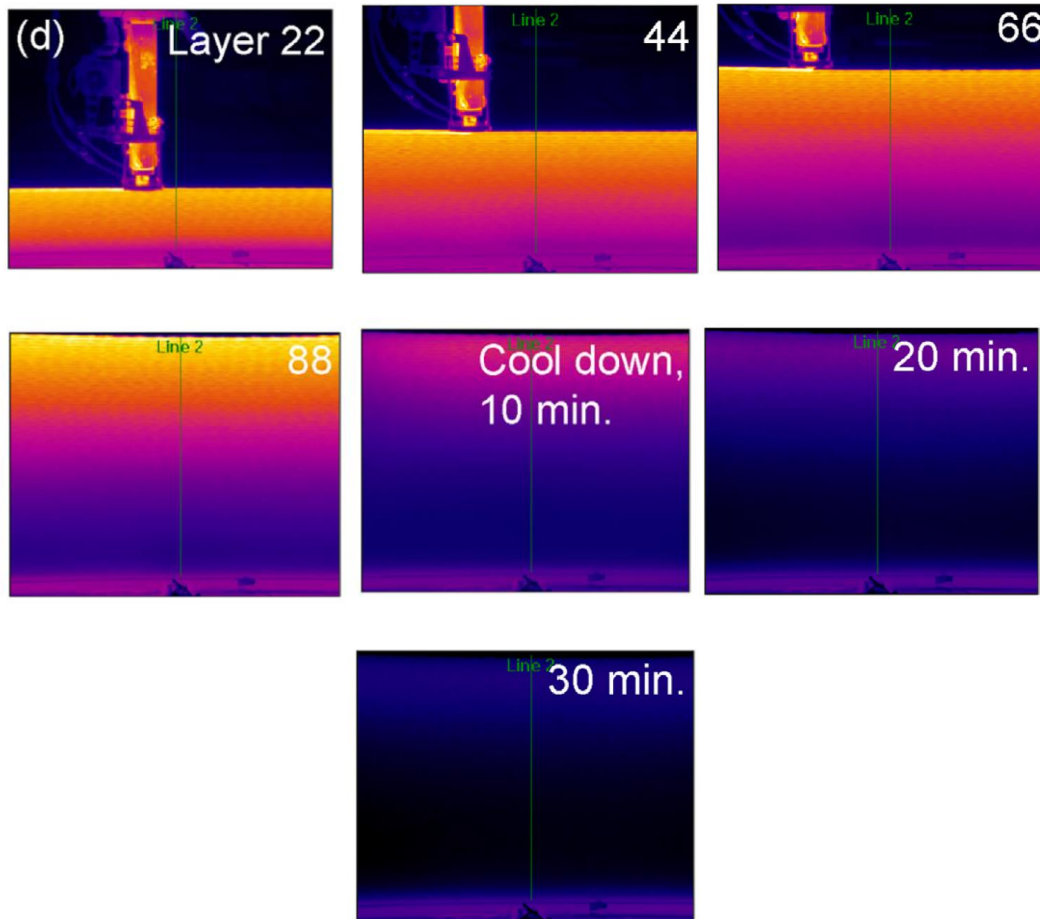


Figure 2.5. Series of images displaying the temperature profile of a printed part during the printing process and the subsequent cooling. The lightest color corresponds to a temperature of about 180 °C, and the darkest color corresponds to a temperature of approximately 20 °C²⁰. Reprinted with permission from Compton, B. G.; Post, B. K.; Duty, C. E.; Love, L.; Kunc, V., *Thermal analysis of additive manufacturing of large-scale thermoplastic polymer composites*. *Additive Manufacturing* **2017**, 17, 77-86. Copyright 2017 Elsevier.

Coogan *et al.* performed a one-dimensional heat transfer analysis to support a bond development model to predict final part strength²¹. For the heat transfer analysis, the authors focused on the interface temperature, and claim to have predicted the temperature with reasonable accuracy. They examined the interface temperature as a function of bed temperature, nozzle temperature, print speed, and fiber width. From this, the authors discovered that bed temperature had very little effect on the thermal profile of the extruded filaments. Varying the nozzle temperature changed the initial temperature of the filaments but did not alter the cooling profiles to a substantial degree. This result was mirrored when the print speed was varied. However,

changing the width of the deposited filaments greatly affected the cooling rates due to the filaments possessing different surface areas and convective behaviors. The researchers noticed that while the interface temperatures matched well with expected values, the part strength predictions were not highly accurate, with the simulation results slightly underpredicted compared to the measured strength. This is most likely due to the single dimension assumption of the heat transfer analysis. The interface temperature might be accurate, but a temperature gradient will exist in the cross-section of the fiber which will affect the mobility of the polymer chains.

Costa, *et al.* further analyzed the cooling rate and its effect on bonding strength using ABS as a representative material^{23, 57}. The researchers used the Biot number to suggest the one-dimensional approach to be valid, and demonstrated good agreement between experimental and predicted values for the surface temperature of the deposited filament, Figure 2.6. However, as shown by Coogan, *et al.*, the predicted bond strength exhibits some discrepancies compared to the experimentally determined values, Table 2.1. This further exemplifies the issue of using a one-dimensional approach to predict the heat transfer of the FFF process.

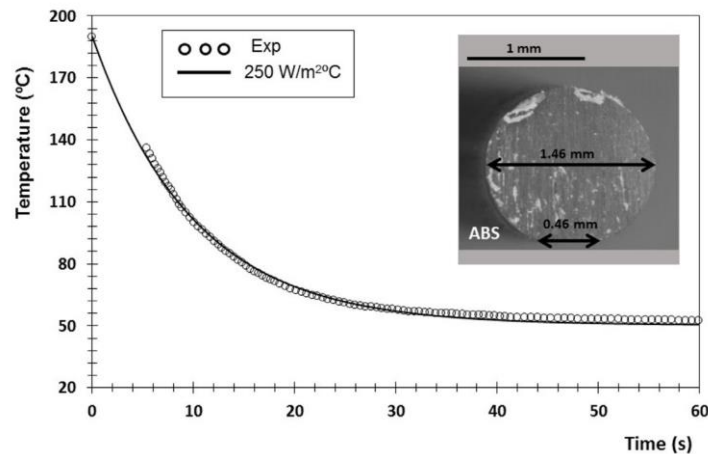


Figure 2.6. Experimental (hollow circles) and predicted (solid line) temperature of an extruded filament showing good agreement of the surface temperature between the two methods²³. Reprinted with permission from Costa, S. F.; Duarte, F. M.; Covas, J. A., Estimation of filament temperature and adhesion development in fused deposition techniques. *Journal of Materials Processing Technology* 2017, 245, 167-179. Copyright 2017 Elsevier.

Table 2.1. Measured and predicted adhesion strength (B_p) of various geometries based on a one-dimensional heat transfer prediction of the cooling rate. Recreated from Costa, et al.²³ A, B, and C refer to three different deposition patterns used to relate the deposition parameters to adhesion. Reprinted with permission from Costa, S. F.; Duarte, F. M.; Covas, J. A., Estimation of filament temperature and adhesion development in fused deposition techniques. *Journal of Materials Processing Technology* **2017**, 245, 167-179. Copyright 2017 Elsevier.

Specimen Type	Die @ 200 °C		Die @ 220 °C	
	Predicted B_p (%)	Measured B_p (%)	Predicted B_p (%)	Measured B_p (%)
A	11	8 ± 5	28	23 ± 8
B	0	0 ± 0	13	9 ± 9
C	0	0 ± 0	0	0 ± 0

2.3.3.4 Examples of Two-Dimensional Heat Transfer Analysis

Adding a second dimension to the heat transfer analysis should increase the accuracy of the predictions. This is demonstrated by Thomas and Rodriguez when they performed a two-dimensional heat transfer analysis to support their model predicting fracture strength^{45, 58-59}. In this analysis, they noticed that the convective cooling term had a noticeable impact on various aspects of the model. As they decreased the value of the convective heat transfer coefficient, h , the cooling time of the filaments increased. Furthermore, when they increased the value of h , the temperature gradient across the cross-section became more pronounced. While the two-dimensional model is generally more accurate than the one-dimensional, it still ignores various aspects of the true system such as conductive heating along the length of the fiber. Thomas and Rodriguez also used a

rectangular cross-section which provided much more contact between layers than a circle or ellipsoid.

Rather than examining the deposited filaments, Edwards and Mackay performed a two-dimensional heat transfer analysis on the material immediately as it exits the nozzle to better understand the development of melt fracture, or “sharkskin”⁶⁰. This group identified the need for an external heating element to increase the temperature of the extruded material to relax the stresses causing the fracture.

2.3.3.5 Examples of Three-Dimensional Heat Transfer Analysis

A few researchers have applied a more thorough, three-dimensional approach to the study of heat transfer in this process⁶¹⁻⁶⁴; however, it has been observed to be very computationally intensive and usually requires significant simplifying assumptions which can lead to lower accuracy in the results⁶⁵. Also, while an article published by Zhang, *et al.* examines the effect of temperature on stress development, most papers published at the start of the research presented in this dissertation utilizing a three-dimensional heat transfer model only study the heat transfer itself, uncoupled from any other analysis^{57, 66-68}.

Costa, *et al.* demonstrated that radiative transfer can be neglected without loss of accuracy when the heat transfer coefficient exceeds 60 W/m²K. The authors also proved that the temperature does not change significantly in small distances along the filament length, suggesting that conductive transfer along the axis of the filament is negligible⁵⁷. These two findings provide proof that simplifying the heat transfer to a two-dimensional, cross-sectional approach can still provide accurate results with significantly less computational power and time.

Another important finding in these studies was produced by Zhang, *et al.* In their study, the authors showed that reheating caused by depositing a new layer on a previously deposited layer occurs primarily in the layer thickness direction⁶⁸. This corroborates the data identified by Costa, *et al.*, suggesting that conduction along the axial length of the deposited roads may be neglected without significant loss of accuracy. Zhang, *et al.* further demonstrated that the magnitude of the reheating is influenced by the layer thickness and print speed, with higher magnitudes realized with thinner layers and slower print speeds.

D'Amico, *et al.* performed a three-dimensional heat transfer analysis by simplifying the system slightly⁵⁰. This group assumed that each layer of material was deposited as a single whole rather than following the deposition with time, and the layers were assumed to have perfect contact with each other. Further, the material properties were assumed to be constant and not influenced by temperature. These assumptions allowed the group to reduce the computation time but resulted in some loss of accuracy. While the trends observed in their study match very closely to experimental results, significant discrepancies exist between the actual values of the predictions and measurements. However, this is useful to highlight the relative trade-off between computing time and accuracy of prediction results.

2.4 Interlayer Bonding and Recovery of Bulk Properties in FFF

The next step in the FFF process involves the impact of layer deposition once it leaves the nozzle and is laid onto the print bed or a previously deposited layer. This aspect is critical because additively manufactured parts are generally mechanically weaker than corresponding parts created using traditional manufacturing methods such as injection molding. This is due in large part to the lack of interlayer adhesion in the z-axis, or axis perpendicular to the layer direction, inherent in parts built using AM. Due to the presence of a series of weld lines in this axis, localized stress

growth will cause failure at much lower loading values than parts created with injection or compression molding. Many researchers have examined AM systems and attempted to predict the bonding between the layers of a print as a function of various parameters including print temperature, print speed, part orientation, time, road orientation, layer geometry, and others as a way to develop methods to increase the bonding^{21, 45-46, 69-70}. Most of these researchers have focused on examining well-understood polymer systems such as PLA⁷¹⁻⁷⁵ and ABS^{19, 21, 23, 45, 51, 69, 76-82}, leaving the high use temperature/high T_g materials largely unexplored. These engineering thermoplastics include polyetherimide (PEI), polyetherether ketone (PEEK) and polyphenylene sulfide (PPS), which are useful in a broader range of practical applications where increased strength and thermal exposure are necessary. Due to larger differences in the deposition and equilibrium temperatures, the thermal gradients and polymer thermal transitions will impact polymer chain diffusion and stress development, suggesting further studies regarding these materials would be greatly beneficial to the field of polymer AM.

2.4.1 Polymer Welding as an Analog to FFF Printing

Investigation into the physical process of the healing of weld lines in general polymeric processes can provide a better understanding of the interfacial bond healing process due to its similarity to what would be observed in AM⁸³⁻⁸⁵. When two pieces of similar polymers contact each other above the T_g of the materials, a bond begins to form, and the interface gradually disappears as the two pieces become one whole.

Wool and O'Connor presented a multi stage mechanism that describes the process of self-healing in polymers⁸⁶. Of the five stages of the mechanism, diffusion played the most significant part in developing the mechanical strength of the interface⁸⁷⁻⁸⁸. Because of this, the visual appearance of the bond is not, necessarily, a good metric to determine the amount of healing that

has occurred⁸⁹. It was shown that complete healing, or a return to bulk properties, is possible, but requires extensive time above T_g ⁹⁰. It was also demonstrated that fractured surfaces are able to heal the polymer-polymer interface to a greater degree than virgin materials⁹¹. This mimics the suggestion made by McIlroy and Olmstead that the disentanglement effect induced by shearing the polymer during AM allows greater healing in the finished product^{46, 92} as well as the results displayed by Bousmina, *et al.* that showed diffusion at polymer/polymer interfaces is greatly dependent on the initial chain end distribution at the interface before diffusion⁹³.

To quantify the required time for the interdiffusion of the polymer chains to return the mechanical properties of the weld to those of the bulk, Pisipati and Baird examined a series of polystyrenes with different weight average molecular weights⁹⁴. Their work measured the amount of time required for a weld line to disappear and the properties to return to those of the bulk. This time is referred to as the complete re-entanglement time, or the time required for the polymer chains on either side of the weld to diffuse across the interface and re-entangle to a state similar to that of the bulk. This group's work was focused on better understanding of injection molding, but can be applied to AM since the layer-to-layer interface is very similar to the weld line formed when the fronts of two flow fields meet in a mold.

The test used to measure the complete re-entanglement time is referred to as an interrupted shear test and is performed using a rotational shear rheometer. The test involves a two-step shearing process with a specified relaxation time between the shearing steps. Due to the inception of shear, a stress overshoot is produced at the start of each shearing step. This overshoot is measured, and the relationship between the two overshoots can provide information on the re-entanglement of the polymer. A representative set of results is displayed in Figure 2.7. The amount of recovery, or healing, can be calculated using Equation (2.15).

$$\% Recovery = \frac{[\tau_m(\dot{\gamma}, t_r) - \tau_{ss}]/\tau_m(\dot{\gamma}, t_r)}{[\tau_m(\dot{\gamma}, \infty) - \tau_{ss}]/\tau_m(\dot{\gamma}, \infty)} \quad (2.15)$$

where $\tau_m(\dot{\gamma}, t_r)$ is the value of the stress overshoot after the relaxation time, $\tau_m(\dot{\gamma}, \infty)$ is the value of the stress overshoot after infinite relaxation time, and τ_{ss} is the steady state stress value. This test can be performed at multiple relaxation times and the results can be extrapolated to 100% recovery.

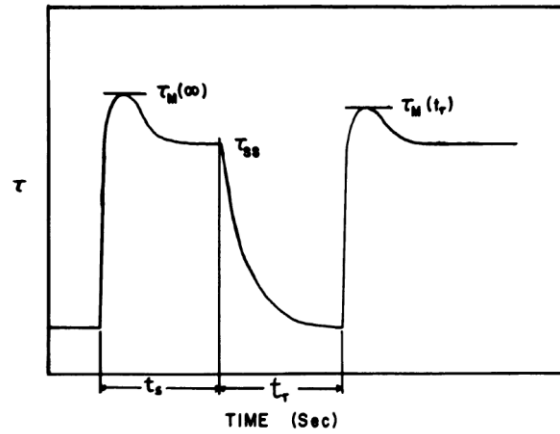


Figure 2.7. Representative results of an interrupted shear test showing the overshoot due to inception of shear, the attaining of a steady state stress value, the cessation of shear, and the subsequent inception of shear producing a smaller overshoot⁹⁴. Reprinted with permission from Pisipati, R.; Baird, D. G., *Correlation of Non-Linear Rheological Properties of Polymer Melts with Weld-Line Strength*. 1 ed.; Astarita, G.; Nicolais, L., Eds. Plenum Press: New York, 1984; pp 215-228. Copyright 1984 Springer.

From this test, Pisipati and Baird determined that the complete re-entanglement time of the polystyrenes ranged from 180 seconds to 445 seconds⁹⁴. The re-entanglement time increased with increasing molecular weight, which agrees with results of craze healing shown by McGarel and Wool⁹⁵. Another interesting discovery was that the complete re-entanglement time appeared to be an exponential or logarithmic function of temperature. Since AM is a non-isothermal process with very little time above T_g , this fact is vital to the development of strong bonds between layers.

2.4.2 Exploration of Bond Development and Healing in FFF

The development of the bond and its accompanying strength is a highly complex problem, as discussed in the previous section. There are two vital aspects required to understand the bond development and its potential in FFF: i) the stages of development and their requirements and ii) the impact of process parameters.

2.4.2.1 Stages of Bond Development

When two polymers contact each other, the interface forms in a multi-step process⁸⁶. According to Wool and O'Connor, the surface rearrangement step involves the polymer chains at the surface of the filament arranging themselves in such a way as to be able to diffuse across the interface⁸⁶. The approach step sets the mode of healing. The wetting stage involves the interface formation and determines the distribution function. The mechanical properties are recovered during the diffusion stage, making this stage the most vital to the bond formation process. Finally, the weld is completely erased during the randomization stage, resulting in material identical to the bulk. An empirical example of the bond growth process is shown in Figure 2.8. Full development of a bond, to the point where the interface is completely erased, may require a substantial amount of time, much longer than the filament is above T_g . However, the bond formation begins very quickly, which is what allows AM to produce parts with near bulk properties.

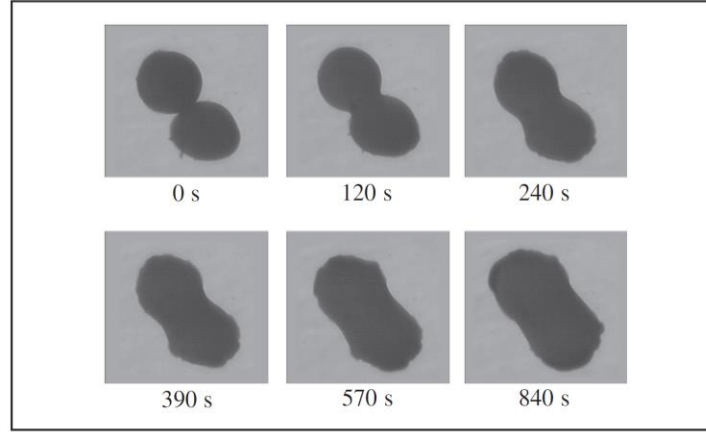


Figure 2.8. Actual representation of the bond formation process¹⁹. Reprinted with permission from Bellehumeur, C.; Li, L.; Sun, Q.; Gu, P., Modeling of bond formation between polymer filaments in the fused deposition modeling process. *Journal of Manufacturing Processes* **2004**, 6 (2), 170-178. Copyright 2004 Elsevier.

The first step of the bond formation requires the coalescence and wetting of the two surfaces. To describe this, Pokluda *et al.* developed a bond formation model that predicted the growth of the bond width, shown in Equation (2.16)^{19, 96}.

$$\frac{d\theta}{dt} = \frac{\frac{\Gamma}{a_0\mu} \left(2^{-\frac{5}{3}} \cos\theta \sin\theta (2 - \cos\theta)^{\frac{1}{3}} \right)}{(1 - \cos\theta)(1 + \cos\theta)^{\frac{1}{3}}} \quad (2.16)$$

$$\theta = \sin^{-1} \frac{x}{a} \quad (2.17)$$

where θ is the bond width, given by Equation (2.17), x is the radius of the neck at time t , a is the particle radius at time t , t is time, μ is viscosity, a_0 is initial particle radius, and Γ is the surface tension. Shahrier, *et al.* applied this analysis to a semicrystalline PEEK material, demonstrating that the model is unable to accurately predict the coalescence of a semicrystalline material below the melting temperature (T_m), but matches experimental values well when the material coalesces

above T_m ⁷⁴. Bhalodi, *et al.* extended this analysis to include a temperature dependent term to account for the non-isothermality of FFF⁹⁷.

2.4.2.2 Impact of Process Parameters on Interlayer Bonding

Recently, numerous researchers have focused on exploring the effect of processing parameters on the bonding phenomenon in FFF⁹⁸⁻¹⁰⁰. These studies include explorations on print speed, layer geometry, bed temperature, deposition/extrusion temperature, environmental temperature, and other similar parameters. Typically, these studies empirically measure a mechanical property such as tensile/compression strength, tear resistance, or critical energy release rate to quantify any sensitivity the system may exhibit to a specific parameter. This section will discuss, in detail, some examples of these studies and their findings to help guide the model development describing the process.

Belleheumer, *et al.* examined the effect of various processing parameters on the neck growth such as extrusion temperature, environment temperature, and convective heat transfer coefficient¹⁹. The authors discovered that environment temperature had little effect on the neck growth. It was generally too low to cause any significant slowing of the cooling rate following extrusion. However, extrusion temperature had a substantial impact on the neck growth. Increasing the temperature at which the material is extruded increases the temperature of the material when contact is made. This allows greater chain mobility and greater neck growth (the first four stages of the bond development process), which agrees with the crack healing results obtained by Jud and Kausch⁸⁹. The convective heat transfer coefficient, likewise, had a significant impact on the neck growth. A lower coefficient, corresponding to a slower cooling of the material, provided the material the ability to grow the neck to a greater degree.

To simplify the modeling process, Coogan *et al.* printed a square box one road wide and tested samples from various locations on the box in tension mode⁶⁹. From this, they developed an empirical model through linear regression to describe the bond strength as a function of the location of the box where the sample was collected (wall), bed temperature (T_p), nozzle temperature (T_N), print speed (S), fiber width (W), and layer height (H). This relationship is shown in Equation (2.18).

$$Bond = 4.09 + 1.01(Wall) + 0.5015(T_p) + 0.125(T_N) + 0.0013(S) + 26.5(W) - 34.6(H) \quad (2.18)$$

Coogan *et al.* determined that the bed temperature and the print speed had very little effect on the bond strength, although increasing print speed did lead to slightly stronger parts due to reduced cooling time between layers. Increasing nozzle temperature increased the bond strength significantly for the same reason as discussed previously. However, fiber width and layer height had the greatest effect on the bond strength. A wider fiber provides more area for the polymer chains to diffuse across the interface. Furthermore, the wider fibers have more thermal mass which reduces the cooling rate of the material and allows it to remain at temperatures above T_g for longer periods of time. The researchers believed the influence of layer height is due to the pressure difference experienced by the materials at different heights from the bed. This pressure affects the bond width and, by extension, the aspect ratio of the interface, causing layer height to have a significant effect on the bond strength.

To better understand the influence of printing temperature, Wu, *et al.* examined this parameter in relation to a polymer's thermal stability and the interlayer bonding force¹⁰¹. The authors measured an approximately 5% decrease in a thermoplastic polyimide's onset temperature (temperature at which the material's weight decreases by 5%) between the raw material and its corresponding filament, suggesting a slight loss of thermal stability in the filament. Upon

examining the effect of printing temperature on the bonding force (force required to pull apart two layers at their interface), the researchers identified a maximum bonding force occurs at 335 °C, which they attributed to higher diffusion rates induced by higher temperatures. Raising the printing temperature above 335 °C caused the polyimide to foam, introducing errors into the print and reducing the bonding force.

Abbot, *et al.* examined the effect of varying extrusion temperature, print speed, and layer thickness on the tensile strength of a printed tensile bar and compared the results of these parameters in two print orientations¹⁰². In this study, the researchers identified that reducing print speed increased the tensile strength in both print orientations, most likely because printing slower allowed the nozzle to transfer more heat to the layers, increasing the time above T_g . Similarly, increasing the extrusion temperature increased the time above T_g , leading to increased strength, although the effect appeared to be less than that caused by print speed. The effect of layer height on the strength changed with print orientation, i.e., a bar printed flat on the bed exhibited greater strength with larger layer height since this increased the bond width between adjacent roads, the bond which was tested. In contrast, when the tensile bar was printed vertically, the tested bond is parallel to the print direction; therefore, smaller layer heights produced greater strengths because the compacting increased the bond width between layers.

The effect of layer time, or time between successive layer depositions, was explored by Morales, *et al.* by pausing a print between layers for a set amount of time and measuring the compressive and shear strength of the resulting parts¹⁰³. In their study, the group observed that the compressive modulus was essentially unaffected by the layer time, but the compressive and shear strength both decreased with increased time between layer depositions. Because the interlayer coalescence and bonding is thermally driven, allowing time to cool between depositions greatly

reduced the bonding that could occur between layers, which caused the decrease in strength. A similar relationship between the temperature of filaments at the time of bonding and the corresponding tensile strength was observed by Lee, *et al.* who studied the effect of airflow on bonding¹⁰⁴.

van Veen proposed to increase the bond strength by maintaining the environment temperature above T_g , thus allowing the material to bond for longer periods of time¹⁰⁵. Through this, he observed significant increases in the tensile toughness, interlayer energy release rate, and tensile strength. Because extended time near and above T_g can cause a change in the geometry of the deposited filament, van Veen also examined these samples using micro CT and optical microscopy and determined that the increase in mechanical properties was not primarily caused by increasing the contacting surface area.

Similar to van Veen, Shelton, *et al.* observed higher bond strengths in parts printed with Ultem 9085 when the environmental temperature was increased¹⁰⁶. Interestingly, the initial cooling rate of the printed specimens is the same even when the environment temperature is raised from 110 °C to 170 °C. The cooling profiles do not diverge until the material has reached nearly 200 °C, suggesting some bonding occurs even below T_g , although this may be small.

Many researchers have shown that changing the processing parameters can also change the interlayer fracture toughness and strength. However, Young, *et al.* showed that changing the processing parameters does not significantly affect the elastic stiffness of the printed part¹⁰⁷. Changing the print temperature, and even changing the infill percentage, did not induce a large change in the slope of the initial loading curve of test blocks exposed to a traveling wedge style test. This suggests that elastic stiffness, unlike fracture toughness, is either inherent in the material or the changes are not significant at the short time scales of testing. A similar result was found by

Allum, *et al.* who demonstrated that the stiffness was consistent when tensile specimens were tested along the length of and perpendicular to the deposited filament⁷¹.

Kuznetsov, *et al.* posited that nearly each of the studies discussed in this section have the potential to be applicable to a very narrow set of printers¹⁰⁸. This group identified that the distance from the filament feeder to the nozzle and the ability to move the nozzle smoothly and accurately significantly affected the influence of print speed and layer thickness on the strength of printed parts as measured by a three point bend test. Because of this dependency, the results found in literature can be correct, even if they disagree with other published sources. It further highlights the need to determine the effect each printer type has on the relationship between process parameters and part properties to be able to accurately optimize a system.

2.4.3 Modification of the Interface or Material to Increase Bonding in FFF

To further the understanding of interlayer bonding, some studies have focused on providing further information regarding the process of interlayer diffusion whereas others attempt to suggest methods for improving the healing with outside stimuli or influences. The previous sections have provided a few examples of these studies, and this section will delve deeper into even more work focusing on improving the bond development in FFF systems by modifying the printing system or the material itself. These modifications provide ample opportunity to also expand the modeling approaches used to predict the bond strength evolution, although that is outside the scope of this dissertation. These attempts are detailed here to provide guidance for future work in this area.

Striemann, *et al.*, Han, *et al.*, and Sabyrov, *et al.* each applied heat to the previously deposited material prior to the deposition of new material with the use of a laser¹⁰⁹⁻¹¹¹. Using this technique, Han, *et al.* showed a 178% increase in the weld strength compared to the control samples that were not exposed to the laser heating. The extra heat allows the previously deposited material to regain

some molecular mobility, increasing the amount of diffusion that can occur before both roads cool below T_g . Deshpande, *et al.* also studied the effect of utilizing a laser to reheat a previously deposited layer prior to laying down a new one⁷⁸. By placing a thermocouple on top of the layer to be heated, they were able to measure the temperature of the layer immediately before the fresh material was deposited, demonstrating a significant increase in the interface temperature at the time of deposition. In their study, this led to an up to 77% increase in the interlayer bond toughness of the final part. Sabyrov, however, also noted that increasing the laser power, while increasing bond strength, also caused cracks and holes to form on the extruded filaments, increasing surface roughness¹¹¹.

Shih, *et al.* modified the interfacial region of a print using cold plasma rather than a laser⁷⁵. By printing a “substrate” (regularly printed part), applying a cold plasma treatment to the top of the substrate, then printing a final layer, the researchers were able to investigate the benefit of this surface modification on the interlayer bonding strength. Their results showed that a 30 s plasma treatment caused the largest increase in the interlayer bonding strength. The primary downside to this technique is the excessive time required for the treatment. Applying this surface treatment to every layer in a print would increase the printing time significantly, even in a relatively small part.

A third technique applied to the interface to increase interlayer diffusion is presented by Tofangchi, *et al.*⁸¹. These researchers applied ultrasonic vibrations to the material during printing to increase the polymer chain reptation to increase the rate of diffusion across the interface. By applying a 34.4 kHz vibration, the researchers measured a 10% increase in the interlayer adhesion measured through a trouser peel test. Jiang, *et al.* likewise saw an increase in the tensile strength of parts printed with applied vibrations¹¹². Compared to the two previously discussed improvement methods, this technique produced the smallest increase in interlayer bonding. However, this

technique is the simplest to apply since it only requires the attachment of an ultrasonic source to the print head rather than the implementation of a high-powered laser or cold plasma.

The use of a new type of material was suggested by Shaffer, *et al*¹¹³. This group noted that most conventional FFF systems require thermally driven diffusion to develop bond strength, thus limiting the ultimate recovery due to the non-isothermality of FFF. Therefore, the researchers investigated the ability of polymers able to be cross-linked with ionizing radiation to create products with desired properties by mixing a radiation sensitive material with PLA. The results from their study demonstrated that the radiation sensitive polymer possessed 1.7 times the toughness of pure PLA, indicating a potential method for improving the bonding in FFF.

Romeijn, *et al.* increased bond strength by adjusting the printing pattern used in FFF¹¹⁴. Typically, FFF prints layers directly on top of previously deposited roads, potentially producing voids between the roads and layers. Romeijn, *et al.* proposed staggering the layers so that the a layer is deposited above the interface of the two roads beneath it, Figure 2.9. This style reduces the space voids present in a printed part, increasing the density of the part and the interlayer contact, leading to a subsequent increase in the maximum in-plane shear stress the part can withstand.

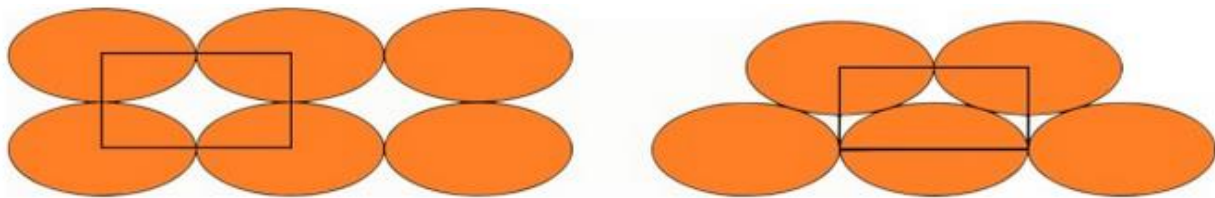


Figure 2.9. Image depicting traditional FFF printing style (left) and the staggered printing style (right) proposed by Romeijn¹¹⁴. Reprinted with permission from Romeijn, T.; Wells, B.; Wei, D.; Paul, G., *Investigation into the shear property of thin-walled additively manufactured structures using staggered fused filament fabrication*. *Additive Manufacturing* 2020, 35, 101259. Copyright 2020 Elsevier.

Different from those before, Ko, *et al.* modified the material to increase the weld strength in FFF⁸⁰. In their study, the authors added up to 10 wt% of a plasticizer to a polycarbonate-ABS material, reducing the T_g by up to 16 °C (15%). This reduction in T_g is indicative of an increase in polymer chain mobility, which should be reflected in a faster reptation time, resulting in a stronger bond development in similar situations. In their study, they do show that increasing the plasticizer by 5% decreases the amount of time required to fully heal the interface by an order of magnitude, validating their hypothesis. The downside to the plasticizer modification is apparent in the bulk modulus of the material. The plasticizer causes a reduction in the bulk properties compared to the unmodified material.

Similarly, Gao, *et al.* added a small amount of a lower molecular weight polymer to PLA to facilitate more rapid diffusion⁷³. By adding up to 5 wt% polyethylene glycol (PEG) with a molecular weight of 4k, 8k, or 20k g/mol, the anisotropy of tensile tested specimens was reduced from approximately 32.5% to approximately 16%. These results indicate that the small amount of PEG acts as a plasticizer, allowing the PLA chains to diffuse across the interface more quickly, recovering more of the bulk strength of the material. However, as noted in Ko, *et al.*'s study, adding too much of the plasticizing agent, even with the higher molecular weight, will reduce the tensile strength of the printed part. In their study, Gao, *et al.* noted that the maximum amount of PEG they should add to reduce the anisotropy of the part is 5 wt%.

Khudiakova, *et al.* explored the interlayer bonding in materials of different stiffnesses by printing with a short carbon fiber reinforced PLA composite and comparing it to pure PLA and testing the results with dual cantilever beam and cracked round bar measurements¹¹⁵. The results of their study showed that introducing a stiff composite material limited bonding due to localized constraints caused by the reinforcing material. This resulted in a lower critical energy release rate

(G_{Ic}) in the composite (stiffer) material. When the two materials were bonded together, the crack in the dual cantilever beam tests continuously propagated toward the stiffer material, suggesting that the bond between the two materials was stronger than the bond of the stiffer material with itself.

A combination of these approaches (modifying the process and modifying the material) was explored by Das, *et al*¹¹⁶. These researchers modified a polypropylene with low molecular weight hydrocarbon resins to delay the crystallization which would otherwise prevent the development of the interlayer bond. By reducing the crystallization temperature from 121.8 °C to 116 °C, the time during which diffusion can occur is lengthened, allowing for a stronger bond between layers. Following printing, the researchers also annealed the printed parts for 24 hours at 120 °C, resulting in a recovery of more than 90% of the properties measured in injection-molded parts using the same material. Fitzharris, *et al.*, Hart, *et al.*, and Dunn, *et al.* also identified post-process heat treatments to significantly increase the mechanical properties of a printed material^{99, 117-118}.

2.4.4 Application of Reptation Theory in Interlayer Bonding

Although empirical exploration of the influence of process parameters on the interlayer bonding can provide some insight into the process, physics-based modeling will allow for a more direct view into the fundamental basis of the bond formation. Modeling the development of the bond strength is typically accomplished by considering the strength as a function of the polymer chain diffusion and is generally achieved by using the reptation theory¹¹⁹⁻¹²⁰. With this theory, Wool and O'Connor developed a model to describe the healing of fracture strength across an interface, shown in Equation (2.19)^{86, 121-122}

$$\frac{\sigma}{\sigma_{\infty}} = \left[\frac{\sigma_0}{\sigma_{\infty}} + \frac{K}{\sigma_{\infty}} * t^{\frac{1}{4}} * \psi(t) \right] * \phi(t) \quad (2.19)$$

where σ_{∞} is the fracture strength of the virgin material, σ_0 is the initial strength developed across the interface due solely to wetting, K is a constant that is proportional to the polymer diffusion coefficient raised to $\frac{1}{4}$ power, $\psi(t)$ is the diffusion initiation function, accounting for any delay to diffusion caused by surface rearrangement, and $\phi(t)$ is the wetting distribution function that provides the total fractional wetted area. This model demonstrates the strength recovering proportional to time raised to $\frac{1}{4}$ power. However, this assumes the recovery is occurring isothermally, which is not the case in the AM process. To account for the non-isothermal behavior of the system, Bastien and Gillespie discretized the equations into temperature dependent portions, allowing them to essentially integrate the function, thereby accounting for the transient heat transfer, Equation (2.20)¹²³. This equation also includes the reptation time, τ_{rep} , which is the longest Rouse time of a polymer chain and indicates the amount of time required for the chain to move a distance on the order of magnitude of its length and can be estimated using the crossover of G' and G'' in a rheological mastercurve¹²⁴. The reptation time can be related to the $\psi(t)$ function presented in Equation (2.19).

$$\frac{\sigma}{\sigma_{\infty}} = \left(\int_0^t \frac{1}{\tau_{rep}} dt \right)^{\frac{1}{4}} \quad (2.20)$$

The diffusion coefficient D can be calculated based on a rheological measurement and material properties such as the molecular weight and density, shown in Equation (2.21)¹²⁵⁻¹²⁶

$$D = \frac{(A\rho kT/36)(R^2/MW)}{\eta} \quad (2.21)$$

where A is Avagadro's number, ρ is density, k is Boltzmann's constant, T is temperature, MW is molecular weight, R^2 is the average square end-to-end distance of the polymer chain, and η is the viscosity of the polymer. Using these equations, Coogan *et al.* verified their empirical bond development model²¹. This work also highlighted the importance of a robust and accurate heat transfer analysis that is able to predict the temperature of the material at multiple locations and times.

McIlroy and Olmstead developed a healing prediction model that has its roots in polymer chain theory, starting with a modified Doi-Edwards model, referred to as the Rolie-Poly model, Equation (2.22) and (2.23)^{46,127-128}. This model examines the conformational tensor and corresponding disentanglement of the polymer chains that is caused during the extrusion process. Understanding the state of the polymer chains as they are deposited will help understand how they will diffuse across the interface.

$$\begin{aligned} \frac{D\mathbf{A}}{Dt} = & \mathbf{K} * \mathbf{A} + \mathbf{A} * \mathbf{K}^T - \frac{1}{\tau_d(T, \dot{\gamma})}(\mathbf{A} - \mathbf{I}) \\ & - \frac{2}{\tau_R(T)} \left(1 - \sqrt{\frac{3}{tr\mathbf{A}}} \right) \left(\mathbf{A} + \beta \sqrt{\frac{tr\mathbf{A}}{3}}(\mathbf{A} - \mathbf{I}) \right) \end{aligned} \quad (2.22)$$

$$\mathbf{A} = \frac{\langle \mathbf{RR} \rangle}{3R_g^2} \quad (2.23)$$

where $\mathbf{A}$ is the conformation tensor described by Equation (2.23), $\mathbf{R}$ is the end-to-end vector for the polymer chains, R_g is the radius of gyration, $\mathbf{K}$ is the velocity gradient tensor, $\text{tr}\mathbf{A}$ is the trace of the conformation tensor, τ_d is the reptation time, τ_R is the Rouse time, $\mathbf{I}$ is the identity matrix. The first term in Equation (2.22) describes the stretching and orienting of the polymer chains in the flow field induced by the printing process. The other two terms define the reptation and Rouse relaxation mechanisms.

The disentanglement caused by the flow field is described in Equation (2.24) where v is the entanglement fraction.

$$\frac{dv}{dt} = -\beta \left(\mathbf{K} : \mathbf{A} - \frac{1}{\text{tr}\mathbf{A}} \frac{d}{dt} (\text{tr}\mathbf{A}) \right) v + \frac{1-v}{\tau_d^{eq}(T)} \quad (2.24)$$

Entanglements can then be reformed through reptation. Through these equations, McIlroy and Olmstead showed how the entanglements of each road decreased during the deposition process, but then recovered and crossed the interface creating a bond. Their results indicate the entanglement fraction can reach upwards of 50%, suggesting the bond should recover a good portion of the bulk properties.

Coasey, *et al.* predicted the evolution of the bond's toughness (G) rather than strength (σ)⁷⁷. To do so, the group utilized Equation (2.25), which shows the toughness is proportional to time raised to the $\frac{1}{2}$ power rather than the $\frac{1}{4}$ power like strength. As with other healing analyses, Coasey, *et al.* demonstrated that the degree of healing increases very quickly in the first second following deposition but remains constant afterward. Their predictions match quite well with the results of single edge notched bend measurements, suggesting that their models do adequately represent the ABS model material they used in the study.

$$D_h^* = \frac{G(t)}{G_\infty} = \left[\int_0^t \frac{1}{\tau_r(T)} dt \right]^{\frac{1}{2}} \quad (2.25)$$

2.4.5 Influences Other than Diffusion on Recovery of Bond Strength

Recent studies have been published that question the previously discussed and explored explanations regarding the degree of healing in AM. Costanzo, *et al.* proposed that the recovery of the weld strength is not limited by the diffusion of polymer chains across the interface⁷². Rather, their research suggests that the configuration of the entangled polymer network is the determining factor in the ultimate weld strength of an additively manufactured part. According to Costanzo, *et al.*, the shearing induced by extruding the molten polymer out of a narrow nozzle causes alignment of the polymer chains, measurable through birefringence. Their study demonstrated that higher birefringence, i.e., the more aligned the polymer chains are, the lower weld strength a part will possess. This is most likely due to the alignment causing a delay where the polymer must relax before the chains may begin diffusing across the interface to heal the weld.

Coogan and Kazmer likewise suggested that the weld strength of an AM part is not significantly affected by the diffusion of the polymer chains across the interface²². These researchers suggest that, in many cases, the polymer chains can diffuse distances greater than their radius of gyration (R_g), which would suggest the weld should be fully healed if that was the sole consideration. Instead, Coogan and Kazmer proposed that the strength is reduced due to a lack of contact between layers. They predicted the interlayer contact with a model based on pressure-driven flow, which they were able to measure using their in-line viscometer¹³. Experimental measurements of the weld strength appear to validate their results suggesting that interlayer contact can play a significant role in the development of the bond between layers.

Allum, *et al.* identified a similar effect, demonstrating that the interfacial bond possesses a similar strength as the bulk material⁷¹. However, this group went further and showed that the strain-at-fracture, specific load bearing capacity, and toughness of the interface were lower than the bulk material and were also dependent on the geometry of the deposited filament. These researchers further posited that other groups may have erroneously suggested that the interface between layers possesses less than bulk strength due to their use of the filament width rather than bond width to determine the strength of the tested bond.

2.4.6 Influence of Crystallization on Interlayer Bonding

Current materials for FFF are primarily amorphous such as ABS or have a nearly negligible amount of crystallizability such as PLA because semi-crystalline polymers often experience significant shrinkage upon cooling and crystallizing which causes warping in the printed part. This greatly limits the material catalog available for FFF, as discussed in Section 2.2. However, semi-crystalline materials are often desired for their advantages over amorphous counterparts. In semi-crystalline materials, the crystallites restrict the movement of the polymer chains, even above T_g , allowing the use of semi-crystalline polymers at elevated temperatures for extended periods of time without loss of mechanical properties whereas amorphous materials would soften and fail. Furthermore, due to their tightly folded nature, polymer crystallites are able to resist penetration by solvent molecules and, thus, often possess great solvent resistance. The primary disadvantage of crystalline materials, other than the shrinkage induced warping, is that the polymer chain restriction that allows their use at elevated temperatures also causes them to be more brittle than amorphous materials. However, the advantages inherent in their use make them highly desirable to companies and universities alike, and their addition to the FFF material catalog would greatly enhance its viability in the industrial and academic spheres.

While crystallinity is well documented to impact welding and interlayer adhesion (as will be discussed in this section), the understanding of the interplay between crystallization and the polymer physics associated with the complex and repeated thermal history is an area that needs to be addressed. Although these aspects are not specifically addressed in this dissertation, these considerations are important to understand how the models developed and discussed in Chapters 4 and 5 should be extended in future work to semi-crystalline engineering thermoplastics, as discussed in Section 6.3.

2.4.6.1 Crystallization Effect on Welding

As mentioned in Section 2.4, the mechanical properties of a printed part are highly dependent on the strength of the bond that is formed at the interface of two layers. This bond will be influenced by the crystallinity of the materials on both sides of the interface. Therefore, it is useful to study not only the effect of crystallinity on the strength of the bond, but also on the effect of crystallinity on the method by which the bond develops.

In wholly amorphous polymers, bonding is dictated by the diffusion of the polymer chains across the interface. This is discussed in detail in Section 2.4. However, the introduction of crystallites has the potential to greatly complicate the diffusion process. Van Alsten, *et al.* suggested that the polymer chain diffusion in semi-crystalline interfaces appears Fickian at short diffusion times, but deviates from this behavior at longer time scales¹²⁹. This was attributed to a mutual diffusion across the interface to completely saturate the available amorphous regions which follows Fickian behavior. The deviation appears after the amorphous region has been saturated. At that point, the polymer chains attempt to diffuse through the crystallite regions, but this proves to be difficult as the chains must move around the crystallites rather than through them. These

results were corroborated by Segalman, *et al.* who generated depth profiles to follow the path of the polymer chains diffusing into a semi-crystalline matrix¹³⁰.

By looking at the development of shear strength in bonded poly(ethylene terephthalate) (PET), Boiko, *et al.* further proved that the development of the bond is a diffusion controlled process⁹¹. In her work, Boiko considered three types of interfaces between amorphous and crystalline PET: amorphous-amorphous, amorphous-crystalline, and crystalline-crystalline. This study proved that the shear strength of the amorphous-amorphous interface and amorphous-crystalline interface both grew linearly with time to the one-fourth power, Figure 2.10 , which is characteristic of diffusion controlled processes. However, the shear strength of the crystalline-crystalline interface actually decreased with increasing time, most likely caused by the difficulty of the polymer chains to diffuse out of one crystalline region and into another one across the interface.

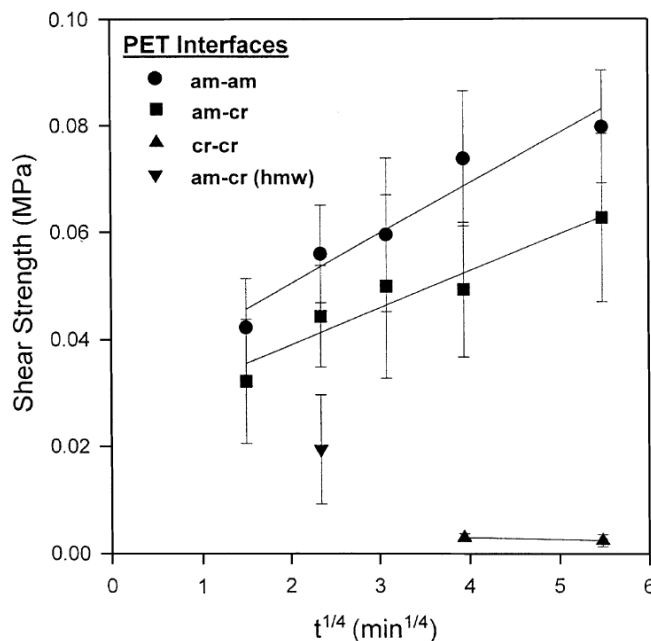


Figure 2.10. Figure adapted from Boiko, *et al.* displaying the growth of the interfacial shear strength as a function of $t^{1/4}$, proving that bond healing at amorphous-amorphous and amorphous-crystalline interfaces is diffusion controlled⁹¹. Reprinted with permission from Boiko, Y. M.; Guérin, G.; Marikhin, V. A.; Prud'homme, R. E., *Healing of interfaces of amorphous and semi-crystalline poly (ethylene terephthalate) in the vicinity of the glass transition temperature*. *Polymer* **2001**, 42 (21), 8695-8702. Copyright 2001 Elsevier.

2.4.6.2 Effect of Crystallinity on Strength of Bond

The strength of the bond will also be affected by the amount of crystallinity present in the materials when they come into contact. Boiko, *et al.* noticed that the bond between two crystalline materials is significantly less than that of two amorphous materials or an amorphous material and a crystalline material at the same processing conditions⁹¹. However, this healing and subsequent measurement was performed on materials that were already in a crystalline state. A similar result was found by Cho and Kardos¹³¹ as well as Awaja, *et al.*¹³² in a semi-crystalline PEEK material.

Boiko, *et al.* continued their investigation and determined that modifying the state of the material following healing can produce exceptional results. The researchers examined crystallizable material that was bonded while amorphous and allowed to crystallize following healing. This method produced bond strengths greater than those produced by purely amorphous

materials. The group believed that this increase in bond strength was due to the organization of polymer chains from the adjacent materials that then proceed to crystallize together in a process referred to as cocrystallization¹³³⁻¹³⁶. This method forms crystallites across the interface which lock the polymer chains in place and prevent them from disentangling and pulling apart.

Schuman, *et al.* had previously shown that cocrystallization did, in fact, occur by examining the interface of two different materials, in this case, high density polyethylene (HDPE) and linear low density polyethylene (LLDPE)¹³³. This group bonded the two materials in the amorphous phase and allowed crystallization to occur, resulting in the cocrystallization phenomenon. DSC curves showing the melting and crystallization curves of the cocrystallized area displayed a single peak for all blend compositions, which is an indication that a single crystal of both materials formed, Figure 2.11.

Bonten and Schmachtenberg further validated this phenomenon by comparing force transmission measurements performed in tension of amorphous and semicrystalline PET to measurements of a bonded material that has crystallized to some degree across the bonded interface¹³⁴. The bonded material displayed a yield stress greater than the bulk amorphous material but less than the bulk semi-crystalline material. If the crystallites formed on either side of the bond, the interface would behave similar to the purely amorphous material. Because the bonded material exhibited a higher yield stress, it was assumed that some crystallites formed across the bond.

Frederix, *et al.* cautioned that the polymer chains must diffuse across the bond to a depth corresponding to the intercrystalline long period in order for cocrystallization to occur¹³⁷. However, by considering the reptation time of the polymer chains in comparison to the amount of time required to develop the weld, the required diffusion length should not be an issue.

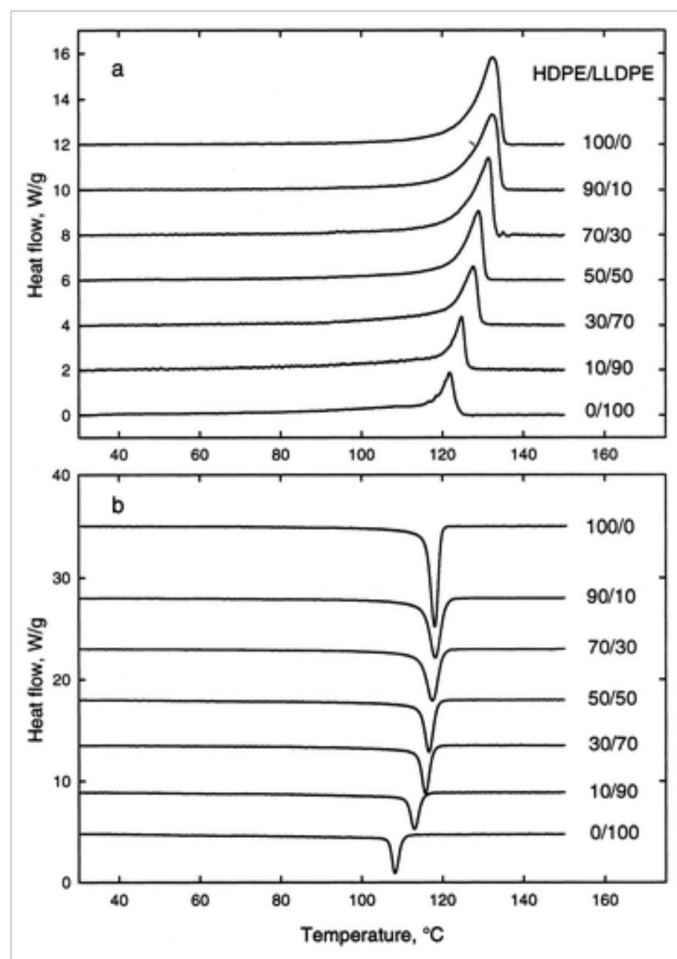


Figure 2.11. DSC plots adapted from Schuman, et al. displaying the melting (a) and crystallization (b) peaks associated with HDPE/LLDPE melt blends of different compositions¹³³. Reprinted with permission from Schuman, T.; Stepanov, E. V.; Nazarenko, S.; Capaccio, G.; Hiltner, A.; Baer, E., *Interdiffusion of Linear and Branched Polyethylene in Microlayers Studied via Melting Behavior*. *Macromolecules* **1998**, 31 (14), 4551-4561. Copyright 1998 American Chemical Society.

2.4.6.3 Application of Crystallization in Fused Filament Fabrication

Researchers have taken the knowledge of cocrystallization and attempted to apply it to FFF printing by developing a core/shell type filament where the core material has a lower crystallization temperature or crystallizability than the shell material¹³⁸⁻¹³⁹. The core of this filament should reduce the warping issue common with semi-crystalline materials while the shell will be able to cocrystallize with the adjacent layers to form a stronger bond. Additive manufacturing companies are also trying to develop semicrystalline polyetherether ketone (PEEK) and polyether ketone

ketone (PEKK) filaments for FFF to take advantage of the benefits crystallinity could bring to printing.

Wittbrodt, *et al.* examined a series of PLA filaments of different colors to determine if the additives used to color the material affected the crystallinity¹⁴⁰. X-ray diffraction (XRD) of samples printed with the same parameters showed the group that the additives, which the company would not disclose, had a significant impact on the crystallinity of the filament, with natural PLA possessing the lowest crystallinity at 0.93%, and the white PLA having the greatest crystallinity at 5.05%. The different crystallinity in each color of material suggests that they will possess different optimal printing temperatures in order to optimize the bond strength of the prints without warping the entire part.

2.5 Development of Residual Strain and Stress in FFF

In recent years, researchers have begun to turn their attention to stress buildup in FFF printed parts with the ultimate goal of predicting stress and warpage in a complete part, similar to the efforts of Talagani, *et al*¹⁴¹. The stress in FFF builds because of a mismatch of temperatures in the polymeric materials upon deposition. A new layer is deposited above T_g , sometimes significantly so, while the previous layer has generally experienced enough time to cool below T_g into a glassy state. The new layer will strain to a greater degree than the previous layer, and since the two layers are bonded, the straining layer will attempt to move the lower one as well, inducing stress in both. This interaction between layers can greatly increase the difficulty in estimating the strain and stress, so current work focuses primarily on either measuring the stress empirically or estimating the stress assuming the strain is only caused by changes in temperature, with no interactions between layers. Some recent work has begun to incorporate the residual thermal stresses in the prediction of part strength¹⁴². However, most studies have focused on the potential of residual

stress to cause warpage and shrinkage in printed parts demonstrating that print speed, road geometry, and part geometry are the most significant influences on the stress development¹⁴³⁻¹⁴⁵. However, most current work simply examines part deformation as a function of process parameters without considering stress as the driving factor¹⁴⁶⁻¹⁴⁸.

One of the earliest works examining the stress development in FFF empirically was conducted by Kantaros and Karalekas¹⁴⁹. These researchers printed rectangular box specimens with ABS, varying layer thickness and road orientation. Using short fiber Bragg grating measurements, Kantaros and Karalekas demonstrated that the residual strain increased when the road direction was changed from parallel to the long dimension (0°) to perpendicular to it (90°) and criss-crossed ($\pm 45^\circ$) when the layer was 0.25 mm thick. This relationship changed slightly when the layer thickness was increased to 0.5 mm. In the case of the thicker layers, the strain in the 0° and 90° specimens were similar. Further, annealing at temperatures less than T_g did not induce any significant change in the material or the max wavelength of the fiber Bragg grating measurement. When the material was annealed above T_g , however, the material experienced strain induced shrinkage, most likely relieving some of the residual stress in the part. Zhang, *et al.* also noticed that road orientation, or raster angle, has a significant effect on the measured residual stress¹⁵⁰. This group also noted that print speed influenced the stress buildup to some degree.

D'Amico, *et al.* measured the irreversible thermal strain in printed parts upon annealing, a parameter that leads to the development of stress and potential failure¹⁵¹. In their study, D'Amico, *et al.* observed that the irreversible thermal strain in the z-axis increases with decreasing layer thickness while the strain in the x-axis decreases with decreasing layer thickness. This leads to a negative relationship between strain in the x- and z-axes. Furthermore, the strain is slightly

anisotropic, i.e., the z-axis strains slightly more than the x-axis in the samples they studied while very little strain occurs in the y-axis.

Brenken, *et al.* examined the stress buildup and resultant deformation in FFF using Abaqus©¹⁵². They accounted for the crystallization kinetics, viscoelastic behavior, and anisotropic shrinkage to accurately determine the deformation that would occur during a routine print. By comparing their predictions to empirical samples, they determined that their modeling process was reasonably accurate, but the applicability of this set of models to larger/different systems is only theorized.

The viscoelastic stresses in a printed filament were explored by Xia, *et al.* paired with an estimation of the temperature profile in a single extruded strand and a stack of three extruded strands¹⁵³. This study showed that the stresses induced changes in diameter of the extrudate, the layer thickness, the profile shape, and the recovery of the shape of the filament. These results are vital to being able to accurately predict the shape evolution of a printed part.

Hébert, *et al.* utilized an holistic simulation approach to explore the stress development and warpage in SLS and FFF printing. While the researchers primarily focused on proving their modeling approach was able to predict stress development in a printed part, they did demonstrate the effect of a couple of process parameters on the stress development¹⁵⁴. First, they examined the effect of voids on the stress development by varying the raster orientations, showing that larger amounts of voids results in a greater degree of anisotropy. Then, the group considered the effect of print orientation, demonstrating that printing with the largest side parallel to the printing direction results in larger amounts of stress.

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Chapter 3

Model Analysis of Feedstock Behavior in Fused Filament Fabrication: Enabling Rapid Materials Screening

3. Model Analysis of Feedstock Behavior in Fused Filament Fabrication: Enabling Rapid Materials Screening

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3.1 Abstract

This research presents a rapid screening process for analyzing the extrudability of polymeric materials for filament extrusion based additive manufacturing (AM) by predicting extrusion

failure. This rapid screening process can further suggest optimal Fused Filament Fabrication (FFF) processing conditions for a specific material. Annular backflow and filament buckling, which are the two primary failure modes during extrusion in FFF, are considered in this study. The screening method focuses on model analysis of annular backflow while simultaneously considering a previously developed model for filament buckling and includes the introduction of a non-dimensional number (Flow Identification Number, or FIN) that predicts a material's propensity to backflow based on a rheological analysis and the system geometry. Annular backflow was modeled by calculating velocity profiles and determining the normalized net flow magnitude. The backflow and buckling models were experimentally verified with acrylonitrile butadiene styrene, low density polyethylene, and sodium sulfonated poly(ethylene) glycol. We empirically validated that the FIN was able to accurately predict backflow and that the potential to backflow and, by extension, propensity to fail during extrusion, is most sensitive to fluctuations in filament diameter and the material's shear thinning behavior. Our results demonstrate the importance of printing in the shear thinning regime to reduce the effect of processing conditions on the extrudability of a polymer.

Keywords: fused filament fabrication; material and process screening; failure mode prediction; backflow and buckling analysis; shear thinning viscosity

3.2 Introduction

Additive manufacturing (AM, also referred to as “3D Printing”) has the potential to revolutionize the manufacturing process for a broad range of products¹. The layerwise approach of AM processes affords the opportunity to create complex geometries that are not possible with traditional manufacturing processes and to produce complete parts and consolidated assemblies

with very little waste. While examples of the use of AM to fabricate end-use products are expanding, widespread industrial adoption of the technologies is limited due to limitations of process repeatability, final part properties, and material selection².

These limitations are especially prevalent in Fused Filament Fabrication (FFF), also trademarked as “fused deposition modeling”, the most prominent type of AM process³. A type of the Material Extrusion AM modality⁴⁻⁵, FFF features the selective deposition of a softened thermoplastic through a nozzle. Specifically, a polymer filament feedstock is fed via counter-rotating rollers into a nozzle where it is heated to a temperature at which it is fluidic. The solid filament above the fluidic zone acts as a piston to extrude the molten polymer out of the nozzle. This process is analogous to the operation of a capillary rheometer, where a metal piston applies force to expel a heated polymer melt through a convergent capillary die. Material extrusion AM is unique in that the filament acts as both piston and extrudate. The FFF system’s motion gantry enables precise deposition of single “roads” of the polymer extrudate to create each layer of a part⁶⁻⁸.

There is extensive current research focus on expanding the capabilities of this process to enable the production of end-use parts. A key need is efficient discovery of a more diverse catalog of available materials to be used in the extrusion AM process¹. The most widely implemented materials in consumer desktop systems currently include polylactic acid (PLA) and poly(acrylonitrile-co-butadiene-co-styrene) (ABS). Poly (ether imide), polycarbonate, polyamide, and other primarily amorphous thermoplastic polymers are also used in a smaller capacity and with restrictions based on machine requirement or physical properties that make complex part geometries difficult, such as crystallization and thermal expansion induced shrinkage and part warping⁹⁻¹². This limited palette serves as the motivation to produce new materials for FFF with a

broader range of thermal and mechanical properties for additional markets and applications. A key challenge hindering this desired discovery is that there is no formalized process for designing, screening, and evaluating materials for FFF. Current approaches tend not to focus on materials-level screening, and are instead focused primarily on the use of design of experiments approaches to identify process parameters, which is both expensive and time consuming¹³.

Development of new materials for the FFF process requires screening across all areas of the printing procedure: (i) filament creation from feedstock, (ii) filament feeding and liquefaction in the nozzle, (iii) liquefied filament extrusion, and (iv) road solidification and geometry formation. The goal of this paper is to provide a model to enable screening of new materials for failure during the filament feeding and liquefaction processes. The three primary failure modes that would prevent a material from being used in FFF, shown in Figure 3.1, include inconsistent filament diameter, annular backflow, and filament buckling⁷.

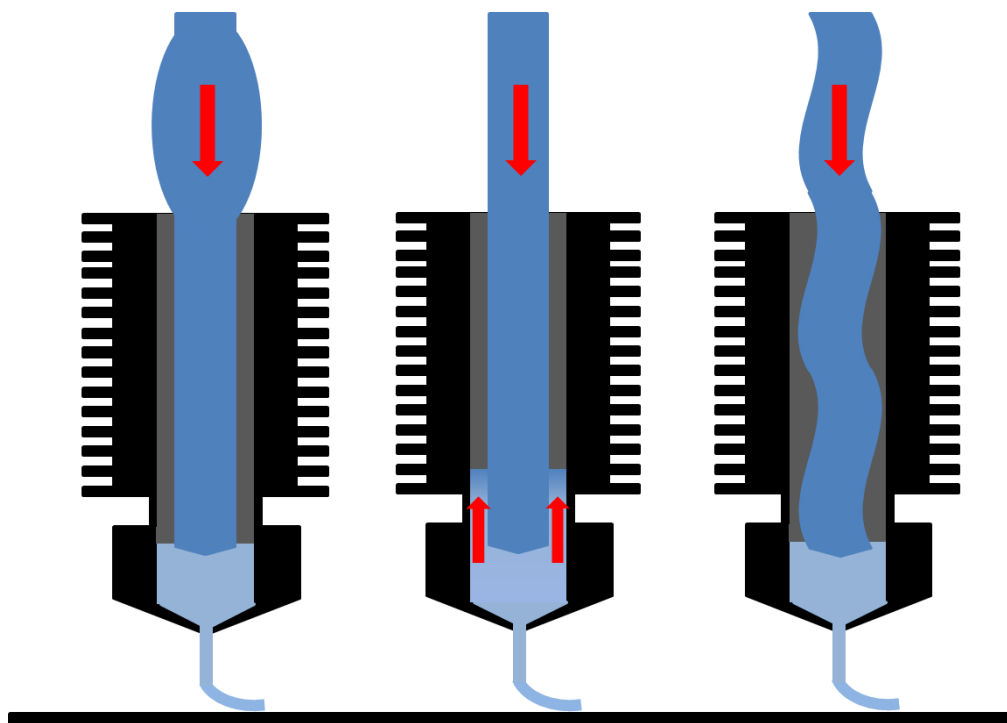


Figure 3.1. Material extrusion failure modes, from left to right: inconsistent filament diameter that exceeds the nozzle diameter, annular backflow, filament buckling.

Improper filament diameter failure can be eliminated by refining the filament fabrication methods with tight diametric tolerances. This failure mechanism will not be discussed further. Filament buckling has been explored by Venkataraman *et. al*⁸. In their work, the authors suggest that a filament will buckle if the pressure applied by the rollers exceeds that of the material's critical buckling stress. The authors estimated this relationship by calculating the ratio of the elastic modulus to the apparent viscosity measured using a capillary rheometer. They discovered that as long as the ratio is greater than a critical value, the material will extrude in FFF for a specific geometry and flow rate. Their work addresses the general buckling failure mode but does not account for the relationship between system geometry and flow behavior of the polymer at the solid-liquid interface, which is necessary for a complete screening analysis.

Annular backflow, shown in Figure 2, which accurately depicts the geometry of an E3D-V6 hot end nozzle as described in schematic diagrams provided by E3D (see supplementary information), is only possible because the filament that acts as a piston to extrude the molten material is not perfectly flush with the liquefier wall. In this failure mode, the molten polymer can flow back up the annular region between the filament and the liquefier wall, escape the heated area, and cool below its solid/fluid transition temperature. Little work has been done to model annular backflow, or to generally characterize the fluid behavior during the liquefaction process in FFF. Understanding this phenomenon is vitally important during the screening process of AM filament material development. For instance, polymeric materials that have low activation energy for flow can experience multiple orders of magnitude drop in viscosity over a narrow temperature range, e.g. in the solid to fluidic transition in the extrusion nozzle. The solid to liquid transition is vitally important to the extrudability of a material and is assumed to be instantaneous, but the behavior of the material at this interface determines the extrudability of the material. A material that has a high modulus but transitions to a very low viscosity fluid upon heating can experience backflow. This is a potential characteristic that can be found in ionomers of highly inviscid polymers¹⁴.

Developing a rapid screening tool to predict failure modes would be a tremendous asset for systematically generating novel materials for FFF. A screening process would remove the current laborious and time consuming trial-and-error methodologies and support efforts to understand the extrudability of materials in regards to their behavior after extrusion such as those by Tekinalp, *et al.*¹⁵. This research takes a continuum-based approach to model the rheological behavior of polymer melts in FFF and presents an efficient dimensionless analysis that predicts filament extrudability based on a rheological measurement and the system geometry. Additionally, this

work highlights the critical importance of shear thinning for successful FFF extrusion. We will demonstrate the applicability of our screening tool by first explaining the model development, proceeded by experimental procedures to validate the model, followed by a comparison of the model predictions and experimental results.

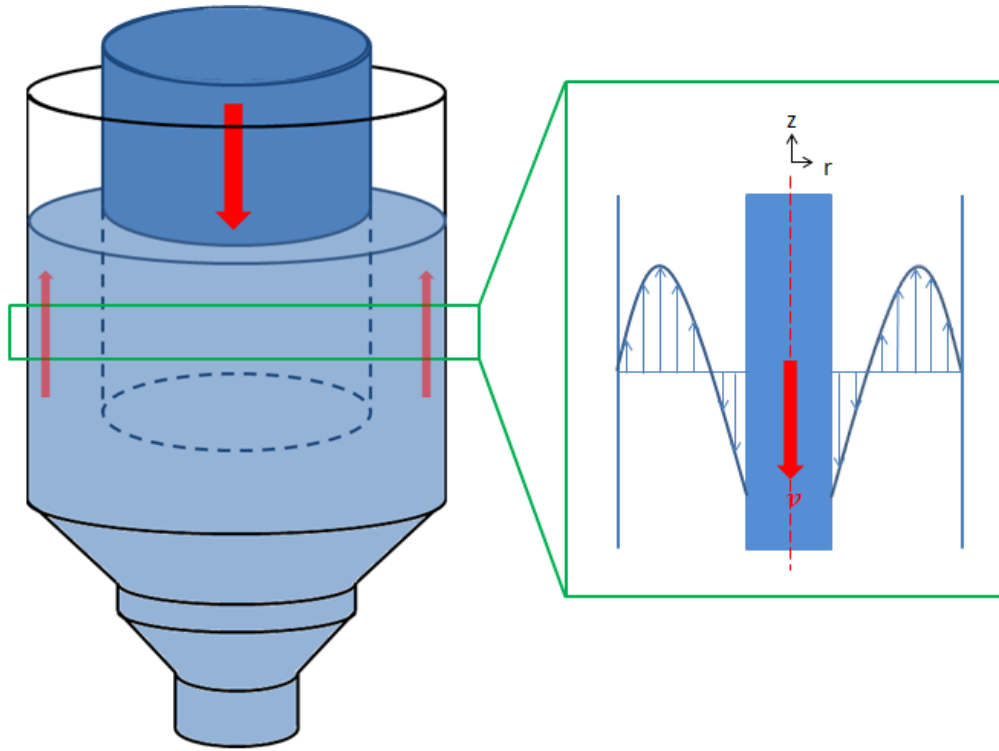


Figure 3.2. Schematic of transition of solid filament to viscous fluid in FFF nozzle. Inset image illustrates representative velocity profile in the annulus between the solid filament and nozzle wall, as would be observed during annular backflow. Note the chosen coordinate system and direction. Geometry of nozzle is based on schematic diagram provided by E3D.

3.3 Numerical Methods

3.3.1 Governing Equations

Nikzad, *et al.* modeled the temperature, pressure, and velocity profiles of a polymer melt in a FFF liquefier geometry¹⁶. However, they assumed that the filament was the same diameter as the liquefier and immediately transitioned to a fluid at the entrance to the liquefier. This allowed

them to model the polymer flow as a purely pressure driven flow that spanned the entire diameter of the liquefier, assuming that the polymer was fluidic along the entire length of the nozzle. Ramanath, *et al.*¹⁷ created a similar model that showed a greater non-isothermal behavior inside the nozzle, but still assumed a purely fluid flow across the diameter and over the complete length of the liquefier. Both groups also focused on the behavior at the nozzle of the liquefier. Our study realizes that the solid to liquid transition is not necessarily instantaneous, particularly at elevated filament feed rates, and also addresses the annular gap between the filament and liquefier wall.

As illustrated in Figure 2, we assume the system is operating at steady state in terms of filament feed rate, and that the fluid is in 1-D flow in the z -direction as a function of the radial position, r . We apply the z -component of Cauchy's momentum equations (Equation 1) in cylindrical coordinates to most accurately represent the geometry found in the FFF liquefier geometry¹⁸,

$$\frac{\partial P}{\partial z} = -\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) \quad (3.1)$$

In equation 1, dP/dz is the pressure gradient in the z direction, r is the radial position, and τ_{rz} is the shear stress acting on the r face in the z direction. Numerous expressions exist to describe τ_{rz} ; however, the generalized Newtonian fluid (Equation 2) incorporates a shear-rate dependent viscosity, and hence can describe the non-Newtonian viscosity behavior¹⁹

$$\tau_{rz} = -\eta(\dot{\gamma})\dot{\gamma} \quad (3.2)$$

In equation 2, $\dot{\gamma}$ is shear rate and $\eta(\dot{\gamma})$ is the shear-rate-dependent viscosity which can be measured directly from small angle oscillatory shear or steady shear rheometric measurements, or approximated using a constitutive relationship.

3.3.2 Boundary Conditions

We modeled a two-dimensional annular region and assumed it was perfectly symmetrical at all points circumferential to the filament. The two boundaries of the system are at the filament surface and at the wall of the liquefier, and we assume a no-slip condition at both boundaries. Therefore, the velocity of the polymer melt at the filament boundary is the same as the solid filament feed rate, and the velocity of the fluid at the liquefier wall is zero.

3.3.3 Constitutive Equations

Empirical analysis of backflow conditions is performed using actual viscosity measurements. However, to model the shear rate dependent viscosity in Equation 2 for a sensitivity analysis of backflow to process parameters, we chose to use the Ostwald–de Waele power law fluid model²⁰⁻²¹. The power law fluid model (Equation 3) is effective at modeling the shear thinning behavior of many polymer melts. We expect most polymeric materials to shear-thin at the shear rates we have calculated for typical filament AM nozzle and annular region, 0.24 and 160 s⁻¹ 22-23. Furthermore, the power law model can be used to approximate a Newtonian fluid by setting the power law index “n” equal to unity and treating the flow consistency index “m” as the zero-shear viscosity. This enables representation of a constant apparent Newtonian viscosity at low shear rates, and shear thinning non-Newtonian fluid at higher shear rates. Realizing the limitations of the power law fluid model, we chose it because of the importance of the shear thinning behavior, which it describes very well¹⁹.

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1} \quad (3.3)$$

In Equation 3, m and n are the flow consistency index and power law index, respectively. Combining Equations 1 through 3 results in a second-order ordinary differential equation.

Decoupling the differential equation and using MATLAB's ode45 function with appropriate boundary conditions, the velocity profile can be solved numerically.

3.3.4 Pressure Drop Estimation

We estimate the pressure drop along the length of the annular region using a power law fluid based momentum balance on the liquefier developed by Bellini *et al.* and by the Hagen-Poiseuille law for the pressure driven flow of a Newtonian Fluid²⁴. The values calculated for both methods were of the same order of magnitude, but Ramanath *et al.* verified the Bellini calculations were comparable to real world values provided by ANSYS simulations¹⁷. Because the solid filament entering the nozzle undergoes a non-isothermal transition from ambient temperature to processing temperature, we cannot treat the system isothermally. In her work, Bellini introduced an Arrhenius relationship into the pressure term that uses the activation energy of flow. This approximates the effect of temperature on the viscosity, and by extension, the pressure drop. Therefore, the Bellini calculations were used to increase the accuracy of the model when calculating pressure drop.

3.4 Experimental

3.4.1 Materials

Three materials were chosen to empirically validate the backflow model. Acrylonitrile-butadiene-styrene (ABS) was purchased from Hatchbox in filament form with a nominal diameter of 1.75, from which constant diameter filament lengths were extracted for empirical analysis. Low density polyethylene (LDPE) with a melt flow index of 25 g/10 minutes was acquired from Sigma Aldrich and extruded into filament using a Filabot EX2 single screw extruder at 180 °C and with a circulating filament cooling water bath and automatic spooler. The Filabot was thoroughly purged with LDPE until no discoloration was apparent to prevent contamination. Filaments lengths

of nominal constant diameter were produced for the empirical validation. The smallest diameter filament lengths were produced with a nominal diameter of 1.65mm, and the largest with a diameter of 1.85 mm.

Sodium sulfonated poly(ethylene) glycol (NaSPEG), an ionomeric polyethylene glycol, was synthesized at Virginia Tech²⁵. This material was processed into filament at 65°C using a Filabot EX2 and automatic spooler. Because of the material's solubility in water, NaSPEG was dried in a desiccator for one week at room temperature to remove any trace moisture. Additionally, the filament was air cooled following filament extrusion. Filament lengths were produced with constant nominal diameters, with the same range of diameters used for LDPE.

We used an open source FFF printer supporting an E3D V6 all-metal-hot-end with a 0.3 mm nozzle and a direct drive feed mechanism to extrude the test materials. The direct drive motor employed speed control to specify the feed rate. The gripping gears were also adjustable to allow specification of the filament diameter. The test materials were printed at feed rates of 5 mm/min, 5 mm/sec, and 10 mm/sec to represent a range of feed rates commonly found in filament extrusion additive manufacturing with systems incorporating a similar nozzle geometry. At higher feed rates, the gripping gears experienced a greater propensity to slip with the nozzle size used for these experiments. In systems that use nozzles with larger diameters, higher feed rates may be more common, but comparable shear rates will be observed and the analysis will scale accordingly. Furthermore, we limited the feed rates to those below 10 mm/sec to conserve limited material quantities, particularly with NaSPEG. Additionally, we emphasized limiting the tests to short filament lengths with high diametric consistency (± 0.01 mm), which further restricted the upper bound of the feed rate to that used in this analysis.

3.4.2 Elastic Modulus

An Instron 5969 load frame with a 50 kN load cell and tensile grips was used to measure the stress-strain relationship of each material at displacement rates that matched the feed rates specified in Section 3.1. Five cylindrical filament samples of each filament material were tested at each displacement rate to obtain a standard deviation. Care was taken to ensure cylindrical sample geometry with no substantial geometric deviation over the tested filament length, ensuring consistent cross-sectional area. All tests were performed at 20 °C. Stress-strain curves provided the measurements necessary to calculate the elastic modulus. The crosshead distance was used as a measurement of the strain with the assumption that all sample deformation occurred in the gauge length between the clamps. The linear region of the stress-strain relationship was used to determine the Young's modulus of each sample by calculating the slope at less than 2% extension.

3.4.3 Shear Rate Dependent Viscosity Measurements

All materials were dried in a desiccator for one week prior to viscosity measurements to remove residual moisture. NaSPEG was pelletized using a Cumberland 6" x 8" Granulator. LDPE was used in pellet form as provided from the manufacturer. ABS filament was pelletized using a 2" Killion pelletizer with a Bronco II speed controller. All materials were compression molded into 1 mm thick disks with a diameter of 25 mm.

An AR-G2 torsional rheometer from TA instruments was used for small amplitude oscillatory shear (SAOS) measurements to determine dynamic viscosity of the filament materials at angular frequencies of 0.1 – 100 radians per second, SAOS data was collected using a 25 mm parallel plate geometry with a 1 mm gap and 7 points measured per decade. The data for each material was collected at the FFF nozzle temperatures corresponding to each material, which was 220 °C for ABS, 180 °C for LDPE, and 65°C for NaSPEG.

An Instron CEAST SR20 capillary rheometer was used to measure the apparent viscosity at shear rates ranging from 100 to 1000 s⁻¹. The capillary die had a diameter of 1 mm and L/D of 30. For each experiment, pelletized material was placed into the capillary barrel and packed manually to expel air bubbles. The piston then applied a continuous force of 500 N during a ten minute preheat cycle to ensure homogenous packing and uniform heating. After preheating, five logarithmically spaced shear rates between 100 and 1000 s⁻¹ were measured. A pressure transducer measured the pressure at each shear rate, and the pressure was converted to shear stress at the wall. The Robinowitsch correction was applied to the shear rate to account for the non-parabolic velocity profile of shear-thinning thermoplastics. A long L/D was chosen to minimize the impact of die entry effects²⁶. Samples were measured at the same temperatures as used for SAOS measurements.

3.5 Results and Discussion

In this study, we present a model to analyze the propensity of a material to backflow. ABS, LDPE and NaSPEG were chosen for empirical validation of the backflow models because of their broad range of fluidic state rheological properties, including large differences in magnitude of viscosity and onset of shear thinning, which are expected to represent a very broad range of polymer flow properties^{23, 25, 27}. Additionally, the three materials have substantially different solid state modulus, which has been documented to impact the propensity to fail during extrusion via buckling⁸. ABS was also chosen as a reference material because it is well documented to extrude successfully in a broad range of FFF systems. We discuss details of the implications of solid and fluidic state properties on the model development, analysis and empirical validation in the following sections.

3.5.1 Model Development to Predict Backflow

Velocity profiles describing the fluid flow of the various materials in the liquefier geometry were created using the differential equation solver in MATLAB. If we consider a “zero” velocity reference point in the inset velocity profile representation in Figure 2, a velocity profile in the downward ($-z$) direction suggests that the fluid is moving towards the nozzle exit, and a velocity profile in the upward ($+z$) direction represents polymer melt that is flowing back towards the solid filament feed. The area under the curve of the velocity profile is indicative of the net magnitude of the cross sectional flow across the annular gap, which was then normalized against an ideal theoretical case in which the velocity profile across the gap was completely in the $-z$ direction (Figures 2,3). This enables calculation of the net flow magnitude as a dimensionless value that describes the velocity profile across the annular gap. This normalization was performed in such a way that a normalized net flow magnitude of zero describes a system identical to the ideal case, i.e., all the material is flowing toward the nozzle exit. As the normalized net flow magnitude becomes more positive, it represents an increasing volumetric flow in the $+z$ direction at the solid/liquid transition of the filament, and that will increase the likelihood for backflow to occur. Using MATLAB and its *trapz* function, the net flow magnitude is quantitatively estimated and normalized across all feed rates and gap sizes. In general, the normalized net flow magnitude can be categorized in one of three ways: no backflow, transition, and backflow. The no backflow condition describes a system where all of the polymer melt flows in the $-z$ direction towards the nozzle exit. The transition condition describes the velocity profile when a small amount of the molten polymer flows in the $+z$ direction of the annular region, but its magnitude is not necessarily sufficient to result in gross backflow and solidification around the filament, which would stop the filament feeding process. However, as we present in the sensitivity analysis, small changes in the

system could easily force the material in a transition state to experience gross backflow and cause a failure.

Here we present a dimensionless number to relate the system geometry and material properties to the material's propensity to backflow. We refer to this dimensionless number as the Flow Identification Number (FIN). The FIN relates the feed rate of the filament, the flow behavior of the polymer melt below the filament, and the difference in cross sectional area resulting from a difference between the diameter of the filament and the diameter of the nozzle. We derived the FIN by examining the fundamental relationship between wall shear rate, wall shear stress, and viscosity in a geometry-normalized manner for ubiquitous FFF machine analysis to arrive at a non-dimensional value, presented in Equation 4¹⁸.

$$FIN = \frac{\Delta P/L}{\eta v} (D_B^2 - D_F^2) \quad (3.4)$$

In equation 4, $\Delta P/L$ is pressure drop of the polymer melt which can be calculated using actual viscosity measurements with the equations developed by Bellini, *et al.*²⁴, η is apparent viscosity, v is filament feed rate in m/s, D_B is the nozzle diameter at the entrance to the liquefier, and D_F is the filament diameter. Physically, the FIN calculates if the pressure differential in the polymer melt is substantial enough to cause the melt to flow into the annular gap created by the solid filament diameter being less than the nozzle diameter. The FIN was calculated with the assumption that the filament feed rate was a finite, non-zero value. A FIN of zero suggests that no flow is occurring during extrusion, which would be represented by the filament and nozzle diameters being identical, viscosity approaching infinity (in which case extrusion cannot occur), or pressure drop approaching zero in which case there would be no driving force for flow. The assumptions used to establish the FIN were validated through multiple empirical trials, supporting the assumption of

the calculation of the velocity profile at the solid-liquid transition as being circumferentially similar around the annular gap.

To illustrate the relationship between the FIN and potential velocity profiles, Figure 3 demonstrates the three aforementioned normalized net flow magnitude scenarios, where the circles, diamonds, and triangles represent no backflow, transition, and backflow, respectively. The graph in Figure 3 displays the entrance to the annular region on one side of the solid filament. Therefore, the left y-axis of the graph ($x = 0.825$ mm) represents the filament boundary of a filament with a diameter of 1.65 mm, and the right y-axis ($x = 1.00$ mm) represents the liquefier wall boundary. The normalized net flow magnitude for each of the three profiles is 0.322, 0.669, and 0.914, and the FIN is 126, 175, and 204, respectively. We will discuss the significance of these values in the following section.

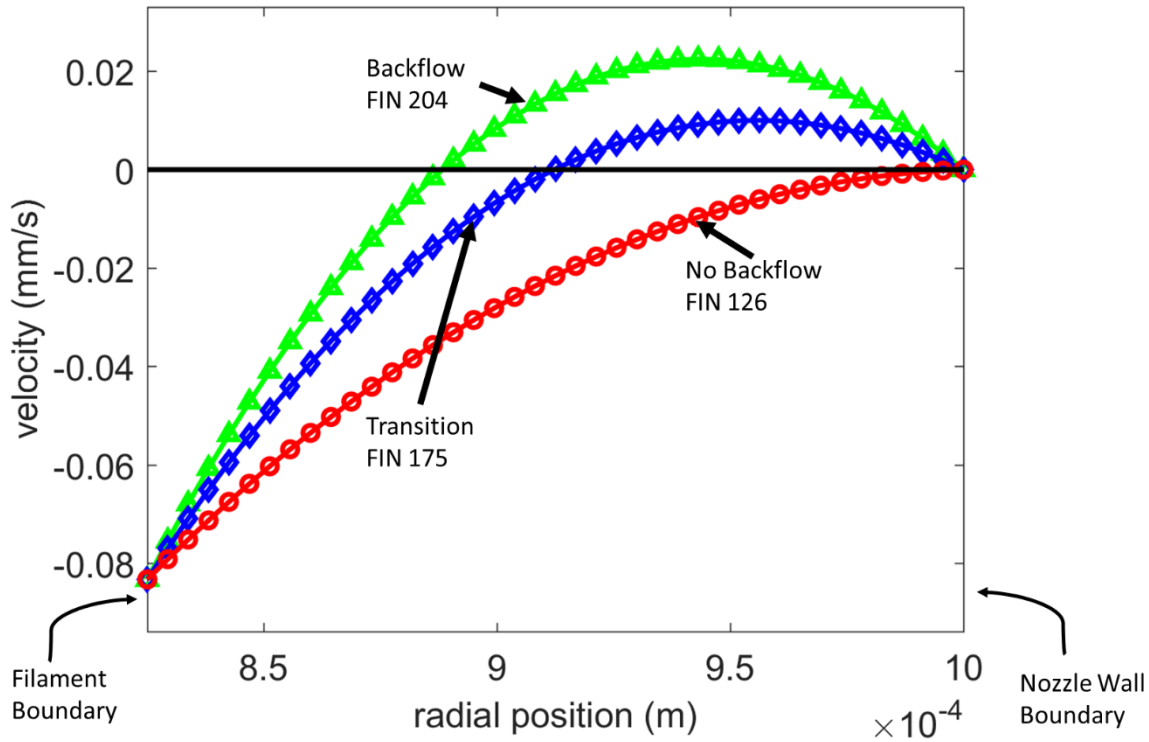


Figure 3.3. Graphical representation of velocity profile of a fluid that is not backflowing (red circles), a fluid in the transition region (blue diamonds), and a fluid that is backflowing (green triangles). Left and right y-axes represent filament (0.825mm) and nozzle (1.00mm) boundaries, respectively. Negative velocity is towards nozzle exit.

3.5.2 Analysis of FIN on Propensity to Backflow

Using the range of parameters in Table 3.1, we analyze the relationship between normalized net flow magnitude and FIN to understand its relationship to flow behavior and propensity to backflow. The values in Table 1 were based on values that could be reasonably expected to be found in an FFF printer with similar nozzle geometry, and the pressure was calculated using Bellini's equations with actual viscosity values. Values for the feed rate, filament diameter, and viscosity within the ranges specified in Table 3.1 were combined in a parametric study (Figure 3.4) to represent a wide range of thermoplastic polymers and processing conditions in FFF. Melt viscosity range is defined to capture a very broad range of thermoplastic behavior, based on our highest measured shear viscosity of ABS (at lowest measured shear rate of 0.1 rad/s,

which is well below typical FFF extrusion shear rates, see Figure 6) and based on the lowest possible expected viscosity based on Ostwald-de Waele power law parameters of $m=100 \text{ Pa}\cdot\text{s}^n$ and $n=0.1$, representative of a very highly shear thinning thermoplastic with a very low viscosity. Importantly, the range of shear rates represented by the feed rates in Table 1 are sufficient to represent much higher filament feed rates in systems with larger nozzle geometries, and therefore capture the flow behavior in a very broad range of FFF systems with varying nozzle geometries.

One can consider the physical interpretation of the FIN and its relationship to normalized net flow magnitude by realizing that the FIN is describing the z-axis location at the transition between solid filament and polymer melt, and relating the conditions of the flowing polymer melt to the geometry of the solid filament. Therefore, the FIN will always be positive assuming that extrusion is occurring, and the normalized net flow magnitude is only describing the net direction of flow at the solid/liquid transition. At a normalized net flow magnitude of zero, flow will still be occurring in the nozzle during extrusion, but all flow is towards the nozzle exit.

The FIN is second order with respect to the filament diameter, as defined in Equation 4. It also exhibits an inverse first order relationship with respect to filament feed rate. The results represented in Figure 3.4 suggest that the FIN has a parabolic, or second order, relationship to the normalized net flow magnitude (R^2 0.9563) over the range of conditions in Table 1, which we expect to encompass the range of interest in currently available FFF systems. As we discuss later in this section, we performed a sensitivity analysis to examine the contributions of each factor in the FIN on the normalized net flow magnitude to analyze the relationship presented in Figure 3.4.

From our analysis of the FIN and normalized net flow magnitude, we determined ranges of values that represent the various stages of backflow potential discussed in Section 4.1. The transition region is broadly represented by velocity profiles that have a normalized net magnitude

of flow greater than 0.5 and less than 0.75. In the transition region, some backflow may occur locally in the annular gap, but it is not expected to be sufficient to result in complete print failure. However, the printed part may suffer from inconsistent deposition rates. The transition region has been empirically observed to coincide with these predicted values and will be discussed later in this manuscript. Normalized net flow magnitudes less than 0.5 will not backflow, and those greater than 0.75 represent conditions that result in backflow and print failure. The FIN at each of these boundaries are 153 and 185, respectively. This transition region was verified through thorough experimentation and as discussed in Section 4.6, identifying the conditions which produced stable, metastable, and unstable extrusion.

Table 3.1. Range of parameters used in FIN analysis and expected to be observed in currently implemented filament AM systems with similar nozzle geometry.

	Low	High
Feed Rate (mm/s)	0.02	30
Filament Diameter (mm)	1.5	1.83
Melt Viscosity at Wall Shear Rate (Pa.s)	1.58	11188
Pressure Drop (MPa/m)	0.0024	939.5

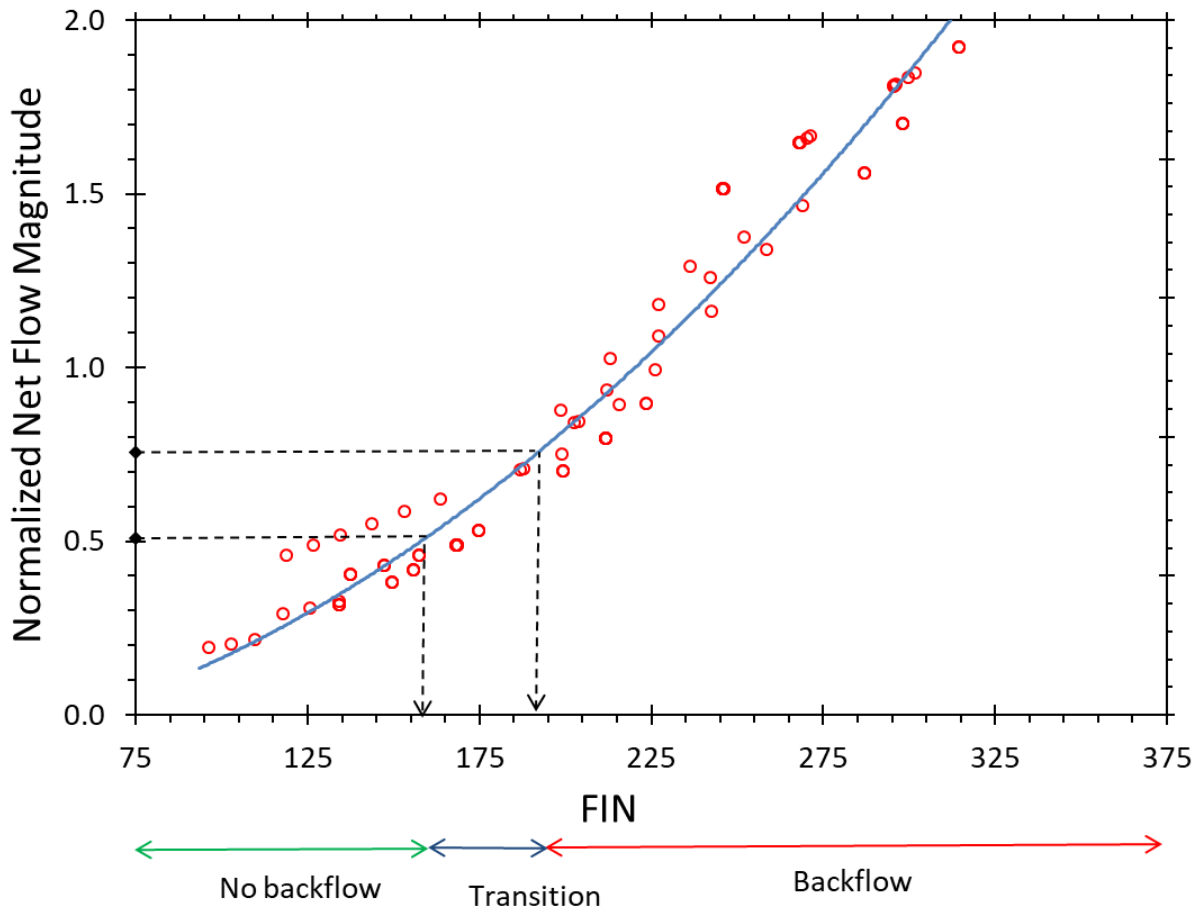


Figure 3.4. A parabolic relationship is observed between FIN and the normalized net flow magnitude. At a normalized net flow magnitude of zero, all material is flowing towards the nozzle exit. Below a FIN of 153, the material is expected to extrude assuming buckling does not occur. Above a FIN of 185, backflow is expected to always occur. A transition region occurs within which inconsistent extrusion may be observed. Open circles are modeled experimental conditions, solid line is a parabolic fit of the data

A sensitivity analysis using the power law constitutive relationship for viscosity was performed to determine the effect of FIN model parameters on the velocity profiles and normalized net flow magnitude. The nominal case is performed at a filament feed rate of 5 mm/s, with a 1.75 mm filament diameter whose power law indices m and n are 20000 Pa.sⁿ and 0.3, respectively. This nominal case was chosen to represent common printing conditions and material parameters. The m power law index was varied by +/- 10000 of its nominal case value, i.e. between 10000 and 30000 Pa.sⁿ. Similarly, the power law index, feed rate, and filament diameter were analyzed with

deviations of 0.1, 4, and 0.1 of the nominal case, respectively. The variations in power law index and flow consistency index represent a broad range of polymer flow properties²⁸⁻³¹. The variation in feed rate represents a range of feed rates found in most FFF printers with similar nozzle geometry. The variation in the filament diameter represents the filament inconsistency of a commercial product. Figure 3.5 analyzes the impact of changing these four FIN parameters on the normalized net flow magnitude.

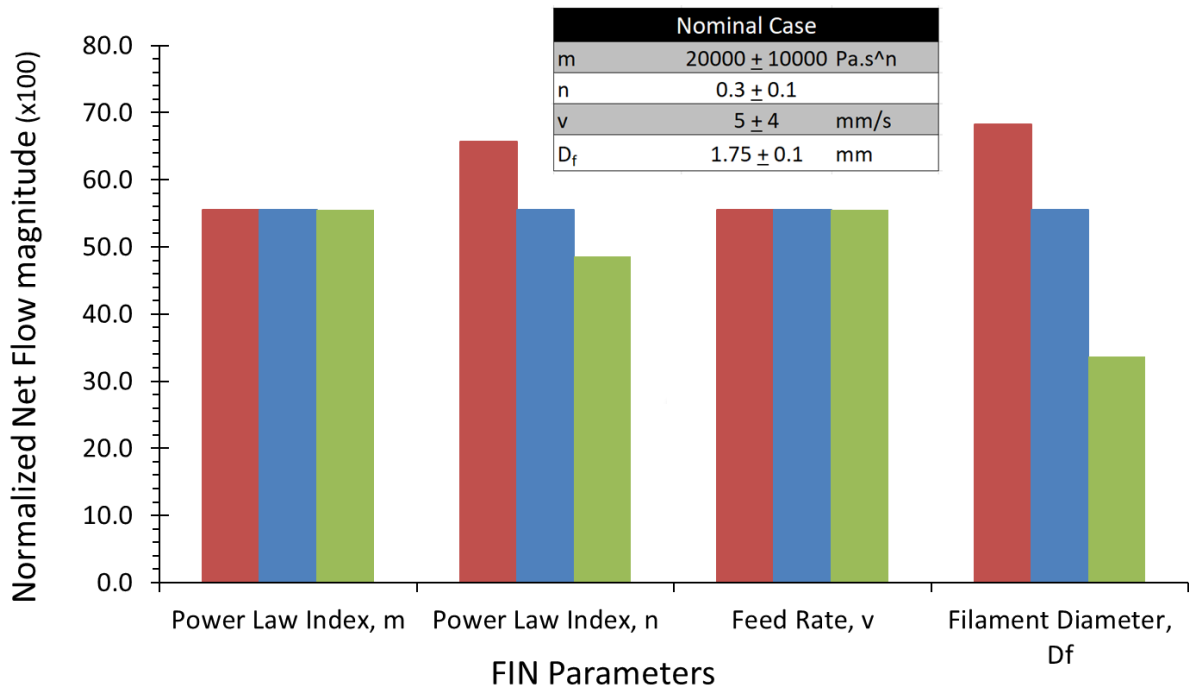


Figure 3.5. Sensitivity Analysis of FIN Parameters on normalized net flow magnitude. Blue represents a nominal case; red and green represent the lower and upper limits of analysis, respectively.

This sensitivity analysis indicates that normalized net flow magnitude has the strongest dependence on filament diameter, with a slightly lesser dependence on the power law index n. Feed rate and flow consistency index both change the normalized net flow magnitude less than 1%

from the nominal case. The filament diameter produces the greatest difference from the nominal case with a 39% decrease in the normalized net flow magnitude measurement when the diameter is changed from 1.75 mm to 1.85 mm. The filament diameter has the greatest effect because it changes the amount of available annular cross-sectional area in which a fluid can flow. By changing the filament diameter from 1.75 mm to 1.65 mm, the cross sectional area in the annular region increases from 0.736 mm² to 1.00 mm². The larger gap size between filament and nozzle wall reduces the pressure resistance in the +z direction. This effect is compounded in low viscosity polymers or polymers with low activation energy for flow, where the resistance to flow is further decreased. As the filament diameter is increased and approaches the barrel diameter, the annular area is reduced, and backflow becomes much less likely.

The power law index, n , describes the shear thinning behavior of the material and shows a large effect on the normalized net magnitude of flow. When the power law index is changed from 0.3 to 0.4, a 12% decrease in normalized net flow magnitude is realized. Small changes in power law index can translate to large changes in the viscosity at a specific shear rate, resulting in large changes in resistance to flow in the annular region between the filament and nozzle wall. As the material is extruded from the nozzle, the shear rate drops exponentially and the material's viscosity increases. These results are consistent with other reports of the benefit of shear thinning in material extrusion printing³²⁻³³.

The results of the sensitivity analysis explain the parabolic relationship between the normalized net flow magnitude and the FIN. As highlighted in Figure 3.5, the diameter of the filament has the greatest impact on the normalized net flow magnitude, but the shear thinning behavior of the polymer is also significant and is the most significant intrinsic property. We therefore suggest that the filament diameter will dominate the correlation of FIN to flow

conditions, but that the degree of shear thinning provides the strongest intrinsic property response on the potential for extrusion failure in appropriate diameter filaments.

3.5.3 Shear Rheology

The rheological properties of ABS, LDPE and NaSPEG were characterized to determine the magnitude of viscosity as well as its shear rate dependence, particularly with respect to the onset of shear thinning. Because we are interested in a broad range of shear rates, we were unable to measure the viscosity with a single technique. Capillary rheometry most closely mimics the system configuration found in FFF printers, but our measurement system configuration was only useful for shear rates greater than 100 s^{-1} . We performed SAOS measurements to analyze dynamic viscosity data at shear rates lower than 100 s^{-1} . Because SAOS are performed in oscillatory shear instead of steady shear, we determined whether there is overlap between the measurement techniques as suggested by the Cox-Merz relationship. Figure 3.6 demonstrates that the dynamic oscillatory measurements match the apparent viscosity provided by capillary rheometry within error of the instrument capabilities. This data suggests that, for the materials analyzed in this study, the dynamic viscosity is an accurate approximation of the steady shear viscosity at low shear rates.

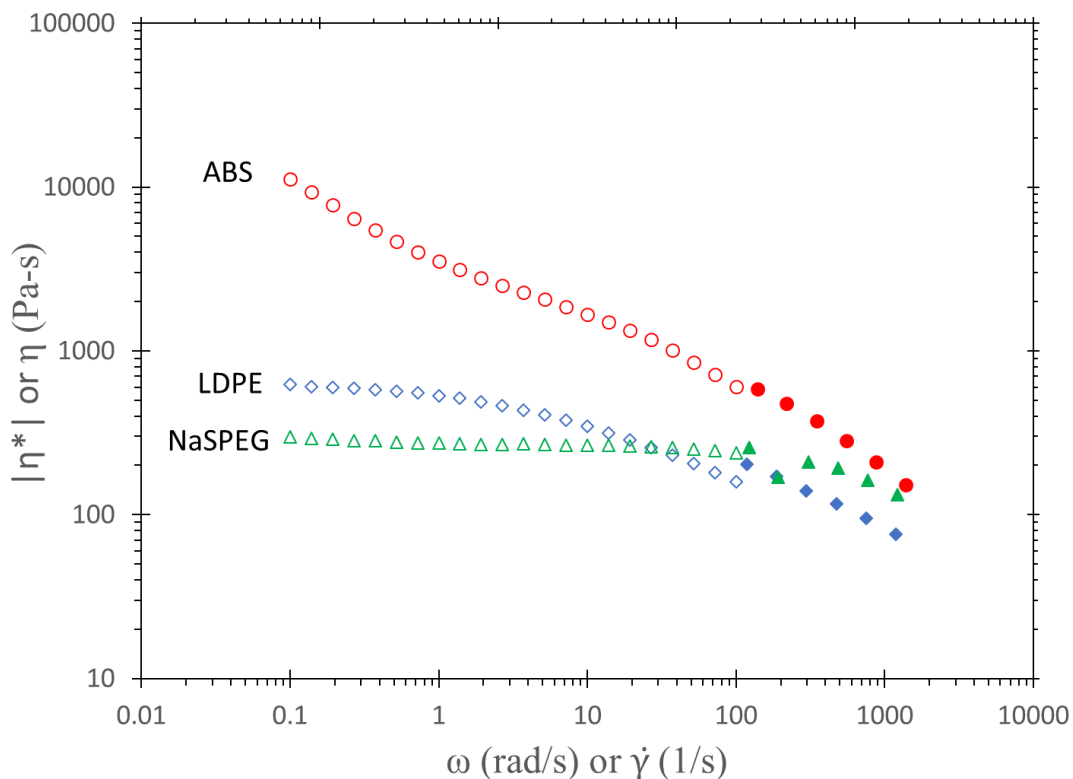


Figure 3.6. Overlay of SAOS (hollow shapes) and capillary steady shear (filled shapes) rheometry to determine correlation between the two measurement techniques for the materials analyzed in this study and to analyze the onset of shear thinning at their respective printing temperatures for ABS (O), LDPE (◇), and NaSPEG (Δ)

For feed rates between 5 mm/min and 10 mm/s, and filament diameters 1.75 ± 0.1 mm the shear rate in the FFF nozzle is between 0.1 and 300 s^{-1} . In this shear rate range, NaSPEG and LDPE transition between Newtonian and shear thinning behavior. Conversely, ABS shows a shear rate dependent viscosity across all measured shear rates, with zero shear viscosity at a shear rate below the measurement capabilities of our instruments in controlled strain mode. Because two of the materials transition between Newtonian and non-Newtonian behavior in the shear rate range of interest, we calculated the velocity profiles for the empirically validated materials with the actual viscosity measurements presented here rather than the power law model viscosity approximation.

3.5.4 FIN Backflow Model Predictions

To validate the backflow model, we calculated the velocity profiles for each of the three test materials at multiple processing conditions. Viscosity values are used at the apparent wall shear rate, calculated based on the filament feed rate and nozzle geometry at the location of the polymer melting, and as represented in Equation 5.

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (3.5)$$

Where $\dot{\gamma}$ is the shear rate of the polymer melt, Q is the volumetric feed rate that accounts for the solid filament feed rate, and R is the wall radius. As illustrated in Figure 2, the FIN is analyzing the transition region between solid filament and flowing polymer melt. We assume that the polymer melt will take the shape of the nozzle immediately below this solid-liquid transition and will be sufficiently represented as simple shear flow through a circular cross section. Therefore, we use wall shear rate that defines the bulk polymer melt in the nozzle below this transition to determine viscosity, which directly relates to the pressure inside the nozzle that could ultimately lead to onset of backflow. Assuming that backflow does occur, it is important to note that the shear rate would rapidly become zero in the annular region because the polymer will solidify above the z-axis location where temperature is not sufficient to transition the polymer to its viscous state. Therefore, we use the “steady state” conditions of flow to evaluate the propensity to backflow, realizing that the backflow phenomenon is an unsteady behavior that will not become a steady state flow condition and, therefore, will actually cease to flow quickly because of fluid solidification in the annular gap.

Figure 3.7 presents the velocity profiles calculated for each material by changing both filament diameter and filament feed rate within practical machine constraints as discussed in Section 4.2, and Table 3.2 lists the FIN values for each of the profiles in Figure 3.7. The velocity profiles indicate ranges of FIN for ABS from 81.1 to 151, which suggest that ABS will extrude well in a variety of FFF systems since it never enters the transition region and should not backflow under any of the tested conditions. Conversely, the FIN of NaSPEG ranges from 99.2 to 204 for the 5 mm/min solid filament feed rate and for diameters ranging from 1.65 to 1.85 mm. These results suggest that the filament may extrude without issue (FIN below 153) or begin to fail as it enters the guaranteed to backflow region (FIN >185) in Figure 4, depending on the combination of feed rate and filament size. For example, NaSPEG with a diameter of 1.65 mm and 5 mm/s is in the backflow region with a FIN of 204. Under these conditions, the material will most likely have flow consistency problems during extruding until the extrusion is stopped by backflowed material that has escaped the molten region and arrested the motion of the filament feed stock. However, the NaSPEG material enters its shear thinning regime as the feed rate is raised to 10 mm/sec (shear rate 272 s^{-1}), resulting in a lower FIN and higher propensity to extrude successfully. These model predictions further emphasize the importance of shear thinning for successful material extrusion in FFF.

LDPE is less likely to backflow than NaSPEG, but at the slowest feed rate and smallest diameter, this material does have a FIN value of 175. Therefore, LDPE has the potential to backflow if it does not buckle in the process. The FIN for LDPE decreases with increasing solid filament feed rate and increasing diameter, similar to the trends observed with NaSPEG.

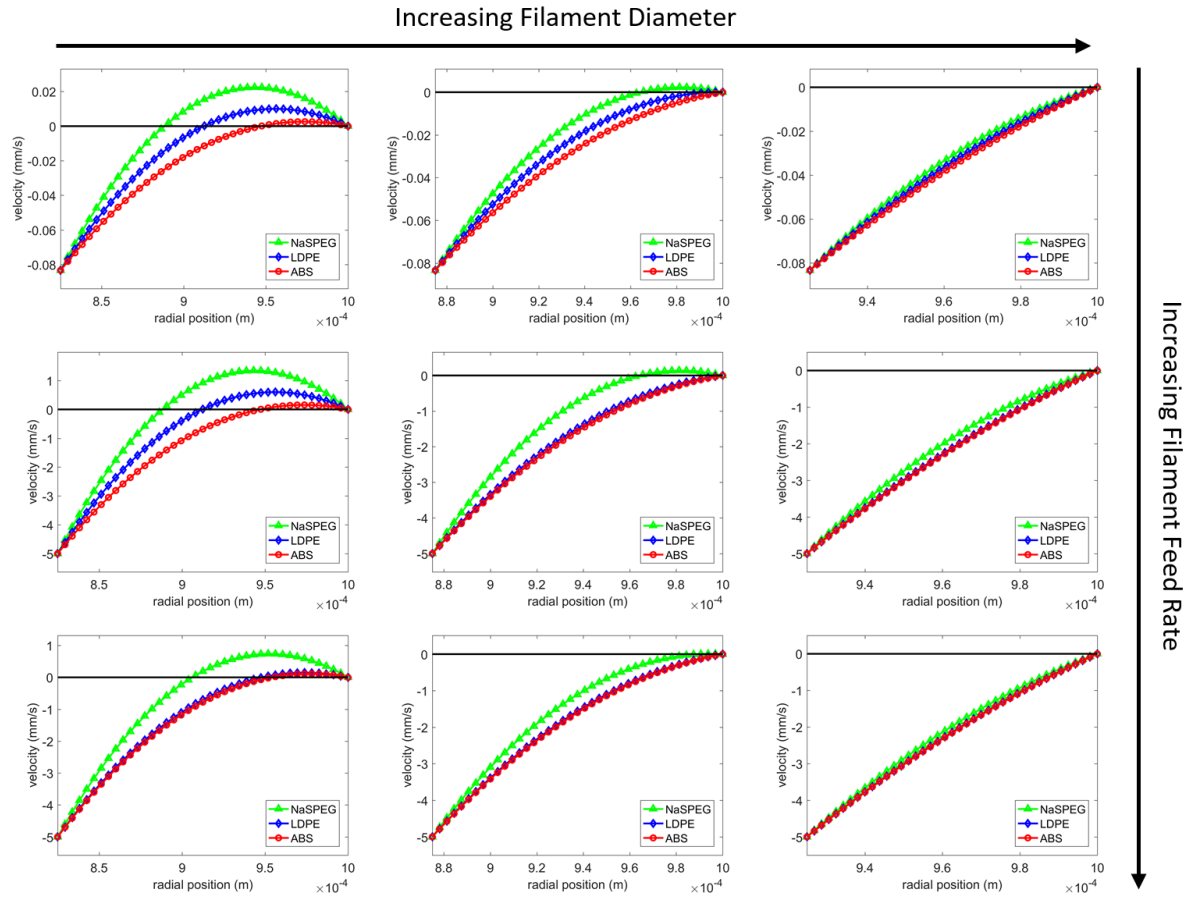


Figure 3.7. Results of backflow model analysis of ABS (O), LDPE (◇), and NaSPEG (Δ). From left to right, diameter: 1.65 mm, 1.75 mm, 1.85 mm. From top to bottom, feed rate: 5 mm/min, 5 mm/s, 10 mm/s. Zero z-direction velocity is represented by the solid line.

Table 3.2. FIN values from modeled velocity profiles for ABS, LDPE and NaSPEG.

Solid Feed Rate	Filament	Material	1.65 mm Diameter	1.75 mm Diameter	1.85 mm Diameter
5 mm/min		ABS	151	114	82.2
		LDPE	175	130	89.8
		NaSPEG	204	149	99.2

5 mm/sec	ABS	150	113	81.8
	LDPE	156	117	83.8
	NaSPEG	204	149	99.2
10 mm/sec	ABS	147	112	81.1
	LDPE	150	114	82.0
	NaSPEG	181	134	91.7

When considering backflow, we refer back to Figure 3.2 and examine the flow behavior in the first two sections of the liquefier. This section of the nozzle is also depicted in the schematic diagram provided in the supplementary information. In the first, and widest, section of the nozzle, the shear rates range from 0.1 to 40 s⁻¹, dependent on the feed rate. The velocity of the polymer increases upon contraction of the nozzle, which increases the shear rates to 2 to 300 s⁻¹. To prevent backflow, the material must be strongly shear thinning before it enters the second section of the nozzle. If the material behaves as a Newtonian fluid in both sections of the nozzle, the material nearer the nozzle exit will strongly resist motion toward the exit and cause the material near the solid to liquid interface to backflow. If the material shear thins in or before the second region of the nozzle, the material nearer the nozzle exit will easily flow toward the exit and prevent motion toward the solid to liquid interface of the material near this region. This is demonstrated by the behavior of ABS and, to a lesser degree, LDPE. The LDPE may be lightly or strongly shear thinning after the contraction dependent on the feed rate, which is reflected by its change in FIN. At feed rates less than 5 mm/sec, the material is only lightly shear thinning after the contraction, and its FIN places it in the transition region. As the feed rate increases, the degree of shear thinning in this section of the nozzle also increases, and LDPE's FIN decreases below the transition point

(to a completely stable, no backflow state). Conversely, NaSPEG does not exhibit substantial shear thinning until shear rates greater than 300 s^{-1} are realized, and remains in the backflow region of the FIN model at all but the fastest tested feed rates when the filament diameter is 1.65 mm. This behavior is further influenced by the degree of shear thinning. As the material becomes less Newtonian, the change in viscosity increases between the two regions of the nozzle at all shear rates. Propensity to backflow is greatly reduced as the degree of shear thinning increases.

The results in Figure 3.7 and Table 3.2 also verify that filament diameter has the greatest effect on the flow behavior inside the liquefier, supporting the results of the modeled sensitivity analysis in Section 3.5.2. The FIN values increase nearly an order of magnitude when the diameter is reduced from 1.85 mm to 1.65 mm. This trend is observed in all materials, highlighting the importance of consistent filament diameter compared to system geometry. However, assuming that filament diameter can be readily controlled via consistent processing approaches to generate the precursor feed, then our results suggest that successful FFF extrusion is most sensitive to the intrinsic shear thinning behavior of the thermoplastic.

3.5.5 Buckling Model Predictions

To capture important failure modes during a screening process, we compared the results of the backflow analysis with failures that may occur via buckling. The buckling predictive method proposed by Venkataraman, *et al.* was implemented with the same conditions used in the backflow models. As shown in Table 3.3, ABS appears to be the stiffest material with an elastic modulus ranging from 1050 MPa to 1230 MPa over the range of rates tested, which are representative of common extrusion rates. LDPE is the softest material in this study with an elastic modulus ranging from 81 MPa to 96 MPa. NaSPEG is more rigid than LDPE, with an elastic modulus ranging from 308 MPa to 435 MPa, because its ionic substituents tend to microphase separate, form ionic bonds,

and increase the strength of the bulk material. The average of the modulus measurements for each material match previously reported literature values and were used for verifying the buckling model³⁴⁻³⁵.

Based on their elastic moduli, we expect that NaSPEG and LDPE are more likely to buckle when used in FFF printers. A sufficiently high modulus is required to allow the materials to act as the piston to expel the fluidic polymer without buckling.

Table 3.3. Modulus measurements of ABS, LDPE, and NaSPEG at 20°C

Material	Speed (mm/sec)	Modulus (MPa)	St. Dev. (MPa)
ABS	0.0833	1230	207
	5.00	1080	30.7
	10.0	1050	34.6
LDPE	0.0833	95.9	6.80
	5.00	95.4	3.60
	10.0	80.8	12.0
NaSPEG	0.0833	435	27.0
	5.00	382	56.0
	10.0	308	45.9

Venkataraman, *et al.* suggested a filament would buckle if the ratio of the elastic modulus to the apparent viscosity dropped below a critical value, somewhere in the range of 3×10^5 to $5 \times 10^5 \text{ s}^{-1}$. Figure 3.8 presents the ratio of elastic modulus to apparent viscosity across a wide range of shear rates. We have denoted a smaller range of shear rates that should be experienced inside the liquefier geometry with vertical dotted lines. The horizontal dotted line is the empirically-placed boundary suggested by Venkataraman. Any filament material below this boundary should fail during the extrusion process due to buckling.

Under the conditions of this study, Venkataraman's model suggest that ABS has no propensity to buckle. By comparison, the model suggests that LDPE should buckle easily at all feed rates tested, and NaSPEG might buckle at feed rates less than 10 mm/sec. At lower feed rates, the molten polymer viscosity is greater, which requires greater rigidity to successfully extrude. The lack of rigidity in LDPE makes it incapable of withstanding the compressive force it needs to overcome this resistance to flow. As a result, LDPE buckles under the compressive stress before it can backflow.

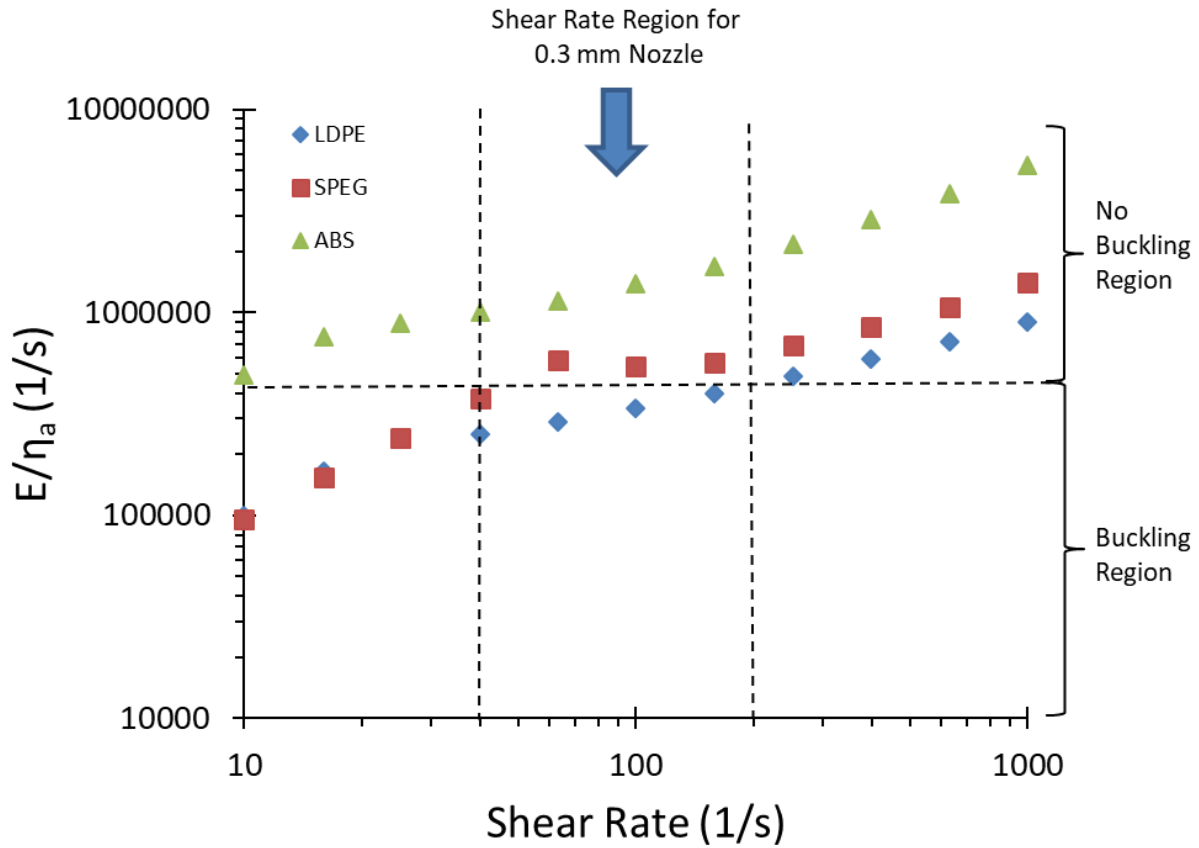


Figure 3.8. Results of buckling analysis. Vertical dotted lines represent range of shear rates that should be experienced inside the liquefier geometry. Data points above the horizontal dotted line should not buckle, and below the dotted line should buckle.

3.5.6 Experimental Validation of Models and Practical Impact on Extrudability

Based on the results provided by the predictive tools presented in this research, we observe a trend in the material properties and propensity to fail. LDPE is predicted to buckle at all feed rates, and also has a small backflow potential at feed rates slower than 5 mm/sec and diameters of 1.65 mm or less. NaSPEG, a material with a high modulus and a nearly Newtonian viscosity, is likely to backflow at feed rates less than 10 mm/sec and filament diameters of 1.75 mm and less. This material should also have a small probability of buckling. ABS, a material with a high

modulus and highly shear thinning viscosity, should not buckle nor backflow under any of the testing conditions.

Multiple trials were performed on ABS, LDPE, and NaSPEG to verify the failure modes predicted by the FIN and buckling models. Tests were performed using sections of filament with constant diameter over the length of the filament (generally +/- 0.01mm or less). To ensure the highest experimental level of diametric consistency for each test, we used the minimum length of filament necessary to perform each analysis. Filament diameters between 1.65 and 1.85 mm were implemented using feed rates between 5 mm/min and 10 mm/s, at the thermal conditions mentioned previously. The commercially available ABS did not buckle nor backflow under the range of processing conditions and filament diameters, which is consistent with previously reported studies. LDPE immediately buckled under all processing conditions and filament diameters and was unable to backflow because it failed via buckling before backflow conditions were reached. NaSPEG buckled at the 10 mm/sec feed rate and all diameters. It backflowed at feed rates of 5 mm/sec and less when the narrowest (1.65 mm) filament diameter was printed. Figure 3.9 displays the results of NaSPEG backflow and LDPE buckling.

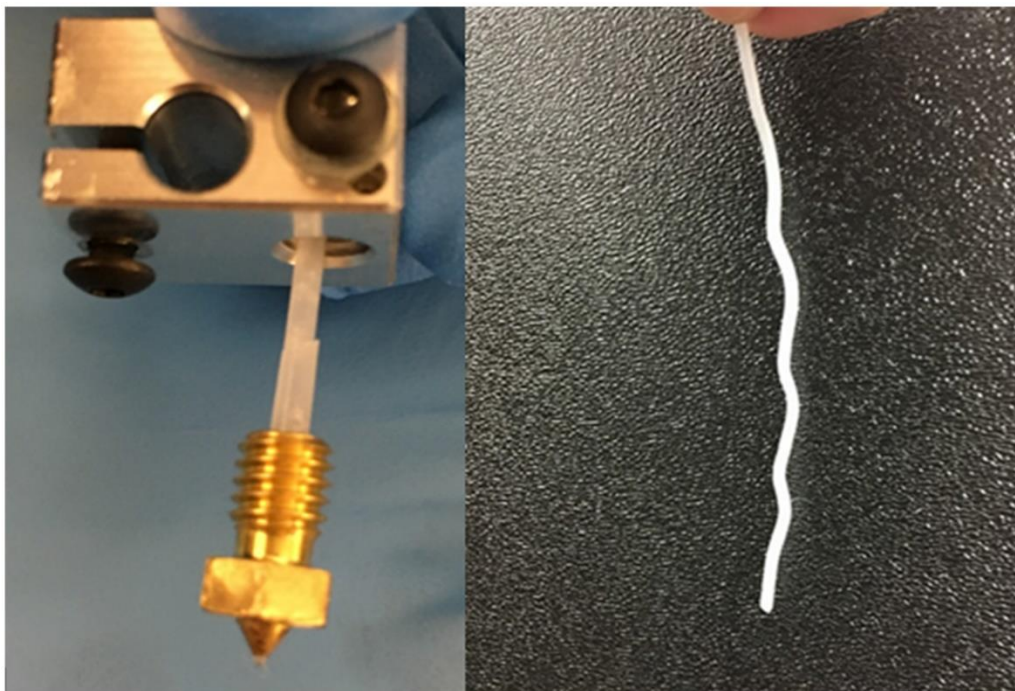


Figure 3.9. Image of NaSPEG backflow (left) and LDPE buckling (right) following attempt for FFF extrusion.

The results in Figure 3.9 suggest general trends related to filament failure in the filament AM process, and corroborate the analysis of ranges of extrusion conditions for materials in FFF geometries. Materials with high tensile moduli, i.e. greater than 1000 MPa, have a smaller probability of buckling under the conditions created in an FFF printer. This is a common property in polymers with a glass transition temperature (T_g) that is sufficiently higher than ambient temperature or in lower T_g materials with sufficient crystallinity to impart substantial rubbery modulus above T_g . Furthermore, materials with an early onset to shear thinning, i.e. shear thin at rates less than 50 s^{-1} , will not backflow except when the filament diameter is very small, i.e. smaller than 1.65mm, which is well below the typical smallest diameter observed in commercially produced filament. If the material has both a low modulus and Newtonian viscosity profile at relevant FFF shear rates, it is expected to buckle before backflow can cause a failure in the printing. If the material has a high modulus and a late onset of shear thinning, i.e. at a shear rate at or above

typical FFF shear rates, then the material will most likely backflow. NaSPEG is a unique example of this last observation. At room temperature, NaSPEG is a rigid solid due to the ionic intermolecular attractions between chains. When the polymer is heated and enters a molten state, the ionic polymer is highly inviscid, resulting from the polymer's low molecular weight and disruption of the ionic interactions in the molten state^{25, 36}. The stiff, solid filament can extrude the molten material without buckling, but the inviscid fluid flows upward in the inherent annular gap.

3.6 Conclusions

This study presents an approach to rapidly screen polymeric materials as potential candidates for filament based material extrusion AM by using a rheological analysis and a tensile measurement to predict extrusion failure. We present a model that describes the magnitude of the velocity profile in FFF hot end geometries, which results in a single dimensionless number, the Flow Identification Number (FIN), that can predict a material's propensity to backflow. A sensitivity analysis indicates that the propensity to backflow is most sensitive to the filament diameter, followed by the degree of shear thinning, in relevant FFF conditions. We applied the model to predict the flow profile of three materials, ABS, LDPE, and NaSPEG, which have significantly different viscosities in terms of magnitude and shear rate dependence, as well as onset of shear thinning. Empirical replication of the flow conditions validated the model prediction, where NaSPEG was observed to backflow at filament feed rates of 5 mm/sec and less and diameter of 1.65, and LDPE was observed to buckle under all feed rate and diameter conditions. Application of a previously developed buckling analysis, with incorporation of the flow and geometry considerations presented here, provides a complete methodology to predict the ability to successfully extrude a filament, and also suggest ranges of processing conditions suitable for successful FFF extrusion.

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Chapter 4

Characterization and Analysis of Polyetherimide: Realizing Practical Challenges of Modeling the Extrusion- Based Additive Manufacturing Process

4. Characterization and Analysis of Polyetherimide: Realizing Practical Challenges of Modeling the Extrusion-Based Additive Manufacturing Process

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4.1 Abstract

This research presents the thorough characterization of a representative material used in material extrusion (MatEx) as the basis for developing a physics based thermal transport and viscoelastic model to capture the highly transient multiphysics associated with extrusion and deposition of an amorphous thermoplastic. The ultimate goal is to develop a process model that can identify critical process parameters in MatEx to target synergistic materials and aid in process design and optimization. Toward this goal, the rheology of Ultem 1010 was characterized to provide information regarding the flow behavior at representative process conditions, including interrupted shear measurements to quantify the complete re-entanglement time and understand the nature of the diffusion process during polymer deposition over previous layers. Scanning electron

microscopy was used to quantify geometric profiles in a printed single road width wall, providing information about the necessary mesh geometry to represent the complex geometry accurately and further serve to establish the capability for viscoelastic models to capture the complex geometry of the deposited road as a function of thermal history. A three-dimensional, transient heat transfer model based on first principles multiphysics analysis is presented, which qualitatively agrees with temperature measurements conducted with an infrared camera. The complexity identified in performing the finite element analysis establishes the practical challenges associated with computational requirements and highly transient response in a complex, free surface flow and solidification process.

4.2 Introduction

Material Extrusion (MatEx), also known by the trademarked name fused deposition modeling, is the most common method of filament extrusion additive manufacturing (AM). It has the ability to create highly complex geometries not possible with traditional manufacturing. AM is further able to create these geometries while producing less waste and using less energy. Currently, MatEx is challenged by the ability to meet quality standards consistently, including both process repeatability and final part properties, for end-use applications. Quality control is a vital aspect of transitioning from rapid prototyping to the manufacturing industry, where repeatability and consistency are required for the parts, machines, and processes to be certified¹. Currently, manufacturers have limited ability to guarantee that every part produced with the use of MatEx will have the requisite mechanical and/or thermal properties, or dimensional accuracy.

A more thorough understanding of MatEx is needed in order to optimize and standardize the printing process to attain the necessary quality control². This understanding can be achieved through physics based process models that incorporate heat transfer, stress development, interlayer

bonding, and crystallization. Computational process models allow for the identification of critical process parameters that influence material behavior during the printing process. This information can then be used to establish acceptable processing conditions to yield the desired printed component performance.

Heat transfer is the driving force behind the evolution of the mechanical properties of a printed part. At elevated temperatures, the polymer layers are able to bond to their adjacent counterparts partially, forming an interface that results in a location of inherent weakness in the final part³⁻⁴. Most current work predicting the evolution of the bond is in the form of empirical models that are only applicable to a small range of systems⁵. Understanding how the thermal energy will travel through the system from the nozzle, bed, and atmosphere will promote a more thorough comprehension of the development of this bond. A geometrically accurate, three-dimensional heat transfer model will greatly aid in predicting these phenomena and will ultimately provide the optimal processing conditions to create consistent parts with properties near, or equal to, corresponding conventionally manufactured counterparts.

Most attempts to generate heat transfer models are only one-⁶⁻⁹ or two-dimensional¹⁰ and assume ideal road shapes such as rectangles, circles, and ellipses in order to simplify the calculations^{3, 9-11}. McIlroy and Olmsted⁹ claim that a one-dimensional model with elliptically shaped roads is able to closely mimic the temperature behavior of the MatEx process as compared to IR camera measurements performed by Seppala and Migler¹². However, IR measurements, such as those reported by Seppala and Migler¹², Dinwiddie *et al.*¹³, and Wolszczak *et al.*¹⁴, only record information on the surface of the printed roads and are incapable of examining the temperature gradient through the cross-section. This is exemplified by Coogan and Kazmer⁷, who predicted the interlayer bond strength of an MatEx printed part with the use of a one-dimensional heat transfer

model. Their model predicted the incorrect bond strength, as demonstrated by their plot comparing predicted bond strength values to measured bond strength values. This comparison resulted in a slope of 0.72 and an R^2 value of 0.795, indicating imperfect agreement between predictions and empirical measurements, as well as some scatter due to the imprecise nature of the printing process. The one-dimensional and, to a lesser degree, the two-dimensional models do not account for the through-thickness temperature gradient, which will affect the cooling rate and mechanical property evolution of the part. Furthermore, these models are not able to capture the viscoelastic properties that create the complex road geometry found in MatEx printing. D'Amico and Peterson¹⁵ developed a coarse three-dimensional heat transfer model, and although it did show similar trends to those observed in empirical measurements, the actual values did not agree well. This model also assumed a rectangular cross-section and a uniform height change across the entire part to simplify the calculations and reduce computation time. Because of these simplifications, the model predicted an average cooling rate 2–3 times greater than experimental rates, resulting in the time required to cool below the glass transition temperature being 2–3 times less than experimental measurements.

To address these issues, the requirements for developing a three-dimensional thermal model that accurately represents the AM process from nozzle extrusion to road deposition and part cooling were identified. This requires extensive knowledge of the thermal properties and flow behavior of the printing material. Herein, we present the characterization of a polyetherimide (PEI) that can provide the necessary parameters for the initialization and optimization of the thermal model, as well as the development of the initial heat transfer model.

4.3 Experimental

4.3.1 Materials and Printer System

Ultem 1010, a PEI with a density of 1.27 g/cm^3 and a glass transition temperature (T_g) of 217°C , manufactured by Sabic, was purchased in 1.75 mm diameter filament form from Stratasys.

The PEI filament was printed with the use of a modified Lulzbot Taz 6 MatEx printer with a maximum nozzle temperature exceeding 400°C and a bed temperature greater than 200°C . The modified Taz 6 was housed in an insulated chamber with 12 Sunlite 35 W halogen lamps directed at the build space. During the print, the environment is able to maintain an approximate temperature of 70°C ¹⁶.

Temperature measurements of the heated build chamber were collected with the use of a type J thermocouple before and during a print. Measurements indicated the ambient temperature of the build chamber to be approximately 43°C during this work. The temperature of the print itself was monitored with a FLIR T650sc IR camera. The nozzle and bed temperatures were set by the system software to be 350 and 200°C , respectively.

4.3.2 Rheology Measurements

The Ultem filament was pelletized with the use of a 5 cm Killion pelletizer with a Bronco II speed controller for preparing samples for rheological testing. The PEI pellets were then compression molded into 1 mm thick disks with a diameter of 25 mm for torsional rheology measurements. The material was dried in a vacuum oven at 125°C and 2.0 inHg overnight prior to all tests.

An AR-G2 torsional rheometer from TA Instruments was used for small amplitude oscillatory shear (SAOS) and steady torsional shear measurements to measure dynamic viscosity of the Ultem at angular frequencies of $0.1\text{--}100 \text{ rad/s}$ and apparent viscosity at shear rates of $0.01\text{--}1 \text{ s}^{-1}$, respectively. SAOS and steady torsional shear data were collected with the use of a 25 mm

parallel plate geometry with a 0.75 mm gap and 5–7 points measured per decade. The data were collected at multiple points within the printing temperatures of 345, 360, and 375 °C.

Interrupted shear experiments were performed on an ARES-G2 torsional rheometer from TA Instruments to determine the re-entanglement behavior of the Ultem as a function of temperature. The measurements were collected at 1 s^{-1} and temperatures of 345, 350, 360, and 365 °C with a 40 min sample equilibration time before the test began. The measurements were collected with the use of a 25 mm 0.1 rad cone and plate geometry. At least three relaxation times were used for each temperature, except 365 °C, because of sample instabilities during the test.

4.3.3 Scanning Electron Microscopy (SEM)

Multiple single road width walls (SRWW) of 10 layers were printed with the same printer parameters to provide measurements that would allow the creation of a meshing model for the finite element analysis (FEA). The printing parameters used to produce these walls included a nozzle diameter of 0.6 mm, extrusion multiplier set to 1, extrusion width set to 0.6 mm, layer height set to 0.5 mm, and print speed set to 10 mm/s. The SRWWs were immersed in liquid nitrogen for 1–2 min and cryofractured to expose the cross-sectional area. The walls were sputter coated with a thin layer of platinum/palladium to provide a conductive coating. Images were analyzed with the use of ImageJ image processing software to obtain measurements describing the shape of the cross-section, as well as the bond width between layers. The measurements were collected at 16 locations across four SRWW samples.

4.4 Modeling

The SRWW thermal model used for this work was developed in several phases. Analysis of the IR temperature data allowed for selection of an initial thermal transport model. Next, analysis of the SEM cross-section data provided the information necessary to construct a three-dimensional

model of the SRWW, leading to the ability to define sufficient viscoelastic models that accurately capture the free surface deformation in future iterations of the multiphysics process model. From this, the mesh of an initial extrudate model was used to construct a full model in the ANSYS Fluent software, including the use of user defined functions (UDFs). The model was initialized by converging to a static steady state solution. A dynamic transient solution was then computed by FEA. The results of the transient model were qualitatively compared to the IR temperature measurements to establish the validity of the model approach.

4.4.1 Governing Equations

Thermal modeling began in the simplest case, with a homogeneous material of constant mass density, thermal conductivity, and constant mass specific heat capacity¹⁷. This reduced the energy balance equation to Equation (4.1):

$$\rho \widehat{C_p} \frac{DT}{Dt} = k \nabla^2 T \quad (4.1)$$

where ρ is the mass density, $\widehat{C_p}$ is mass specific heat capacity, k is thermal conductivity, t is time, and T is temperature. After the initial wetting takes place, no significant flow was assumed to occur, which further reduced the material derivative to a simple partial derivative with respect to time. Rearranging and grouping the thermal conductivity, mass density, and mass specific heat capacity into a single term yielded Equation (4.2):

$$\frac{\partial T}{\partial t} = \alpha \nabla^2 T \quad (4.2)$$

where α is the thermal diffusivity. Thus the model was reduced to that of a simple case of heat diffusion in a system with moving boundaries. This is a reasonable assumption, assuming that radiation is not significant in conventional prototyping MatEx systems when compared to other

heat transfer mechanisms^{12, 15, 18}. Applicable viscoelastic models are not presented in this work but will be considered for future application to develop a predictive tool capable of capturing the coupled thermal diffusion and flow behavior. These two phenomena, which are linked and strongly affect each other, ultimately determine the complex MatEx road geometry and final part properties.

4.4.2 Model Analysis of IR Temperature Measurements

Monochromatic IR video recordings were analyzed with the use of custom lab made video software to determine the cooling rate. The analysis was performed by extracting the structure tensor from each frame of video. The simplest form of the structure tensor is defined by the dyadic product of the gradient of an image field with itself. For monochromatic thermography, the grayscale color intensity of each pixel is a function of the observed temperature. The square root of the trace of the structure tensor is thus proportional to the observed change in temperature. The structure tensor from each input video frame was extracted and converted to an output frame representing the change in temperature.

4.5 Results and Discussion

The purpose of this study was to develop a physics based process model that describes the heat transfer of a polymer system during the filament extrusion AM process. Ultem 1010 PEI was thoroughly characterized to provide initial parameters for the model development and to establish a baseline set of empirical conditions for model validation. After complete characterization of the material, a three-dimensional heat transfer model was produced with the goal of incorporating fluid flow and polymer chain diffusion and re-entanglement into the model at a later time.

4.5.1 Analysis of IR Temperature Data

IR thermography was used to estimate the surface temperature of the extruded layers and extrapolate the cooling rate from those temperatures. An IR video captured the thermal behavior

during the printing of a rectangular prism (approximately $50 \times 10 \times 5.5$ mm), which was assumed to have a cooling rate similar to that of a SRWW. Specifically, the first road of a new layer should possess a similar cooling rate as a SRWW because of the lack of adjacent roads. The output of the custom analysis software, shown in Figure 4.1, provides information regarding the change of temperature. The data from the converted IR video allowed the determination of the time required for the temperature to cool from the extrusion temperature, ~ 350 °C, to the bulk part temperature, ~ 220 °C. It was estimated that this cooling time was approximately 3 s, resulting in a cooling rate of about 43 °C/s. These results suggest that very little flow should occur following the initial wetting because the heat transfer occurred on a time scale sufficiently shorter than other phenomena.

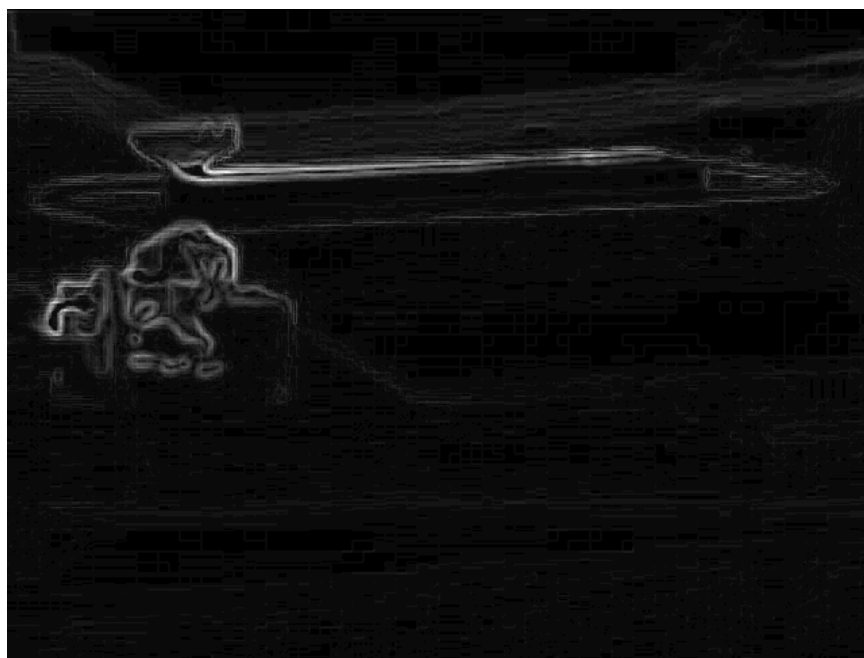


Figure 4.1. Image from IR video processed with the use of custom software demonstrating the cooling rate of the deposited filament. Lighter colored areas represent changing temperature, and dark colored areas represent material with a constant temperature.

4.5.2 Shear Rheology

The rheological properties of Ultem 1010 were measured to characterize its flow behavior throughout the AM process for future application in the addition of viscoelastic constitutive models. During the extrusion and deposition of a layer, the polymer may experience a broad range of shear rates, e.g., less than 0.01 s^{-1} and possibly exceeding 500 s^{-1} . The rheological properties were measured with the use of steady and oscillatory torsional rheometry to capture this broad range of shear rates. The material experiences the highest shear rate as it is extruded from the nozzle. The shear rates associated with material deposition on the heated bed, or on top of a previously placed layer, are much lower than those at the nozzle. If the Cox–Merz rule holds¹⁹, then the viscosity of the material during the extrusion and road deposition process can be represented by the SAOS data. In order to verify the applicability of the Cox–Merz rule and to allow extension of the rheology measurements to lower shear rates, steady shear torsional measurements were performed. These low shear rates, $\dot{\gamma} \leq 0.1 \text{ s}^{-1}$, provide information regarding the zero-shear behavior of the molten polymer. Because the polymer experiences minimal shear following deposition, knowledge of this behavior is vital to modeling the viscoelastic processes that lead to the final road geometry. The viscosity profiles in Figure 4.2 suggest that the complex viscosity matches the apparent viscosity within the error of the instruments, verifying the applicability of the Cox–Merz rule for this material.

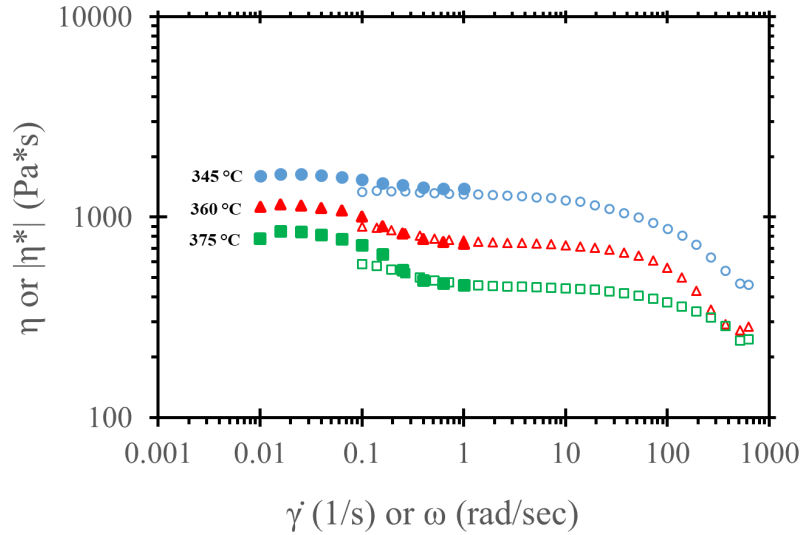


Figure 4.2. Overlay of small amplitude oscillatory shear (hollow shapes) and steady torsional shear (filled shapes) rheometry of Ultem 1010 at 345 (●), 360 (▲), and 375 °C (■).

From the data in Figure 4.2, PEI will be in the shear thinning regime within the nozzle during the extrusion process. This is important for successful extrusion²⁰. Furthermore, after deposition onto the heated bed, the polymer will become highly viscous with rapid cooling, which will allow it to retain its shape.

After the polymer has exited the hot end orifice, it will experience a nearly zero shear environment. From the data in Figure 4.2, the material becomes highly viscous in the low shear regime and will likely not deform to a large degree; therefore, very little flow should occur following initial wetting, further verifying the assumption presented in a previous section. This is vital to modeling bond development; although the flow phenomena are not included in the heat transfer modeling work presented in this study, they will be incorporated in future work.

4.5.3 Complete Re-Entanglement Time

The dominating factor contributing to the strength of an additively manufactured product is the bond between the individual layers, driven by the thermal transport of the MatEx process. The bond formation process is comprised of two steps (following wetting): sintering and diffusion. In sintering, the interface between the two adjacent surfaces forms and expands. This step only occurs at high temperatures, greater than T_g . Diffusion involves the transport of the polymer chains across the interface formed during sintering and the subsequent re-entanglement of the chains.

When complete re-entanglement is achieved, the bond strength theoretically returns to that of the bulk polymer. However, the polymer chains are only mobile above the T_g . Because the polymer cools quickly after being printed, the newly printed road will only remain above T_g for less than 3 s^{12} . This indicates that the polymer must diffuse quickly while above the T_g to achieve a bond with mechanical properties similar to that of the bulk. To characterize the bond development in Ultem 1010, an interrupted shear experiment was performed on the material to quantify the complete re-entanglement time at different isothermal temperatures.

The interrupted shear experiment²¹ applies a shear rate to a fresh sample, i.e., a sample that has experienced infinite relaxation time, until an equilibrium is reached, which implies all entanglements are separated. The stress overshoot created at the inception of shear is measured. Once equilibrium is attained, the shearing is stopped and the sample is allowed to relax. During the relaxation period, the chains begin to re-entangle. After a set amount of relaxation time, shearing is restarted and the stress overshoot is measured again. The degree of re-entanglement can be calculated with the use of Equation (4.3). With multiple relaxation times, the degree of re-entanglement can be extrapolated to 100%:

$$\% \text{ recovery} = \frac{\tau_m(\dot{\gamma}, t_r) - \tau_{ss}/\tau_m(\dot{\gamma}, t_r)}{\tau_m(\dot{\gamma}, \infty) - \tau_{ss}/\tau_m(\dot{\gamma}, \infty)} \quad (4.3)$$

where $\tau_m(\dot{\gamma}, t_r)$ is the value of the stress overshoot after the relaxation time, $\tau_m(\dot{\gamma}, \infty)$ is the stress overshoot at infinite relaxation time, and τ_{ss} is the equilibrium, or steady state, value of the stress.

Figure 4.3 displays the results of the interrupted shear measurements. The complete re-entanglement time for each temperature was calculated based on at least three relaxation times except for 365 °C, because of some sample instability at that temperature. The complete re-entanglement time exhibits an inverse relationship with temperature. This follows the expected trend, i.e., the polymer is less mobile at lower temperatures. However, the rate at which the complete re-entanglement time increases is vital to understanding how the bond will develop before the part cools below the T_g . The trend that is displayed in Figure 4.3 suggests the complete re-entanglement time is an exponential or logarithmic function of the temperature. The re-entanglement's logarithmic dependence on temperature implies that the majority of the entanglements form quickly, in the first few seconds. The remaining time is spent forming a small number of entanglements to return the bond to bulk polymer properties. This result suggests that the bond strength should also increase logarithmically.

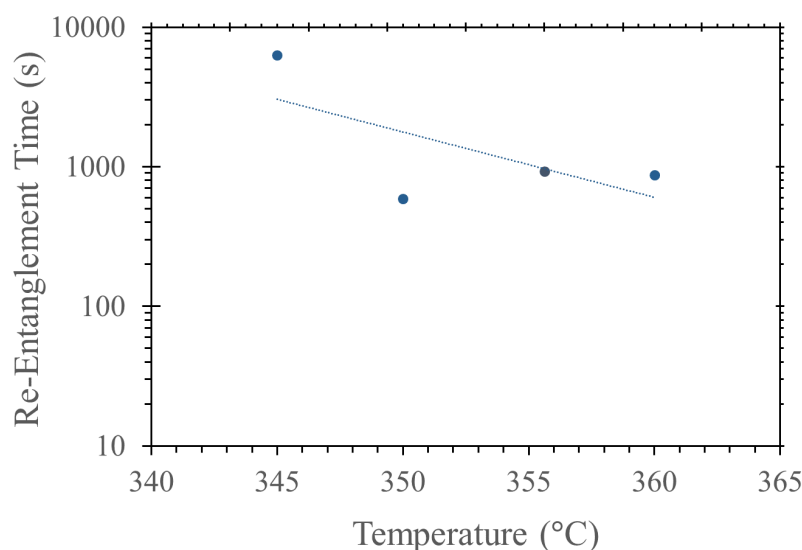


Figure 4.3. Relationship between the complete re-entanglement time of Ultem 1010 and isothermal temperature.

The complete re-entanglement times displayed in Figure 4.3 were measured isothermally. The relationship it demonstrates with temperature allows extrapolation of the nonisothermal behavior of the chain diffusion at the road interfaces. With this method, detailed information regarding the reptation time or theoretical diffusivity of the polymer chains is not required.

4.5.4 SEM

Following characterization of the rheological behavior of the material, the SEM images of the SRWW were examined to ascertain the shape of the individual layers as well as the contribution of the distance from the heated bed to the width of the layer interfaces, and by extension, the available area for interlayer bonding, which are dependent on the rheological properties presented in previous sections. These SRWWs were all printed with the printer parameters specified previously to eliminate variation due to varying parameters. The goal of this study is not to determine the effect of the various parameters on the final shape of the road, but rather to determine the general effect of the distance from the heated bed. Figure 4.4 displays the shape of the bottom

and top layers. These images suggest that the shape of the cross-sections appears as a flattened ellipsoid. This directly verifies the earlier assumption that idealized shapes such as circles and rectangles would not accurately mimic a representative part, although it does lend some support to the assumption of an elliptical cross-section⁸⁻⁹. Figure 4.4 further suggests that the shape changes to some degree as a function of the distance from the bed. Figure 4.4 shows the bottom layer possessing a wider profile, whereas the top layer exhibits a taller profile. This is assumed to be caused by the heat from the bed rising through the layers and allowing the bottom layer to maintain an elevated temperature for a longer period of time. This extended time at elevated temperature would allow it to deform to a greater degree, especially following the deposition of subsequent layers. However, thermal measurements of the individual layers would be required to verify this assumption. These results are critical to establish a methodology for accurate meshing of the extrudate in the FEA process as well as to enable correct implementation of a viscoelastic constitutive model to capture the real shape of the filament resulting from flow at the confined and free surfaces of the extrudate during road deposition.

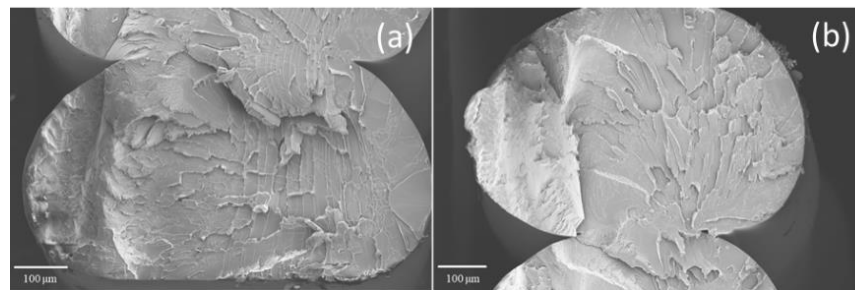


Figure 4.4. Cross-section image of a single road width wall (SRWW) displaying ovular shape. (a) The bottom layer of a 10-layer SRWW. (b) The top layer of the SRWW, illustrating differences in shape and weld width as a function of distance from the print bed.

Figure 4.5 shows the average value of the width of the bonds for the 10-layer SRWW. The bond number is counted from the bottom layer of the weld, e.g., Bond 1 corresponds to the

interface between Layers 1 and 2, which also corresponds to dimension D in Figure 4.6. This information corroborates the assumption that the heat from the bed only extends to the first two layers. The interface between these layers is widest because the heat from the bed provides enough thermal energy to deform the material after deposition and broaden the interface between the layers. Layers above the first two do not receive as much thermal energy from the heated bed, and therefore cool more quickly and do not deform to the same degree as the first layers. This result has important implications in regards to the strength development of the printed part. The interfaces between the higher layers provide less area for polymer chain diffusion and re-entanglement to occur and are expected to result in weaker bond strength.

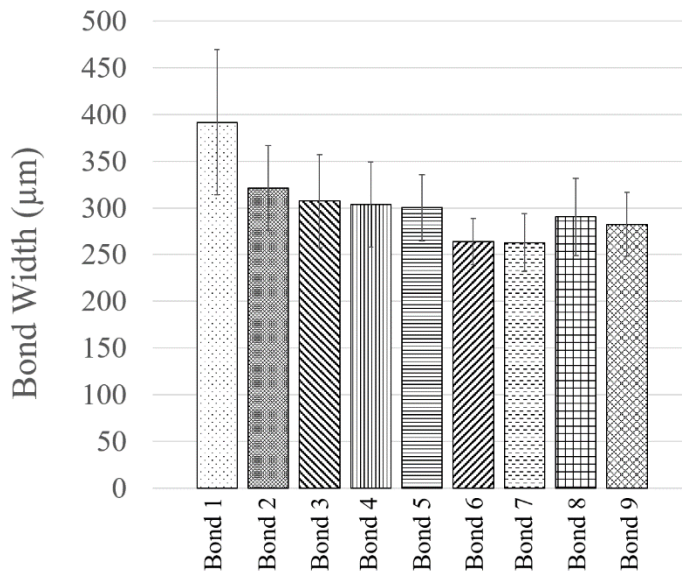


Figure 4.5. Distribution of weld width as a function of layer height. Bond number corresponds to the bottom layer creating the weld.

4.5.5 Development of Representative Mesh Geometry from SEM Cross-Section Data

The first step toward describing the geometry of SRWWs was constructing a representative parametric model of the road cross-section. This was done to reduce the parameter space, implied by fitting mesh points to individual images, to a significantly smaller size while still representing the average of experimental observations. The parametric model was developed with measurements performed on the cross-sectional SEM images. The measurements required for the specification of the model are represented in Figure 4.6 and compiled in Figure 4.7. Measurement A represents the widest point of the layer measured from the middle of the layer, and measurement B represents the height of point A from the bottom of the layer. Measurement E corresponds to the thickness of the layer. Measurements C and D are not included in Figure 4.7, because these measurements are captured by the bond width between layers, and the measurements are displayed in Figure 4.5. The layers were assumed to be symmetrical about the center line. The values reported in Figure 4.7 represent the average measurement calculated from the 16 samples, and the error bars represent a single standard deviation.

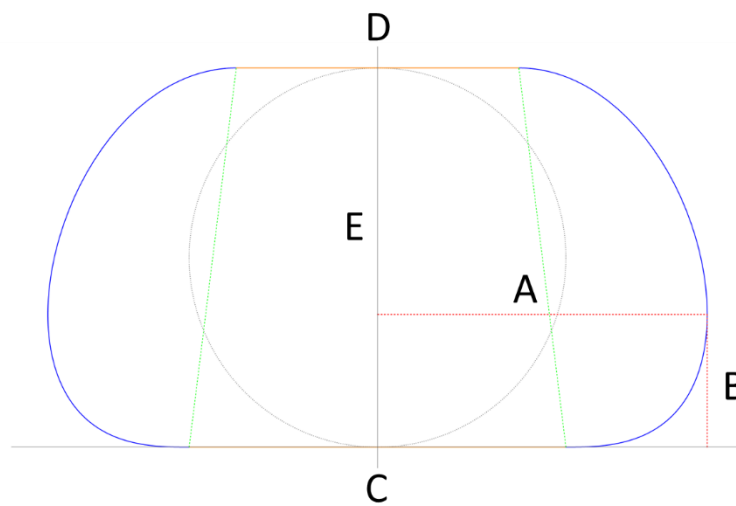
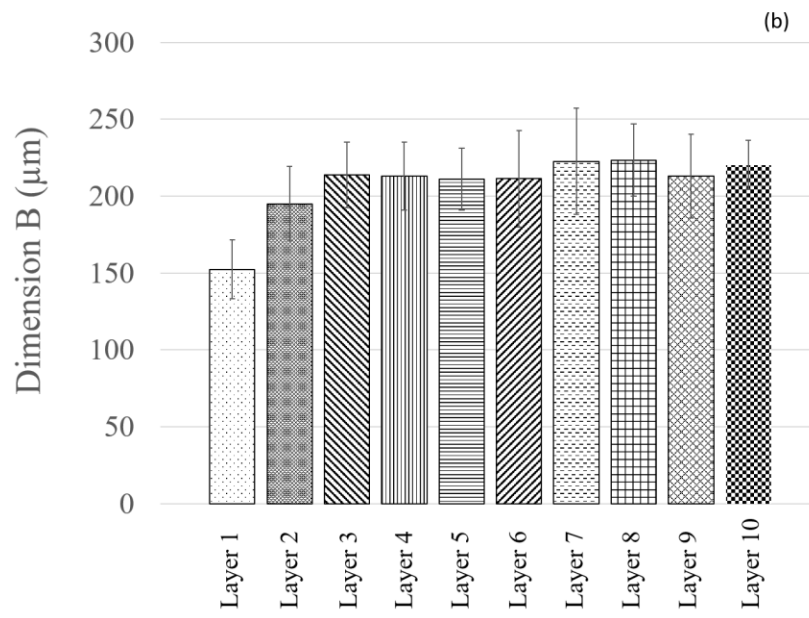
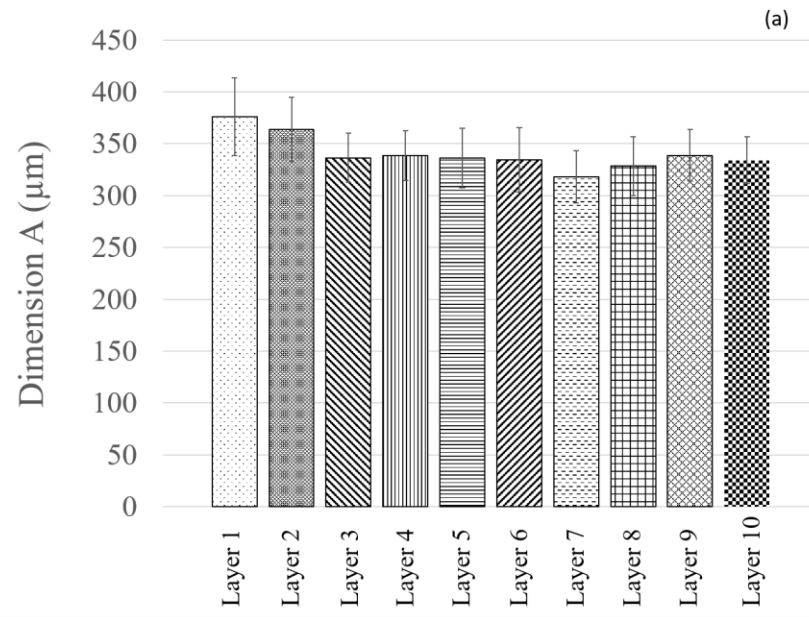


Figure 4.6. Measurements required to develop geometry for meshing that represents the shape of the SRWW.



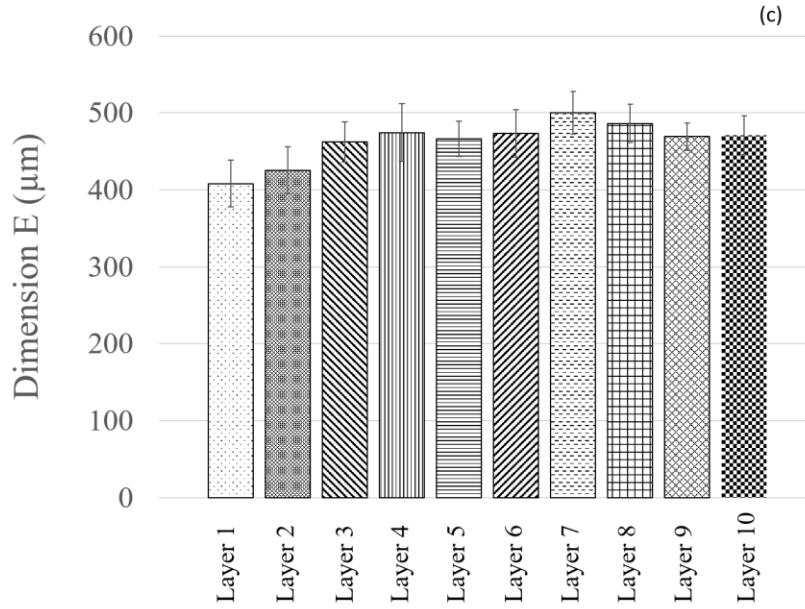


Figure 4.7. Measurements used to describe the representative shape of the individual layers in a single road width wall. (a) Corresponds to dimension A, (b) corresponds to dimension B, and (c) corresponds to dimension E from Figure 5.

A three-dimensional model representing the SRWW was developed from these measurements, i.e., a flattened ellipsoid that changes dimensions as a function of layer height. The parametric model was slightly modified to produce individual layers with a curved top surface that can be flattened upon deposition of an additional layer to allow FEA of each road in sequence or isolation, as illustrated in Figure 4.8. A mesh geometry was developed from the parametric model, and a mesh with a reasonable node density was implemented for the FEA (Figure 4.9).

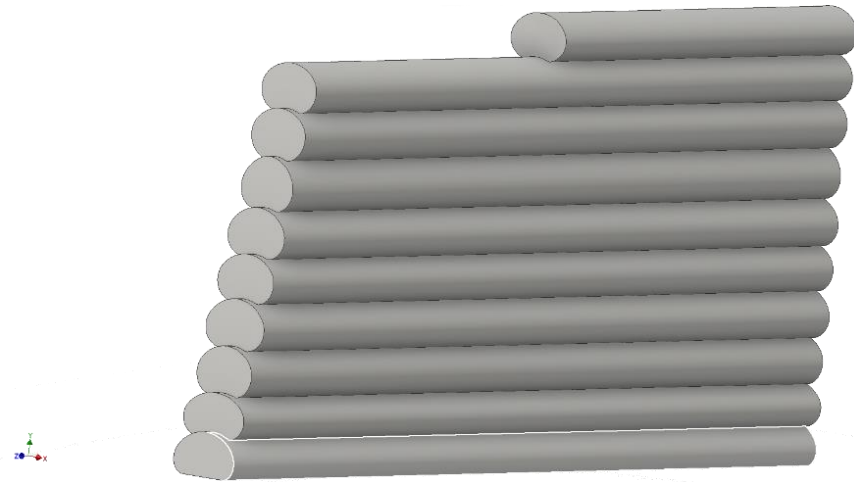


Figure 4.8. Three-dimensional image describing the shape of the individual roads of a single road width wall. The curved top surface allows the analysis of the roads in sequence or isolation.

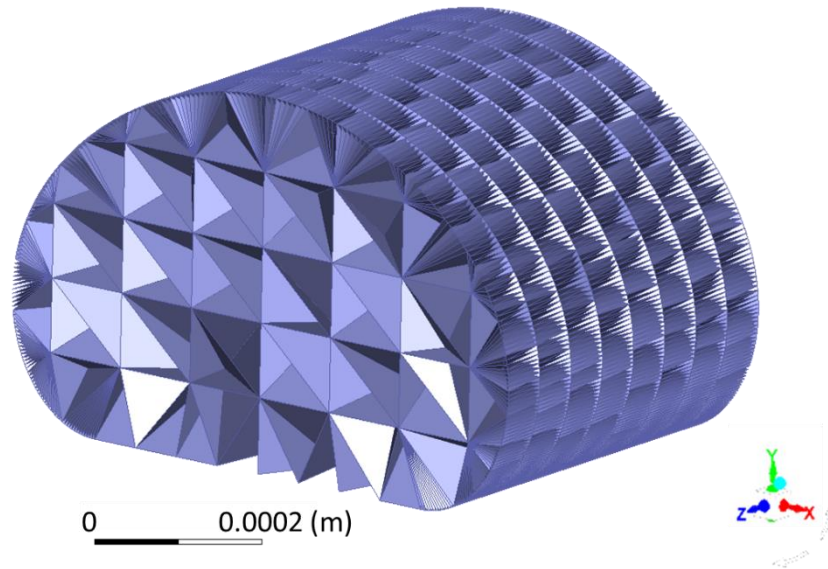


Figure 4.9. Image depicting node density used in the heat transfer finite element analysis of a single road width wall based on the parametric model.

4.5.6 Thermal Model

ANSYS FEA software, which can take UDFs, was employed to simulate the evolution of an extruded filament and predict the thermal profile produced while cooling. UDFs allow for extension of the ANSYS FEA solver to cover specialized problems. They are written in the ANSI C/C++ programming languages and compiled to a dynamic link library prior to running a simulation. During simulation, the motion of the front face, representing the extrudate leaving the

nozzle, was controlled by a UDF assigned to that region of the mesh. A nominal rate of 1 $\mu\text{g}/\text{min}$ was used for the mass flow rate. The rear of the extrudate and the bed contacting surface were set to a fixed temperature of 523.15 K. The extending surface representing fresh extrudate was held at 623.15 K. The air contacting surface was initialized to 523.15 K, and a nominal heat transfer coefficient of 5 $\text{W}/\text{m}^2 \text{K}$ was assumed. The far field air temperature was set to 523.15 K. An initial steady state solution was converged with zero mass flow to initialize the transient simulation. The transient model was then solved numerically, with a convergence threshold for the residual value of 10^{-6} for the energy equation. To achieve this convergence, a time step of 0.005 s was used with a maximum of 500 iterations allowed for each time step. This model was carried out to 86 full time steps, or 0.43 s, the results of which are displayed in Figure 4.10. It was noted that the residual values, while low at very short time scales, increase with increasing time steps, suggesting the error in the model grows as a function of time. When compared to the IR video discussed in a previous section, the simulation results qualitatively match the observed rapid drop in temperature and transient profile along the length of the deposited filament because of convective and conductive heat loss away from the nozzle and center of the road. However, because the model was limited to less than 0.5 s, detailed quantitative comparisons cannot be made and are, therefore, outside the scope of this study. The simulations do validate the purpose of this study, however, which was to demonstrate the ability to model the three-dimensional heat transfer phenomenon in MatEx, resulting in a complex, transient thermal profile.

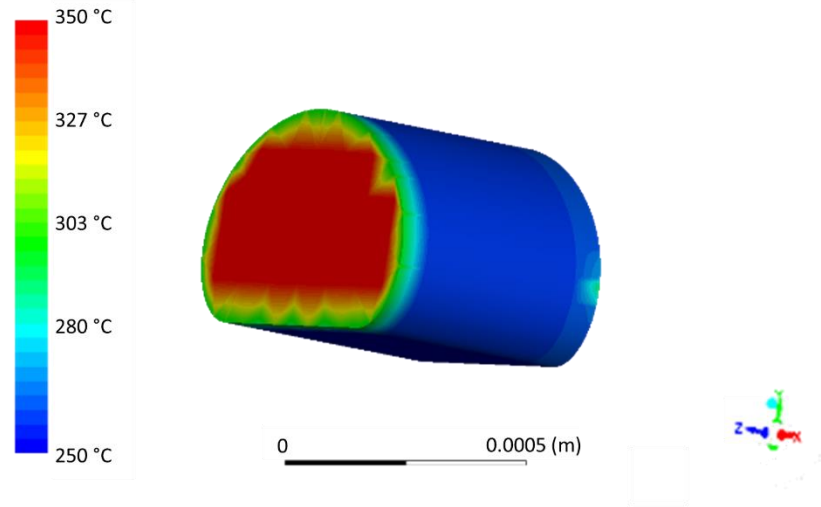


Figure 4.10. Image displaying the thermal profile of an extruded filament at the end of 0.43 s.

A compounding error was noted when calculating the thermal profile displayed in Figure 4.10, which leads to the primary challenge of the three-dimensional heat transfer modeling. In order to achieve a high level of precision, well converged initial steady state solutions are required. Furthermore, these models require excessive computing power and time, requiring multiple days to calculate the thermal profile of the extruded filament representing less than half a second of printing time. Extending these calculations to a full scale part would require either an excessive amount of time to converge or a simplifying assumption. However, extension to higher layers is required for verification that the thermal energy from the heated bed only extends primarily through the first two layers. Further addition of a coupled viscoelastic model would exponentially increase the complexity of the computations and would intensify these issues because of the relationship between the temperature of the extrudate and its flow and viscoelastic properties.

4.6 Conclusions

In this work, the thermal energy from the heated bed of a material extrusion AM printer has been suggested to only extend to the first two layers of a printed object, within the context of the thermal gradient between print and bed temperatures presented in this study. The lack of thermal

energy, and by extension, rapid cooling of higher layers, results in the layer-to-layer interface being a function of the layer height. The cooling rate of the deposited layers was also shown to be rapid enough to prevent further deformation following the initial wetting of the layers. A method was utilized to determine the complete isothermal re-entanglement time of a material, which can aid in understanding the bond formation of a printed part during the cooling process. The initial stages of a three-dimensional thermal transport model are presented. These initial attempts at modeling the temperature profile of a SRWW as a function of time and location demonstrate the challenges in predicting the temperature of a MatEx printed part to capture the full three-dimensional profile in the real, complex road geometry. The highly nonuniform cross-section thermal profile and rapid transient cooling process emphasize the need for a high precision, three-dimensional heat transfer model with a detailed node network, combined with more efficient numerical tools for solving the governing transport equations that provide information on this system.

4.7 Acknowledgments

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Chapter 5

Temperature, Diffusion, and Stress Modeling in Filament Extrusion Additive Manufacturing of Polyetherimide

5. Temperature, Diffusion, and Stress Modeling in Filament Extrusion Additive Manufacturing of Polyetherimide: An Examination of the Influence of Processing Parameters and Importance of Modeling Assumptions

(This chapter reproduces work which is in preparation for publication, expected submission to Additive Manufacturing in Q3 2020)

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5.1 Abstract

Fused filament fabrication (FFF), a form of filament-based material extrusion additive manufacturing (AM), is an extremely useful technique for the rapid production of highly customized products; however, most of the current understanding of this process is based in empirical evidence. Initial modeling attempts have traditionally focused on predicting heat transfer and either interlayer diffusion and adhesion or stress development but have not taken a combined approach to analyze all three components in a multiphysics model. In this study, we implement finite difference models to examine the combined heat transfer, polymer diffusion represented as degree of healing (D_h), and residual stress development in FFF of poly(ether imide) (PEI). Printing with PEI is of great interest because of its desirable mechanical properties and high use temperatures, but also creates a more challenging modeling problem with higher thermal gradients and greater potential thermal processing window compared to traditionally modeled AM materials, such as ABS and PLA.

In this study, experimental analyses including trouser tear tests and part warpage measurements provide correlation to predicted D_h and stress levels. The models suggest that the temperature of a layer is influenced by the subsequent printing of up to at least three layers in this geometry. The results of this study demonstrate that, particularly at slow print speeds, the relaxation and recovery of bulk strength is highly sensitive to analysis of the relaxation behavior of the polymer, highlighting a need for careful interpretation of this parameter when designing models. An investigation into the sensitivity of the degree of healing and stress development highlight the importance of environment temperature and print speed/layer time on the final printed part properties.

5.2 Introduction

Fused filament fabrication (FFF), a type of filament-based material extrusion additive manufacturing, is a well-established method for producing highly customized parts on a small scale. Although vast improvements have been realized in recent years, this production modality is generally limited to prototype production. One goal of additive manufacturing is to expand into the end-use market. However, several aspects of the process currently prevent the widespread adoption of this production method for the end-use market, notably a significant reduction in part properties when compared to traditionally processed materials. In particular, anisotropy and poor z-axis properties primarily stem from poor interlayer adhesion¹⁻³. Currently, FFF is primarily commercially limited to polylactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS), with other polymeric materials used in specialized prototyping applications and/or academic research studies. PLA and ABS have weak mechanical properties and low use temperatures, especially compared to engineering thermoplastics such as poly(ether imides) (PEI) and polyether ether ketones (PEEK). Even though limited commercial FFF printing of PEI filament is currently available, studying PEI provides insight into the interaction between the FFF process and polymeric materials with processing temperatures much higher than traditionally studied materials, such as PLA and ABS, to draw conclusions about the broader applicability of modeling approaches to guide machine design and process optimization⁴. In order to better understand the AM process as well as expand the material catalog and increase the viability of FFF in the end-use market, the effect of the various printing parameters and materials on the bond strength and dimensional stability must be more thoroughly understood.

Multilayer modeling can be particularly useful to understand thermal behavior of the FFF process and the translation to the transient, non-isothermal polymer diffusion process at deposited

layer interfaces⁵. The lack of sufficient interlayer adhesion at these interfaces is an issue inherent to the FFF process that exacerbates the weak z-direction bulk properties of many current AM materials. During the FFF process, a layer is deposited as a molten material. The heat from this freshly deposited layer transfers to the adjacent layers, inducing polymer chain mobility and permitting interlayer wetting and diffusion⁶⁻⁷. This process is referred to in this manuscript as healing, and the amount of healing that occurs will be referred to as the degree of healing (D_h). The heat from the freshly deposited layers is vital to the healing process as it allows a previously deposited and cooled layer to regain the mobility required for the diffusion to occur. At 100% D_h , the interface disappears and the properties of the bond return to that of the bulk material. However, this process can only occur above the glass transition temperature (T_g) of the material, when the polymer chains possess enough energy for long range motion, on the order of its radius of gyration, often referred to as reptation. In FFF processing, the layers have been shown to remain above T_g for a total of approximately 3 seconds when using ABS⁸.

The resulting dimensional accuracy of FFF produced parts is also partially governed by the thermal expansion and contraction of the polymers during the deposition and cooling process. Printed parts will cool unevenly due to differences in part geometry and environmental conditions including layer distance from the heated bed, bed temperature, nozzle temperature, print speed, and temperature uniformity in the build chamber. However, the contraction will be constrained by the adhesion of the polymer to the heated bed as well as the other deposited layers. This constraint results in the development of stress within the layers. This residual stress within the part will act as a driving force to cause deformation of the layers, often resulting in warping of the printed part away from the heated print bed, delamination, and, in extreme cases, failure to completely print the desired object⁹.

First principles multiphysics-based predictive models offer a powerful tool to capture heat transfer, polymer chain diffusion, and residual stress buildup^{5, 10}. However, the models required to provide detailed information regarding the AM process can be computationally intensive and require excessive amounts of time to complete¹¹⁻¹². To reduce the complexity of the models, most current work has focused on the modelling of one-^{7, 13-15} and two-dimensional¹⁶ systems. These models have employed simplifying assumptions such as a uniform cross-sectional temperature or a negligible transfer of heat along the axis of the deposited filament. Some of these models are able to provide some insight into the FFF process, but they are not thorough, focusing on one or two aspects at a time, such as heat transfer and/or interlayer wetting^{12-15, 17}. Furthermore, most current work focuses on common polymer materials such as ABS as their model material due to its well-defined properties. Few reports have studied higher use temperature engineering thermoplastic materials such as PEI.

Outside of limited recent manuscripts, relatively little research can be found that predicts the degree of healing that occurs during FFF printing based on modeling of the non-isothermal behavior. Coogan and Kazmer developed an empirical model to predict the interlayer bond strength based on a sample's location in a single road width wall, its geometry, as well as the bed and nozzle temperature and print speed¹⁸. They later expanded this study by modeling the non-isothermal healing during the deposition process with the assumption of one-dimensional heat transfer¹⁴. Similarly, many of the current healing models utilize a one-dimensional heat transfer to simplify the required calculations, but doing so causes loss of information regarding the thermal gradient across the cross section of the deposited road, which could influence healing of the interlayer bond. Further studies have demonstrated the effect of nozzle temperature and layer geometry on the recovery of the interfacial bond in FFF¹⁸. On the other hand, interfacial healing

in polymers has been studied quite thoroughly in prior studies for application to processes such as injection molding and thermoplastic tape placement¹⁹⁻²⁰.

Here we implement a two-dimensional heat transfer model which is combined with interlayer diffusion and stress development models to explore the FFF printing process of the PEI Ultem 1010. Through this analysis, we simultaneously capture the heat transfer, degree of healing, and stress buildup as a function of time and location. We then explore the validity of these models by comparing them to empirical measurements of bond tear resistance and warping, which are functions of the degree of healing and residual stress development, respectively. We conclude with an analysis of the comparison between predictions and empirical results and suggest further modifications to increase the accuracy and precision of the predictive models. These comparisons further provide insight into the influence of various process parameters and relaxation behavior on printed part properties.

5.3 Modeling

The following sections discuss our modeling approach for heat transfer, interfacial polymer diffusion, and stress buildup in a multilayer FFF system.

5.3.1 Heat Transfer

In the FFF process, heat from the bed, environment, and nozzle will significantly influence the transport of thermal energy through a layer. The thermal transport will be further influenced by the convective heat transfer coefficient since much of the layer will be exposed to convective cooling conditions. These parameters along with the layer time, or time required to deposit each layer, were user-defined constants for the model development. These parameters were further assumed to be constant throughout the print. In this work, we assumed radiative heat transfer from

the nozzle to be negligible, an assumption that has been shown to be appropriate in similar systems^{12, 21}.

To simplify the model development, a finite difference approach was adopted. While a finite element model may more accurately predict the system, it has been shown that a fully specified and geometrically accurate model greatly increases the required computation power and time beyond the capability of widely available computing resources¹¹. Using finite difference limits the model by requiring a rectangular geometry for the layers, which in practice typically have an ellipsoid or flattened ellipsoid geometry. However, the rectangular cross-section provides an estimate for the total distance and area across which diffusion may take place at the layer interface, and we will compare the results of these models to experimental measurements to assess potential discrepancies caused by this assumption. Some of the cooling effects caused by the geometry may not be captured, but it enables analysis of many build layers to facilitate the rapid collection of information regarding diffusion and stress development as a function of process parameters.

Each layer was assumed to be instantaneously deposited¹² at the nozzle temperature with perfect contact with the previously deposited layer below it. A finite difference mesh was imposed on each layer through the placement of rectangular elements of dimensions dx and dz , resulting in a layer comprised of n_x and n_z elements in the x and z directions, respectively. An example of this mesh is depicted in Figure 5.1, although the number of nodes in the mesh was reduced in the figure to more easily display the general appearance of the mesh.

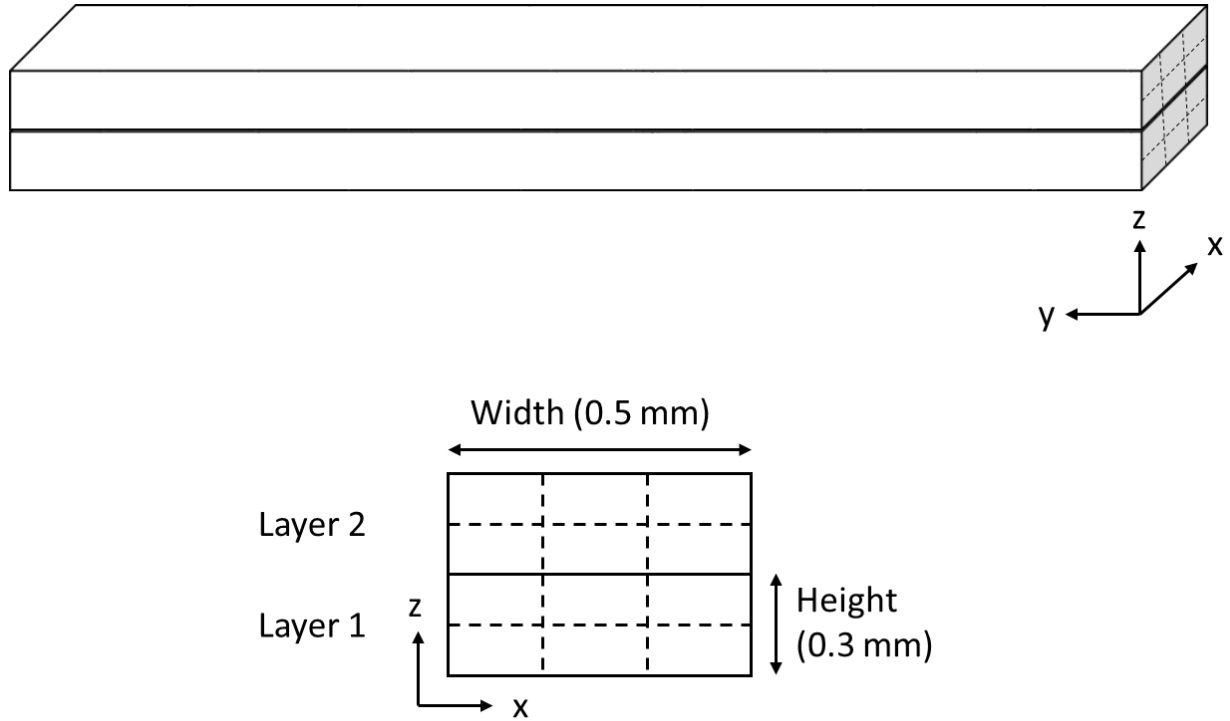


Figure 5.1. Example of finite difference mesh used to predict heat transfer in FFF, not representative of mesh size used in analysis but simplified to highlight node matrix geometry. Top image depicts the full layer geometry, showing all axes. Bottom image depicts the cross-section of the layers, indicating the x - and z -axes.

We focus on the conductive and convective heat transfer in the x - and z -directions because the heat transfer should behave consistently at all points in the y -direction. When using the central difference finite difference method, this reduces the heat transfer equation to that shown in Equation (5.1) where T is temperature; T_r , T_l , T_t , and T_b are the temperatures of the nodes to the right, left, top, and bottom of the node being modeled, C_p is the heat capacity, ρ is the density, h is the convective heat transfer coefficient, A is the surface area exposed to convection, and T_{env} is the temperature of the environment. This equation can be modified depending on the location of the node being calculated. For example, an internal node would not include the convective term, while a corner node would not have conductive terms on two sides.

$$\frac{dT}{dt} = \frac{k}{C_p \rho} \left(\frac{T_r + T_l - 2T}{dx^2} + \frac{T_t + T_b - 2T}{dz^2} \right) + \frac{hA}{C_p \rho dx dy dz} (T_{env} - T) \quad (5.1)$$

The temperature at each node can then be calculated by combining the influences from the x- and z-directions as shown in Equation (5.2).

$$T_{i+1} = T_i + \left(\frac{dT}{dt_l} + \frac{dT}{dt_r} + \frac{dT}{dt_t} + \frac{dT}{dt_b} \right) dt \quad (5.2)$$

5.3.2 Degree of Healing

The bond strength in the final part will depend primarily on the degree of healing, or the amount of chain interdiffusion and re-entanglement that occurs between layers and returns the interfacial properties to those of the bulk material^{14, 19, 22}. This study assumes an equal contribution to the interfacial healing from both adjacent layers and that the temperature of the bond is the average of the temperatures of the layers on either side of the interface, illustrated in Equation (5.3).

$$D_h(t_h) = 0.5D_{h1} \left(t_h, \frac{T_1 + T_2}{2} \right) + 0.5D_{h2} \left(t_h, \frac{T_1 + T_2}{2} \right) \quad (5.3)$$

In Equation (5.3), D_h is the degree of healing, t_h is the time during which healing can occur, and T_1 and T_2 are the temperatures of the bottom and top layers of the interface being modeled, respectively. At the maximum D_h of 100%, the polymer chains have completely diffused across the interface and re-entangled to provide properties of the bulk polymer. When this occurs, all history of the interface disappears and the sample regains the mechanical and viscoelastic properties of the bulk material. It has been shown that the degree of healing in amorphous materials increases in proportion to time raised to the one-fourth power as a function of the reptation time

as shown in Equation (5.4)²⁰. Because the reptation time is a function of temperature, an integration over the time of the print is required to account for the non-isothermal temperature profile.

$$Degree\ of\ Healing = \left(\int_0^t \frac{1}{\tau_r(T)} dt \right)^{\frac{1}{4}} \quad (5.4)$$

In Equation (4), τ_r is the reptation time, T is temperature of the material (expressed in this study as the temperature of a specified node), and t is time following deposition. By combining Equation (5.3) and (5.4), averaging the degree of healing for the entire layer, and converting the integration to a summation, we arrive at Equation (5.5) to describe the total healing of the bond between layers. In this work, we analyze reptation times using multiple approaches, including previously published reptation time for PEI provided by Bastien and Gillespie²³. We also estimated the reptation time for Ultem 1010 similar to the analysis performed by Bartolai, *et al.*, and approximated with a pseudo-Arrhenius analysis of the temperature dependence of reptation time from Bastien and Gillespie, highlighted in Equation (5.6)¹⁷. We further approximated the reptation time using a Williams-Landel-Ferry (WLF)²⁴ analysis of small amplitude oscillatory shear (SAOS) rheology data. Finally, a relaxation time was estimated for Ultem 1010 based on the approach discussed by van Meerveld using the zero-shear viscosity measured as part of a previous study, Equation (5.7), and the reptation time was approximated utilizing the approach developed by Likhtman and McLeish and demonstrated by McIlroy and Olmstead^{11, 15, 25-26}. The temperature dependence was approximated with an Arrhenius analysis represented by Equation (5.6)²³.

$$D_h(t_h) = \frac{dt^{\frac{1}{4}}}{nx * rows} \left(\sum_{\tau=0}^t \sum_{x=1}^{nx*rows} \frac{1}{\tau_r(T)} \right)^{\frac{1}{4}} \quad (5.5)$$

$$\tau_r(T) = A * \exp\left(\frac{B}{T}\right) \quad (5.6)$$

$$\eta_0 = 0.064\tau_e \frac{\rho RT}{M_e} \left(\frac{M}{M_e}\right)^{3.4} \quad (5.7)$$

In these equations, A is a pre-exponential factor, B is related to the activation energy to flow, τ_e is the relaxation time of an entangled strand, ρ is the density, R is the ideal gas constant, M_e is the critical entanglement molecular weight, and M is the molecular weight.

5.3.3 Shear Stress Development

Most polymers undergo thermal contraction upon cooling which may be quantified by the coefficient of thermal expansion. However, the layers are adhered to each other and the heated bed, limiting the contraction and thus developing stress. Stress in a printed part will subsequently act as a driving force for deformation, potentially leading to loss of geometric accuracy and delamination from the heated bed and/or between individual layers.

Although stress development can be driven by a multitude of factors, this study assumes that stress is solely facilitated by thermal contraction to enable a rapid approximation. A plane strain assumption was further implemented, limiting the contraction to only the y-direction under the assumption that the contraction in the other dimensions was negligible²⁷. It is also assumed that no stress develops above T_g because the polymer chains are able to move and relax relatively quickly in their rubbery state above T_g . Equation (5.8) forms the basis of the stress development analysis, where σ represents stress, E represents the elastic modulus, α represents the coefficient of thermal expansion, and ΔT represents the temperature difference above T_g at any given time.

$$\sigma = E\alpha\Delta T \quad (5.8)$$

These assumptions are expected to underestimate the total stress developed during printing because they do not include the interactions between layers, which in reality leads to additional constraint resulting in an increase in the contractive stress of adjacent roads. However, this approximation provides insight into the primary driving force behind the warping phenomenon in FFF of amorphous polymers following the deposition of a series of layers.

5.4 Experimental

5.4.1 Sample Preparation

For FFF printed specimens, Ultem 1010 filament, T_g of 217 °C, was purchased from Stratasys and Push Plastic with a nominal diameter of 1.75 mm. Single road width hollow boxes of dimensions 76 x 76 x 25 mm were printed using a modified Lulzbot Taz 6 printer and relevant procedures²⁸. Printing temperatures examined in this study include 345 °C and 375 °C. The bed temperatures included 175 °C and 200 °C. Print speeds of 15 mm/s and 60 mm/s were also examined.

Melt-pressed films were produced by pelletizing filament using a 2 inch Killion pelletizer with a Bronco II speed controller. PEI pellets were pressed at 343 °C into 75 x 75 mm films of thicknesses ranging from 166 to 434 μm .

5.4.2 Degree of Healing Measurement

The degree of healing was measured according to ASTM standard D1938-14²⁹. The force required to pull apart the layers was determined by averaging the measurements collected between the initial peak of the force displacement curve and the peak prior to complete failure. Degree of healing was calculated from the ratio of the tear force of the printed samples to the tear force of the bulk samples. An average degree of healing for each set of conditions was measured using at

least 5 samples per set of conditions. The weld thicknesses were measured after testing using a Phenom Pro scanning electron microscope (SEM). 13 mm long samples were cut from the end of the tear region of the tested specimens and coated with a 5nm layer of Au/Pd with the use of a Cressington sputter coater. Bulk properties were also measured using ASTM D1938-14 from the melt-pressed films.

5.4.3 Reptation Times

A number of approaches were used to describe and approximate the reptation time in this study to better understand the influence of relaxation behavior. The parameters that describe the reptation times are displayed in Table 5.1. The data from Bastien and Gillespie was used as represented in their publication²³. Viscoelastic SAOS data for Ultem 1010 was used to determine the crossover point of G' and G'' , as demonstrated by Bartolai, *et al.*¹⁷. Extrapolation to lower temperatures was performed using two different approaches: the pseudo-Arrhenius method demonstrated by Bastien and Gillespie, Equation (5.6), and WLF. The fourth approach implemented relaxation time of an entangled strand, τ_e , estimated using the approach discussed in van Meerveld, Equation (5.7), which uses zero-shear viscosity measurements to calculate τ_e ; the reptation time was then estimated using the molecular weight and critical entanglement molecular weight of Ultem 1010, similar to the approach developed by Likhtman and McLeish and utilized by McIlroy and Olmstead^{15, 25-26}. Temperature dependence was similarly approximated using Equation (5.6).

Table 5.1. List of parameters used to estimate the reptation time based on different approaches

Reptation Time	Measurement Technique	Material	Pseudo Arrhenius Approximation		WLF Approximation		
			A (K^{-1})	B	C ₁	C ₂ (°C)	T _{ref} (°C)
1	Bastien and Gillespie data	PEI	59728	1.38 E-46	20.9	388.5	310
2	SAOS - Crossover of G' and G''	Ultem 1010	14869	3.26 E-13			
3	SAOS - Crossover of G' and G''	Ultem 1010					
4	Zero-shear viscosity – Pseudo Arrhenius	Ultem 1010	14419	5.24 E-13			

5.4.4 Determination of Printing Conditions

The bed and environment temperatures were measured using a forward-looking infrared (FLIR) camera. To measure the bed temperature, black electrical tape was attached to the heated bed and allowed to equilibrate for 10 minutes at 175 °C and 200 °C and subsequently imaged. The electrical tape was assumed to have an emissivity of 0.95³⁰. To measure the air temperature, a roll of electrical tape was placed in the chamber on top of a 20 mm thick platform made of fiberglass insulation and allowed to equilibrate for 20 minutes while surrounded by an 80 mm diameter PEI cylinder.

The convective heat transfer coefficient was measured by using a 0.7 mm wide PEI part that was heated externally to 200 °C and equilibrated for 10 minutes. The part was then placed in the printing chamber on a 20 mm thick platform made of fiberglass insulation to prevent interference caused by conductive heat transfer and allowed to cool. The temperature profile of the cooling part was captured using a FLIR camera, and a heat transfer equation was fit to the experimental data by varying the heat transfer coefficient.

Comparing setpoint temperatures to FLIR measured temperatures, measurements of 164.0 °C and 188.4 °C were obtained for the set points of 175 ° and 200 °C, respectively. The air temperature above the heated bed was measured to be 97.1 °C and 100.4 °C for bed temperatures of 175 °C and 200 °C, respectively. The emissivity of the PEI was measured to be 0.87. The convective heat transfer coefficient for the system was calculated to be 29 W/m²K.

5.5 Results and Discussion

For the model analyses in subsequent sections, printing parameters include an environmental temperature of 100.4 °C, a bed temperature of 188.4 °C, a deposition temperature of 375 °C, a convective heat transfer coefficient of 29 W/m²K, and a print speed of 15 mm/s that resulted in a layer time of 20.3 seconds. The reptation time determined using the approach of van Meerveld (Reptation time 4 in Table 5.1) was used to produce the degree of healing results in Figure 5.4.

5.5.1 Heat Transfer Model Results

The temperature profile was monitored at multiple mesh nodes within a layer as depicted in the simplified representation in Figure 5.2 to analyze the non-uniform thermal profile across the cross-section of a layer. Layers were also assumed to be symmetrical about their center axis such that locations 1, 2 and 3 in Figure 5.2 are representative of either side of the layer. Figure 5.3 displays the thermal profiles of layers 1 and 22 of a representative single road width wall for one set of printing parameters.

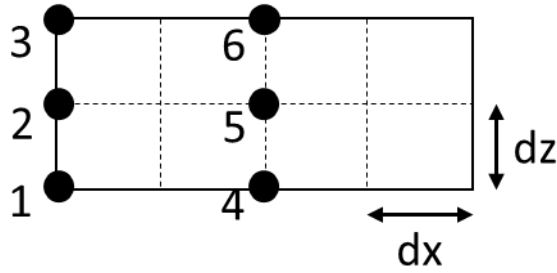


Figure 5.2. Depiction of the locations used to determine the localized behavior during layer deposition. The image shows a radial cross-section of a deposited layer with the deposition direction going into the page.

Figure 5.3a and b display the representative temperature profiles at locations 1 – 6 for two different layers, illustrating our ability to capture the transient information at various locations inside a layer. These results indicate that the initial temperature of each layer matches the deposition temperature but rapidly quenches to a near equilibrium plateau value that is dependent on the location in the print, e.g. locations 3 and 6 display a lower equilibrium temperature in layer 1 because they are further from the heated bed. Furthermore, the equilibrium temperature is affected not only by location within the layer but also within the printed part itself. The results in Figure 5.3 suggest that the equilibrium temperature of layer 1, approximately 185 °C, is strongly influenced by the heated bed while the equilibrium temperature of layer 22, approximately 120 °C, is determined primarily from the environmental temperature.

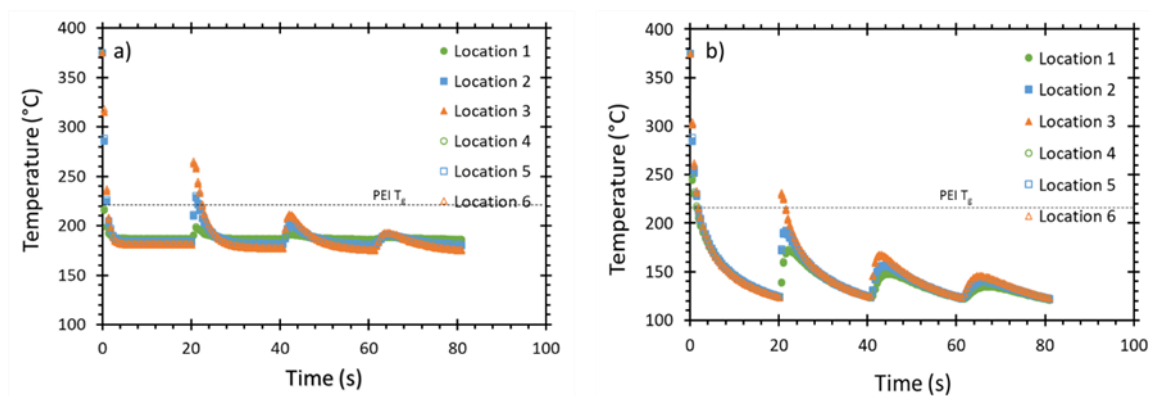


Figure 5.3. Predicted temperature of layer 1 (a) and layer 22 (b) at different locations (described in Figure 5.2) in the layer as a function of time after deposition. A limited, coarse time step is represented in the plot for ease of visualization; however, a time step of approximately 0.007 s was utilized in the analysis.

The results in Figure 5.3 depict the rapid cooling of the deposited filament, showing that the material remains above T_g for approximately one second following deposition. This time is extended for the short layer time, particularly in higher layers, potentially reaching nearly 10 s above T_g . For this layer geometry, the heat from subsequently deposited layers increases the temperature of the modeled layer, potentially providing enough energy to exceed the T_g for approximately two more seconds in layer 1 and less than a second in layer 22, similar to results reported by Seppala, *et al.*⁸.

5.5.2 Tear Strength: Measurement and Predictive Analysis

The thermal profile results suggest that the interlayer healing must occur quickly to form a strong bond between layers. Figure 5.4a demonstrates this by depicting an extremely rapid rise in the D_h , exceeding 100% in the bottom layer, followed by an immediate plateau that corresponds to the temperature of the interface dropping below the T_g . The reliance of the diffusion and healing on the temperature of the layers is further exemplified by a small increase of approximately 4% in D_h observed at 20 s, corresponding to the deposition of a new layer transferring thermal energy to

previously deposited layers and briefly extending their time above T_g . This relationship between temperature and healing allows the bond between layers 1 and 2 to heal to a significant degree because the temperature of layer 1 will rise to approximately 253 °C at the time that layer 2 will be near 375 °C, resulting in an average bond temperature near 314 °C. Furthermore, the temperature of layer 1 will not decrease below T_g again for nearly 2 seconds, providing the polymer chains significant time and energy to diffuse across the interface and recover the bulk strength. The temperature of layer 22, on the other hand, only increases to approximately 213 °C upon deposition of the subsequent layer, resulting in an average bond temperature near 294 °C, and the temperature of layer 22 will remain above T_g for less than a second. Therefore, the overall molecular mobility experienced at this interface is substantially less than that of layer 1, resulting in a lower degree of healing in layer 22 compared to layer 1, 112% compared to 206%. This relationship was further substantiated by the results displayed in Figure 5.4b, which displays the final degree of healing for each layer of a 40-layer SRWW. It is apparent from these results that the degree of healing significantly decreases as a function of the distance from the heated bed until an equilibrium is reached at approximately layer 15, beyond which (at these printing conditions and geometry) the thermal energy from the heated bed no longer influences the thermal profiles and degree of healing. In studying these phenomena, it should be noted that the analysis in this study predicts degrees of healing greater than 100%, a physical impossibility; however, the trends observed are useful in understanding the interplay between temperature, time, and interfacial healing. We will address the magnitude of this value later in this section.

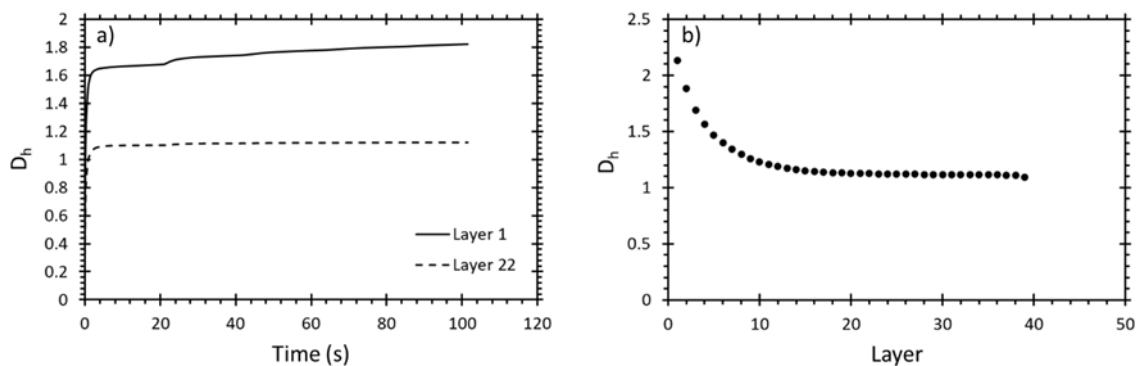


Figure 5.4. a) Predicted degree of healing as a function of time after deposition for layer 1 and layer 22 and b) the predicted degree of healing as a function of the layer number

Tear strength provides empirical insight into the degree of healing that has occurred in a printed sample when compared to bulk polymer properties. We measured the tear strength of parts produced with varying nozzle temperature, bed temperature, and print speed; a representative plot of the force measurement during the Type III test is shown in Figure 0.1 in the supplementary information. In this study, the tear strength was determined by averaging the force between the initial peak of the force-displacement curve and the peak prior to failure. Table 5.2 lists the sets of parameters used to print the SRWW samples.

Compression-molded film sheet samples were also measured using a Type III tear test to represent the bulk tear strength of Ultem 1010. The tested films spanned a range of thicknesses from 166 to 434 μm , which span the ranges of interlayer bond widths in the printed parts, providing information regarding the tear strength of the bulk PEI as a function of thickness and is presented in Figure 0.2 in the supplementary information. Tear strength was then normalized for printed parts based on actual layer widths measured with SEM. Degree of healing is subsequently calculated using a ratio of printed to bulk tear strength, and compared to the various model results produced using different reptation times as presented in Table 5.2

Table 5.2. Comparison of final degrees of healing using different methods of approximating reptation time as a function of specified process parameters. Reptation time approximation techniques are specified in Table 5.1.

T_{dep} (°C)	T_{bed} (°C)	t_{layer} (s)	Empirically Measured	Reptation Time 1	Reptation Time 2	Reptation Time 3	Reptation Time 4
345	164	20.3	0.31	0.02	0.80	0.49	0.90
345	164	5.1	0.20	0.31	1.63	1.29	1.80
345	188	20.3	0.30	0.03	0.83	0.51	0.93
345	188	5.1	0.17	0.33	1.66	1.32	1.83
375	164	20.3	0.43	0.06	0.98	0.68	1.09
375	164	5.1	0.36	0.82	2.04	1.77	2.22
375	188	20.3	0.37	0.06	1.01	0.71	1.13
375	188	5.1	0.29	0.88	2.08	1.81	2.28

Table 5.2 presents the degree of healing across all tested and modeled parameter combinations, demonstrating the importance of the reptation time measurement and approximation when determining the recovery of the interlayer bond. While trends can be ascertained from the model results, the absolute value of D_h can vary significantly by modifying the approximation technique used to determine and extrapolate reptation time. At a deposition temperature of 375 °C, bed temperature of 188 °C, and layer time of 20.3 s, the D_h changes from 101% to 71% to 113% using reptation times 2, 3, and 4, respectively. Comparing these reptation times at 375 °C, reptation time 2 is approximated to be 0.003 s, reptation time 3 is approximated to be 0.002 s, and reptation time 4 is also approximated to be 0.002 s. This discrepancy imposed by the approximation technique can become more significant as the temperature changes, with reptation times 2, 3, and 4 estimated to be 4.92 s, 28.2 s, and 3.16 s, respectively, at 217 °C, demonstrating the extent to

which the approximation technique can influence the reptation time of the same material, even when the same viscoelastic data is utilized.

Although the absolute values of the degree of healing are highly sensitive to the approximation and extrapolation of reptation time, the general relationships between the processing parameters and D_h are insensitive to the reptation time. Therefore, for the purposes of comparison to empirical data, the trends observed in the predictions produced using the reptation time approximated with the approach of van Meerveld (reptation time 4 in Table 5.1) will be discussed. The results in Table 5.2 indicate that increasing the deposition temperature from 345 °C to 375 °C (while maintaining bed temperature and layer time at 164 °C and 20.3 s) will also increase D_h due to more molecular mobility at the initial deposition, increasing D_h from 31% to 43% experimentally and from 90% to 109% in the predictions. A higher deposition temperature will also increase the amount of thermal energy transferred to the previously deposited layer. The predictions exacerbate this to a slight degree, increasing D_h by 29% rather than the 12% observed experimentally, most likely because the models assume the material is deposited at the same temperature as the nozzle; although, a number of studies have shown this is not always an accurate assumption³¹⁻³³. Increasing the bed temperature from 164 °C to 188 °C and maintaining the deposition temperature and layer time at 345 °C and 20.3 s has little effect on the degree of healing, either experimentally or in the predictions, changing D_h from 31% to 30% and 90% to 93%, respectively. This relatively small influence is a result of the distance of the tested/modeled layer from the heated bed which greatly reduces the impact of this processing parameter.

A discrepancy in the influence of the print speed is observed when comparing the predicted and empirical values. Increasing the print speed (decreasing the layer time) changes the D_h from 31% to 20% empirically and from 90% to 180% in the predictive results when the deposition and

bed temperatures are maintained at 345 °C and 164 °C, respectively. The models indicate that decreasing the layer time would increase the D_h because a new layer would be deposited before the previous layer fully equilibrated, extending its time above T_g and increasing the overall molecular mobility. However, the models in this study did not account for the thermal energy conductively supplied to the deposited layer by the heated nozzle. Conduction from the heated nozzle would provide a significant thermal energy source at sufficiently slow speeds, particularly when the geometry is large/complex enough that the previous layers are able to reach an equilibrium temperature prior to the deposition of a new layer. This interaction would increase the temperature of both the deposited layer and the previous layer and increase D_h as observed experimentally. A more thorough examination of the predicted influence of various printing parameters on the degree of healing and stress development can be found in Figure 0.3 and Figure 0.4 in the supplementary information.

To investigate the molecular level effects that can contribute to the potential discrepancies in predicted vs. experimental D_h , we considered the impact of disentanglement and molecule extension/relaxation on the time scales associated with interlayer diffusion, Figure 5.5. The analysis based on work performed by McIlroy and Olmstead examines the time required to relax the molecular extensions caused by shearing from the nozzle because interlayer diffusion cannot occur until the polymer chains are no longer distended^{15, 34}. We considered changes such as 2x and 3x increases to the relaxation time of an entangled strand because large changes can be observed in the relaxation behavior based on the approximation technique. This approach allowed us to investigate the differences that appear in the molecular mobility as demonstrated by the onset of and ultimate value of entanglement recovery, Figure 5.5, utilizing the same parameter set as Figure 5.3, Figure 5.4, and Figure 5.6. These results demonstrate that these relatively small changes

to the relaxation behavior, which our approximations suggest are realistically potential variations, can delay the onset of entanglement recovery by nearly an order of magnitude because of the slower molecular motion. This retarded molecular mobility can further substantially reduce the recovery of the entanglements because the polymer is typically above T_g for only 2-3 s, lessening the time during which the bond strength can increase. Figure 5.5 demonstrates this by showing that the 2x and 3x increase in the relaxation times can result in an approximately 10% and 20% reduction in the recovered entanglements, although this reduction can become less apparent as the time above T_g increases, such as the case when the layer time is 5.1 s. These results suggest that if the approximation of the relaxation behavior is incorrect by a small amount, the ultimate recovery could be vastly over- or under-estimated.

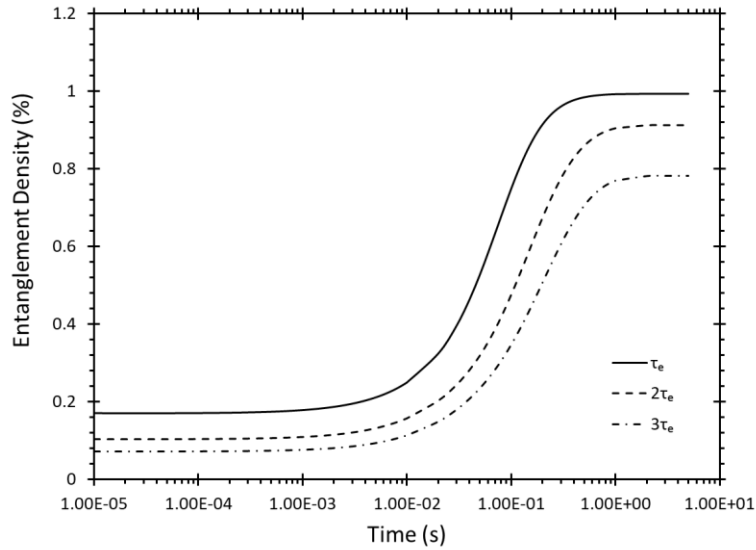


Figure 5.5. Analysis performed using method introduced by McIlroy and Olmstead demonstrating delay in entanglement recovery and sensitivity to minor changes in relaxation spectrum.

5.5.3 Warpage measurements: Comparison to Stress Predictions

Figure 5.6a and b depict the stress buildup in the first layer as a function of time and the final stress buildup in each layer of a 40-layer print, respectively. The oscillation of the stress

buildup with time is exacerbated in these results (Figure 5.6a) because we assume that the stress state development is solely facilitated by polymer thermal contraction and expansion. As the deposited layer cools below T_g , stress builds with decreasing temperature because the polymer chains are unable to relax into a thermodynamically favorable position. When a subsequent layer is deposited and the temperature of the original layer sharply increases, the stress correspondingly decreases drastically, leading to the oscillating behavior observed in Figure 5.6a. As the number of layers continues to increase and deposition occurs at locations far away from the layer in question, temperature attains an equilibrium value and so does the developed stress state.

Figure 5.6b depicts the final average stress in each layer of the modeled print. The results indicate that the bottom layer possesses the lowest amount of thermal stress in the entire part due to the influence of the heated bed. As the distance from the heated bed increases, the equilibrium temperature of the layer decreases, as demonstrated in Figure 5.3, resulting in a corresponding increase in the equilibrium stress value of each layer. In the SRWW geometry considered in this study, a plateau in stress is observed at approximately layer 15. The cumulative stress may lead to the part warping away from the heated bed to attempt to relieve the stress, or potentially result in interlayer debonding, depending on the location of the weakest interface.

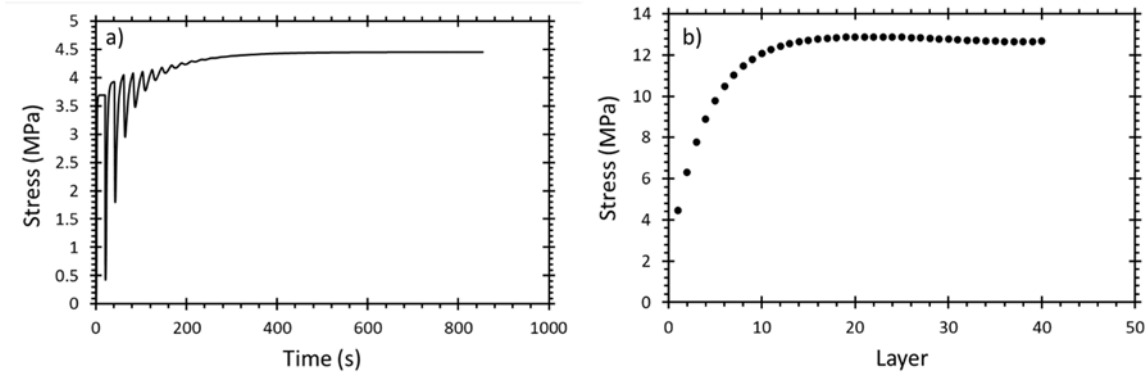


Figure 5.6. a) Stress developed in layer 1 as a function of time and b) final stress developed in each layer as a function of the layer number

Because warping is primarily caused by stress buildup in the part, we have related the predicted stress in the final layer to the warping measured at the corner of a printed part, Figure 5.7. Printing will fail at a certain level of warping. In our system, this point was identified empirically to occur when the corners of a printed part warp approximately 2.6 mm off the heated bed by measuring the warpage of a sample that had pulled off the bed during the printing process.

We can observe from the results in Figure 5.7 that layer time is a dominating factor in both stress buildup and warpage. At 345 °C deposition temperature and 164 °C bed temperature, decreasing layer time from 20.3 s to 5.1 s correspondingly reduced the predicted stress and measured warpage from 13.1 MPa to 6.84 MPa and 2.37 mm to 1.88 mm, respectively. Experimentally, this is most likely caused by an increase in the duration of time the material remains above T_g and a reduction in the cooling rate, which allows the material to relax to a more thermodynamically favorable state. The predictive results are lower due to the interaction between layer time and final temperature; the models allow the full part to cool for a time equal to twice the layer time after the final layer is deposited, which is not long enough to attain a true equilibrium

temperature when the layer time is 5.1 s. Because of this, the predicted stress is lower at shorter layer times.

Deposition temperature has a slight effect on the warping and stress, especially at the shorter layer time, changing from 1.88 mm to 1.22 mm and 6.84 MPa to 6.18 MPa, respectively, when T_{dep} is increased from 345 °C to 375 °C and T_{bed} and t_{layer} are held constant at 164 °C and 5.1 s. The higher deposition temperature provides slightly more time and energy to relax to a thermodynamically favorable state experimentally, similar to the interactions observed with the layer time. A lower bed temperature increased both stress and warpage because the bed temperature has a small influence on the environmental temperature, which would influence the equilibrium temperature and stress state of the final layer. A decrease in the bed temperature caused the predicted stress and measured warping to change from 6.57 MPa to 6.84 MPa and 1.37 mm to 1.88 mm, respectively, when the deposition temperature and layer time are maintained at 345 °C and 5.1 s. These results produce a linear relationship between experimentally measured warpage and predicted stress that can provide a tool to predict potential failures during the printing process. This relationship may allow us to much more quickly estimate whether a part will fail due to warpage.

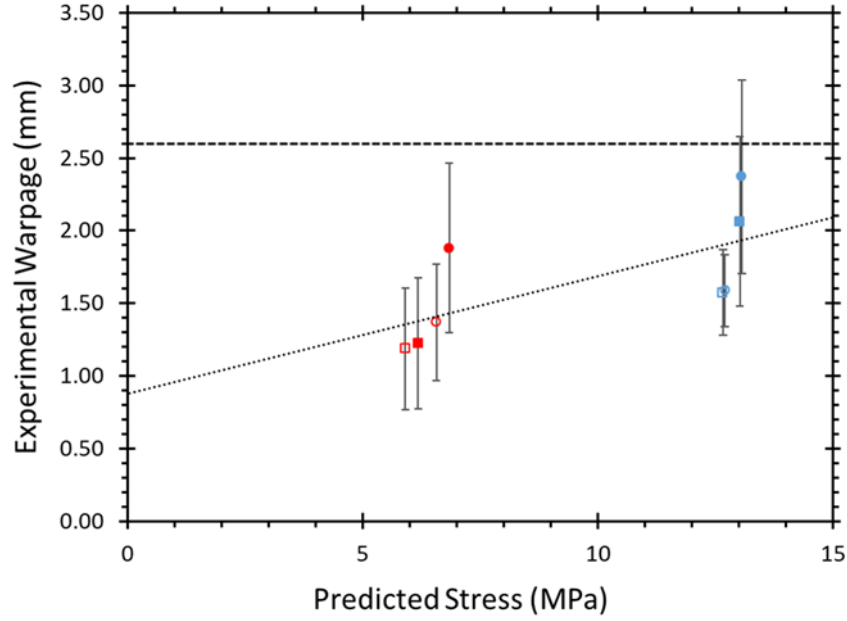


Figure 5.7. Average warpage at the corners of each part as a function of the predicted stress developed in the final layer. Error bars represent a single standard deviation. A linear fit of the data is included. Deposition temperatures included 345 °C (●) and 375 °C (■). Bed temperatures included 175 °C (solid shapes) and 200 °C (hollow shapes). Print speeds included 15 mm/s (blue shapes) and 60 mm/s (red shapes).

5.6 Summary and Conclusions

In this study, we present an investigation into the influence of process parameters and relaxation behavior on the degree of healing and stress development in FFF processing of the polyetherimide Ultem 1010 based on a transient, cross-sectional thermal profile developed utilizing a two-dimensional finite difference heat transfer analysis. The results presented herein demonstrate the ability to explore the complex multiphysics-based processes inherent in FFF with great efficiency and reduced time with a basic software such as MATLAB or Mathematica. Further understanding of these aspects of FFF printing will aid in the development of predictive models that can efficiently and rapidly estimate the mechanical properties of a printed part, reducing the need for extensive trial and error testing.

The degree of healing, a metric for the polymer diffusion between layers, primarily occurred in the first few seconds following deposition, when the temperature of adjacent layers exceeded T_g . The D_h exhibited a sensitivity to the layer number caused by the decreasing equilibrium temperature, and the predicted D_h values further displayed an extreme sensitivity to the approximation and extrapolation of the reptation time, τ_{rep} . These results demonstrated that small changes in the extrapolation of τ_{rep} to lower temperatures can result in significant differences in the predicted value of D_h . However, the trends produced by the healing models remained consistent, producing information that will provide a more thorough understanding of the FFF process. These trends suggested that the deposition temperature would have some effect on the healing due to its control of the molecular mobility immediately following deposition. Bed temperature should not significantly influence the interlayer healing except in the first few layers. A discrepancy in the influence of layer time indicated the assumption of negligible heat conduction from the nozzle was incorrect, particularly in parts produced with slow print speeds/long layer times. Further, molecular level interpretations suggest that the polymer chains are deformed due to the shearing from the printer nozzle experienced during extrusion. An increase in the relaxation behavior by a factor of 2 or 3 can cause an almost order of magnitude increase in the time required for the distended polymer chains to relax prior to re-entanglement, greatly reducing the amount of time available for recovery of the interlayer bond.

Predictions of the shear stress development based on plane strain and thermal contraction illustrate an oscillatory relationship between stress and time due to the influence of the temperature profiles. The stress development exhibited a low sensitivity to changes in the deposition and bed temperatures because of the relatively small influence on equilibrium temperature that determines the final layer stress state. The results suggest that layer time, on the other hand, will have a

significant influence on the equilibrium stress, primarily influenced by the time the part is allowed to cool. Experimentally, layer time should provide the largest impact on the stress because it would most strongly affect the cooling rate of the layers.

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6. Conclusions and Recommendations for Future Work

6.1 Conclusions

1. In order to continue expanding the limited material catalog in FFF, a rapid screening tool is needed to examine the printability of novel chemistries or modified commercial feedstocks. The first step in printability is extrudability, so a technique to predict failure to extrude is the starting point for the development of a screening tool. In the work presented in this dissertation, failure to extrude was identified to be caused by three primary issues: inconsistent filament diameter, filament buckling, and annular backflow. A predictive model for filament buckling was identified, which demonstrated that buckling was dependent on the ratio of stiffness of the material and its viscosity. Annular backflow was examined by modeling the flow field of the molten polymer inside the liquefier, resulting in the development of a dimensionless number, the FIN value, based on material properties and system geometry. According to the analysis, a system and material with a FIN value less than 153 should not backflow, and a system and material with a FIN value greater than 185 should fail because of backflow. Between these two values is the transition region, in which the extrusion may be inconsistent. A sensitivity analysis demonstrated that the most influential parameters for backflow are the polymer's shear thinning characteristics and the filament diameter. Empirical validations of the buckling and backflow models suggest that they can adequately predict the behavior of a material in the FFF system.
2. Polyetherimide was characterized in order to support the development of thermal transport and viscoelastic model describing the deposition, transient thermal profile, and road shape evolution of a material in FFF. The characterization included rheological measurements to determine the temperature dependent viscosity and complete re-entanglement time of the polyetherimide Ultem 1010. From this characterization, it was determined that, even if the material was held at the deposition temperature, it would require over 10 minutes to completely re-entangle, or

completely recover. Since FFF is a non-isothermal system, this suggests that it should be nearly impossible to completely recover bulk properties at the interface of two layers in Ultem 1010. However, the re-entanglement time appears to be exponential or logarithmic with temperature, and most likely time, suggesting that most recovery occurs at very short time scales. The results of the thermal profile did indicate that little heat traveled along the axis of the material, while a significant gradient existed in the cross-section, indicating a two-dimensional approach might be valid. However, the thermal transfer analysis proved that a well-defined, highly accurate three-dimensional model requires extensive computation power and time, such that modeling 0.5 s of printing time required more than a week of computing. This demonstrated the need for simplifying assumptions or alternate computing methods to approach this issue without reducing accuracy.

3. A two-dimensional, transient heat transfer model was developed to support the prediction of the recovery of the interlayer bond and the development of residual thermal stresses. These models were applied to a PEI material, Ultem 1010, to investigate the behavior of a high-use temperature material. Due to the large temperature difference between the printing temperature and bed/environment temperature, large gradients may form in the material during this process, influencing the heat transfer and molecular mobility in ways not observed in traditional FFF materials. A finite difference approach was adopted to model the heat transfer while interlayer bonding was modeled using a method described in literature where the ratio of recovered bond strength to bulk bond strength was proportional to bonding time raised to the $\frac{1}{4}$ power. Residual stress was modeled using a plain strain assumption, reducing it to a single dimension. The results of the thermal profiles indicated that the time above T_g is dependent largely on the layer time, ranging from 2 s to 10 s in this study based on the print geometry and corresponding raster speed. The literature healing model significantly overpredicted the recovery of bulk strength, predicting

recovery over 100% for all sets of parameters examined, while the empirical counterparts all exhibited recovery less than 50%. A separate analysis using the approach developed by McIlroy suggested that, at the longer layer times, small changes in the relaxation behavior of the polymer can have significant effects on the predicted recovery, suggesting a need for very careful and exact measurement of the relaxation times of the polymer as well as accurate temperature profiles to adequately capture the thermal influence on the molecular mobility.

6.2 Scientific Contributions

1. Development of a non-dimensional number that can predict the backflow of a specified material based on the shear thinning behavior of the polymer, the feed rate into the nozzle, and the system geometry, including the filament diameter and liquefier diameter
2. Validated the buckling model published previously by another group and suggested its use as a part of a rapid screening tool to predict the extrudability of a polymer in FFF
3. Characterized Ultem 1010 rheologically in order to facilitate viscoelastic modeling
4. Demonstrated that the road geometry of a printed part is not consistent throughout all layers, but is dependent on the distance from the heated bed
5. Demonstrated some of the limitations inherent in highly accurate three-dimensional heat transfer modeling of the FFF deposition process
6. Proposed that a two-dimensional heat transfer model can adequately capture the transient and repeated thermal history in FFF deposition
7. Coupled degree of healing and stress development models to a heat transfer model to more accurately predict the bond strength and deformation that occurs during FFF printing
8. Proposed a modelling approach that provides a measurable metric by which the predictive results can be compared.

9. Demonstrated that the healing of an interlayer bond in FFF is highly sensitive to the relaxation behavior of the polymer molecules, although this can be difficult to observe experimentally if the healing exceeds 100%, suggesting a reason why the healing is strongly influenced by print speed/layer time

6.3 Recommendations for Future Work

1. Agreement was observed between the FIN value predictions and empirical observations. However, only three materials were examined. A broader range of materials should be tested to explore the effect of large thermal gradients, semi-crystalline behavior, and inclusion of composite material.
2. A three-dimensional finite element heat transfer model with a relatively dense node network prevented rapid calculation of the thermal profile of a deposited filament. The trade-off between accuracy of results and density of node network should be examined to determine if a sparser network would allow the three-dimensional calculation of the thermal profile in a reasonable time frame. The convergence criteria can likewise be examined to determine its influence on the computation power and time requirements.
3. Once an accurate three-dimensional finite element model is developed, the viscoelastic models should be re-visited to investigate the road shape evolution and allow more detailed study of the stress development. These approaches will greatly expand the understanding of FFF as a process and allow better design of both printers and materials.
4. Currently, the only comparison available for the two-dimensional heat transfer model is that which can be found in literature. Because the results observed in this study were so dependent on the layer time, it would be useful to thermally image the material being printed with the same conditions as those in the study to determine if the material truly remains above T_g for such extended times.

5. The conclusion that the bond healing predictions are so sensitive to the relaxation behavior of a material suggests further characterization of the model material could illuminate the cause of the significant discrepancy between the predicted healing and the empirical measurements. Validation of the relaxation times previously measured could suggest the lack of healing is caused by influences other than those examined in this study such as cracks or voids appearing at the interface of the layers.
6. The degree of healing model presented in this study assumes that adjacent layers immediately contact, and an interface fully forms upon deposition. However, it has been shown in literature that the interface formation can be driven by numerous factors and should be accounted for in the degree of healing calculations. Therefore, an extension of this modeling approach should include the different mechanism-dominant aspects of the healing process, including intimate contact driven by temperature and pressure and then developed through squeeze flow followed by the interlayer diffusion of polymer chains across the developed interface.
7. The simplifications regarding stress development assumed in the study presented in this dissertation would, most likely, result in an underestimation of the total stress in an FFF produced part. To address this, the model would need to be modified to include interaction between layers, as this would closely mimic the actual behavior in FFF. Further, the model should include the transient behavior of the polymer chains, especially regarding their behavior caused by extended times above T_g and their interaction with the cooling rate, to accurately estimate the stress development during the FFF process.
8. The bond healing in PEI, an amorphous polymer, was explored in this dissertation. Examining a similar analysis using a semi-crystalline material such as PEEK would be useful to determine the influence of crystallinity on bonding, particularly in high temperature materials.

- Use the models described in Chapters 3, 4, and 5 to develop a fully defined predictive model set to describe the FFF process from material insertion to road coalescence. Following this, extend the use of the model to explore the experimental methods of increasing bond strength discussed in Section 2.4.3 to explore their relative value to the advancement of FFF.

Publications

Peer Reviewed Journal Manuscripts

- Das, A.; Chatham, C.A.; Fallon, J.J.; Zawaski, C.E.; Gilmer, E.L.; Williams, C.B.; Bortner, M.J. Current understanding and challenges in high temperature additive manufacturing of engineering thermoplastic polymers. *Additive Manufacturing* (34) 101218, 2020
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Articles in Preparation for Peer Review

- Das, A.; Biria, S.; **Gilmer, E.L.**; Bortner, M.J. Importance of polymer rheology on material extrusion additive manufacturing: Correlating process physics to print properties. *Expected Q4 2020*

2. **Gilmer, E.L.**; Anderegg, D.; Gardner, J.M.; Siochi, E.J.; Dillard, D.A.; McIlroy, C.; Bortner, M.J. Temperature, Diffusion, and Stress Modeling in Filament Extrusion Additive Manufacturing of Polyetherimide. *Expected Q3 2020*

Conference Presentations

1. **Gilmer, E. L.**; Anderegg, D. A.; Dillard, D.; McKnight, S. H.; Bortner, M. J.; “Modeling of Poly(ether imide) in Material Extrusion Additive Manufacturing” **2019 AIChE Annual Meeting**, Orlando, FL, November 13, 2019; Oral Presentation
2. **Gilmer, E. L.**; Anderegg, D. A.; Bryant, H. A.; Ruffin, D. C.; Skrip, Jr., S. M.; Fallon, J. J.; Bortner, M. J.; “In-Situ Monitoring of Extrusion Based Additive Manufacturing” **MII Material Innovations and Instrumentation Expo**, Blacksburg, VA, May 7, 2019; Poster Presentation
3. **Gilmer, E. L.**; Anderegg, D. A.; Gardner, J. M.; Siochi, E. J.; Dillard, D.; Bortner, M. J.; “Validation of Material Extrusion Degree of Healing and Residual Stress Models with the Use of Poly(ether imide)” **Chemical Engineering Graduate Student Association Symposium**, Blacksburg, VA, April 19, 2019; Oral Presentation
4. **Gilmer, E. L.**; Mansfield, C.; Baird, D. G.; Bortner, M. J.; “Characterization of Poly(ether imide) for Development of a Physics-Based Process Model to Simulate Thermal Transport During Fused Deposition Modeling” **Society of Plastics Engineers ANTEC 2018**, Orlando, FL, May 7-8, 2018; Poster Presentation.
5. **Gilmer, E. L.**; Mansfield, C.; Baird, D. G.; Bortner, M. J.; “Characterization of Poly(ether imide) for Development of a Physics-Based Process Model to Simulate Thermal Transport During Fused Deposition Modeling” **MII Technical Conference and Review**, Blacksburg, VA, April 17, 2018; Poster Presentation.
6. **Gilmer, E. L.**; Miller, D.; Bortner, M. J.; “Modeling Flow Phenomena in Fused Filament Fabrication (FFF) Geometry” **Chemical Engineering Graduate Student Association Symposium**, Blacksburg, VA, April 11, 2018; Oral Presentation.
7. **Gilmer, E. L.**; Miller, D.; Bortner, M. J.; “Modeling Flow Phenomena in Fused Filament Fabrication (FFF) Geometry” **2017 AIChE Annual Meeting**, Minneapolis, MN, November 3, 2017; Oral Presentation
8. **Gilmer, E. L.**; Miller, D.; Bortner, M. J.; “Modeling Flow Phenomena in Fused Filament Fabrication (FFF) Geometry” **2017 Southeast Polymer Forum**, Blacksburg, VA, June 5-7, 2017; Poster Presentation.
9. **Gilmer, E. L.**; Mansfield, C.; Baird, D. G.; Bortner, M. J.; “Characterization of Poly(ether imide) for Development of a Physics-Based Process Model to Simulate Thermal Transport During Fused Deposition Modeling” **Chemical Engineering**

Graduate Student Association Symposium, Blacksburg, VA, April 13, 2017; Oral Presentation.

10. **Gilmer, E. L.**; Miller, D.; Bortner, M. J.; “Modeling Flow Phenomena in Fused Filament Fabrication (FFF) Geometry” **33rd Annual Graduate Student Assembly Research Symposium and Exposition**, Blacksburg, VA, March 29, 2017; Oral Presentation
11. **Gilmer, E. L.**; Gigliotti, N.; Bortner, M. J.; “Investigation of Nanoparticle-Polymer Interphase in Thermosetting Systems” **The Food, Energy, and Water Nexus: Challenging Scientists and Engineers in the 21st Century**, Blacksburg, VA, October 10-12, 2016; Poster Presentation.

Appendix A – Supplementary Information

A.1 Supplementary Information for Chapter 5

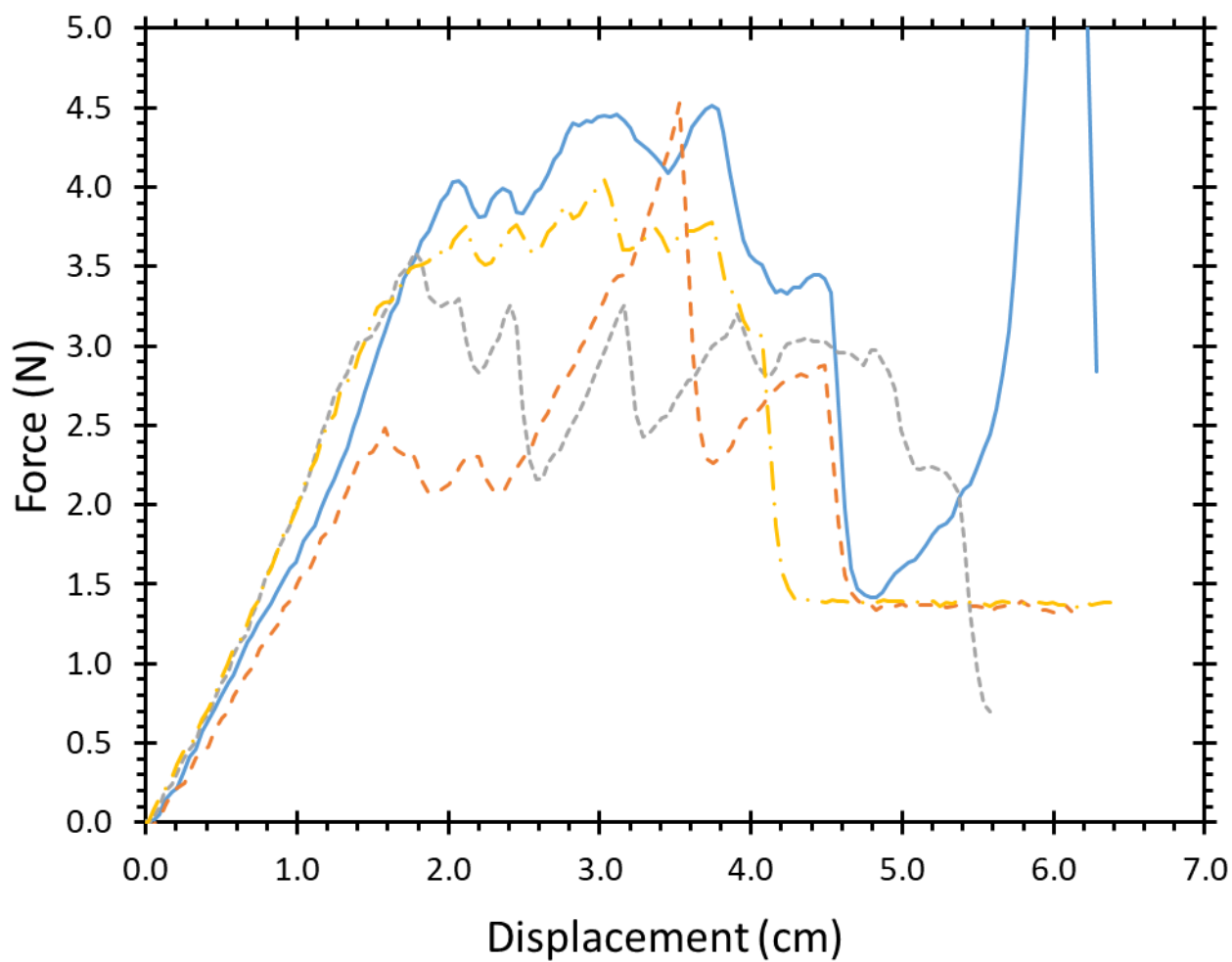


Figure 0.1. Tear test results of sample printed with $T_{dep} = 375\text{ }^{\circ}\text{C}$, $T_{env} = 164\text{ }^{\circ}\text{C}$, and $t_{layer} = 15\text{ s}$

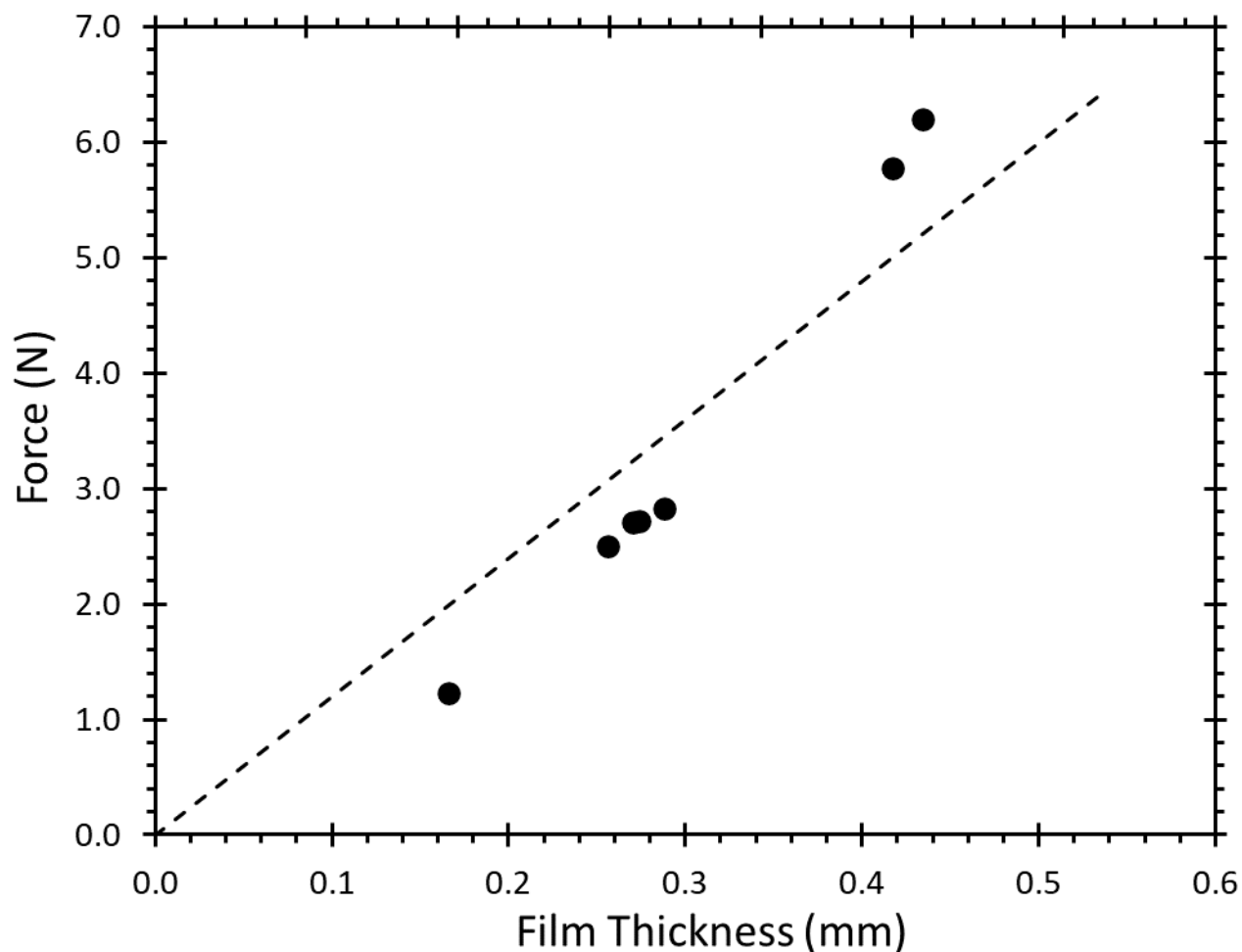


Figure 0.2. Tear test results of compression molded PEI sample compared to the thickness of the film

To further explore the trends observed when comparing the empirical and predicted measurements, we performed sensitivity analyses examining the influence of layer time, environmental temperature, convective heat transfer coefficient, bed temperature, and nozzle temperature on the degree of healing and stress development. The ranges of the parameters are specified in Table 0.1 and are representative of machine constraints in our system¹. For each variable analysis, the other parameters were used at their design midpoints. The number of layers modeled was reduced to 24, and the time step was extended to approximately 0.02 s to facilitate

more rapid data collection. In this study, layer time was used rather than print speed because the effect of print speed on a printed part would be highly dependent on the part geometry, leading us to focus on layer time as a more representative parameter.

Table 0.1. Ranges of variables used in the sensitivity analysis

Variable	Min	Max	Step
t_{layer} (s)	1	20	1
$T_{\text{environment}}$ (°C)	20	160	10
T_{bed} (°C)	20	200	10
$T_{\text{deposition}}$ (°C)	345	375	3
h (W/m ² K)	10	100	10

The sensitivity analyses for the degree of healing are presented in Figure 0.3. The absolute values of the degrees of healing often exceed 100%, a physical impossibility, and is most likely attributable to a slight error in the approximation of the reptation time. However, the trends produced remain valid and vital to understanding the FFF process, specifically to help guide future optimization studies. The results in Figure 0.3 demonstrate that D_h increases with increasing bed temperature in layer 1. Increasing the heat from the bed also increases the equilibrium temperature of the first layer, resulting in more healing, thus raising the D_h from approximately 39% at 20 °C to approximately 171% at 200 °C. However, layer 22 is not influenced by the heated bed at all due to its distance.

The degree of healing in layers 1 and 22 increased following an increase in the environmental temperature because of a slower cooling rate resulting from the smaller difference

between the deposition temperature and the environmental temperature. Furthermore, a higher environmental temperature would increase the equilibrium temperature of the layers following deposition, particularly those further from the heated bed. Therefore, increasing the environmental temperature from 20 °C to 150 °C raises the D_h for layer 22 from 51% to 147% in the case of this study. Increasing the heat transfer coefficient, h , also decreases the degree of healing due to a similar argument, i.e. a change in the cooling rate. Higher values of h represent a greater degree of convection, which would increase the cooling rate and, thus, reduce the amount of time spent above T_g and decrease the degree of healing, even in layer 1, whose cooling rate is primarily dominated by the heated bed.

Increasing the deposition temperature from 345 °C to 375 °C increases the degree of healing for both layer 1 and layer 22 from 73% to 88% and 77% to 95%, respectively. Increasing the deposition temperature would increase the initial temperature of the deposited filament which would also increase the polymer chain mobility. However, the additional time spent at the elevated temperature is quite small because of a higher cooling rate resulting from the greater temperature difference between the deposition temperature and the environmental temperature. As a result, a relatively minor increase in D_h is realized.

The relationship between layer time and D_h appears to be inverse and dependent on the layer number, or distance from the heated bed. Layer 1 does not display a strong influence from the layer time, exhibiting an increase in D_h only when the layer time is 1 or 2 seconds. At times longer than 1 second, the heated bed quenches the layer to an equilibrium value prior to the deposition of a new layer supplying thermal energy to the layer. Further from the heated bed, the layer equilibrates more slowly, as can be observed in Figure 5.3b. Because of this, the layer time has a greater influence for times up to approximately 10 seconds, where the impact of layer time

on D_h significantly lessens, although D_h does continue decreasing with increasing layer time for the entire 20 seconds examined in the sensitivity analysis. This relationship would change to some degree with the introduction of the heat transfer from the nozzle, with the D_h most likely increasing with increasing layer time.

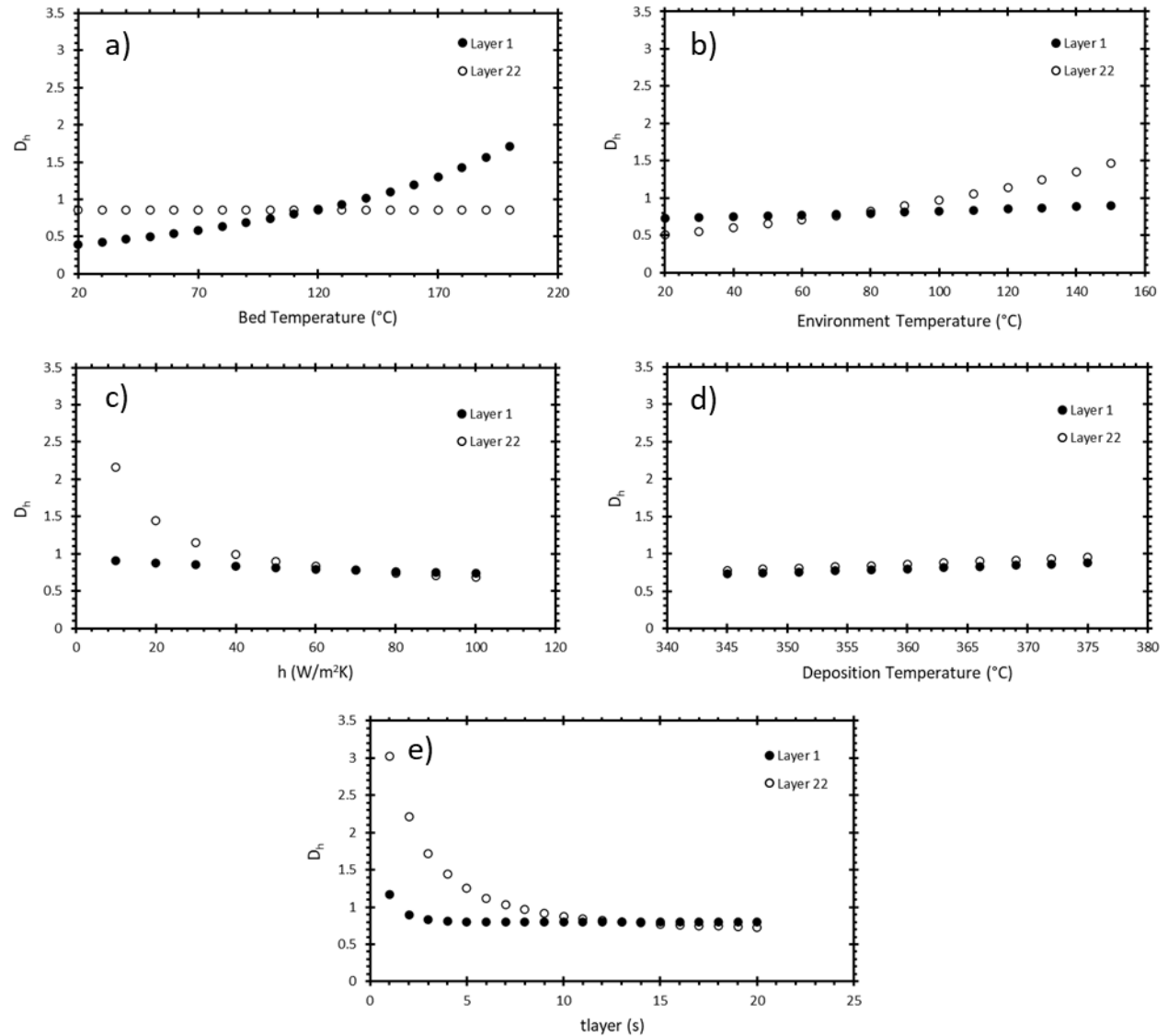


Figure 0.3. Sensitivity analysis of the degree of healing examining the effect of varying bed temperature (a), environment temperature (b), heat transfer coefficient (c), nozzle temperature (d), and layer time (e).

The sensitivity analyses of the stress development, depicted in Figure 0.4, display the calculated stress values for the first and last layers of a 24-layer print. In this study, the stress development will only be influenced by the temperature difference between the glass transition temperature and the final, steady state temperature. The final layer, however, may not attain a true steady state temperature in some situations because, following deposition of the final layer, the printed part is only allowed to cool for an amount of time equivalent to twice the layer time.

Figure 0.4a depicts the sensitivity of the stress development to the bed temperature. The final layer is not influenced by the bed temperature at all, maintaining a stress measurement of ~14 MPa across the entire temperature range of 20 °C to 200 °C. On the other hand, the stress in layer 1 is linearly dependent on the bed temperature. Due to this, the stress in layer 1 ranges from 20.4 MPa to 4.07 MPa based on the bed temperature.

According to Figure 0.4b, the environment temperature causes only a slight change in the stress developed in layer 1, from 13.6 MPa to 10.9 MPa when T_{env} is increased from 20 °C to 150 °C. As discussed previously, the temperature of the bottom layer is controlled primarily by the temperature of the heated bed, although the environmental temperature can influence it slightly, particularly at the top of the layer. The stress developed in the final layer appears to be linearly dependent on the environmental temperature because the equilibrium temperature of that layer is determined by the environmental temperature. Thus the stress varies from 21.2 MPa to 6.95 MPa in the temperature range explored in this study.

Figure 0.4c indicates that increasing the heat transfer coefficient does not affect the shear stress in layer 1 to any significant degree because the temperature of layer 1 is controlled almost entirely by the adjacent heated bed, significantly reducing the influence of the convective heat transfer. The figure further indicates that the heat transfer coefficient can cause a relatively large

change in the stress present in the final layer when h is small. When the heat transfer is low, the final layer is unable to reach a true steady state temperature before the completion of the model, resulting in a higher temperature and correspondingly lower stress value.

Figure 0.4d suggests that the deposition temperature does not have a noticeable effect on the final stress of either the first or last layer. Layer 1 maintains a stress value of 12.2 MPa whereas the final layer changes only slightly, from 14.1 MPa to 14.0 MPa across the 30 °C temperature range. However, compared to the other parameters, this influence is negligible.

The influence of layer time mimics that of the heat transfer coefficient, as can be observed in Figure 0.4e. The final stress of the first layer is not significantly influenced by the layer time because it has excessive time to attain a steady state temperature except at the shortest layer times. The stress in this layer ranges from 11.6 MPa to 12.2 MPa across the 20 second range of layer times. The temperature of the final layer, however, is unable to reach steady state in two layers worth of deposition time when the deposition time is extremely short. However, it plateaus at approximately 14.0 MPa when the layer time is approximately equal to 10 seconds.

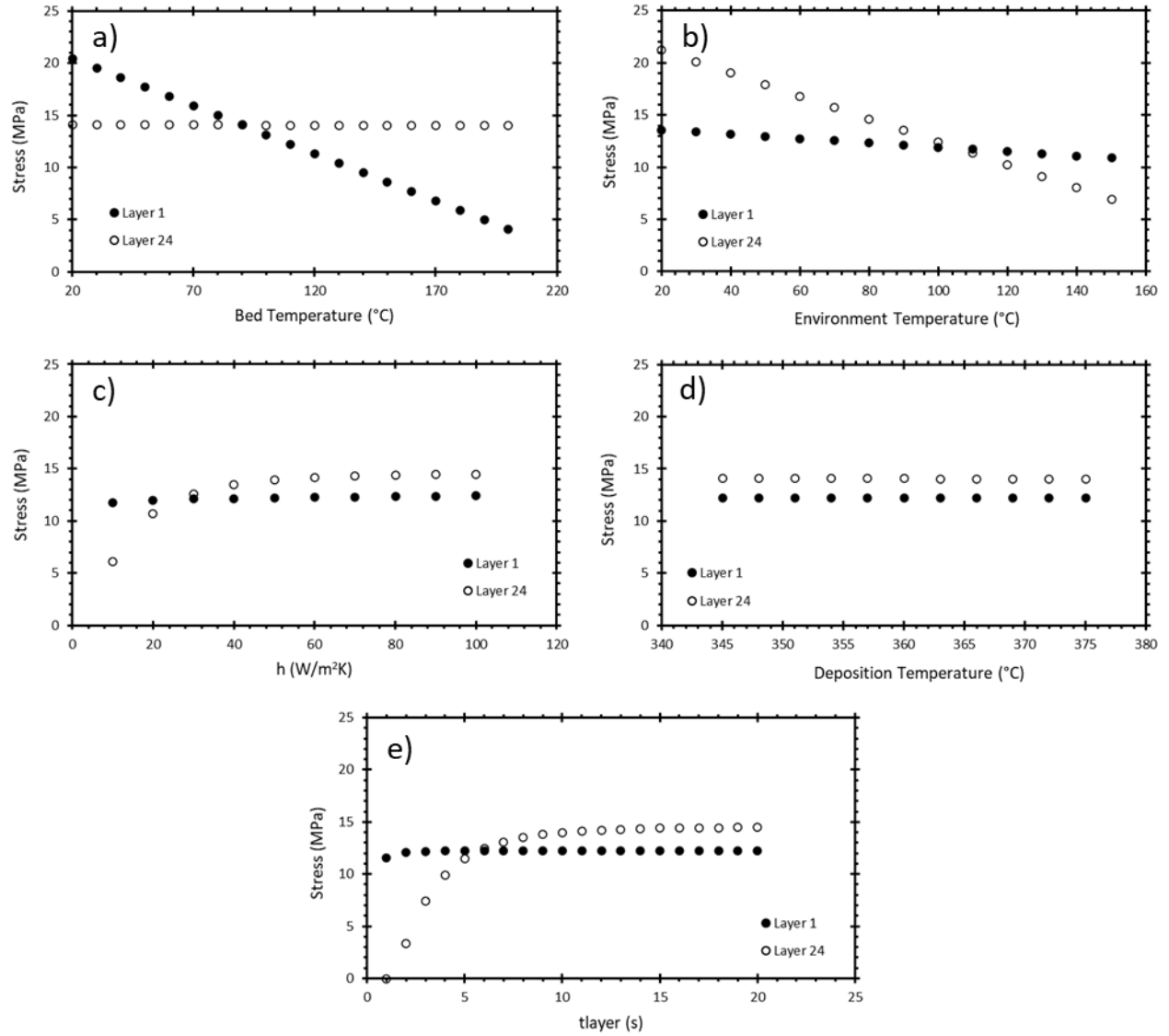


Figure 0.4. Sensitivity analysis of the shear stress present in layer 1 and layer 24 examining the effect of varying bed temperature (a), environment temperature (b), heat transfer coefficient (c), nozzle temperature (d), and layer time (e).

A.1.1 References

1. Gilmer, E. L.; Mansfield, C.; Gardner, J. M.; Siochi, E.; Baird, D. G.; Bortner, M. J., Characterization and Analysis of Polyetherimide: Realizing Practical Challenges of Modeling the Extrusion Based Additive Manufacturing Process. In *Polymer-Based Additive Manufacturing: Recent Developments*, ACS Publications: 2019; pp 69-84.