Process/Structure/Property Relationships of Semi-Crystalline Polymers in Material Extrusion Additive Manufacturing

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Abstract

Material Extrusion additive manufacturing (MEX) represents the most widely implemented form of additive manufacturing due to its high performance-cost ratio and robustness. Being an extrusion process in its essence, this process enables the free form fabrication of a wide range of thermoplastic materials. However, in most typical MEX processes, only amorphous polymers are being used as feedstock material owing to their smaller dimensional shrinkage during cooling and well-established process/structure/property (P/S/P) relationship. Semi-crystalline polymers, with their crystalline nature, possess unique properties such as enhanced mechanical properties and improved chemical resistance. However, due to the inherent processing challenges in MEX of semi-crystalline polymers, the P/S/P relationships are much less established, thus limits the application of semi-crystalline polymers in MEX.

The overall aim of this thesis is to advance the understanding of P/S/P relationship of semi-crystalline polymers in MEX. This is accomplished through both experimental and simulation-based research. With a typical commodity semi-crystalline polymer, Poly (ethylene terephthalate) (PET), selected as the benchmark material.

First, we experimentally explored the MEX printing of both neat and glass fiber (GF) reinforced recycled PET (rPET). Excellent MEX printability were shown for both neat and composite materials, with GF reinforced parts showing a significant improved mechanical property. Notably, a gradient of crystallinity induced by a different toolpathing time was highlighted.

In the second project, to further investigate the impact of MEX parameter on crystallinity and mechanical properties, a series of benchmark parts were printed with neat PET and analyzed. The effect of part design and MEX parameter on thermal history during printing was revealed though a comparative analysis of IR thermography. Subsequent Raman spectroscopy and mechanical test indicated that crystallinity developed during the MEX process can adversely affects the interlayer adhesion.

In the third project, a 3D heat transfer model was developed to simulate and understand the thermal history of MEX feedstock material during printing, this model is then thoroughly
validated against the experimental IR thermography data. While good prediction accuracy was shown for some scenarios, the research identified and discussed several unreported challenges that significantly affect the model's prediction performance in certain conditions.

In the fourth project, we employed a non-isothermal crystallization model to directly predict the development of crystallinity based on given temperature profiles, whether monitored experimentally or predicted by the heat transfer model. The research documented notable discrepancies between the model's predictions and actual crystallinity measurements, and the potential source of the error was addressed.

In summary, this thesis explored the MEX printing of semi-crystalline polymer and its fiber reinforced composite. The influence of MEX parameters and part designs on the printed part's thermal history, crystallinity and mechanical performance was then thoroughly investigated. A heat transfer model and a non-isothermal crystallization model were constructed and employed. With rigorous validation against experimental data, previously unreported challenges in MEX thermal and crystallization modeling was highlighted. Overall, this thesis deepens the understanding of current semi-crystalline polymer’s P/S/P relationship in MEX, and offers insights for the optimization and future research in the field of both experiment and simulation of MEX.
Material extrusion additive manufacturing (MEX), also known as fused filament fabrication (FFF), is a popular form of 3D printing known for its cost-effectiveness and versatility in creating objects from plastic materials. Traditionally, MEX utilizes amorphous polymers because they are less prone to shrinkage and thus easier to print. However, semi-crystalline polymers, offer enhanced strength and chemical resistance, yet they pose significant challenges in printing due to a limited understanding of their process/structure/property (P/S/P) relationships in MEX.

This research aims to improve our understanding of P/S/P relationships of semi-crystalline polymers in MEX. The study utilizes a typical semi-crystalline polymer, Poly (ethylene terephthalate) (PET), as the benchmark material.

The study begins with the exploration of the MEX printing of recycled PET (rPET) and its glass fiber composite, finding that with appropriate MEX parameters, both feedstocks are highly printable, and the incorporation of glass fibers substantially increased the strength of the printed parts.

Subsequently, a comprehensive investigation regarding the intricate relationship between crystallinity development, mechanical properties, and the MEX printing process is conducted. Our research revealed that the MEX process and the design of the part both considerably affect the crystallinity of the final part, thereby influencing its mechanical properties.

In the third chapter, a 3D heat transfer model is constructed to better understand and predict the temperature evolution of materials during MEX printing. Most importantly, the modeling results are rigorously validated against experimental data, showing promising results. However, it also reveals challenges in precisely predicting the temperature of parts under certain conditions.

The research then evaluates the applicability of Nakamura non-isothermal crystallization model for MEX printing scenarios. It is found that this model underestimates crystallinity in MEX, primarily because it does not account for shear-induced crystallization, a critical factor in
the process. This finding underscores the necessity for more advanced models that can effectively capture the complex dynamics of MEX.

In summary, this dissertation significantly enhances our understanding of the behavior of semi-crystalline polymers in MEX printing. It sheds light on the complex relationship between the printing process, the structure of the material, and the final properties of the printed object. This work not only advances our knowledge in 3D printing but also paves the way for more sophisticated modeling approaches, optimizing the MEX process and expanding its potential applications.
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1. Chapter 1

Challenges in Printing Semi-Crystalline Polymers with Material Extrusion Additive Manufacturing: A Review

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1.1. Abstract

Semi-crystalline polymers provide improved thermo-mechanical properties compared with amorphous polymers, finding diverse applications in industries across aerospace, tissue engineering and medical components. However, these sectors frequently demand the production of complex or customized parts, a challenge that traditional manufacturing methods often struggle to meet in an efficient and cost-effective manner. Material extrusion additive manufacturing (MEX), emerges as a potential solution, given its suitability for low-cost, customizable and rapid production. Combining the unique properties of semi-crystalline polymers with the flexibility of MEX unlocks a wide array of applications and functionalities. Nevertheless, current MEX feedstocks are predominantly limited to amorphous polymers, which have well-established process/structure/property (P/S/P) relationships. In contrast, the P/S/P relationships of semi-crystalline polymers in MEX are far more complex and thus poorly understood, primarily due to the crystallization that occurs during the printing process. This knowledge gap often leads to inconsistent and undesired print qualities, such as weak interfacial adhesion and significant warpage. This review seeks to deepen the understanding of the complexities and challenges involved in printing semi-crystalline polymers via MEX. As different semi-crystalline polymers exhibit different kinetics, this review categorizes a series of semi-crystalline polymers into three groups based on their crystallization rate. Following this trend, a discrepancy in their corresponding MEX processability is shown.

1.2. Introduction

Material extrusion additive manufacturing (MEX), alternatively known as Fused Filament Fabrication (FFF) or Fused Deposition Modeling (FDM), stands as a prevalent modality of additive manufacturing. This technique involves feeding a filament form of polymer material through a pinch roller mechanism, which is then extruded through a heated nozzle. Controlled movement of the nozzle lay down each layer of material, cumulatively forming the intended 3D structure.

MEX offers considerable advantage in terms of ease of deployment, cost-efficiency, and rapid production capabilities. However, its primary application still remains in prototyping rather than in the direct fabrication of end-use products. One key obstacle to its broader application lies in the limited selection of suitable materials. Most commonly, amorphous polymers are employed in MEX owing to their minimal shrinkage and well-studied process/structure/property (P/S/P) relationships [1-3].

Compared to amorphous polymers, semi-crystalline polymers offer improved thermo-mechanical properties, chemical resistance, and wear resistance [4, 5]. Ideally, the combination of these unique attributes with MEX’s advantage would enable rapid, customizable manufacturing of complex parts that can be particularly beneficial in sectors such as aerospace, medical device and personalized equipment [6, 7], which often demand highly customized, intricate components – a demand well-suited to MEX’s capabilities.
However, the use of semi-crystalline polymers in MEX comes with challenges. These difficulties stem primarily from semi-crystalline polymer’s crystallization process, which induce additional volume reduction beyond thermal shrinkage during material solidification [8-15]. This phenomenon is illustrated in a pressure-volume-temperature (pvT) diagram (Fig. 1). Unlike amorphous polymers, which display a minor inflection point at temperatures around $T_g$, semi-crystalline polymers experience a sharp decline in specific volume as the molecules pack in an orderly way at temperature where significant crystallization starts ($T_c$) [16-19]. This extra shrinkage makes semi-crystalline polymers more susceptible to larger overall shrinkage compared to amorphous polymers [20-23]. For instance, from 300° C to room temperature at a cooling rate of 10° C/min, polyethylene terephthalate (PET) can exhibit as much as 18% shrinkage [23], whereas amorphous ABS only experiences around 10% shrinkage [21].

Moreover, the properties of semi-crystalline polymer parts are significantly influenced by their degree of crystallinity. Properties such as modulus and tensile strength can differ substantially depending on the degree of crystallinity, which in turn is affected by factors such as cooling rate and processing conditions [24]. This added layer of complexity further complicates the material’s P/S/P relationship, leading to inconsistent mechanical properties across different batches of MEX printed parts. Issues such as weak interlayer adhesion and significant warpage are often encountered.

To facilitate advancements in MEX with semi-crystalline polymers, an in-depth understanding of these challenges is essential. This review aims to deliver both a summary and comprehensive analysis of the issues encountered when printing semi-crystalline polymers via MEX. Recognizing that these challenges stem from the polymer’s crystallization process and that different semi-crystalline polymers exhibit distinct crystallization kinetics, we categorize them based on crystallization rates into three groups, namely, semi-crystalline polymers with fast, intermediate and slow crystallization rates. Contrary to the common belief that semi-crystalline polymers are generally difficult to print in MEX, our analysis revealed a more nuanced picture. Specifically, semi-crystalline polymers with fast crystallization rates pose the most significant challenges, while those with slower crystallization rate are relatively easier to print and share similarities with amorphous polymers in MEX.
Fig. 1. Typical pvT diagram for amorphous and semi-crystalline polymers
1.3. Roadmap

As discussed previously, the difficulties in printing semi-crystalline polymers via MEX primarily stem from their inherent crystallization characteristics. This additional crystallization process results in issues such as large volume shrinkage, weak layer bonding and warpage, etc. At a microscopic level, it should be noted that different semi-crystalline polymers possess distinct crystallization kinetics, particularly in terms of crystallization rates. For example, some polymers are generally known to crystallize fast, such as polyethylene (PE), while others crystallize slower, such as poly(lactic acid) (PLA). More precisely, this crystallization rate is essentially temperature dependent, being slowest near the melting temperature \( T_m \) and glass transition temperature \( T_g \). This behavior can be quantified using the crystallization half-time \( t_{1/2} \), which represents the time required to reach half of the final crystallinity. Notably, the rate peaks at a specific temperature, which corresponds to the minimum \( t_{1/2} \), as depicted in Fig. 2.

![Fig. 2. Relationship of crystallization half time vs. crystallization temperature](image)

Recognizing the temperature-dependent nature of crystallization rate, we use the minimum \( t_{1/2} \) as the benchmark value (Fig. 2) for comparing different semi-crystalline polymers. All reviewed semi-crystalline polymer’s minimum crystallization half-time \( t_{1/2-min} \) are summarized in Fig. 3. We categorize those with \( t_{1/2-min} \) shorter than 30s, around a few minutes and larger than 10 minutes as fast, intermediate and slow crystallizing polymers, respectively.
Fig. 3. summary of minimum $t_{1/2}$ for: PPS[25-27], PP[28], PEEK[29], PEKK80/20[30], HDPE[31], PEKK 70/30[32], PET[24, 33, 34], PEKK60/40[32] and PLA[35]

In addition, changes in specific volume due to crystallization for these semi-crystalline polymers are presented in Fig. 4:
Interestingly, in Fig. 4, the fitted lines for each set of data are nearly parallel (except for PPS), indicating that each unit incremental in crystallinity results in a similar change in specific volume. This concludes that, the final degree of crystallinity is the dominant factor influencing shrinkage due to crystallization.

For polymers like HDPE or PEEK, the rapid crystallization rate quickly results in a high degree of crystallinity, introducing large amount of shrinkage and making them challenging in MEX process. Conversely, for polymers with intermediate or slow crystallization rate, the development of crystallinity can be minimized through optimization of the print parameters. In such case, thermal shrinkage becomes the dominant contributor to in-process shrinkage (similar to amorphous polymers). And post-annealing can be applied after printing to increase crystallinity in a uniform manner to improve mechanical properties.

In summary, semi-crystalline polymers of different crystallization rates present different levels of challenge in MEX. This logic serves as the basis for this review paper, guiding the categorization of semi-crystalline polymers into three groups based on their crystallization rates. The challenges or difficulties regarding each group of polymers in MEX are explored. By doing so, we aim to deepen the understanding of the material’s P/S/P relationships and offer
insights for the parameter optimization, as well as modification or synthesis of existing and new semi-crystalline polymers with better compatibility for MEX.
1.4. Material extrusion additive manufacturing of semi-crystalline polymers

1.4.1. Semi-crystalline polymers with fast crystallization rate

1.4.1.1. Overview

As previously highlighted, fast-crystallizing polymers rapidly attain high levels of crystallinity during MEX printing, introducing significant shrinkage that often leads to warpage failure. This issue becomes particularly severe for polymers with a low surface energy, such as polyolefins, as in this case, the freshly deposited material may easily peel off due to their poor adhesion to the print bed.

Moreover, the highly crystalized underneath layer acts as a barrier to polymer chain entanglement at the welding interface, impeding the formation of a robust interlayer adhesion. Achieving strong interlayer adhesion with fast-crystallizing polymers typically require an interfacial temperature close to or above melting temperature ($T_m$). However, reaching such an elevated temperature without causing material degradation is often challenging and costly. Collectively, these challenges make fast-crystallizing semi-crystalline polymers exceptionally difficult to print in MEX. Various strategies to enhance the printability of this group of polymers have been explored and will be discussed in this section.

1.4.1.2. Poly(etheretherketone) (PEEK)

Polyaryletherketone (PEAK) represents a group of high-performance, semi-crystalline engineering polymers. These polymers feature a backbone composed of alternately ketone and ether groups. By modifying the chemical structure and adjusting the ratio of the backbone units, the resulting polymers can be tailored to exhibit different melting temperatures and crystallization behaviors to meet various application demands. For instance, Poly(etheretherketone) (PEEK), the most widely recognized member of the PEAK family, possesses fast crystallization kinetics which can effectively shorten the temperature holding time in injection molding to achieve the required crystallinity, thus providing beneficial to traditional polymer processing techniques.

However, processing PEEK via MEX presents certain challenges. The high melting point of PEEK, with a $T_m$ of 343°C, surpasses the temperature capabilities of most standard desktop MEX printers. This scenario either necessitates modifications to existing printers or the employment of specialized printers, both of which incur additional costs and design efforts. Moreover, the high shrinkage rate of PEEK, attributed to both crystallization [1, 29, 41-43] and thermal shrinkage makes PEEK particularly susceptible to warpage. A commonly adopted solution to minimize thermal shrinkage while maintaining the desired crystallinity is the use of a heated chamber.

Han et al. [44] simulated the temperature and stress field development during the MEX printing process of PEEK. Their findings suggest that faster print speeds and higher chamber
temperatures leads to smaller maximum stress and more uniform stress distribution, thereby reducing overall warpage. These simulation results were further validated with experimental data, confirming good agreement between the two.

Wu et al. [45] studied the impact of build chamber temperature on the warpage of a square plate benchmark part (20 × 20 × 3 mm) printed with PEEK using a custom-built MEX printer. The chamber temperature ranged from 90°C to 130°C, while the build plate temperature remained constant at 150°C. By comparing the surface point cloud of the printed part with the original CAD model, it was demonstrated that warpage can be significantly reduced through increasing the chamber temperature up to 130°C.

Hu et al. [46] developed a custom MEX printer equipped with a heated chamber and a novel heat collector (Fig. 5) to concentrate the local thermal energy around the forming area. The degree of warpage was investigated by altering the temperature of the heated chamber from 25°C to 60°C, while maintaining the print bed temperature at 135°C. The results revealed that increasing the chamber temperature reduced the average degree of warpage from over 20% to 6.1%. Further utilization of the heat collector led to an even lower warpage of 5.0%.

These observations for neat PEEK align well with the simulation results presented by Han et al. [44]. However, an interesting contrast is seen in the case of short carbon fiber reinforced PEEK, where Yang et al. [47] reported an opposite trend. They noted a continuous increase in the degree of warpage from 0.2% to 1.6% as the chamber temperature was raised from 20°C to 150°C. It was only at 200°C that the warpage decreased to 0.4%.

It is worth noting that besides chamber temperature, other factors such as build plate adhesion, printing toolpath, part design, infill pattern and infill density, etc., also impact warpage. Unfortunately, quantifying the influence from these variables is challenging, hence they are seldom investigated. With the influences from all these different factors coupled together, it’s conceivable that the occurrence of warpage might not precisely follow the reported trends with a different machine or part design. Nonetheless, these findings hold considerable significance for guiding the optimization of PEEK MEX printing processes to mitigate the risk of warpage.
While warpage poses a significant challenge in the MEX of PEEK, an even greater challenge lies in the anisotropic properties of the printed parts. Typically, MEX printed parts exhibit much higher strength in the intra-layer direction compared to the inter-layer direction. This anisotropy is well-documented for many MEX feedstock materials [48-61], yet the investigations are relatively limited for PEEK. SEM images of the tensile fracture surfaces in most PEEK MEX studies depict significant delamination between layers, implying weak interlayer adhesion. For example, Arif et al. [62] highlighted a difference as large as 88% in both tensile strength and flexural strength between the X and Z directions for MEX printed PEEK specimens. This substantial anisotropy stems from the very limited polymer chain entanglement and co-crystallization occurring at the layer interface.

Jarrousse et al. [63] explored the self-adhesion behaviors of semi-crystalline polymers, revealing that robust adhesion between two pre-annealed semi-crystalline polymer plates only develops when the average interface temperature — determined by the mean of the upper and lower surfaces’ temperature — reaches or exceeds the melting temperature. This finding has significant implications for MEX printing of PEEK, which frequently utilizes heated chambers [62]. In such condition, PEEK’s crystallization process is significantly accelerated [26], resulting in the preceding layer attaining high crystallinity prior to the deposition of the subsequent layer. However, if the temperature of the heated chamber is insufficiently high, the interfacial temperature may not reach the polymer’s melting point, resulting in insufficient bonding between layers. This is in agreement with observations from Collinson et al. [64], who reported that that PEEK components printed within 70°C to 100°C chamber temperature range had low crystallinity (around 8%), contrasting with a significant increase in crystallinity (approximately 32%) at 130°C. Mechanical testing indicated that samples with lower crystallinity displayed considerably enhanced interlayer adhesion than those with higher crystallinity, highlighting the complexity between crystallization and interlayer adhesion in MEX-printed PEEK structures.

As highlighted previously, achieving robust interlayer adhesion in the presence of high crystallinity necessitates an interfacial temperature close to or above PEEK’s melting point. PEEK begins to melt around 310°C [65]. Utilizing a 420°C nozzle, an ambient temperature of 200°C is necessary to attain an average interface temperature of 310°C, assuming that the ambient temperature equals that of the previously deposited layer. However, designing a printer capable of maintaining such a high chamber temperature presents substantial challenges, including high energy demands and the protection of delicate electronic components. With an ambient temperature set lower, achieving a solid weld at the interface becomes problematic. Many studies, summarized in Table 1, report print conditions with chamber and nozzle temperatures below 200°C and 400°C, respectively. Development of effective interlayer adhesion is unlikely under these conditions.

The existing literature often omits detailed data on the Z-direction tensile strength of PEEK samples - a critical measure of interlayer adhesion. Only a few studies have explored this area. Xu et al. [66] demonstrated that a nozzle temperature of 420°C within a 230°C chamber
temperature significantly enhance interfacial welding, as evidenced by SEM images (copied here in Fig. 6). Similarly, Wächter et al. [67] observed that increasing the chamber temperature to 250° C significantly improved interlayer adhesion. Specifically, at nozzle temperatures of 430°C and 450°C within a 250°C chamber, the Z tensile strength reached approximately 75 MPa and 90 MPa, respectively. These values correspond to a welding factor ranging from 0.8 to nearly 1 (where the welding factor is the ratio of interlayer bonding strength to the base material's tensile strength), indicating a minimal difference in tensile strength between the X and Z directions. Their SEM image further substantiated this improvement, showing that the typical layer welding lines disappeared at higher temperatures.

![Fig. 6](image-url)

*Fig. 6. (a) Morphology of PEEK-033G after tensile fracture with different temperatures. SEM images of fracture surface of PEEK-033G with different nozzle temperatures (b) 380°C, (c) 390 °C, (d) 400°C, (e) 410 °C, (f) 420°C, reported by Xu et al. [66]*

Another issue regarding the MEX printing of PEEK that has not been extensively studied is the presence of numerous pores found on the fracture surface within the printed samples, as observed in the SEM images from various authors (corresponding MEX parameters summarized in Table 1). While other studies present a slightly better fracture surface without the spherical pores, the phenomenon remains puzzling.

*Table 1. References with spherical pores found on the fracture surface*

<table>
<thead>
<tr>
<th>Reference</th>
<th>Ambient temperature</th>
<th>Print bed temperature</th>
<th>Nozzle temperature</th>
<th>Drying of raw material</th>
<th>Printer</th>
<th>Pore defects (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berretta et al. [68]</td>
<td>Open air</td>
<td>300°C</td>
<td>350-380°C</td>
<td>✓</td>
<td>Modified MendleMax v2.0</td>
<td>Y</td>
</tr>
<tr>
<td>Basgul et al. [69, 70]</td>
<td>Not mentioned</td>
<td>100°C</td>
<td>390-410°C</td>
<td>Not mentioned</td>
<td>Indmatec HPP 155</td>
<td>Y</td>
</tr>
</tbody>
</table>
In a typical MEX process, the cross section of a deposited print road resembles a rounded-rectangle, leading to a triangular void due to insufficiently infill between the adjacent print roads [86-97]. However, these PEEK printed samples differ noticeably: the pores are spherical rather than triangular, and are found in greater numbers than would be expected from unfilled corners alone. Moreover, these pores are also located within the printed roads, suggesting insufficient corner infill is not the root cause.
Thermal degradation could be an intuitive explanation, but several factors suggest otherwise. First, a review of temperature settings in Table 1 reveals no substantial differences between the instances where pores are present and where they are absent. Second, according to Patel et al. [98] and Tsai et al. [99], the onset for PEEK’s thermal degradation occurs around 450° C in an inert atmosphere, and the threshold remains similar in the presence of oxygen [100]. This degradation temperature is well above the nozzle temperatures referenced in Table 1 by at least 30° C. Additionally, the degradation process starts with random chain secession [101], it is quite unlikely for significant amount of gaseous degradation products to form within the short dwell time of the MEX extrusion process. Lastly, FTIR results from Ding et al. [72] confirmed no chemical degradation in PEEK filaments printed at a 420° C nozzle temperature.

Currently, the origin of these pores observed inside PEEK printed parts remains unstudied. These random pore defects are undesirable and may contribute to the considerable variability in the mechanical properties of MEX PEEK parts reported in the literature, as summarized in Fig. 7.

As shown in Fig. 7, samples without the pore defects generally exhibit a slightly better tensile strength. It should be noted that the mechanical property data reported in these
references are based on a variety of factors, such as nozzle temperatures, nozzle diameters, ambient temperatures or annealing temperatures, etc. Therefore, in Fig. 7, the highest tensile strength from each study is displayed to represent the best outcome achieved under each set of variables.

1.4.1.3. High density polyethylene (HDPE)

High density polyethylene (HDPE) is characterized by a rapid crystallization rate, with many components achieving final crystallinities exceeding 50% [102-106]. This high crystallinity inevitably leads to a significant volume reduction during the MEX process.

To mitigate this large shrinkage, incorporating fillers into the HDPE matrix has become a common approach in MEX [107-109]. Fillers, typically having a lower coefficient of thermal expansion (CTE), result in composites that demonstrate reduced volumetric changes upon cooling and solidification post-extrusion [110, 111]. Various studies have investigated different filler materials in combination with HDPE for filament fabrication. For instance, Singh et al. [112] utilized recycled HDPE to create ZrO$_2$ reinforced filaments, optimizing processing parameters for enhanced filament tensile strength. In a similar study, Singh et al. [113] combined recycled HDPE with SiC/Al$_2$O$_3$ reinforcements, which was shown to improve filament tensile strength. Other fillers such as graphene [114] have also been reported. Unfortunately, the actual MEX printing of these filled filaments was not reported.

Natural fillers have also been considered by various authors, Gregor-Svetec et al. [115] proposed a printable HDPE filament filled with cardboard dust. While good printability of this composite was demonstrated with a few benchmark parts, an increase in cardboard dust content led to a notable decrease in mechanical properties, likely due to the inherent weaknesses of the dust and its incompatibility with HDPE. Similarly, Tarrés et al. improved the printability and mechanical property of HDPE through the incorporation of thermomechanical pulp fiber (TMP) [116], using maleic anhydride functionalized polyethylene as a compatibilizer. An increase in tensile strength with higher fiber content was revealed. Despite the improved printability of TMP filled HDPE, the SEM image showed substantial horizontal voids indicative of poor layer adhesion of printed layers, such voids have also been reported in other work [117]. Koffi et al. [118] enhanced the printability of HDPE by adding yellow birch fibers along with a coupling agent. The oil-canning deformation of the printed parts was reduced significantly by 80% at 30 wt.% birch fiber content, demonstrating improved printability. However, it was shown that the addition of Birch fiber did not improve the tensile strength of the printed part.

Without the particle or fiber filler to reduce the large volumetric shrinkage, printing HDPE becomes more challenging. Gudadhe et al. [119] have proposed two strategies to reduce warpage and improving printability. The first method involves blending HDPE with a small portion (less than 0.5 wt.%) of dibenzylidene sorbitol (DMDBS) for increasing the melt stiffness, along with approximately 10 wt.% linear low density polyethylene (LLDPE) to suppress crystallinity. The second method is directly printing HDPE with a thin brim around the part, coupled with a polyvinyl acetate-based adhesive applied to the print bed to improve the initial
adhesion. Both methods showed a reduction in warpage, indicating enhanced printability. However, it was found further increase the infill density to above 20% still leads to undesired large warpage, indicating the proposed solutions are effective only up to a certain threshold of infill density.

The most notable advancements in neat HDPE MEX printing were reported by Schirmeister et al. [120]. Addressing the challenge of HDPE’s adhesion to the print bed due to its inherently low surface energy [121, 122], Schirmeister et al. experimented with various substrates, including glass, with and without adhesive spray, PEI-coated plates, PP, steel brush-roughened HDPE, Polyolefin elastomers (POE), olefin block copolymers (OBC), and poly(styrene-block-ethene-co-butene-block-styrene) thermoplastic elastomer (SEBS). Their findings indicated that SEBS alone provided sufficient adhesion to counteract warpage while still allowing for the removal of printed parts.

Schirmeister et al. also noted that HDPE’s rapid crystallization and consequent shrinkage led to voids due to inadequate infill at the standard extrusion rates. By slightly over-extruding, they achieved a much denser cross section. As discussed previously in Section 1.4.1.2, achieving adequate interlayer adhesion in highly crystalline polymers is challenging without reaching an interface temperature near or above the melting point. While high-temperature build chambers facilitate this for PEEK, HDPE can be effectively welded at higher nozzle temperatures without such chambers, due to its lower melting point of around 130°C and processability up to temperatures close to 280°C. The nozzle temperatures investigated by Schirmeister et al. ranged from 190°C up to 260°C. It was revealed by mechanical testing that when nozzle temperature is above 210°C, both Young’s modulus and tensile strength along Z direction reached nearly identical values to bulk HDPE property. This finding highlights the achievement of nearly isotropic mechanical properties in HDPE MEX prints — a feature that is notably difficult for other semi-crystalline materials without the support of a heated chamber, as the nozzle temperature necessary to reach an interface temperature proximate to the melting point would typically surpass the degradation threshold of the material; at the same time, shape loss due to too low of a viscosity at extreme temperature is also a concern.

### 1.4.1.4. Polypropylene (PP)

Worldwide, polypropylene (PP) constitutes the second largest consumer polyolefin market [123, 124] (after polyethylene). The PP market is segmented into homopolymer PP, with its commendable heat resistance and stiffness, and copolymer PPs, both random and block types, which offer enhanced low-temperature impact strength relative to homopolymer PP.

PP shares many characteristics with high-density polyethylene (HDPE) such as a high crystallization rate [125], high crystallinity, and low surface energy, etc. These attributes make PP susceptible to warpage as well. Bachhar et al. [126] demonstrated that applying adhesive to the build plate and using a large brim effectively mitigates the warpage in MEX printing of neat PP, but only at lower infill densities (< 50%).
Given the similarities between HDPE and PP, similar strategies have been investigated to enhance the printability of PP, including the incorporation of natural fillers. Stoof et al. [127] experimented with sustainable PP composite filaments by mixing pre-consumer recycled PP with various natural fillers such as hemp fiber, harakeke fiber, and recycled gypsum powder. To estimate material shrinkage post-deposition, they proposed a test specimen design and a corresponding mathematical model that calculates linear shrinkage based on the printed specimen’s curvature radius of warpage. Their work reported an estimated 2.13% linear shrinkage with neat pre-consumer PP, and incorporation of 30 wt.% hemp or harakeke fiber effectively reduced this shrinkage down to 0.47% and 0.34%, respectively. Conversely, gypsum was less effective; a 50 wt.% inclusion only cut shrinkage from 2.13% (neat pre-consumer PP) to 1.15%, equating to the reduction offered by only 10 wt.% hemp. Beyond shrinkage reduction, the addition of fiber increased the tensile strength as expected. The tensile strength of MEX printed neat PP increased from 17.02 MPa to 22.45 and 23.55 with 30 wt.% of hemp and harakeke fiber, respectively. Another study by Wang et al. [128] focused on isotactic PP homopolymer and the impact of spray-dried cellulose nanofibril (SDCNF) on the crystallization kinetics. It was discovered that 10 wt.% of SDCNF not only suppressed PP’s crystallization rate, but also decreased the coefficient of thermal expansion (CTE). This suggests that, a 10 wt.% SDCNF incorporation could mitigate PP’s shrinkage due to crystallization and thermal contraction in the MEX process, potentially enhancing PP’s printability. But unfortunately, the study did not extend to actual printing trials.

Compared to fiber-like fillers, low aspect ratio fillers are less effective in reinforcing tensile properties, yet they remain effective in mitigating shrinkage post deposition. Spoerk et al. have conducted extensive research on PP MEX feedstocks, incorporating various low-aspect ratio fillers [129-131]. In their 2017 study [130], they investigated the impact of expanded spherical perlite filler content on PP random copolymer’s volumetric shrinkage as temperature decreased from 230°C to 40°C. It was found that the volumetric shrinkage was decreased from approximately 17% (neat PP) to about 11% with the addition of 30 vol.% expanded perlite filler. DSC results indicated that the filler did not substantially alter the polymer's crystallinity. Consequently, the observed reduction in shrinkage is attributed primarily to the filler's lower coefficient of thermal expansion (CTE) [107, 108].

Incorporating fillers into polymers to mitigate shrinkage and warpage is indeed effective, yet it introduces the issue of increased brittleness, which can lead to filament fracture during printing or spooling — a critical concern that, if ignored, results in printing failures. Spoerk et al. [130] were among the first to address this issue, suggesting the solution of blending the PP random copolymer /expanded perlite composite with a small amount of amorphous polyolefin (am.PO). This approach significantly lowered the risk of filament breakage during printing or spooling, ensuring a more reliable printing process. Several 3D geometries were successfully printed with this composite, demonstrating an improvement in the printability of PP through filler integration. Although mechanical properties of the printed parts were not examined this study, Spoerk et al. in other research [129, 131] demonstrated that the inclusion of different
glass sphere fillers substantially reduced the notched impact strength of the parts by 60% to 90%. These fillers act as initiation points for cracks [132-134], with larger glass microspheres causing a more significant reduction in impact strength [129]. Thus, while fillers improve the MEX printability of PP, they may significantly compromise certain mechanical properties.

Another unique challenge involves MEX printing of PP is presented by the control and optimization of the resultant crystal structure. Typically, PP can adopt various crystalline structures [135-137] – predominantly α (monoclinic), and β (hexagonal) [138-142], with γ (triclinic) being less common and beyond the scope of this discussion. Each form of PP has different and unique properties. α-PP exhibits higher elastic modulus and better heat/chemical resistance and considered to be quite durable, while β-PP has improved elongation at break and higher impact strength [138, 143-147]. In commercial PP products, whether extruded, blown, spun or molded, the fraction of β-form crystal is usually negligible [148], partially owing to the reason that the formation of β-PP requires annealing at a higher temperatures, typically in the range of 100 to 132° C [138] – a step not commonly integrated into the processing of PP products.

Interestingly, MEX appears to facilitate the formation of β-PP [149]: it has been reported that shearing – a process that consistently occurs within the nozzle throughout the MEX printing process – can promote the development of β-PP [150, 151]. Furthermore, the layer-by-layer fabrication manner of MEX extends the processing time beyond those of traditional manufacturing techniques. This provides the opportunity of annealing the previously printed layers at various temperatures. Through precisely controlling the MEX environmental temperature, the resultant crystalline structure can be tailored. Spoerk et al. [129] studied the effect of chamber temperature on the crystal structure of the printed parts. The comparative analysis of DSC and XRD results from samples printed under 25° C and 55° C revealed that higher chamber temperature increased the presence of β-form crystal, although the predominant crystal form remained α-form. Given the low fraction of β-form crystal, the impact strength of 55° C sample exhibit only a marginal increase compared to that of 25° C. However, it is reasonable to conjecture that a further elevation in chamber temperature could yield a more pronounced distinction in impact properties.

In addition, PP is known for its broad processing window. It melts at approximately 160° C and can be processed at temperatures up to 280° C, or even 300° C for brief periods [152]. Thus, besides the previously discussed chamber temperature, the nozzle temperature can also be varied to induce different temperature profiles, thereby favoring the formation of specific crystal structures. For instance, Wang et al. [153] explored the effect of two nozzle temperatures – 200° C and 250° C – on the resultant crystalline structure and mechanical properties of samples printed with a PP homopolymer filament (Moplen HP741T). Evidences from the DSC confirmed the presence of β-PP in samples printed with a lower nozzle temperature (200° C). With results from XRD, it was calculated that the fraction of β-PP can be increased dramatically from ~10% up to ~75% by using a 200° C nozzle along with 130° C build
plate. The inclusion of β-crystals, as anticipated, significantly enhanced the impact strength. And specimens printed at the lower temperature of 200°C showed a substantial increase in notched impact strength by up to 70% compared to those printed at 250°C.

Last but not least, the issue of print bed adhesion with PP feedstock has not been thoroughly addressed in the literature, with some studies omitting the build platform material selection [130, 154-156], other successful printing on PP print bed has been documented [127, 129-131, 157]. Printing PP directly onto a PP platform risk forming a permanent bond that prevents the removal of the finished part. Spoerk et al. [158] encountered this problem when printing random copolymer PP. One proposed solution to prevent irreversible adhesion is using ultra-high molecular weight polyethylene (UHMWPE) as the build platform material. Enhancing adhesion with UHMWPE can be achieved by either increasing the print bed temperature or by roughening the surface of the plate. At a bed temperature of 50°C and a surface roughness of 9.7 μm, satisfactory adhesion was attained without permanent bonding. Parts made from composite or neat PP, printed using this method, showed minimal warping, indicating that UHMWPE is a viable print bed material for PP in Material Extrusion (MEX) processes.

Furthermore, Leng et al. [159] proposed an alternative design approach to enhance adhesion — creating a build plate with arrays of conical holes, as illustrated in Fig. 8. As the molten material forms anchoring pin through filling the holes post deposition, initial layer can be firmly secured to the build plate and effectively minimizing warpage. This technique has been successfully applied to print several 3D benchmark parts with high quality.

![Fig. 8. Schematic of the platform with arrays of conical holes and its geometric dimensions proposed by Leng et al. [159]](image.png)

1.4.1.5. Polyphenylene sulfide (PPS)

Polyphenylene sulfide (PPS) is a rigid semi-crystalline polymer composed of para-phenylene units, with a melting temperature around 285°C. It is renowned for its superior mechanical properties and resistance to high temperatures and solvents. Although PPS is classified as a fast-crystallizing semi-crystalline polymer in this review, its crystallization rate is relatively slower than other polymers of this category, such as HDPE or PEEK, with the shortest $t_{1/2}$ ranging from a few seconds to around 30 seconds [27, 160].
Moreover, PPS displays a unique characteristic where it experiences less volumetric shrinkage with each increment of crystallinity. This is evidenced by the less steep slope of the specific volume versus crystallinity line, as depicted in Fig. 4. The slightly slower crystallization rate, together with smaller shrinkage from crystallization, suggests that PPS could have a better printability compared to previously discussed polymers like PEEK or HDPE. Indeed, successful MEX printing of both unfilled PPS and filler-reinforced PPS has been reported by various researchers [161, 162].

For instance, Garmabi et al. [163] delved into the optimization of the MEX printing process for PPS. The influence of chamber temperature, nozzle temperature and layer height were investigated with a response surface methodology. According to their optimized settings, they reported a Z tensile strength around 37 MPa, as detailed in Table 2.

A particularly intriguing aspect of PPS in the context of MEX is the material's post curing: in the presence of oxygen under elevated temperature, PPS will partially go through branching, chain extension, and crosslinking, leading to an increased molecular weight and some thermoset-like properties [164, 165]. This characteristic presents a unique opportunity to enhance the properties of MEX printed PPS parts through post-processing.

Fitzharris et al. [166] conducted a systematic study using the Taguchi method to optimize MEX parameters and maximize the Z-axis tensile strength of printed PPS parts. They also explored the effects of post-curing time and temperatures up to 180°C. The study highlighted that with appropriate post curing treatments, the Z ultimate tensile strength could be increased from approximately 52% of that of PPS film to about 80%. Furthermore, the peak Z tensile strength and Young’s modulus achieved were around 61 MPa and 2230 MPa, respectively. These enhancements, especially in interlayer adhesion, are particularly promising for the properties of MEX-printed parts.

Also with post heat treatment, a wider range up to 240° C was investigated by Geng et al. [167]. In this work, they printed PPS parts under active air cooling, which initially had a crystallinity of around 19%. These parts then underwent various thermal post curing conditions at 130, 150, 200, or 240°C for a duration of 100 minutes. The treatment at the highest temperature (240°C) increased the crystallinity to approximately 64%. SEM of the fractured surface revealed a notable reduction in void size and improved layer coalescence after thermal post curing. Most significantly, post-curing increased the XY plane tensile strength dramatically from 27.2 MPa to 57.3 MPa, marking an improvement of 108%. Similar results were also reported by Magri et al. [168], where post curing at 200°C for one hour raised the XY modulus and tensile strength from 2170 MPa and 51.6 MPa to 2390 MPa and 63.1 MPa, respectively.

Utilizing a Design of Experiments (DOE) approach and ANOVA analysis, Zirak et al. [169] reported the as printed specimens with an interlayer tensile strength of approximately 6 MPa. Following 6 hours post curing at 200° C, the highest interlayer tensile strength recorded was around 13 MPa, corresponding to an enhancement over 100%. While this tensile strength is
significantly lower than that reported in other studies (as summarized in Table 2), this result underscores the significant potential of post curing treatments to substantially improve the mechanical properties of PPS printed parts.

Table 2. Parameters and resultant properties for MEX printing of PPS reported by various authors

<table>
<thead>
<tr>
<th>Reference</th>
<th>Printing parameter</th>
<th>Mechanical properties</th>
<th>Post curing protocol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Garmabi et al. [163]</td>
<td>Nozzle - 310 - 340° C Chamber - 55 -75° C Layer thickness - 0.1 -0.3 mm Print speed – 40 mm/s Print orientation - Z</td>
<td>Z tensile strength = 17.93 ± 0.95 MPa to 37.53 ± 1.1 MPa</td>
<td>No post curing investigated</td>
</tr>
<tr>
<td>Fitzharris et al. [166]</td>
<td>Nozzle - 290 - 310° C Layer thickness - 0.2 mm Print orientation - Z</td>
<td>Z tensile strength = 39.5 ± 4.1 MPa to 50.1 ± 0.3 MPa</td>
<td>140 – 180° C 10 min – 24 hr.</td>
</tr>
<tr>
<td>Geng et al. [167]</td>
<td>Nozzle - 285° C Layer thickness - 0.3 mm Print speed - 680 mm/min Cooling condition - air-forced cooling, natural cooling Print orientation - XY</td>
<td>XY tensile strength ~ 27 MPa to 38 MPa</td>
<td>130 - 240° C 100 min</td>
</tr>
<tr>
<td>Magri et al. [161]</td>
<td>Nozzle – 320 - 350° C Layer thickness – 0.15 mm Print orientation - XY</td>
<td>XY tensile strength ~ 42 MPa to 47 MPa</td>
<td>No post curing investigated</td>
</tr>
<tr>
<td>Magri et al. [168]</td>
<td>Nozzle – 320 - 340° C Layer thickness – 0.1 - 0.2 mm Print speed - 20 - 40 mm/s Print orientation - Z</td>
<td>XY tensile strength = 40.3 ± 1.4 MPa to 51.6 ± 1.4 MPa</td>
<td>180 – 220° C 1 hr.</td>
</tr>
<tr>
<td>Zirak et al. [169]</td>
<td>Nozzle – 320 - 350° C Print speed – 10 – 40 mm/s Print orientation - XY</td>
<td>XY tensile strength ~ 6 MPa</td>
<td>200° C 90 min to 24 hr.</td>
</tr>
</tbody>
</table>

1.4.2. Semi-crystalline polymers with intermediate crystallization rate

1.4.2.1. Overview

Polymers with an intermediate crystallization rate opens unique opportunity to keep the development of crystallinity under control during the MEX process, thus the process can be optimized for a lowered amount of shrinkage as well as better interlayer adhesion, which collectively enhances the printability of the material.

In comparison to polymers with fast or slow crystallization rate, the most noteworthy feature for polymers with intermediate crystallization rate is their responsiveness to print parameters, which stems from the fact that the resultant crystallinity can be strongly influenced
by the MEX parameters for this group of polymers. When parameter selected favors the 
accumulation of heat, the material crystallizes more during the process, thus the printed parts 
exhibit a higher in-plane tensile strength and modulus, while the impact strength is worsened. 
In contrast, when the parameter favors the dissipation of heat, the printed parts tend to remain 
closer to an amorphous state during the MEX process, enhancing their impact strength while 
potentially reducing tensile strength and modulus.

For optimal use of polymers with an intermediate crystallization rate in MEX, it is essential 
to adjust printing parameters to suit the specific application, whether it requires impact 
resistance or structural strength.

1.1.1.1. Polyetherketoneketone 70/30 (PEKK 70/30)

Polyetherketoneketone (PEKK) is another member of the polyaryletherketones (PEAK) 
family besides the previously mentioned polyetheretherketone (PEEK) in section 1.4.1.2. On a 
molecular level, PEKK differentiates itself from PEEK by substituting one of the ether linkages 
with a more rigid ketone group, contributing to a slightly higher $T_g$ [170-173]. Furthermore, the 
synthesis of PEKK can result in two isomeric forms depending on the site of the addition 
reaction. The introduction of the second ketone group via a 1, 4 - addition (terephthalic radical) 
leads to a more linear and rigid polymer backbone, denoted as the “T” form. In contrast, a 1, 3 
-addition (isophthalic radical) results in a less linear backbone with greater flexibility, denoted as 
the “I” form [174]. The ratio of these isomeric units, referred to as the T/I ratio, influences the 
material properties: a higher T/I ratio correlates with faster crystallization and stiffer 
mechanical behavior, whereas a lower ratio yields a material with more amorphous 
characteristics.

Due to the challenges associated with MEX printing of PEEK, many companies, such as 
Stratasys, have opted to offer PEKK as an alternative in their PEAK product lines. The isophthalic 
structure of PEKK, which imparts a kink in the polymer backbone, reduces its overall 
crystallization rate (the shortest $t_{1/2}$ for PEEK is approximately 1s, while for PEKK it is around 
60s), thereby mitigating the degree of shrinkage post-deposition. This endows PEKK with a 
significant better printability in MEX than PEEK. However, PEKK's introduction to the market is 
not solely due to the printing difficulties associated with PEEK. In addition to possessing similar 
mechanical strength, PEKK also has its own set of advantages. For example, according to Yuan 
et al. [175], PEKK contains a greater proportion of ketone groups than PEEK, which provides 
additional sites for surface chemical modifications. As a result, after sulfonation, PEKK offers a 
better osteointegration performance for surgical implants.

In terms of melt processing, PEEK has a fixed $T_m$ of around 350° C. PEKK, however, by 
adjusting the T/I ratio, the melting temperature can be tuned from near 300° C with a T/I ratio 
of 60/40 to around 350° C with a T/I ratio of 80/20 [176]. Notably, its degradation temperature 
remains stable at approximately 500° C [177]. Thus, PEKK offers a relatively wider melt 
processing temperature range compared with PEEK. Other benefits of PEKK includes 
significantly higher compression strength etc. [178-180]. Since PEKK with a 60/40 T/I ratio
exhibits an excessively slow crystallization rate, often it is described as a pseudo-amorphous polymer [181], thus will be discussed later in Section 1.4.3.3 instead. PEKK 70/30 and 80/20 present typical semi-crystalline polymer characteristics. However, due to the scarcity of literature on PEKK 80/20, this section will primarily be focused on PEKK 70/30.

While the printability and performance of PEKK 70/30 are remarkable, research into the process-property relationship within MEX for this polymer is not as extensive as that for PEEK. The most pertinent study to date appears to be the patent US20200276760A1 filed by Arkema in 2018 [182]. According to the patent, maintaining a build chamber temperature at least 50°C, and preferably 80°C, below the cold crystallization temperature of PEKK 70/30 (190°C [176]), effectively prevents the material from fully crystallizing during the MEX process. XRD analysis of the “as printed” parts showed peaks that were less defined compared to those observed in parts that had undergone annealing at 200°C, indicating a lower crystallinity in the samples printed under cooler chamber conditions (chamber temperature = 80°C). The patent also includes a modeling result depicting the impact of the build chamber temperature on the crystallinity of “as-printed” parts (Fig. 9). The result corroborates the XRD findings by showing low crystallinity for “as-printed” parts when the build chamber temperature is maintained below 150°C.

![Modeled crystallization % vs heat chamber temp](image)

*Fig. 9. The modeled "as printed" crystallinity vs ambient temperature, imported from reference [182]*
The superior printability of PEKK 70/30, relative to PEEK, was highlighted by the authors when printing parts under identical conditions. Common issues associated with PEEK such as warping, poor interlayer adhesion, and non-uniform shrinkage were notably absent with PEKK 70/30. The patent provides quantitative shrinkage data, which is presented here in Table 3. This data reveals that the shrinkage experienced by PEKK 70/30 in MEX process is comparable to that of ABS, and considerably less than that of PEEK. Subsequent to the annealing process, there is an observed increase in shrinkage up to 3%. However, the uniformity of this shrinkage mitigates potential problems.

Table 3. Shrinkage data imported from reference [182]

<table>
<thead>
<tr>
<th>Material</th>
<th>% Distortion on Thin Wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEKK 70/30 as printed</td>
<td>1.2%</td>
</tr>
<tr>
<td>PEKK 70/30 after post processing</td>
<td>3.0% uniform shrinkage</td>
</tr>
<tr>
<td>PEEK as printed</td>
<td>4.4%</td>
</tr>
<tr>
<td>ABS</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

In addition to enhanced dimensional stability, the slower crystallization rate of PEKK 70/30 contributes to improved interlayer adhesion. As outlined in Section 1.4.1.2, achieving strong bonding between PEEK layers necessitates maintaining the printer chamber at temperatures above 200°C to ensure the interface temperature approaches the T_m of PEEK. Such high-temperature chamber designs are complex and costly. Lower temperature chambers, however, do not adequately raise the interface temperature to the Tm, and PEEK's high crystallinity limits polymer chain mobility within the amorphous regions, consequently restricting diffusion, entanglement, and co-crystallization at the interface. In contrast, the predominantly amorphous state of PEKK 70/30 during printing allows for greater chain mobility, which facilitates diffusion and entanglement at the interface at temperatures above T_g, resulting in significantly stronger bonding. This property also simplifies printer design and reduces associated costs [183].

The crystallinity and mechanical properties of samples printed in a 75°C chamber, as reported by the patent authors, are documented in Table 4. its rapid crystallization leads to a final “as-printed” crystallinity of 21%, sufficient to hinder polymer chain diffusion and entanglement at the interface, as indicated by a large disparity between the XY maximum stress (79 MPa) and Z maximum stress (5 MPa) — a difference as large as 94%. Conversely, for PEKK 70/30, the “as printed” crystallinity is nearly amorphous (0-2.5%), and the maximum stress disparity is notably lower with XY maximum stress at 84 MPa and Z maximum stress at 51 MPa, a 39% difference. This represents a substantial improvement over PEEK. Moreover, post-annealing can enhance the XY and Z strengths of PEKK 70/30 printed samples by approximately 8%, although the level of anisotropy remains unchanged.
Table 4. Crystallinity and mechanical properties from reference [182]

<table>
<thead>
<tr>
<th></th>
<th>Crystallinity (wt.% via WAXD)</th>
<th>XY maximum stress (MPa)</th>
<th>XY elongation to break (%)</th>
<th>Z maximum stress (MPa)</th>
<th>Z elongation to break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEKK 60/40</td>
<td>As printed</td>
<td>0%</td>
<td>83</td>
<td>10.4%</td>
<td>48</td>
</tr>
<tr>
<td>PEKK 60/40</td>
<td>Post treatment</td>
<td>0%</td>
<td>87</td>
<td>11.0%</td>
<td>n/t</td>
</tr>
<tr>
<td>PEKK 70/30</td>
<td>As printed</td>
<td>0-2.5%</td>
<td>84</td>
<td>13.0%</td>
<td>51</td>
</tr>
<tr>
<td>PEKK 70/30</td>
<td>Post treatment</td>
<td>22%</td>
<td>90</td>
<td>8.2%</td>
<td>56</td>
</tr>
<tr>
<td>PEEK</td>
<td>As printed</td>
<td>21%</td>
<td>79</td>
<td>19.9%</td>
<td>5</td>
</tr>
</tbody>
</table>

The processing parameters of PEKK 70/30 extend their influence beyond tensile properties to include flexural properties as well. Xu et al. [184] studied the relationship between processing parameters and the flexural properties of PEKK 70/30 printed specimens. Their study investigated the impact of various nozzle temperatures ranging from 345°C to 385°C, finding that a nozzle temperature of 375°C yielded the optimal flexural modulus and strength. In contrast, the highest investigated nozzle temperature, 385°C, resulted in the lowest flexural properties. SEM imaging revealed random pore defects in the PEKK 70/30 specimens, similar to those observed in PEEK samples (as discussed in Section 1.4.1.2), with the exception of specimens printed at 355°C. The authors proposed that the decrease in mechanical properties at the 385°C nozzle temperature could be attributed to an increased presence of these defects, though the underlying cause of the defects remains unexplored.

Further research by the same team, under a consistent nozzle temperature of 375°C, assessed other parameters such as layer thickness, infill density, and build orientation. Results indicated that thinner layers enhanced flexural modulus and strength due to improved layer bonding; increased infill density reduced the presence of air gaps, thereby enhancing flexural properties; and vertical build orientation was linked to the weakest flexural properties.

1.1.1.2. Polyethylene terephthalate (PET)

Poly(ethylene terephthalate) (PET) is a commercial semi-crystalline polymer widely used in packaging, such as water bottles and various product containers. In the realm of MEX, most of the PET filaments available are derived from glycol-modified PET, known as PET-G. The synthesis process of PET-G is akin to that of PET, involving polycondensation. The principal distinction lies in the synthesis ingredients: along with terephthalic acid (TPA) and ethylene glycol (EG) — the two primary components of PET — a third monomer, cyclohexane dimethanol (CHDM), is incorporated. When the fraction of CHDM in the copolymer exceeds 50%, the resulting product is classed as PET-G [185]. The bulky nature of CHDM molecules interferes with the regular alignment of PET-G polymer chains, significantly diminishing its overall crystallinity, making PET-G an amorphous material.
Within the context of MEX, it is often assumed that the amorphous nature of PET-G would be more advantageous over PET due to its resistance to shrinkage from crystallization, which could enhance printability. However, this perspective over-simplified the challenge involved with printing semi-crystalline polymers. In practice, PET exhibits great printability. Owing to its intermediate crystallization rate, PET parts can be printed with a relatively low crystallinity, analogous to PEKK (Section 1.1.1.1), thereby avoiding warpage and non-uniform shrinkage. Additionally, the mechanical properties of these parts can be enhanced post-printing through thermal treatments such as annealing, in order to meet specific application needs.

Currently, PET-G is the primary focus within PET related MEX research, with studies on semi-crystalline PET being relatively rare. Zander et al. [186] addressed this gap by experimenting with filaments from recycled PET (rPET) flakes. They successfully printed tensile specimens and a radio bracket at a nozzle temperature of 270°C and a bed temperature of 30°C. The tensile testing revealed that the mechanical properties of the rPET prints were comparable with those fabricated from filaments produced from commercial PET. Notably, the uniform and cohesive fracture surfaces of the rPET samples imply robust interlayer adhesion. These results highlight the impressive printability of rPET, and also suggesting that commercial PET, which closely resembles rPET chemically and physically despite rPET's potential impurities and slightly higher crystallinity, should exhibit at least equivalent if not enhanced printability.

The author of this review paper also studied the MEX printing of semi-crystalline rPET and the corresponding glass fiber (GF) reinforced composite (
Chapter 2). In the experiment, neat rPET demonstrated excellent printability and enhanced layer adhesion, yielding Z axis mechanical properties that were roughly 70% of those measured in the X axis. This is notable as Z strengths in MEX processes are often significantly lower [187-189]. The addition of 20 wt.% GF to rPET markedly increased modulus and tensile strength in the X axis by 71% and 25%, respectively. However, this incorporation of GF also led to a diminished Z strength due to the presence of GF at the interfaces, which does not contribute to layer adhesion. 20 wt.% GF eventually resulted in about a 31% reduction in the sample’s Z tensile strength.

A significant observation from this research is the influence of the MEX process and parameters on the crystallinity of PET and its composites. Depending on the thermal history imparted by the MEX process, the resultant printed part may range from nearly amorphous to exhibiting crystallinity levels exceeding 25%. Such variations in crystallinity substantially alter the optical and mechanical properties of the final product. The addition of glass fibers has been noted to decrease total crystallinity but only to a limited extent. Challenges arise when the design of the part or the chosen printing strategy restricts heat dissipation, leading to uneven crystallinity across different locations of the same part. To date, there still remains a lack of comprehensive research on the relationship between part design, MEX processing parameters and the resultant crystallinity of PET.

Last but not least, some methods have already been proposed in order to mitigate the risk of embrittlement in PET parts when elevated crystallinity is encountered. For example, Zander et al. [190] tested the incorporation of various elastomers – 5 wt.% of either styrene ethylene butadiene styrene (SEBS), maleic anhydride functionalized SEBS (SEBS-MA) or micronized rubber – to an rPET matrix. These modified materials were then fabricated into filaments and subjected to mechanical test after printing. The results showed that, the introduction of these elastomers did not significantly alter the ultimate tensile strength of the material. However, there was a notable variance in terms of the toughening performance: while micronized rubber led to a modest toughness increase of 86%, the smaller particle size of SEBS and SEBS-MA yielded far greater improvements, enhancing toughness by 350% and 550%, respectively.

1.4.3. Semi-crystalline polymers with slow crystallization speed

1.4.3.1. Overview

Semi-crystalline polymers with slow crystallization rate exhibit behaviors similar to amorphous polymers in MEX. Due to the significantly extended time required for crystallization, the printed parts tend to remain largely amorphous irrespective of the print parameters. This group of polymers usually exhibit very good printability. Therefore, this section will only briefly review some of the related works.

1.4.3.2. Polylactic acid (PLA)

Polylactic acid (PLA) is a linear polyester typically synthesized through the ring-opening polymerization of lactide, a method preferred in industrial settings [191]. There are three
stereoisomeric forms of the lactide monomer: L-lactide, D-lactide, and meso-lactide, composed of two L-, two D-, or one of each L- and D- lactic acids, respectively. PLA derived from solely L- or D-lactides (PLLA and PDLA) are semi-crystalline. In contrast, PLA derived from meso - lactide is amorphous [191]. Interestingly, a 1:1 mixture of PLLA and PDLA forms stereo-complex crystals (sc-PLA), characterized by a substantially higher melting point (approximately 220° C) compared to pure PLLA or PDLA (approximately 160° C). The elevated melting temperature enhances PLA’s heat deflection resistance. Additive manufacturing of sc-PLA has been reported for selective laser sintering (SLS) [192], but unfortunately not for MEX to the best of the author’s knowledge.

While stereo-complex PLA (sc-PLA) applications in Material Extrusion Additive Manufacturing (MEX) remain underexplored, commercially available semi-crystalline PLA filaments have long been established in the market, commanding a significant share [193]. The popularity of PLA stems from its affordability, biodegradability, diverse color options, and, notably, its user-friendliness: PLA filaments do not require high printing temperatures, which minimizes nozzle clogging due to degradation. Simultaneously, occurrence of warpage in PLA’s MEX printing is minimal.

Notably, PLA provides strong welds at the interface, potentially achieving bulk material strength. Allum et al. [194] reported that PLA, when printed with a nozzle temperature of 210° C and build plate temperature of 60° C, exhibited comparable strength in both the X and Z directions, with values ranging approximately from 50 to 70 MPa, indicative of robust welds. However, the analysis of strain-at-fracture, specific load bearing capacity as well as toughness showed a weaker value along Z direction. With finite element analysis (FEA), it was found that the localization of strain caused by the print road geometry was the reason of this anisotropy. Finally, the influence of varying layer time and printing speed on mechanical properties was investigated, and no significant differences in strength associated with these two parameters were found, implying PLA is less sensitive to print speed related MEX parameters.

1.4.3.3. Polyetherketoneketone 60/40 (PEKK 60/40)

PEKK 60/40, as discussed in Section 1.1.1.1, is a copolymer similar to PEKK 70/30 but with a lower ratio of terephthalic to isophthalic components. The lower T/I ratio significantly decelerates the crystallization process, making PEKK 60/40 a pseudo-amorphous semi-crystalline polymer [181]. It has been commercialized as a filament for MEX, with products available from companies such as Stratasys and VisionMiner.

Currently research work focusing on the MEX of PEKK 60/40 are still limited. Davis et al. [195] explored the mechanical properties of vertically printed PEKK tensile specimens under various layer times ranging from 3.6s to 43.9s. The inherent slow crystallizing nature of PEKK 60/40 negates the impact of crystallization on interlayer bonding, leaving the temperature-dependent molecular diffusion as the primary determinant, which is intrinsically linked to the layer time. According to Davis’ findings, all specimens appeared amorphous, regardless of the layer time. The vertical tensile specimens printed with the shortest layer time of 3.6s exhibited
the highest tensile strength at 53.8 MPa due to optimal interlayer bonding. While the tensile strengths for other specimens printed with longer layer times — 13.8s, 31.5s, and 43.9s — did not show a statistically significant difference and were only approximately 20% lower than the peak value, demonstrating the potential of PEKK 60/40 as a promising, reliable and robust MEX feedstock.

1.5. Conclusions

In Material Extrusion Additive Manufacturing (MEX), the general belief is that semi-crystalline polymers pose greater challenges in printing than amorphous polymers. This paper has presented a more nuanced view, suggesting that the crystallization rate of the material is a critical factor that should be considered. We have categorized semi-crystalline polymers into three groups based on their crystallization rates: fast, intermediate, and slow. And the according key findings are presented as follow:

For semi-crystalline polymers with fast crystallization rate:

- High crystallinity causes significant shrinkage, potential infill gaps, and residual stress. Warpage frequently encountered if print bed adhesion is insufficient.
- High crystallinity also hinders polymer chain entanglement and co-crystallization across the layer interface, resulting in poor interlayer adhesion.
- Achieving sufficient interlayer adhesion requires an interface temperature near or above the polymer's melting temperature ($T_m$). Usually realized with a high temperature printing chamber, or high temperature nozzle, or both.

For semi-crystalline polymers with intermediate crystallization rate:

- heated environment is not critical for good interlayer adhesion.
- Proper parameters can maintain low crystallinity, reducing warpage and facilitating better chain diffusion.
- More sensitivity to printing parameters; print speed and layer time can substantially affect crystallization and, consequently, the mechanical properties.

For semi-crystalline polymers with slow crystallization rate:

- Crystallization process is usually too slow to cause any significant impact on their MEX process
- Generally possess great printability and interlayer adhesion

In summary, it is crucial in MEX to embrace a tailored approach to each semi-crystalline polymer based on its crystallization rate. This perspective in turn, will pave the way for innovations in both print strategies and material formulations. It is the author's hope that this work catalyzes further research and forward the boundaries of additive manufacturing.
2. Chapter 2

Material Extrusion Additive Manufacturing of Glass-Reinforced Recycled Poly (Ethylene Terephthalate) Composite

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2.1. Abstract

Poly (ethylene terephthalate) (PET) is a commodity thermoplastic. For example, it is predominately used in drink bottles, of which material the global demand is forecast to be 42 million metric tons by 2030. With the rapid accumulation of waste PET plastics, there have been significant efforts to identify novel ways for turning recycled PET (rPET) into end-use products with value. One application of rPET is as a cost-effective, robust feedstock for Material Extrusion (MEX) additive manufacturing (AM), enabling customized, free-form manufacturing without the need to rely on conventional larger-scale molding equipment. Printing of pure PET and rPET has been shown in prior research. To improve the mechanical properties of rPET, we explore combining this waste with reinforcement fiber and upcycle it into a composite part for end use applications.

The goal of this study is to explore the impact of glass fiber (GF) reinforcement on rPET’s MEX processability and resultant mechanical properties. To achieve this goal, a custom-made MEX 3D printer was used to print filaments produced from recycled PET and GF at varying concentrations. It was found that 20 wt.% of short GF tripled the viscosity of rPET, as well as enhanced the shear thinning effect. Printed tensile bars showed a decreasing trend in crystallinity with glass fiber loading. It is shown that GF leads to an increase in both elastic modulus and tensile strength of the printed parts. However, compared with the modulus increase (71%), the increase in tensile strength is relatively small (25%), mainly due to the significant fiber breakdown throughout the processing procedure. Evaluation of the printability of this rPET as well as its glass fiber reinforced composite is demonstrated by printing several complex geometries, including components for an unmanned air vehicle (e.g. a fixed-wing drone).

2.2. Introduction

Poly(ethylene terephthalate) (PET) is a semi-crystalline thermoplastic, characterized by its high strength-to-weight ratio [196, 197], excellent electrical insulation [198] and good gas barrier property [199, 200]. These benefits make PET an ideal choice for a variety of applications. Currently, one of the major market sections for neat PET is packaging such as water bottles and containers. With fiber reinforcement, PET composites are widely used in electrical devices, switches and structural panels, etc. [201].

Since the first commercialization of PET in the early 1950s, there has been a significant increase in the global consumption level. Over the decades, this growing market demand caused a significant accumulation of PET waste. For example, the current global production rate of plastic bottles is around one million per minute [202, 203], and for the period of 2020-2025, the market of plastic bottles is forecast to reach 240 billion at a compound annual growth rate (CAGR) of 5.5%. In the US, more than 70% of PET bottles produced are not recycled but instead end up in landfills or incinerators [204, 205].
As a high performance and well-developed thermal plastic, the growing market demand for PET and its corresponding products seems to have an irreconcilable conflict against sustainability. One novel pathway for reusing waste PET and extending its lifecycle could be as a feedstock for additive manufacturing (AM, also referred to as 3D Printing). Material Extrusion additive manufacturing (MEX), a modality of AM that produces parts by selectively hot-melt extruding thermoplastic filament in a layer-wise fashion, is a suitable technology for processing recycled PET (rPET). MEX systems are cost-effective [206, 207], simple in machine configuration, and feature a breadth of build envelopes – ranging from industrial-scale (~20 × 20 × 20 in. or even larger) to desktop-scale (~4 × 4 × 5 in.). MEX is capable of fabricating robust thermal plastic products as well as fiber reinforced composite parts of sufficient quality for end-use application and is easily deployable to resource-poor areas that benefit from onsite manufacturing.

Both PET and rPET has been reported to have good MEX processability despite their semi-crystalline nature. For example, Zander et.al [186] demonstrated an rPET printed radio bracket with filament directly made from recycled water bottle flakes. Three-point bending test of the printed bracket showed nearly identical load at failure compared to the same part printed from commercial ABS filament. Voorde et.al [208] examined both molecular weight and polydispersity of virgin and recycled PET and found no inferior values for the recycled material; the mechanical tests of printed specimens also showed comparable properties between recycled and virgin feedstocks, once again demonstrating the feasibility of directly using rPET as an MEX feedstock.

MEX is also a preferable AM technology for printing composite parts compared with other types of AM. For example, Ning et.al [209] studied the incorporation of carbon fiber (CF) on the mechanical properties of MEX printed ABS part; significant improvement of tensile strength and Young’s modulus was achieved even with only 5 wt.% CF loading. Similar improvement from fiber reinforcement in MEX has been reported [210-214]. Shulga et.al [215] investigated the MEX of glass fiber reinforced polypropylene (PP). X-ray micro-computed tomography (micro-CT) results showed an obvious fiber alignment with the direction of toolpath. This directional orientation of reinforcing fiber in MEX often leads to a larger degree of anisotropic properties [212, 216], but with design optimization following the principles of DfAM (design for additive manufacturing) [217], this shortcoming of anisotropy can be minimized to the greatest extent possible. Katalagarianakis et al. [218] demonstrated the MEX of carbon fiber reinforced rPET. Through pvT measurement, it was shown that the addition of CF can significantly reduce the volumetric shrinkage up to 42% compared to neat PET. In addition, the CF were shown to act as a nucleating agent and increase the crystallization temperature of the PET matrix.

In MEX, glass fiber and carbon fiber are the two most widely used reinforcing filler. While they are both capable of enhancing the mechanical properties of the end product, they possess different characteristics in terms of strength, stiffness [219-221] and electrical insulation capabilities [222]. Most importantly, when mixing with semi-crystalline polymers, there
characteristics in altering the nucleation and crystallization rate is different. For example, it is reported that carbon fiber exhibits a significantly higher nucleation efficiency than glass fiber [223]. Furthermore, the crystallization rate of semi-crystalline composites containing carbon fiber surpasses that of their glass fiber counterparts [223, 224].

While prior literatures have shown successful MEX of PET & rPET homopolymer, as well as rPET/CF composite, there has been no research regarding the glass fiber reinforced rPET composite fabricated via MEX. The objective of this work is to explore the process/structure/property (P/S/P) relationship of this composite. Specifically, we explore how the addition of glass fiber affects the mechanical property, the degree of anisotropy, as well as the resultant crystallinity of printed parts. To further validate this approach, example products featuring complex geometries were successfully printed with rPET and its GF composites. Considering the lower cost of glass fiber compared with carbon fiber [225], directly printing GF reinforced composite from rPET provides the possibility to fabricate high performance parts for underdeveloped and resource poor areas, while extending the lifecycle of waste PET at the same time.

2.3. Material and Methods

2.3.1. Materials & filament fabrication

Recycled PET (rPET) flakes (provided by UNIFI Inc.) from a mixed stream recycle facility were used to prepare the filament. Owens Corning 183F short glass fiber (GF) with a diameter of 11 μm and length of 4 mm were also incorporated at varying concentrations (levels of GF loading: 0, 1, 3, 5, 10, 20 wt.%) with a Leistritz ZSE 18 twin screw extruder and a water bath. In order to promote uniform mixing with the glass fiber, the larger original rPET flakes are first granulated down to a smaller size. Both ground rPET flakes and short GF were dried overnight at 90° C under vacuum, then mixed by shaking before extruded. The extruder’s eight temperature-controlled zones were set as 230° C, 240° C, 240° C, 250° C, 250° C, 250° C, 250° C, 260° C, 260° C from feed port to die, and screw speed was set to 200 rpm. The extrudate was pelletized and vacuum dried at 90° C overnight. A Filabot EX2 filament extruder was used together with a custom-made conveyer belt for making ⌀1.75 mm rPET/GF filament, with the extruder’s temperature set to 270° C.
2.3.2. Rheology testing

To evaluate the rheological behavior of GF filled rPET filaments, the extruded filaments were cut into small pieces and tested at steady state with a TA instrument HR1 Discovery Hybrid rheometer. Tests were conducted at the extrusion temperature (270°C) using 25 mm parallel plates with a 1 mm gap. A flow sweep was conducted with a shear rate ramping from 1 to 100 s⁻¹.

2.3.3. 3D printing with GF reinforced filament

In this work, a custom-made, delta-bot MEX 3D printer was used. Slic3r software was used to generate printing toolpath. To prevent the nozzle from being damaged and clogged by the GF filler, a 0.6mm hardened steel nozzle was installed. Two types of specimens for mechanical testing were printed, as shown in Fig. 11.

![Fig. 11. Illustration of two test specimens, (a). ASTM D1708 tensile specimen, (b). single layer geometry, with orientation of punched tensile specimens indicated](image)

The first specimen is an ASTM D1708 tensile specimen with a thickness of 3 mm. This multiple layer specimen is selected in order to better represent the mechanical property when a multiple layer object needs to be printed in real application. The second specimen is a single wall geometry where mini tensile specimens along both the X and Z directions are punched off in order to evaluate the influence of GF loading on the resultant degree of anisotropy. Several complex geometries were also printed to demonstrate the printability of this material, details shown in Section 2.4.2.

The applied printing parameters are listed in Table 5. A nozzle temperature of 270°C was selected based on the DSC analysis of the composite feedstock (Supplementary Information Fig. A1) to ensure a complete melt of rPET. Different infill densities were selected for different parts: for the ASTM D1708 tensile specimen and the single layer geometry, an infill density of 100% was used. For demonstrating the material’s printability, a lower infill density (20%) was used to shorten fabrication time when the part size was significantly larger.
Table 5. Printing parameters for the two types of specimens

<table>
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<tr>
<th>Nozzle temperature (°C)</th>
<th>Bed temperature (°C)</th>
<th>Layer height (mm)</th>
<th>Shell perimeters</th>
<th>Infill density</th>
<th>Infill pattern</th>
<th>Print Speed (mm/s)</th>
<th>Fan cooling</th>
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</thead>
<tbody>
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<td>Room temperature</td>
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<td>3</td>
<td>20-100%</td>
<td>Rectilinear</td>
<td>15</td>
<td>N/A</td>
</tr>
</tbody>
</table>

2.3.4. Measuring residual fiber length distribution

The reinforcing capability of embedded GF is heavily dependent on its residual length. However, GF’s inherent brittleness often leads to its breakdown during mixing or extrusion processes [226]. To evaluate how the mixing and MEX printing impact the residual length of the embedded GF in both the filament and the printed composite parts, we recover the embedded GF using TGA (TA Q50) at 600° C for 4 hours, then dispersed in a small amount of distilled water for better observation. Images from the optical microscope (ZEISS Axio Vert.A1 Inverted Microscope) were processed with ImageJ software to analyze the length distribution of recovered GF.

2.3.5. Mechanical testing

To evaluate the impact of GF on mechanical properties, uniaxial tensile testing on of ASTM D1708 tensile bars printed in XY orientation (section 2.3.3) was conducted with an Instron 5984 Universal Testing System at a displacement rate of 1 mm/min. Seven tensile bars were printed and tested for each composition.

To determine the level of anisotropy in the mechanical properties of printed specimens, small tensile dog bones (10 mm gauge length and 3 mm neck width) from the printed single wall geometries along both X and Z directions as illustrated previously in Fig. 11. A smaller Instron machine (Instron 5500R) was used to account for the smaller punched tensile specimens.

2.3.6. SEM

In order to examine the GF dispersity and the quality of printed parts, both rPET/GF filaments and printed tensile bars were cryofractured with liquid nitrogen, then sputter coated with Cressington 208HR sputter before examined using a LEO (Zeiss) 1550 field-emission SEM.

2.3.7. Differential scanning calorimetry (DSC)

The crystallinity of printed ASTM D1708 tensile bars was measured using a differential scanning calorimetry (TA Q20). DSC Specimens were taken from the same position (indicated in Fig. 12) of each tensile bar and tested with a heating rate of 10° C/min. Crystallinity (X%) was calculated through the following equation:

\[ X\% = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \times V_{rPET}} \]  Eq. (1)
where $\Delta H_m$ and $\Delta H_{cc}$ are the area of the melting peak and cold crystallization peak, respectively. $V_{rPET}$ is the volume fraction of the rPET in the composite, which is calculated using a density value of 2.62 g/cm$^3$ [227] and 1.38 g/cm$^3$ for the density of the 183F short glass fiber and rPET, respectively. $\Delta H_f$ (120 J/g [228]) is the heat of fusion for 100% crystallized PET.

2.4. Results and Discussion

2.4.1. Filament fabrication and rheology testing

1.75 mm rPET/GF filament was made with Filabot EX2 filament extruder and a custom-made conveyer belt (installed with cooling fan). Fig. 13 shows the cryofractured surfaces of filaments with different GF loadings. Over the fractured surface, no bundles of GF were observed, indicating good compatibility between 183F short GF and the rPET matrix. In addition, it is observed that the GF are mostly aligned with the direction of filament extrusion, indicated by the protruding residual GF on the fracture surface. Overall, the fabricated rPET/GF filament is free of pores and consistent in diameter.

Fig. 13. Cryofractured surface of rPET/GF filaments with varying GF loading
To investigate the influence of GF addition on the rheological behavior of rPET, the shear viscosity of filaments with various GF loadings were measured at steady state, as shown in Fig. 14.

![Shear viscosity of each rPET/GF composition](image)

**Fig. 14. Shear viscosity of each rPET/GF composition**

For the low shear rate region (1 to 10 s\(^{-1}\)), all the samples demonstrated a Newtonian fluid behavior, as the shear viscosity remained almost constant versus the shear rate. Such a Newtonian behavior would suggest that the GF filler was well incorporated in the polymer matrix [229]. Adding fillers to the polymer matrix can effectively increase the material’s viscosity [229-231]. As seen in Fig. 14, the zero-shear viscosity for pure rPET is around 250 Pa·s, relatively lower than virgin PET (~700 Pa·s [186, 232]). It is observed that viscosity increased with GF loading; the viscosity nearly tripled (around 720 Pa·s) at 20 wt.% GF. Since the viscosity for pure rPET is relatively low, a higher extrudate viscosity from the incorporation of GF can increase the resistance against bead deformation and nozzle oozing, as well as improving the bridging performance in MEX printing [233].

As the shear rate increases, all specimens show a shear-thinning characteristic, which can be observed in the stress vs. shear rate diagram shown in Fig. 15.
At a shear rate above 20 s⁻¹, the slope of the stress curve for all samples starts to decrease, indicating a typical shear thinning behavior. Note that if the shear rate further increases above 50 s⁻¹, the samples will start to have gap failure in the rheometer (indicated by the decreasing of stress), so only data points between 20 s⁻¹ and 50 s⁻¹ are used to fit into the power law model. The power law index was calculated using the Oswald de Waele Power Law model:

\[ \tau = K \gamma^n \]  Eq. (2)

where \( K \) is viscosity constant, \( \tau \) is shear stress, \( \gamma \) is shear rate, and \( n \) is power law index. The fitted results for each composition are listed in Table 6.

**Table 6. Power law index calculated for each composition**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Power law index, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure UNIFI rPET</td>
<td>0.59</td>
</tr>
<tr>
<td>1 wt.% GF</td>
<td>0.45</td>
</tr>
<tr>
<td>3 wt.% GF</td>
<td>0.51</td>
</tr>
<tr>
<td>5 wt.% GF</td>
<td>0.26</td>
</tr>
<tr>
<td>10 wt.% GF</td>
<td>0.18</td>
</tr>
<tr>
<td>20 wt.% GF</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Generally, as the content of GF increases, the power law index decreases, which corresponds to GF enhancing the shear-thinning behavior of the material. Such results are intuitive as GF will significantly increase the viscosity of the composite material; however, when under the influence of shear flow, GF will gradually orient along the flow direction, which decreases viscosity.

2.4.2. 3D printing with rPET/GF composite filament

A custom-made MEX printer was used to print specimens with filaments from various GF loadings, as shown in Fig. 16. To further examine the quality of different rPET/GF filament printed parts, printed ASTM D1708 tensile specimens (Fig. 16 (b)) were cryofractured and examined under SEM (Fig. 17). Fig. 18 provides a magnified view of the fracture surfaces imaged in Fig. 17.

*Fig. 16. Test specimens printed with various GF loadings. (a): single layer geometry for anisotropy test. (b): ASTM D1708 tensile bars printed in XY orientation*
In Fig. 18, the triangular voids typical of MEX process are highlighted by the red circles. With a dimension around 35 μm; these voids originate from insufficient contact between adjacent printed roads due to the rounded rectangular cross-sectional shape of the printed road. In Fig. 17 and Fig. 18 it can be seen that all the fractured surfaces showed a typical ductile fracture characteristic. In addition, the fractured surface is generally dense and solid, with no evident debonding between printed layers.

It is also observed that, on the fracture surface, most of the glass fibers are oriented outwards. This is because, during both the filament extrusion and the printing process, the
material was forced to flow through a small orifice, during which the GF aligned with the
direction of the flow field. This gives rise to an anisotropy of reinforcement in the printed part,
which is further investigated in Section 3.4.

To demonstrate the printability of this rPET/GF composite, several other geometries were
printed, Fig. 19 a shows printed, pure rPET components of a fixed-wing autonomous air vehicle
specifically designed for on-site fabrication & deployment in resource-poor areas [234]. The
assembled drone and video of this aircraft in flight is included in the Supplementary
Information. In addition, parts printed with a variety of rPET/GF compositions are shown in Fig.
19 b to d including a small “strandbeest” (Fig. 19 b) and two micro-quadcopters (Fig. 19 c, d). In
general, all of the printed parts presented a surface finish and mechanical properties suitable
for part production.

Fig. 19. Various complex parts printed with rPET/GF filaments. (a). Components for a low-cost drone designed
by the Virginia Tech Unmanned Systems Laboratory [234]; (b). a small “strandbeest” [235]; (c) and (d). micro
quadcopter chassis [236, 237]
2.4.3. GF length distribution

Fig. 20 presents a comparison between the GF length distribution of filament and printed parts for different rPET/GF compositions.
Fig. 20. Distribution of residual GF length inside filament and printed parts
It is shown that for both filaments and printed parts, the largest portion of residual GF is all below 240 μm. This significant reduction in fiber length compared with the original length (4000 μm) is due to the multiple extrusion processes: the materials were first extruded from the twin screw extruder, extruded again with Filabot EX2 filament extruder, then extruded a third time during printing. This is reflected in Fig. 20, where the printed parts featured a smaller mean residual fibers length than those seen in the filament. This fiber length reduction is closely related to the printed part's macroscopic mechanical performance, which is explored in the following section.

2.4.4. Mechanical testing

The results of uniaxial tensile test of ASTM D1708 tensile bar printed in XY orientation with rPET/GF filaments at various GF wt.% are plotted in Fig. 21 and Fig. 22.

![Elastic modulus vs. GF content](image)
It is observed that the modulus of printed rPET/GF composites increased with GF content, and with 20 wt.% GF, the modulus is nearly doubled that of neat rPET (Fig. 21). Usually, the macroscopic properties of composite material are affected by factors including interfacial adhesion, shape, and orientation of dispersed phase [238, 239]. As seen in the SEM images of cryofractured surface (Fig. 17 and Fig. 18), the good dispersion and interfacial adhesion of GF inside the printed parts increases the material’s stiffness without causing a catastrophic loss in ductility (i.e., the printed tensile bars with 20 wt.% GF still showed a semi-ductile failure during the tensile test). The increase in tensile strength is limited compared with modulus due to the reduction of GF size reduction over the course of multiple extrusions.

According to the theory of Kelley and Tyson [219, 228, 240, 241], the critical fiber length $l_c$ for reinforcement is calculated as

$$\frac{l_c}{d} = \frac{\sigma_{fu}}{2\tau_y}$$

Eq. (3)

where $\sigma_{fu}$ is the ultimate fiber strength (3100 - 3800 MPa according to Owens Corning [242], here 3450 MPa is used) and $\tau_y$ is the interfacial shear strength (45 MPa for the perfectly bonded condition with PET [228]). Thus $l_c$ is calculated to be 421.6 μm. According to the fiber length distribution (Fig. 20), most of the fibers inside the filament (< 240 μm) are shorter than this calculated $l_c$ value. When fibers are shorter than the critical length, they tend to pull out
under tension rather than fracture; thus, the increase in ultimate tensile strength is not as significant.

As mentioned in Section 3.2, the orientation of the dispersed phase is another key factor that affects the composite’s macroscopic property. Inside the printed parts, the GF was well-aligned with the printing direction (Fig. 17 and Fig. 18), which leads to an increase in the anisotropy of the material.

Tensile test results for these tensile bars printed in different orientation are shown in Fig. 23 and Fig. 24. The tensile data from the XY orientation-printed multilayer ASTM D1708 tensile bars are included for comparison.

Fig. 23. Elastic Modulus vs GF content for punched tensile bars
As seen in Fig. 23, the modulus of X and Z oriented specimens were similar at lower GF concentration. As GF content increases, the difference in tensile modulus between two orientations gradually increases. Given that the GF inside the printed parts is oriented along the printing direction, it is reasonable that more GF will lead to increased anisotropy in modulus.

By comparing the tensile strengths of specimens in Fig. 24, it is also found that increasing the content of GF decreases the ultimate tensile strength in the Z direction, which corresponds to a decrease in interlayer adhesion. It is shown that when GF reinforced PET exits an orifice, the variation of wall shear rate can change the orientation of GF on the surface of the extrudates [243]. Wall shear rate can be calculated by:

$$\gamma_w = \frac{4Q}{\pi R_c^3}$$  \hspace{1cm} Eq. (4)

where $Q$ is the volumetric flow rate (estimated by 15 mm/s print speed $\times$ 0.2 mm layer height $\times$ 0.6 mm extrusion width). $R_c$ is the radius of the flow channel, taken to be the radius of the nozzle (0.6 mm). The calculated wall shear rate is thus 85 s$^{-1}$, under which condition, according to the literature [243], the GF will still orient parallel to the flow direction, rather than protrude out of the surface of the extrudates. In this scenario, the addition of GF decreases the contact area of rPET matrix between printed layers, which leads to a decrease in the interlayer bonding strength and results in the decrease of the ultimate tensile strength along the Z direction, similar findings have been reported in other works [216, 244].
2.4.5. Crystallinity of printed parts

Currently, almost all of the commercial off-the-shelf PET filaments are actually PET-G, which is molecularly modified to be amorphous. While PET itself is a semi-crystalline polymer, so is its recycled version: rPET. The crystallinity of semi-crystalline polymers has a large effect on its mechanical behavior. A low crystallinity PET or rPET is flexible and ductile, while higher crystallinity leads to brittle fracture under impact. To understand the influence of adding GF on crystallinity, DSC measurements were conducted on the printed ASTM D1708 tensile bars. The specimens for DSC were taken from the same position (refer to Section 2.7) on each tensile bar to make sure their data are comparable.

Fig. 25 is the measured crystallinity plotted versus the GF content (raw data included in the Supplementary Information Table A1). An overall decreasing trend is observed here, but the crystallinity data is scattered over a wide range. Literature has very contradictory findings on how GF affects the crystallinity of the PET/GF composites. Some report that the crystallinity of PET will decrease after incorporation of GF [230, 245, 246], while others found that increasing the content of GF actually increased the degree of PET’s crystallinity [231]. It seems more authors have found that GF will decrease the crystallinity of PET, which is in accordance with what is observed in this study. It is worth noting that, Reinsch and Rebenfeld reported that adding GF to PET will cause a decrease in crystallinity under isothermal crystallization condition [246], but when GF is added to PET matrix with additives like plasticizers or nucleating agents, the final crystallinity under isothermal crystallization will not be affected by the GF [247]. Although in a typical MEX process of a semi-crystalline polymer, the material goes through a non-isothermal crystallization process instead of an isothermal one, but the result from isothermal experiment still has certain reference value here. For rPET used in this study, it is very likely some of the recycled flakes will contain additives or some other unknown contaminant, thus, although a decreasing trend in crystallinity is observed, the data varies from batch to batch of rPET flakes, which causes a large deviation on each data points.
It is noted that the MEX printing conditions and specimen toolpath also have a large effect on the final appearance of the printed parts. Fig. 26 shows a series of 100 % infilled cones printed from a variety of GF concentrations at a printing speed of 15 mm/s without a cooling fan during printing.

Although GF did slightly decrease the crystallinity of rPET in this study (Fig. 25), GF is not considered to be a PET crystallization inhibitor. If an elevated temperature can be maintained during the process (such as additional of newly extruded molten material or insufficient convective cooling during printing), rPET/GF composite will still crystallize to the degree that the material shows a relatively brittle fracture under tension load rather than a ductile fracture. Usually for PET, this macroscopic transition in property is indicated by the appearance of white
color on the material. This can be observed in the upper portions of the printed cones shown in Fig. 26. This is observed as layering speed increases with shorter layer times associated with the shorter toolpaths at the top of the cones. At these shorter layer times, the previous layer does not have enough time to sufficiently cool down, so it continues crystallizing during the printing process. To make a more uniform print for this geometry, it might be necessary to apply a fan cooling and lift the printing nozzle after each layer to accelerate extrudate cooling; however, it is not yet clear how active cooling affects the interlayer bonding. We do not imply that the lower crystallinity form of rPET and its GF composites are better than the higher crystallinity one; however, a printed part with uncontrolled non-uniform properties is usually not desired. Thus, a topic of further study is how to precisely control the printing process of rPET (or virgin PET) and its composites to enable homogenous material properties throughout the printed shape.

2.5. Conclusions

In this study, the authors investigated the influence of GF on the material properties of rPET, its processability for MEX, and the mechanical properties of the resulting printed parts. It was found that GF significantly increased the viscosity of rPET. The composite was still printable at highest GF loading of 20 wt.%. The size of the GF filler reduces during the multiple extrusion process, which limits its performance in enhancing the ultimate tensile strength of printed parts; however, the increase in modulus with increasing GF was noteworthy. In addition, the tensile test of printed single layer specimens revealed that increasing the loading of GF will lead to an increase in the anisotropy of printed parts, due to a minor decrease in interlayer bonding strength. Overall, the rPET/GF composite showed both great printability and resultant mechanical properties. Several complex parts were successfully printed, including components for a low-cost drone that was designed for delivery and remote sensing applications in the developing world [234], (Fig. 19).

While the material has demonstrated remarkable printability (i.e., absence of warpage and good layer adhesion), it is noted that uneven cooling (due to uncontrolled printing environment and/or print time between layers) can cause different levels of crystallinity in the final part (e.g., Fig. 26). To further refine this approach, and to optimize printed rPET quality for all printed geometries, additional research in MEX heat transfer modeling, rPET crystallization kinetics, and novel MEX toolpath strategies is needed to precisely control the printing process.

2.6. Acknowledgement

This work is sponsored by SERDP (WP18-C4-1291). The authors would like to thank UNIFI® and Owens Corning® for the generous providing of materials. The authors acknowledge Moby Ahmed of Ambercycle Inc. for the collaboration.
2.7. Supplementary Information

**Fig. A 1.** DSC curves of rPET flakes provided by UNIFI Inc. (the bottom curve corresponds to the heating cycle and the top curve corresponds to the cooling cycle, both at a rate of 10° C/min)

**Fig. A 2.** rPET printed parts assembled in EcoSoar drone vehicle [234]
<table>
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<th>GF wt.%</th>
<th>volume percent of rPET, V_{PET}</th>
<th>cold crystallization peak, ΔH_{cc}</th>
<th>melting peak, ΔH_{m}</th>
<th>crystallinity%</th>
<th>average</th>
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3. Chapter 3

Material Extrusion Additive Manufacturing of Semi-crystalline Polymers: Exploring the Effects of Specific Area and Layer Time on Crystallinity and Mechanical Properties

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3.1. Abstract

Due to the shrinkage and poor adhesion during the printing of semi-crystalline polymers, most material extrusion additive manufacturing (MEX) feedstocks predominantly consist of amorphous polymers. As such, the process/structure/property (P/S/P) relationship for semi-crystalline polymers in MEX is less established than for amorphous polymers. Given that MEX processing introduces variable thermal histories during printing, the resulting crystallinity of a part can significantly vary across different printed parts, inhibiting MEX’s capability to consistently produce semi-crystalline parts with optimal performance. In this study, a typical semi-crystalline polymer, poly(ethylene terephthalate) (PET), is selected as the benchmark material for MEX processing to explore the P/S/P relationship of semi-crystalline polymers. Recognizing this relationship’s strong dependence on thermal history, the authors investigate two critical factors that influence thermal history during the MEX process: the part’s specific area (SA), which affects convective cooling efficiency, and the printing layer time (LT), which impacts the interlayer cooling. It is shown that a shorter LT, coupled with a smaller SA, extends the time at which the layer experiences elevated temperatures, thus leading to an increased crystallinity. Raman spectroscopy shows that, with intermediate and extended LTs, the crystalline domain in the previous layer forms before the deposition of the next layer and impedes the welding between layers and leads to decreased Z tensile strength. However, with a short LT, material can be deposited before significant crystallization of the previous layer occurs, resulting in improved Z tensile strength. Furthermore, higher crystallinity enhances both modulus and tensile strength along the X direction.

3.2. Introduction

3.2.1. Process/structure/property relationships of polymers in material extrusion additive manufacturing

Additive manufacturing (AM) has gained a significant attention over the past decade owing to its capability of free form fabrication. Material extrusion additive manufacturing (MEX), a modality of AM, utilizes thermoplastic filament feedstocks and deposits molten material layer-by-layer through a heated nozzle with a pinch roller mechanism. MEX is currently the most widely implemented form of additive manufacturing, particularly because of its affordability and scalable build envelope size. It offers a broad selection of commercial polymer feedstock materials that are suitable for various applications. In order to maximize the mechanical properties of the printed parts, and to enable the discovery of future materials, it is crucial to have a comprehensive understanding of the materials’ process/structure/property (P/S/P) relationships, which describes how MEX processing parameters affect the resulting microstructure and, ultimately, the performance of printed parts.

Polymer materials used in MEX can generally be categorized into two types: amorphous and semi-crystalline polymers. Amorphous polymers, such as ABS, are defined by their disordered molecular orientation, resulting in a glassy-like microstructure without a distinct melting point...
Semi-crystalline polymers, on the other hand, possess both crystalline and amorphous regions [249, 250]. The enhancement from the crystalline regions endows semi-crystalline polymers with benefits such as improved strength, toughness, controlled permeability and better resistance to chemicals and creep, etc. [249, 251, 252]. However, enabling the MEX printing of semi-crystalline polymers can sometimes be more challenging than amorphous polymers due to the higher risk of warpage and delamination caused by the crystallization during cooling following deposition.

The P/S/P relationships in MEX of amorphous polymers suggests that higher interfacial temperature and longer time above glass transition temperature ($T_g$) during printing leads to better welding between printed roads and layers, resulting in enhanced mechanical properties [253, 254]. Abbott et.al [255] used in-situ IR thermography to discover that the print speed and the layer height negatively affected the time above $T_g$, while the extruder temperature positively affected the time above $T_g$. Mechanical testing of the specimens showed that with longer time above $T_g$, the specimens exhibited better mechanical properties. Similar findings were also reported by Sun et.al [256], Yu et.al [213] and Tyagi et.al [257]. As such, for amorphous polymers in MEX, as long as the dimensional accuracy is maintained, it is always preferable to proceed the MEX process with elevated temperature to promote coalescence between print roads.

However, for semi-crystalline polymers, their P/S/P relationship is much more complicated due to the crystallization that occurs during the process. Collinson et.al [64] investigated the influence of chamber temperature on the weld strength of a single-layer geometry of printed PEEK. Mechanical testing showed significantly weaker bonding between layers in PEEK specimens printed with elevated chamber temperature. Such findings contradicted the results shown by amorphous polymers like ABS, and it was demonstrated that the development of crystallinity during the MEX process can impede the formation of bonding between layers [63, 258, 259]. Wang et.al [153] studied the influence of layer height and nozzle temperature on the resultant impact strength of a MEX part printed with polypropylene (PP). It was demonstrated that with different levels of layer height and nozzle temperature, the printed specimens formed different crystal morphology (a, β, β' crystals) and thus exhibited significantly different impact strength. Very similar results were also reported in a study of PP by Leng et.al [159].

These findings reveal the significant influence of various MEX printing parameters on printed semi-crystalline polymer’s microstructure, resultant crystallinity, and corresponding mechanical properties. However, one limitation of prior research in semi-crystalline polymers’ P/S/P relationships is that their experiments are based on a fixed geometry – typically a dog bone shaped tensile specimen or a single layer geometry. However, in MEX, when a different geometry is printed, even with the same set of parameters, the temperature profile of each layer during the printing process can be significantly different. Thus, conclusions generalized from a fixed geometry are not necessarily applicable when different geometries are printed. The research question of how MEX printing parameters and printed part geometry affect the in-
situ temperature profile, thus the development of crystallinity throughout the part, and consequently, the resultant mechanical property, remains unanswered.

3.2.2. Research questions and hypotheses

Addressing the aforementioned research question necessitates a clear understanding of the thermal behaviors involved in the MEX process, specifically how they are impacted by changes in the toolpathing time (represented by layer time, equals print time per layer) and part geometry (represented by specific area, equals surface area/volume). The research hypotheses formulated for this investigation are thus designed to delve into these relationships. By examining the heat dissipation efficiency affected by specific area (SA) and the peak temperature influenced by layer time (LT), these hypotheses will provide critical insights into how crystallinity and mechanical properties are developed during the MEX process. This approach not only assists in answering our main research question, but also paves the way for optimizing the MEX process for semi-crystalline polymers.

The first hypothesis follows the principle of heat transfer, where an expanded surface area of an object yields greater degree of interaction with its surrounding environment, thereby enhancing its heat dissipation efficiency. Based on this principle, it is hypothesized that an increased SA will facilitate more rapid cooling of the component during the MEX printing process.

The second hypothesis is rooted in the layer-by-layer fabrication method of MEX. This process allows the deposited material to cool down within the layer intervals. A shorter LT outputs more thermal mass per unit time and shortens the layer intervals allowed for cooling the materials. Importantly, this higher rate of material deposition combined with shortened cooling window, concentrates the thermal energy, leading to an increased peak temperature until the influence of re-heating from freshly deposited material diminishes due to sufficient layer build-up. This logic guides the second research hypothesis for this work: with a shorter LT, the peak temperature (the highest temperature in the printing process monitored by the IR camera) during the MEX process will be higher.

In the experimental work, specimens with different levels of SA and LT will be printed and the in-situ temperature profile will be monitored with IR camera to test the two research hypothesis. The resultant crystallinity will be correlated with the two process parameters (SA and LT), and mechanical test will reveal how MEX process-induced crystallinity influence the final part property.

3.3. Material and Methods

In this work, we address the research gap by selecting a typical semi-crystalline polymer: poly(ethylene terephthalate) (PET), as a benchmark material. The minimum hot crystallization (crystallize from melt) half time \( t_{1/2} \) of PET is approximately five minutes \[260\]. This contrasts with two other frequently studied semi-crystalline polymers in MEX: PLA and PEEK, which have
minimum crystallization half time of over 1000s [35] and ~1s [29], respectively. As a result of the extreme crystallization half times of PLA and PEEK — indicating very slow or very fast crystallization rates — their MEX resultant crystallinities are less sensitive to processing variables. In contrast, PET, with an intermediate crystallization rate, is hypothesized to offer a broader range of potential crystallinities during MEX processing, and by extension, a wider variety of mechanical properties.

Building upon the hypothesis surrounding PET's broader range of potential crystallinities in MEX processing, a comprehensive experimental framework was established to analyze the effects of varying process parameters and printed geometries on the mechanical properties of printed semi-crystalline polymers. Specifically, the authors designed several prismatic geometries with different levels of SA to be printed at various LT to represent the actual scenario of printing different geometries at different print speeds. The corresponding in-situ temperature profiles are monitored with an IR camera, and the resultant degree of crystallinity was evaluated using DSC. More importantly, the development of such crystallinity during the layer deposition process was investigated by using Raman spectroscopy on specimens that were printed and quenched at different process intervals. Finally, tensile specimens were cut from the printed geometries to evaluate the mechanical properties along both the X and Z directions. These experiments allow the synthesis of process (i.e. varying parameters and geometries), structure (i.e. via Raman spectroscopy), and property (i.e. via tensile testing) relationship of semi-crystalline polymers in MEX.

3.3.1. Design of specimens

In the experimental setup for this work, the design of the specimen must satisfy two criteria. First, given that IR thermography only captures the surface temperature of a layer, it is crucial to ensure that the temperature gradient beneath the surface is negligible. This ensures that the IR temperature accurately represents the entire layer. Second, under the same level of LT, to isolate the temperature profile (controlled by SA) as the sole variable influencing the development of crystallinity, the impact of strain-induced crystallization must be consistent for each specimen. In other words, given a fixed level of LT, differences in the material’s shearing history during the printing processes should be negligible for each specimen.

The first criterion is accomplished by a lumped-capacity assumption, which has been used in prior MEX research [261-265]. Under a lumped-capacity hypothesis, the temperature gradient inside the body is small enough to be ignored so that the temperature profile can be assumed to be uniform across the characteristic dimension. For the lumped-capacity approximation to be accurate, a group of dimensionless number called Biot number (Bi) needs to be small, usually ≤ 0.1 [266]:

\[
Bi = \frac{hL}{k}
\]
\[ Bi = \frac{h(L/2)}{k} \]  
\[ \text{Eq. 5} \]

In Eq. 5, the \( h \) is the convective heat transfer coefficient, \( L \) is the thickness of the geometry, and \( k \) is the thermal conductivity of the material. With the estimated value of \( h = 11.5 \text{ W/m}^2 \) and \( k = 0.15 \text{ W/m·K} \) [267] (Supplementary Information), the maximum value of \( L \) satisfying \( Bi \leq 0.1 \) is calculated to be 2.6 mm. Referring to the thickness indicated in Fig. 27, it is obvious that all of the designed specimens meet the lumped capacity assumption.  

![Fig. 27. Dimensions of the four designed prismatic geometries and corresponding infill toolpath during printing](image)

The second criterion is accomplished by designing each specimen such that the cross-sectional (i.e., layer) area (width*thickness) is roughly consistent across all specimens, as illustrated in Fig. 27. This design consideration ensures a similar infill area across all specimens. As a result, the actual print nozzle speed remains the same for all specimens at the same level of LT. Crucially, maintaining the same print nozzle speed across all specimens under the same LT ensures that all specimens undergo the same extrusion shear history. This eliminates the influence of strain-induced crystallization across different specimens printed at the same level of LT.

### 3.3.2. Filament fabrication and printing of specimens

The virgin PET pellets (PolyQuest PQB7-080, with an intrinsic viscosity of \( 0.80 \pm 0.02 \text{ dL/g} \) and \( T_g = 75^\circ \text{C} \)) were kindly provided by PolyQuest Inc. Before further processing, the PET pellets were first vacuum dried overnight at 130° C to remove any absorbed moisture.

A Filabot EX2 desktop extruder together with a custom-made conveyer belt were applied to extrude the dried PET pellets into 2.85 mm filament. For this work, an Ultimaker3 MEX printer was used. In order to maintain the natural convection heat transfer condition during printing, the cooling fan power was set to 0%. In addition, both of the cooling fan ducts were sealed by Kapton tape to block any possible leaking air flow from the front axial fan.

To accomplish the designated layer times (LT = 3, 6 and 9 seconds), the “Minimum Layer Time” setting in the Cura slicing software was employed. In this approach, the minimum layer time was first adjusted to match the planned LT value, and then the print speed in Cura was set to an extreme value (400 mm/s), which enabled the software to automatically reduce the
actual print speed in order to meet the minimum layer time requirement. This method ensures that the time taken to print each layer exactly matches the target minimum layer time.

Other relevant printing parameters are summarized in Table 7, and the actual print speed corresponding to each levels of LT are summarized in Table 8.

**Table 7. Printing parameters for the designed geometries**

<table>
<thead>
<tr>
<th>Nozzle temperature (°C)</th>
<th>Bed temperature (°C)</th>
<th>Minimum layer time setting (sec)</th>
<th>Layer Thickness (mm)</th>
<th>Infill density</th>
<th>Fan cooling</th>
<th>Infill pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>275</td>
<td>Non-heated</td>
<td>3, 6, 9</td>
<td>0.2</td>
<td>100%</td>
<td>0%</td>
<td>concentric</td>
</tr>
</tbody>
</table>

**Table 8. Levels of layer time (LT) and the corresponding actual print speed**

<table>
<thead>
<tr>
<th>Layer Time (LT)</th>
<th>“Minimum layer time” set in Cura software (sec)</th>
<th>Actual print nozzle speed (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s – short LT</td>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>6s – intermediate LT</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>9s – extended LT</td>
<td>9</td>
<td>27</td>
</tr>
</tbody>
</table>

**3.3.3. IR in-situ temperature recording**

The in-situ temperature evolution of the designed specimens was tracked throughout the MEX printing process using an IR camera (Micro-Epsilon/TIM640). To facilitate this monitoring, a custom-designed IR camera holder was mounted to the left side of the print bed (as illustrated in Fig. 28a), thereby positioning the IR camera to focus on the central area of the parts under fabrication (as illustrated in Fig. 28b).
Fig. 28. In-situ monitoring of temperature evolution of print: (a) location of IR camera, (b) example snapshots from in-situ temperature monitoring video at different times, temperature values taken from the cross pointer location

3.3.4. Differential scanning calorimetry (DSC)

To evaluate the degree of crystallinity of the printed parts, samples of mass around 5 -10 mg were taken from the center of the printed geometries (as illustrated in Fig. 29). Differential scanning calorimetry (DSC) scans from 10 to 270° C were performed on a TA Instrument DSC Q2000, with a ramp heating rate of 10° C/min.

Fig. 29. DSC sampling site (highlighted in red) for the printed geometries

The degree of crystallinity was calculated based on Eq. 6:

\[ X\% = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f} \]  

Eq. 6

Where \( \Delta H_m \) and \( \Delta H_{cc} \) is the area of the melting peak and cold crystallization peak, respectively, and \( \Delta H_f \) is the heat of fusion for 100% crystallized PET. In this study, a \( \Delta H_f \) value of 120 J/g is used [228].
3.3.5. Raman spectroscopy

A HORIBA XploRA™ PLUS Raman spectrometer was used to study the development of crystallinity during layer deposition. To prepare the specimens for Raman, the print was first stopped at approximately 60% of completion as illustrated in Fig. 30a. Immediately upon stopping the print, the few uppermost layers were rapidly quenched using cold compressed air to prevent the material’s further crystallization (Fig. 30a). After cold air quenching, specimens were cut in half across layers with an Allied TechCut 4™ low speed saw at a speed of 400 rpm (Fig. 30b). Raman spectroscopy was then performed with the mapping function on two locations on the exposed cross section (i.e., the top three layers and another three consecutive layers located further down in the middle, Fig. 30c). The quenched top layers served to represent the material’s “as deposited” state, while the bulk layers further down in the middle represent the material’s “final” state after the completion of the print. Raman intensity data were collected with Raman shift from 1040 to 1220 cm$^{-1}$.

Fig. 30. Preparation of specimens for Raman spectroscopy

3.3.6. Mechanical testing

To investigate the resultant mechanical properties along both the Z and X directions, tensile specimens (dimensions illustrated in Fig. 31) were cut from the printed geometries using a WAZER™ desktop waterjet cutter to avoid sample heating. Tensile testing was completed with an Instron 5984 Universal Testing System at a displacement rate of 1mm/min.

Fig. 31. Dimensions (in mm) for the tensile specimen
3.4. Results and Discussion

3.4.1. In-situ temperature profile measurements

The recorded in-situ temperature profile of specimens with different SA and printed under different levels of LT are summarized in Fig. 32 and Fig. 33.

Across all levels of LT (Fig. 32), the temperature of the specimens with a larger SA is consistently lower than the specimens with a smaller SA throughout the process. This pattern indicates a more efficient convective cooling due to the larger SA, thus verifying the first research hypothesis (Section 3.2.2).
Fig. 33. In-situ temperature profile from specimens with different SA (a) SA = 1.07, (b) SA = 1.72, (c) SA = 2.54, (d) SA = 3.37

Fig. 33 plots the temperature profiles from Fig. 32 for comparison based on different levels of LT. Under the same SA, the peak temperature (or highest temperature) of each IR temperature curve is lower for those with a larger LT than a smaller LT, which supports the second research hypothesis (Section 3.2.2). This trend is most prominent for the specimens with smaller SA. As a specimen’s SA increases, the convective cooling efficiency is enhanced significantly, which makes the difference in peak temperature less noticeable.

Interestingly, while a shorter LT results in a higher peak temperature, it also induces faster cooling, as indicated by the steeper slope at the initial stage and the lower temperature at the later stage of the printing process. One potential explanation for this observation is depicted in Fig. 34: with a shorter LT, although more thermal mass was initially deposited, the printer’s hot end rapidly ascends away from the monitored layer, leading to less radiation heat transfer from the hot end. Conversely, an extended LT results in the opposite situation, with accumulated radiation heat transfer causing a slightly slower cooling rate and subsequently a higher...
temperature at the later stage. Similar findings have been reported by Abbott et.al [255], where a faster print speed eventually leads to a faster cooling rate in a vertical print.

Fig. 34. Influence from the hot end on cooling under smaller and larger LT (a) under short LT, layers build up quickly with less accumulated radiation heat during cooling phase. (b) under extended LT, layers build up slowly with more accumulated radiation heat during the cooling phase

Considering the process as a whole, a short LT offsets the higher starting peak temperature with a more rapid cooling rate. Taking “time above $T_g$” as a metric of crystallizable time window, Fig. 33 reveals that, across all levels of SA, the time above $T_g$ under different LT are relatively similar ($T_g \approx 75^\circ C$ for PolyQuest®080 PET). This similarity suggests that the influence of LT on crystallinity is much less significant than that of SA, as explored in Section 3.4.2.

3.4.2. Resultant crystallinity of the printed parts

As demonstrated in the previous section, varying levels of SA and LT can induce differences in thermal history, and potentially lead to varying degrees of crystallinity in semi-crystalline polymers. Fig. 35 plots specimens of different SA and LT levels against their respective degrees of crystallinity as measured by DSC. As the filament used in this experiment is custom made, the slight variation in diameter can introduce a variation in the flow rate during extrusion. Consequently, the SA of the printed geometry may not precisely match the intended designed. To account for this discrepancy, Fig. 35 utilizes the actual printed SA value (calculated based on measured dimensions) for plotting instead of the designed values.
Fig. 35. Measured Crystallinity vs. SA and LT. Legend corresponds to crystallinity %.

Moreover, as currently there’s no established mathematical foundations which describe the relationship between crystallinity, SA, and LT, a second order polynomial fit was employed here. The high $R^2$ value (Table 9) builds confidence of the response surface presented in Fig. 35. It should be emphasized that the fitted model is strictly applicable only within the plotted region and should not be extrapolated beyond this scope.

Table 9: Crystallinity data fitting parameters and results

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>Z0</td>
</tr>
<tr>
<td>Fitted values</td>
<td>50.7791</td>
</tr>
</tbody>
</table>

In Fig. 35, it can be seen that the influence from SA on the resultant crystallinity significantly outweighs that of the LT. The reason of such differences originates from how varying SA and LT influence the in-situ temperature profile (Section 3.4.1). For each LT level, a change in the part’s SA can significantly alter a part’s convective cooling efficiency during the process (Fig. 32), thereby leading to a wide spectrum of achievable crystallinity. However, within a fixed SA, although a shorter LT initially creates a higher peak temperature, this higher temperature is subsequently counterbalanced by a faster cooling rate, thus making the influence of LT on the resultant crystallinity less significant compared to that of SA. Overall, the MEX of PET can yield a broad range of resultant crystallinity with different levels of SA and LT.
3.4.3. Crystallinity development during the MEX process

As previously mentioned, the crystalline region of an already printed layer can hinder the entanglement of the polymer chain, and cause a decrease in interlayer adhesion [64]. Therefore, optimal printing involves completing layer deposition before the majority of the previous layer has crystallized, thereby facilitating polymer chain entanglement across the layer interface [63]. To evaluate the development of crystallinity during layer deposition, we characterize a cold air quenched sample with Raman spectroscopy.

Fig. 36. Illustration of Raman mapping with micrograph from a specimen with SA = 1.07 (thickness 2 mm) under LT = 9 sec (extended LT)
Fig. 36 illustrates the Raman mapping function applied in this work. Basically, the top three layers (quenched with cold air after deposition) and another three bulk layers positioned at the middle of the specimen were probed by Raman spectroscopy with Raman shift ranging from 1040 to 1220 cm$^{-1}$. For PET, it has been reported that the more crystalline sample exhibits two peaks at approximately 1095 cm$^{-1}$ and 1120 cm$^{-1}$, while the amorphous sample shows only one peak at ~1120 cm$^{-1}$ [268, 269]. Examining the relative intensity of these two peaks allows the quantitative determination of relative crystallinity at the particular location on the specimen.

As shown in Fig. 36, a total of 50 mapping points across the three layers were probed to capture potential crystallinity variations within the layer. The results revealed that the relative intensity of the two peaks within each layer remained largely consistent, indicating that the degree of crystallinity within each layer does not vary significantly. Consequently, Fig. 37 only displays one representative Raman spectrum for each layer. Across all the spectrums for the three bulk layers (Fig. 37d, e and f), both peaks at ~1095 cm$^{-1}$ and ~1120 cm$^{-1}$ can be clearly

![Typical Raman spectrums for the specimen with SA = 1.07 (thickness 2 mm) under LT = 9 sec (extended LT)](image-url)
seen, indicating a higher degree of crystallinity for these bulk layers. However, for the air quenched top layer (Fig. 37a), only one peak at about 1120 cm\(^{-1}\) is seen, indicating that this first layer is relatively amorphous after deposition. For the second and third layers (Fig. 37b, c), the presence of two peaks at approximately 1095 cm\(^{-1}\) and 1120 cm\(^{-1}\) indicates a higher degree of crystallinity.

In this example, it is known that the printed parts eventually reached a high crystallinity, as observed in the Raman results from the bulk layers. The nearly amorphous nature of the first layer indicates that the newly deposited molten material doesn’t initiate crystallization immediately upon deposition. However, the simultaneous high crystallinity of the second and third layers implies that this “newly deposited” first layer is welding against an underlying crystalline layer, a condition less ideal for promoting interlayer adhesion. We mark this specific scenario as “crystallization > deposition”, which corresponds to significant crystallization of the previous layer has occurred before the deposition of the subsequent layer (the opposite scenario is marked as “crystallization < deposition”, meaning significant crystallization of previous layer has not occurred at the deposition of the subsequent layer). The crystallinity development across layer deposition for other specimens are summarized in Table 10, and the mechanical properties corresponding to these scenarios are presented in Section 3.4.4.

**Table 10. Summary of crystallinity development across layers for all specimens**

<table>
<thead>
<tr>
<th>Layer Time (LT)</th>
<th>Specific Area (SA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.07 (thickness 2 mm)</td>
</tr>
<tr>
<td></td>
<td>1.72 (thickness 1.2 mm)</td>
</tr>
<tr>
<td></td>
<td>2.54 (thickness 0.8 mm)</td>
</tr>
<tr>
<td></td>
<td>3.37 (thickness 0.6 mm)</td>
</tr>
<tr>
<td>3 sec</td>
<td>crystallization &lt; deposition</td>
</tr>
<tr>
<td></td>
<td>crystallization &lt; deposition</td>
</tr>
<tr>
<td></td>
<td>crystallization &lt; deposition</td>
</tr>
<tr>
<td></td>
<td>low crystallinity**</td>
</tr>
<tr>
<td>6 sec</td>
<td>crystallization &gt; deposition</td>
</tr>
<tr>
<td></td>
<td>crystallization &gt; deposition</td>
</tr>
<tr>
<td></td>
<td>low crystallinity</td>
</tr>
<tr>
<td></td>
<td>low crystallinity</td>
</tr>
<tr>
<td>9 sec</td>
<td>crystallization &gt; deposition</td>
</tr>
<tr>
<td></td>
<td>crystallization &gt; deposition</td>
</tr>
<tr>
<td></td>
<td>low crystallinity</td>
</tr>
<tr>
<td></td>
<td>low crystallinity</td>
</tr>
</tbody>
</table>

** low crystallinity stands for the scenario in which the entire part came out nearly amorphous after printing due to fast convective cooling when SA is large enough.

3.4.4. Mechanical property characterization

Mechanical tensile tests of waterjet cut samples (Fig. 38) were performed to evaluate the mechanical properties of specimens with different levels of SA printed under different levels of LT. To correlate the specimen’s mechanical properties with estimated degree of crystallinity, the real SA values (calculated from the measured dimensions of the specimens) together with the corresponding LT are substituted into the fitted polynomial function (Section 3.4.2).
Mechanical properties were evaluated in both the Z and X directions. The Z direction allows for the assessment of interlayer adhesion across different specimens. Additionally, comparing the Z direction properties against those in the X direction allows for a qualitative estimation of the anisotropy. Because the influence of LT on crystallinity is minimal compared with influence from SA (Section 3.4.1), the mechanical properties are all plotted against varying SA for each level of LT to provide a better visualization.
Fig. 39. Z direction modulus of specimen under different LT and SA. (a) LT = 3 sec, (b) LT = 6 sec, (c) LT = 9 sec

Fig. 39 shows the modulus of the Z specimens plotted together with the degree of crystallinity, estimated based on corresponding SA and LT values. As can be seen in Fig. 39, across all levels of LT, a part’s Z modulus and crystallinity generally exhibit a coherent increasing trend with decreasing SA. However, at very low SA, the modulus eventually levels off at around 1400 MPa despite an increased crystallinity.
While the modulus in Fig. 39 displayed a monotonic increasing trend, the ultimate tensile strength along the Z direction (Fig. 40) showed a more complicated trend. Under the two relatively larger LT (6 and 9 sec; Fig. 40 b and c), it was found that the UTS of Z samples with a smaller SA are lower than those with a larger SA; i.e., the crystallinity and UTS present an opposite trend under LT 6 and 9. Reflecting on the temperature profiles presented in Section 3.4.1, smaller SA specimen’s temperature history during printing is hotter, and yet these small SA specimens formed weaker interlayer adhesion compared with larger SA specimens. Such finding is quite opposite to what’s established for amorphous polymers (e.g. ABS etc.), where it is shown that a hotter interface temperature promotes welding of the interface and increases UTS across the layer.

At short LT (3 sec), this trend is reversed: the UTS along Z direction tends to increase with the decreasing SA. This phenomenon can be rationalized with the insights obtained from Raman spectroscopy (Section 3.4.3). First, under the two larger levels of LT (6 and 9 sec), significant crystallization occurred at smaller SA values before the deposition of the next layer.
(Table 10), thus the crystalline domain of the previous layer impeded the diffusion and entanglement of the polymer chain from the subsequent layer, leading to weakened interlayer adhesion. However, if the printing process is conducted at sufficient high speed, i.e., $LT \leq 3$ sec, the layer deposition outpaces the major crystallization of the previous layer underneath, leading to improved interlayer adhesion.

This observation suggests that, in MEX printing of semi-crystalline polymers, the crystallization process and the layer deposition process are competing, and there exists a critical LT threshold for enhancing the interlayer adhesion. For LTs below this threshold, it may be beneficial to increase the cooling efficiency (e.g., design part’s with larger SA or increasing the cooling fan power) to print parts with reduced final crystallinity, as this may lead to an improvement in interlayer adhesion.

Fig. 41 and Fig. 42 show the measured modulus and UTS along the X direction, respectively. Similar to the Z direction, the X direction modulus increased with the degree of crystallinity and eventually levels off at approximately 1400 MPa. Since the UTS along the layer (i.e., X direction) is not affected by the interlayer adhesion, it also showed a coherent increasing trend with the degree of crystallinity, which is in accordance with previous literature [24].
Fig. 41. Modulus of each specimen along the X direction. (a) LT = 3 sec, (b) LT = 6 sec, (c) LT = 9 sec
By comparing the modulus between X and Z specimens, it is revealed that the printed specimens display nearly isotropic modulus values (Fig. 43 a, b and c). However, the tensile strength of the specimens is highly anisotropic (Fig. 44 a, b and c), with the X direction UTS approximately twice of the Z direction. Interestingly, it was found that reducing the LT does not reduce this anisotropy. This could potentially be attributed to the orientation of the polymer chain or crystalline domain as influenced by the extrusion process. Quantifying the orientation of the polymer chain vis WAXS/SAXS is outside the scope of the current work, and will be considered for future investigation.

Fig. 42. UTS of each specimen along the X direction. (a) LT = 3 sec, (b) LT = 6 sec, (c) LT = 9 sec
Fig. 43. X and Z modulus comparison. (a) LT = 3 sec, (b) LT = 6 sec, (c) LT = 9 sec
3.5. Conclusion

To explore the P/S/P relationships of semi-crystalline polymers in MEX, various studies have delved into the impact of print parameters on the properties of MEX printed semi-crystalline polymer parts. One notable limitation of these prior works is their focus on fixed geometries, such as Type I tensile specimen. This limitation restricts the applicability of their findings from being applied in printing other different geometries. In order to address this gap, this work extends beyond these prior studies by not only considering the influence from print layer times (LT), but also the part geometry, specifically, variations in the part’s specific area (SA).

Utilizing IR thermography, by monitoring the printing process across various specimens with different levels of SA and LT, this study validated the research hypotheses that: first, an increase in SA enhances the part’s cooling efficiency, leading to a lower in-process temperature. Second, a shorter LT concentrates the thermal mass, resulting in higher peak temperatures in the printing process. Interestingly, a shorter LT also triggers a higher cooling rate, potentially
due to the reduced accumulation of radiative heat transfer from the hot end in the quick printing process.

The printed specimens’ crystallinities were evaluated using DSC, demonstrating that by adjusting the levels of SA and LT, a wide range of crystallinity outcomes for PET can be achieved in MEX. Specifically, a larger SA significantly reduces crystallinity, while the impact of LT is less significant in comparison, with a shorter LT only slightly increase the final crystallinity.

Another critical finding from this work is that crystallization appears to hinder the development of interlayer adhesion. Through examining the evolution of relative crystallinity with Raman across layer deposition and correlating this with mechanical testing data, we conclude that either efficient cooling or an extremely small LT is needed to facilitate material deposition prior to the crystallization of the underlying layer, thereby enhancing the interlayer adhesion in MEX of semi-crystalline polymers.

3.6. Acknowledgement

The author acknowledges the company PolyQuest for kindly providing the materials.
3.7. Supplementary information

Natural convection heat transfer coefficient is estimated with Eq. 7:

\[ h = \frac{Nu \times k_{\text{air}}}{D} \]

\[ \text{Eq. 7} \]

where \( Nu \) is the Nusselt number, \( k_{\text{air}} \) is the thermal conductivity of the air, and \( D \) is the characteristic dimension. Here, \( D \) equals the height of the vertical slab specimen.

Nusselt number is estimated by Eq. 8:

\[ Nu = \begin{cases} 
0.59Ra^{1/4} & 10^4 < Ra < 10^9 \\
0.1Ra^{1/3} & 10^9 < Ra < 10^{13} 
\end{cases} \]

\[ \text{Eq. 8} \]

Where \( Ra \) is the Rayleigh number, estimated by Eq. 9:

\[ Ra = Gr \times Pr \]

\[ \text{Eq. 9} \]

Where \( Gr \) is the Grashof number, estimated by Eq. 10:

\[ Gr = \frac{D^3 \times \rho^2 \times g \times \Delta T \times \beta}{\mu^2} \]

\[ \text{Eq. 10} \]

Where \( \Delta T \) is the difference in temperature between the specimen (\( T_{\text{specimen}} \)) and the environment (\( T_{\text{env}} \)). \( \rho \) is the fluid's (i.e., air in this work) density, based on the air film temperature (\( T_{\text{film}} = (T_{\text{specimen}} + T_{\text{env}})/2 \)). \( g \) is the gravitational acceleration. \( \mu \) is the viscosity of the air, also based on the air film temperature. \( \beta \) is the volume expansion coefficient, for ideal gas, \( \beta = 1/T_{\text{film}} \).

\( Pr \) is the Prandtl number, estimated by Eq. 11:

\[ Pr = \frac{\mu \times C_p}{k} \]

\[ \text{Eq. 11} \]

Where \( C_p \) is the heat capacity of the air based on the air film temperature.

All the values of these parameters are summarized in Table 11:

\textit{Table 11. Parameters and corresponding values used for estimating } h

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D )</td>
<td>0.05</td>
<td>m</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
<td>Unit</td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>g</td>
<td>9.81</td>
<td>m/s²</td>
</tr>
<tr>
<td>( T_{\text{specimen}} )</td>
<td>543.15</td>
<td>K</td>
</tr>
<tr>
<td>( T_{\text{env}} )</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>( T_{\text{film}} )</td>
<td>420.65</td>
<td>K</td>
</tr>
<tr>
<td>( \rho )</td>
<td>0.839</td>
<td>kg/m³</td>
</tr>
<tr>
<td>( \beta )</td>
<td>0.0024</td>
<td>1/K</td>
</tr>
<tr>
<td>( \mu )</td>
<td>23.7×10⁻⁶</td>
<td>Pa·s</td>
</tr>
<tr>
<td>( C_p )</td>
<td>1.017×10³</td>
<td>J/kg·K</td>
</tr>
<tr>
<td>( k_{\text{air}} )</td>
<td>34.84×10⁻³</td>
<td>W/m·K</td>
</tr>
</tbody>
</table>

With the above parameters, the natural convection coefficient is estimated to be 11.5 W/m²·K. This estimated value is of the same magnitude to literature values with good fit to the experimental data [261, 270, 271]. With \( h = 11.5 \text{ W/m}^2\cdot\text{K} \) and \( k_{\text{PET}} = 0.15 \text{ W/m}·\text{K} \), the maximum thickness \( L \) satisfying \( \text{Bi} \leq 0.1 \) is calculated to be 2.61 mm (Section 3.3.1). Given the maximum thickness of the designed specimens is 2 mm, it is concluded that the designed specimens meet the lumped capacity assumption.
4. Chapter 4

Validating a 3D Heat Transfer Model for Material Extrusion Additive Manufacturing via In-situ Thermography

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4.1. Abstract

The thermal history a polymer experiences during material extrusion additive manufacturing (MEX) significantly impacts interlayer adhesion, crystallinity, and final bead shape. Given the complex interactions and impacts of print parameters, toolpath, and part geometry on material's thermal history, many thermal models to predict MEX process/structure/property (P/S/P) relationship have been proposed. However, the vast majority of these models are relatively simplistic 1D or 2D models. Although they have been shown to accurately predict transient thermal behaviors of single-walled geometries, they fail to capture the effects of 3D part geometry or inter- and intra-layer interactions. Capturing the temperature evolution during the printing process for a more complex 3D object requires a full 3D heat transfer model. Unfortunately, the prediction accuracy of current 3D models has not been thoroughly assessed, as these studies solely focus on improving the computational efficiency of the algorithm. Thus, to address this gap, a 3D heat transfer model capable of directly parsing the printing toolpath file (e.g., gcode) is constructed. This model is then validated by comparing its predicted temperature profile against experimental infrared (IR) thermography for a variety of 3D geometries. Our investigation has revealed two previously unreported challenges that still hinder 3D MEX models from producing accurate temperature predictions, namely, the accurate determination of the convective heat transfer coefficient, and the assignment of distinctively different boundary conditions for different surfaces of the same part. Moreover, our model assessment indicates that the inclusion of active cooling during the printing process mitigates the influence of such challenges, and improves the agreement between model prediction and the experimental data.

4.2. Introduction

Material extrusion additive manufacturing (MEX), commonly known as fused filament fabrication (FFF) or fused deposition modeling (FDM), is the most prevalent form of additive manufacturing [272-281]. MEX creates intricate and customized parts layer by layer through the deposition of molten thermoplastic polymers. The MEX printing process typically imparts a significant non-isothermal characteristic on its deposited materials with large thermal gradients, resulting from the rapid heating, cooling, and intermittent re-heating of the materials as they are extruded and solidified [7, 167, 281-285]. These imposed temperature gradients, and the overall thermal history experienced by the material, determine the final quality of the printed parts, including mechanical strength, dimensional accuracy, surface quality, and, specifically for semi-crystalline polymers, the degree of crystallinity [45, 195, 255-257, 286-290]. To better understand and control the impact of thermal history on resultant part quality, accurate heat transfer modeling is essential. By providing a comprehensive understanding of the temperature profiles and gradients, such models could enable researchers and engineers to correlate the thermal history with the part’s final properties. Identifying the critical process parameters and the polymer's corresponding process-structure-property (P/S/P) relationship ultimately leads to improved part performance and reduced manufacturing defects.
Existing literature presents various heat transfer models for MEX, ranging from relatively simple to complex. Among these models, the simplest and least computationally expensive form is the 1D model, which only accounts for the processing thermal gradient in one direction, typically the build direction (i.e., the Z direction). In a typical 1D model, each layer is assumed to be deposited as a whole solid uniform layer, with a time interval between the deposition of layers equal to the actual time for printing each specific layer [291, 292]. To initiate the heat transfer calculation, surfaces exposed to the surrounding environment are assigned with a convective and radiational (if not ignored) cooling boundary condition, while surfaces in contact with other layers are assigned with a conductive boundary condition.

To date, 1D models have been applied by various authors for understanding the process/structure/property (P/S/P) relationship of different polymers. For instance, Basgul et.al [261] investigated a 1D heat transfer model and validated the model prediction with the infrared (IR) temperature data collected during the printing of a 10 × 10 × 10 mm³ cube geometry with polyetheretherketone (PEEK). The model predictions were found to be closer to the experimental data for the mid-layers of the cube, while significant under-prediction and slightly over-prediction were reported for the bottom and top layers, respectively. The authors attributed the under-prediction at bottom layers to a potentially higher actual bed temperature in the print area than the value used in the model, while the over-prediction at the top layers resulted from the accumulation of errors from all the underlying layers. More importantly, the simulated results from the 1D heat transfer model were further coupled with a non-isothermal healing model to investigate the influence of printing thermal history on the degree of interlayer welding. Results highlighted that the model helped to identify insufficiently healed layers within the PEEK part built by MEX.

Generally, 1D heat transfer model offer a basic understanding of temperature evolution in the MEX process. While these models are very simple, computationally efficient, and capable of providing some initial insights, they are limited in their ability to capture the complexity of temperature evolution during the MEX process. To overcome the limitations of the 1D model, other researchers have investigated 2D heat transfer models that consider temperature variations and heat flow in two dimensions [265, 293]. The majority of 2D models continue to operate under the previous assumption in the 1D model, that each layer is deposited as a whole entity [265, 293]. However, instead of treating the layer using a lumped capacitance model, thermal gradients along the layer cross section are incorporated in 2D models. For instance, Pooladvand et.al [294] constructed a 2D heat transfer model simulating the printing process of a cylindrical test specimen. It was reported that the 2D model effectively captured the temperature gradient from the inside of the specimen towards the outside, and provided decent agreement between the simulated and the experimental temperature profile. In addition to its utility in desktop-scale MEX, the application of a 2D heat transfer model is particularly well-suited for scenarios involving Big Area Additive Manufacturing (BAAM). Given the significant temperature gradients observed in the cross-sectional area of the BAAM deposited print road, a 2D model is necessary to accurately capture these complex thermal
characteristics. Owens et.al [295] presented a scalable 2D model for simulating both desktop and BAAM-scale MEX. Utilizing a two-dimensional implicit numerical strategy, their model effectively reduced the required computational cost while offering decent agreement with the experimental data.

Obviously, compared with 1D model, the 2D models offer a more detailed representation of the temperature profiles and gradients within the MEX process, enabling a better understanding of the thermal behavior of materials during printing. However, 2D models still lack the capability to fully capture the intricacies of the thermal interactions and complex geometries resulting from the complex toolpathing strategies in most MEX processes. This necessitates the development of 3D heat transfer models for a comprehensive understanding of the process. Currently, in terms of constructing a 3D model, the two most recognized difficulties are: 1) The model needs to comprehend the toolpathing strategy specified by the machine code, i.e., the model should understand how the part is planned to be printed and 2) the model needs to be computationally efficient. The computational cost for a full-scale 3D model is significantly larger than the most common 1D and 2D models. If the model simulation time is orders of magnitude longer than the actual print time, the modeling approach might quickly become less practical than just directly printing the part and subsequently updating/optimizing the parameters accordingly.

Compared to the aforementioned 1D and 2D heat transfer models, the number of reported works regarding a full-scale 3D model are significantly fewer due to these existing challenges. Zhang et.al [296, 297] proposed a unique 3D heat transfer simulation method for MEX, in which the part to be printed is discretized into small elements along the specified nozzle toolpath. By applying an “active body” approach (assuming that the re-heating effect is limited to a certain range near the freshly deposited material), the model achieved linear time complexity, thus significantly reducing the computational cost for simulating the MEX process of a real 3D part with complex geometry. Bhandari et.al [298] proposed another 3D model based on meshing where each meshed element is activated chronologically based on the g-code specified toolpath. Similarly, their work also applied an “active body” approach to improve computational efficiency. Results demonstrated that this approach can be 300-500 times faster than the conventional finite element method. Besides the “active body” approach, other methods for improving the computational efficiency, such as artificial neural network [299, 300] have been proposed with promising improvement. Unfortunately, even though these 3D models improved the computational efficiency together with the capability of toolpath-recognition, the aforementioned works did not validate the model predictions against real experimental data. Meanwhile, other authors, such as Stockman et.al [301], compared their 3D heat transfer model results to experimental data collected from a single-walled geometry. Although good agreement between model prediction and experimental results was reported, their model does not possess the capability of parsing/understanding the machine code specified toolpath, thus limiting its application for more complex geometries and processes.
Indeed, the high computational demand of 3D model is a remarkable challenge. However, the ultimate goal for any MEX heat transfer models is always to achieve a good prediction of the temperature profile during the printing process. This is specifically important for the case of printing semi-crystalline polymers, as small variations in the temperature profile can significantly alter the development of crystallinity during printing, thus change the resultant mechanical properties including interlayer adhesion, ultimate tensile strength and Young’s modulus, etc. However, vast majority of the current 3D models focus solely on improving the computational efficiency, without a rigorous validation of the model predictions against experimental data. This leads to uncertainty about the accuracy of the models’ predictions under various MEX printing scenarios. Thus, this work aims to address the discrepancies between the 3D model predictions and actual experimental data.

To fulfill this objective, our first step involves constructing a 3D model capable of parsing the machine g-code and executing numerical heat transfer calculations. The framework of this 3D model is inspired by several reported works that utilize a discrete-event, finite difference approach, a method widely adopted in existing 3D modeling studies [296-298, 301-304]. Following this, a critical aspect of our study is to validate the model simulated results by comparing them against temperature profile obtained from in-situ IR thermography. This comparison is essential to assess the model’s predictive accuracy. In addition to the commonly used single-walled geometry, our study expands the scope to includes a variety of new benchmark geometries. These additional geometries are representative of typical conditions encountered in MEX printing of actual components, yet they are overlooked in the current modeling research. Examples include varying dimensions, loose infill, and overhangs requiring support structures. The results of the model validation illuminate scenarios in which the model can provide accurate predictions, as well as identify those situations that present greater challenges for accurate modeling.

4.3. Framework of MEX 3D heat transfer model

The main objective of this study is to validate the model’s prediction across diverse MEX printing scenarios. Consequently, this section provides only a concise summary of the model’s operational process. For a more detailed explanation regarding the construction and functioning of this 3D model, readers are directed to Appendix Section 4.7.4 to 4.7.7 of this paper.

Briefly, in this study, a 3D heat transfer model for the MEX process is constructed. This model, programmed in Python 3.8, employs the reported discrete-event, finite difference approach [296, 298, 301], with the printing road discretized into individual elements and activated chronologically to simulate the actual MEX printing process.

Since the toolpath planning is usually complicated for a 3D object in MEX printing, to be able to simulate the heat transfer during the printing process, the model first needs to interpret the printing command specified by the slicing software. This process begins with importing
an .stl file into the Cura slicer, after which a corresponding printing g-code file is generated. The custom-constructed model program then analyzes the g-code file, collecting information such as build envelope dimensions, nozzle movement coordinates, and printing speed, etc. This analysis allows the model to determine the nozzle's location at any given moment during the printing process.

Furthermore, the model hypothesizes that the entire part, consist of deposited print roads, can be discretized into individual elements along the toolpath direction, as illustrated in Fig. 45. Each element is assumed to have a uniform temperature distribution within. And whenever a nozzle movement passes the location of an element, the corresponding element will be activated.

Based on the spatial arrangement of all currently activated elements, their contacting condition can be analyzed. This information determines the heat transfer mechanism across the surfaces of the element: if a surface is shared by two contacting elements, heat transfer across the contacting surfaces $q_{cond}$ is governed by conduction, using a finite difference approach, expressed as Eq. 12:

$$Q_{cond} = k \cdot A \cdot \frac{(T_{elm} - T_{neighbor})}{d} \cdot dt$$

Eq. 12

Where $k$ is the material’s thermal conductivity, $A$ is the contacting area between the elements, and $d$ being the distance between the elements.

Conversely, heat transfer across free surfaces is governed by convection and radiation, using a finite difference approach, expressed as Eq. 13 and Eq. 14.

$$Q_{conv} = h \cdot A \cdot (T_{elm} - T_{env}) \cdot dt$$

Eq. 13

$$Q_{radi} = \varepsilon \cdot \sigma \cdot A \cdot [(T_{elm} + 273.15)^4 - (T_{env} + 273.15)^4] \cdot dt$$

Eq. 14

Where $h$ is the convection coefficient, $A$ is the exposed surface area, $\varepsilon$ and $\sigma$ are the emissivity of the material and the Stefan-Boltzmann constant, respectively.

This analysis in the model is dynamic: with each new element activation, the contacting condition of all element is re-assessed and updated, ensuring an accurate representation of the heat transfer mechanisms through all the surfaces throughout the duration of the print.
During the simulation, heat transfer calculations for all currently activated elements are performed numerically using a finite difference method. In parallel with these calculations, the model also dynamically tracking the nozzle’s locations, which determines the activation of new elements. The simultaneous execution of new element activation and heat transfer calculation effectively mirrors the process of material deposition and heat transfer in an actual MEX printing operation. As a result, the model eventually generates a simulated transient temperature profile for each elements of the 3D part, and providing a comprehensive view of the polymer’s thermal history during the printing process. The model’s overall operational flowchart is depicted in Fig. 46.
4.4. Material and Experiment

4.4.1. Material selection

The material selected for this work is PolyQuest 080® poly(ethylene terephthalate) (PET), kindly provided by PolyQuest, Inc. There are two main reasons behind this selection:

First, previous works [186] have shown that PET does not require heated bed to ensure a warpage-free printing. This helps protect the electronic components of the IR camera lens from potential damage caused by a direct exposure to elevated temperature. And a room temperature print bed also provides a better contrast between the part and the background in the IR camera imagery.

Second, the PET’s appearance shifts from transparent to opaque upon crystallization. This provides a visual indication of areas of excessive thermal mass accumulation during the printing process. This indicator of thermal gradient can be used to quickly, qualitatively evaluate the model's prediction. Additionally, heat generated by the crystallization of PET is dismissed in the model. This is a widely accepted assumption in reported works [261, 265, 305], and has been further substantiated by our experimental evidence (as detailed in Appendix 4.7.1).

4.4.2. Print parameters

Benchmark parts was printed on an Ultimaker3 with PET using the print parameters listed in Table 12. The infill density and print speed varied according to geometries.
### Table 12. Print parameters applied for this work

<table>
<thead>
<tr>
<th>Nozzle temperature</th>
<th>Print road width</th>
<th>Print bed temperature</th>
<th>Cooling fan power</th>
<th>Infill pattern</th>
<th>Layer height</th>
</tr>
</thead>
<tbody>
<tr>
<td>270° C</td>
<td>0.4mm</td>
<td>Room temperature</td>
<td>0% 50% 100%</td>
<td>Concentric</td>
<td>0.2 mm</td>
</tr>
</tbody>
</table>

#### 4.4.3. Experimental setup

To monitor the temperature profile during the printing process, an IR camera (Micro-Epsilon TIM640) was attached to the print bed of the Ultimaker3 using a custom designed camera holder (Fig. 47). This arrangement maintained a fixed point of observation, ensuring consistent focus on the targeted point within the IR video footage.

Subsequently, to validate the model’s predictions across different benchmark geometries, heat transfer simulation results from an element positioned at the focal point of the IR camera were obtained, and then directly compared with the in-situ IR thermography measurement.

![Fig. 47. Recording the in-situ temperature profile with IR camera](image)

#### 4.4.4. Part design for model validation

Prior research has predominantly utilized a simple single-walled geometry, thereby overlooking the influence of diverse geometries, complex toolpaths and varying thermal histories on the simulation outcomes. To address this gap, our study strategically designed an array of parts with different geometries for MEX printing. These parts, showcased in Fig. 48,
were specifically chosen to rigorously test and validate the efficacy of our model in accurately predicting thermal history in a broad spectrum of MEX scenarios.

Fig. 48. Design of benchmark geometries for printing

Part 1 embodies a single-walled box geometry. As mentioned previously, it is a benchmark part frequently employed in the vast majority of reported 1D and 2D models. Despite its commonality, the information and conclusion gathered from a single part like this can be largely limited, thus we introduced additional parts for a more in-depth model validation.

Parts 2 through 4 represent a prismatic geometry with varying cross-sectional dimensions. A comparative analysis of the model prediction across these samples unveils the influence of a varying dimension on model’s prediction accuracy.

Further, Part 5 introduce a conical geometry, which has not been presented previously in other MEX modeling works. Contrary to parts 1 - 4, which eventually reach a thermal equilibrium state as the layer deposition process proceeds (i.e., temperature profiles of all the layers above certain distance from the build plate become identical), Part 5 features a varying dimension from the base to the apex. This variability within a single part impacts the accumulation rate of thermal mass throughout the printing process. Validating the model’s performance at different points within this conical structure (i.e., bottom, middle, top) offers valuable insights into the prediction accuracy under fluctuating thermal mass accumulation rates – a factor highly relevant to many real-world MEX printing scenarios. Furthermore, the comparison of results from part 1, 2 and 5 also shows the model prediction performance for distinctively different geometries.

Part 6 showcases an overhang geometry, which necessitates a support structure during the printing process. In practical MEX applications, support structures are commonly encountered, yet previously reported models have not scrutinized prediction performance in these scenarios.
Finally, Part 7 comprises a cubic geometry with sparse infill (20%). Like support structures, sparse infill is a prevalent feature in real-world MEX applications. However, such geometries remain largely untested in current existing models.

The inclusion of these diverse geometries in this study allows for a comprehensive evaluation of the predictive capabilities of our model, thus contributing to the ongoing refinement of modeling heat transfer of the MEX processes. Given the rarity of these structures in previously reported modeling works, examining these geometries offers valuable insight into our model predictions.

4.5. Results and Discussion

4.5.1. Model validation – printing with active cooling

![Diagram](image)

*Fig. 49. Part 4 to 7, drawings vs. the actual printed part (with active cooling)*

Most commercial MEX printers, either desktop or industrial scale, are equipped with cooling fans directed at the tip of the nozzle. These fans play a crucial role in optimizing the cooling process post-deposition, effectively mitigate excessive heat build-up that could lead to unwanted material spreading and deformation. This enhancement ensured both an improved surface finish and the dimensional accuracy of printed parts. Consequently, the default configurations in a majority of MEX slicer software have this cooling feature activated to leverage these advantages. In this section, our focus will be on scenarios involving active cooling.

We selected several benchmark parts to demonstrate our model’s prediction performance, showing in Fig. 49. The column (Part 4) represents cases with uniformly dimensioned printed parts from bottom to top, while the cone (Part 5) exemplifies parts with varying dimensions along the same axis. Additionally, in the practical application of MEX, two features that are often encountered are sparse infill and support structures for overhangs. Despite their common occurrence, the MEX heat transfer simulation of parts with these features has not been explored extensively in previous studies. Thus, in this work, we include the overhang geometry
(Part 6), illustrating scenarios necessitating support structures during MEX printing, and the 20% infilled geometry (Part 7) represents those printing process utilizing a loose infill.

Collectively, these parts encapsulate common scenarios in MEX printing, offering valuable insights into our model’s efficacy in real-world applications. The appearance of printed Part 4 to 7 – namely, the column, cone, overhang and 20% infill – with active fan cooling is depicted in Fig. 49. Notably, under active cooling conditions, these parts predominately displayed a translucent appearance, indicative of a reduced degree of crystallinity.

With the implementation of active fan cooling in MEX printing, heat transfer predominantly occurs through forced convection, a process primarily influenced by the airflow generated by the cooling fan rather than the air density gradient characteristic of natural convection. This leads us to hypothesize that the convection coefficient $h$ for forced convection remains relatively constant, irrespective of the part’s shape, due to the uniform nature of forced airflow. In our modeling approach, we therefore consistently apply the same $h$ value for parts subjected to identical fan cooling levels, as exemplified by the column, overhang, and 20% infill geometries (Fig. 49). Furthermore, it is important to reiterate that our methodology for temperature data acquisition involves using IR thermography to record a specific point at the front center of the layer of interest. This recorded temperature profile is then compared with the temperature of an element at the same spatial location in the model.

However, given the unknown air velocity from the cooling fans, determining the convection coefficient required a trial-and-error approach. For instance, we determined that a forced convection coefficient $h = 30 \text{ W/m}^2\cdot\text{K}$ accurately predicts the temperature profile of the 55th layer (a layer roughly in the middle of the entire part) of the column geometry (Part 4) when printed with 50% fan cooling power, as illustrated in Fig. 50c.

**Fig. 50.** Part 4 printed with cooling fan power = 50% (a) IR camera snapshot at the deposition of layer 55, (b) model simulation result at the deposition of layer 55 (c) temperature profile of layer 55, model vs. IR data
For the cone geometry (Part 5), a higher cooling fan power (100%) was utilized to prevent deformation due to excessive heat accumulation at the cone's tip. Accordingly, we set the convection coefficient at 35 W/m²K, slightly higher than that for the column (Part 4, 30 W/m²K). As depicted in Fig. 51, the model's predictions closely align with the experimental data across all three measured locations. It is worth mentioning that in Fig. 51c, the IR thermography diverges from the predicted curve after the print process finishes. This deviation occurs because the hot end and cooling fan move away upon completion of the print, transitioning the cooling of the part from forced convection to natural cooling, which would require a much smaller convection coefficient that was not utilized in this simulation.

![Fig. 51. Part 5 printed with cooling fan power = 100%, (a) IR camera snapshot at the deposition of layer 14, 33 and 57, (b) model simulation result at the deposition of layer 14, 33 and 57 (c, d, e) temperature profile of layer 14, 33 and 57, model vs. IR data](image)

Both the overhang (Part 6) and the 20% infilled geometry (Part 7) were printed using a 50% fan cooling power, identical to the setting for the column (Part 4), thereby justifying the use of the same convection coefficient, $h = 30$ W/m²K. Despite all being subjected to active cooling, the modeling results for the overhang (Fig. 52) and 20% infilled (Fig. 53) are marginally less accurate compared to the column (Part 4, Fig. 50) and cone (Part 5, Fig. 51), with predicted temperatures about 5 to 10°C lower than the actual measurements. This discrepancy may stem from the structural configuration of the support and infill. Typically, the infill and support structures within a 3D printed part consists of a complex network of crisscrossing or zigzagging material, forming a lattice-like framework with numerous cavities and intersecting paths. This intricate structure can impede the airflow from the cooling fan, preventing it from effectively reaching and uniformly cooling the lower areas of these structures. Consequently, part of these surfaces receives less direct cooling air flow, leading to a reduced impact of the active cooling. This uneven cooling distribution may contribute to the error observed between the model's temperature predictions and the actual measurements captured by IR thermography, as the deeper sections of the support or infill are less influenced by the forced convection provided by the fan.
Overall, the model demonstrated a good prediction performance for MEX parts printed under active fan cooling, which is the most common scenario in MEX applications. This highlights the model’s robustness and applicability in real-world printing conditions. However, within the current modeling framework, some challenges arise when attempting to predict temperature profiles for MEX printing processes without active fan cooling. These challenges, along with their origins and potential solutions, will be thoroughly explored in the subsequent sections.

4.5.2. Model validation – printing without active cooling

In contrast to typical MEX applications, sometimes the benchmark parts used in existing MEX heat transfer modeling studies are printed without active fan cooling. This is probably due
to the use of very simple benchmark geometries in the 1D or 2D models, such as the single-walled box geometry (Part 1 in this work, illustrated in Fig. 48). For this basic shape, active cooling is not required to maintain surface finish quality, as the deposited material already cools efficiently during the printing process. However, without the implementation of active fan cooling, our study recognizes a few challenges that arise when attempting to extend the model simulations beyond the very basic single-walled box geometry. To showcase these challenges in greater detail, we break down the MEX printing process into several key scenarios: printing parts with variable shapes, dimensions, and those involving infill or support structures. Additionally, we have expanded some of our selection of benchmark parts. The results detailed in these following sections not only demonstrates the complexity inherent in modeling the temperature profile for the MEX process without active fan cooling but also offers a more nuanced understanding of the associated challenges.

4.5.2.1. Without active cooling – model validation across varied shapes

In this section, we explore our model’s prediction performance across distinct different shapes, printed without active fan cooling. The single-walled box, the thin wall and the cone (Part 1, 2 and 5) is selected as benchmark. The actual appearance of the printed parts is depicted in Fig. 54. A noticeable difference in the appearance can be observed. The single-walled box (Part 1) and the thin wall (Part 2) exhibit a translucent color, indicating a lower degree of crystallinity. This suggests a thermal history characterized by lower temperatures during the printing process. In contrast, the cone (Part 5) demonstrated a distinct gradient, transitioning from translucent at the bottom to opaque at the top. This indicates a gradual increase in temperature, due to a shortened layer time in the printing process towards the top.

Prior to initiating the simulation, a value for the natural convection coefficient \( (h) \) was first determined. As the single-walled box and the thin wall both feature a vertical surface, the corresponding natural convection coefficient was calculated using a reported empirical
equation [271], resulting in $h = 13.8 \text{ W/m}^2\text{K}$. For the cone geometry, a separate empirical equation specific to conical shape was utilized [306], resulting in $h \approx 17.3 \text{ W/m}^2\text{K}$. A detailed description of these empirical equations is provided in Appendix 4.7.2.

![IR camera and simulation](image)

**Fig. 55.** Part 1 printed without active cooling (a) IR thermography vs. (b) model prediction at the onset of printing layer 55, (c) temperature profiles of layer 55, IR thermography vs. model prediction

Utilizing $h = 13.8 \text{ W/m}^2\text{K}$ for the single-walled box (Part 1), the model's prediction of the thermal history of layer 55 is presented with the IR thermography data in Fig. 55. The comparison illustrates that the model accurately predicted the temperature evolution of the 55th layer throughout the printing process. However, as shown in Fig. 56, the simulation for the thin wall (Part 2) – utilizing the same natural convection coefficient – diverges from the IR thermography, showing an error of approximately 20° C. It was found that adjusting $h$ down to $5 \text{ W/m}^2\text{K}$ provides a more accurate prediction for the thin wall.

![IR camera and simulation](image)

**Fig. 56.** Part 2 printed without active cooling. (a) IR thermography vs. (b) model predictions at the onset of printing layer 55, (c) temperature profiles of layer 55, IR thermography vs. model prediction
Similarly, in Fig. 57, the empirical equation estimated natural convection coefficient for the cone \( h \approx 17.3 \text{ W/m}^2\text{K} \) significantly under-predicted the temperature profile for all locations (the bottom, middle and top location are represented by layer 14, 33 and 57, respectively). This error increases sharply as the location of interest moves up, implying that the error accumulated through the simulated layer deposition process. The underlying cause of this error accumulation for the cone is more complicated than simply inaccurate natural convection coefficient, and will be elaborated in the subsequent section.

It is obvious that determining a suitable natural convection coefficient \( h \) for MEX heat transfer model is crucial for an accurate prediction. In the prior section which active fan cooling is employed, a single \( h \) worked for all benchmark parts as long as the fan cooling power is kept the same. However, from the results of single-walled box and the thin wall alone, it is evident that without active fan cooling, the most suitable natural convection coefficient \( h \) might vary for different parts, as this parameter is intrinsically dependent on both geometry and temperature. Empirical equations can be used to determine the value of \( h \), but the outcome of this approach can sometimes be flawed as shown in Fig. 56 and Fig. 57. What’s more, most empirical equations might not be suitable for the MEX process due to the significant non-isothermal characteristic of this process, as well as the constantly changing dimensions during the layer deposition process. Current literature addressing this issue for MEX modeling is still limited.

### 4.5.2.2. Model validation across varied dimensions

In this section, modeling results of the thin wall, thick wall and column geometry (Part 2 – 5) are compared with their corresponding IR thermography collected during the printing process. As outlined in Section 4.4.4, Part 2 to 4 are prismatic geometry with uniform cross-sectional dimensions from the bottom to the top, each differing in aspect ratios. Their model validation results offer insight into the model prediction performance across parts with different
dimensions printed without active fan cooling. Additionally, the cone (Part 5), with its non-uniform dimensions at different heights, serves as a unique case to evaluate the model’s accuracy in predicting for parts with variable dimensions.

The drawings and the actual printed specimens of these benchmark parts are shown in Fig. 58. Note that visual inspection shows more opaque regions for the thick wall, the column and the cone, suggesting presence of higher crystallinity, which would come from slower cooling, or in another word, a higher temperature during the printing process.

![Fig. 58. Part 2 to 5, drawings vs. the actual printed part (without active cooling)](image)

In the preceding section (Section 4.5.2), we demonstrated that using $h = 5 \text{ W/m}^2\text{K}$ yielded accurate simulation results for the thin wall (Part 2), as shown in Fig. 56. Considering the geometric similarities between the thin/thick wall and the column, we applied this same coefficient to these parts.

In addition, unlike the single-walled box (Part 1) and the thin wall (Part 2), the thick wall (Part 3) and the column (Part 4) feature top surface dimensions comparable to the size of the hot end. With the hot end constantly hovering above the top surface, a different boundary condition specifically for the top surface is needed during the heat transfer simulation (further detailed in Appendix 4.7.3).

For the heat transfer simulation of the thick wall (Part 3) and the column (Part 4), we simply employed an adiabatic boundary condition to the top surface, implying the absence of convective and radiational cooling, while retaining $h = 5 \text{ W/m}^2\text{K}$ as the natural convection coefficient for the other surfaces. The simulation results, shown in Fig. 59 and Fig. 60, demonstrated good agreement with the in-situ IR thermography observations.
Fig. 59. Part 3 printed without active cooling (a) IR camera snapshot at the deposition of layer 55, (b) model simulation result at the deposition of layer 55, top surface assigned with adiabatic boundary condition (c) temperature profile of layer 55, model vs. IR data

Fig. 60. Part 4 printed without active cooling (a) IR camera snapshot at the deposition of layer 55, top surface assigned with adiabatic boundary condition (b) model simulation result at the deposition of layer 55 (c) temperature profile of layer 55, model vs. IR data

However, for the cone-shaped benchmark Part 5, an interesting variation in model prediction accuracy was observed across different positions. At the layer near the bottom (layer 14), the model’s prediction generally aligned well with the experimental data. However, as the position moves to the middle (layer 33), a gradual deviation between the simulation results and the IR data becomes apparent with the progression of printing. This discrepancy becomes even
more pronounced at the top layer (layer 57), where the modeled results exhibited notable errors even from the onset. In short, for the cone-shaped Part 5, the accuracy of the model predictions deteriorates progressively from the bottom (layer 14) towards the top (layer 57).

This error in modeling the cone-shaped Part 5 primarily stems from its varying dimensions. This variation leads to more surface area (top surface plus the side surface) being affected by the heat from the hot end. Accurately simulating such a geometry with its changing dimensions necessitates more complex boundary conditions (more information provided in the Appendix 4.7.3).

Overall, without active fan cooling, the results presented in this section demonstrated the model's capability to accurately predict the temperature profile for parts with uniform dimensions from bottom to top, given the correct boundary conditions are applied. However, challenges increase with parts that exhibit variance in dimensions within a single geometry, as this complexity necessitates more sophisticated boundary conditions. It's noteworthy that in practical 3D printing scenarios, many parts feature such dimensional variations, posing a significant challenge to current 3D modeling approaches in accurately predicting thermal behavior across diverse geometries.
4.5.2.3. Model validation with presence of infill or support structure

In this section, we evaluate the model prediction performance for parts that require support structures or loose infill, printed without active fan cooling. Utilizing the overhang (Part 6) and the 20% infilled geometry (Part 7) as the benchmark, the comparison between simulation result and experimental IR thermography is presented in Fig. 63. It should be noted that given the dimensions (comparable to the size of hot end) of both parts, the adiabatic top surface boundary condition is also employed here in the simulations.

It is reasonable to suspect that the presence of support structure underneath might influence the temperature of the supported overhang portion. However, due to the entire overhang portion being parallel to the build plate, direct temperature measurement at this
location was impossible for the IR camera. Therefore, we utilized temperature readings from the front surface of the overhang geometry (Part 6), specifically from layer 32 (near the bottom) and layer 63 (near the top). These measurements, along with their corresponding simulated temperature profiles, are depicted in Fig. 63.

Examining Fig. 63c and d, it is evident that the two simulated thermal histories are identical, reflecting that an equilibrium state has been reached in the simulated printing process. Importantly, the recorded IR temperature is significantly hotter than the model’s prediction. Correcting this error falls outside the scope of this work, but a potential explanation is offered: in MEX, the distance between support structure trusses as well as the space between the part and the support structure tend to be quite narrow, typically at the scale of millimeters. These confined spaces largely restrict the temperature gradient of the air within, resulting in a significantly decreased local convective cooling efficiency. Consequently, an excessive amount of heat becomes entrapped within these locations, as depicted in Fig. 64. Such entrapped heat directly impacts the in-situ temperature of the adjacent part being printed, creating a disparity between simulated and actual temperatures. Apparently, this source of error is not accounted for in the model. To address this error, a unique boundary condition must be once again assigned to these affected surfaces within the support structure. However, identifying and quantifying the area of these surfaces presents a significant challenge that has not been discussed in existing MEX modeling works.

![Fig. 64. Illustration of limited convection within the support structure](image-url)
Similarly, in the case of Part 7 (20% infilled), a similar issue arises. The confined space between the infill structures also restricts the natural convection within these locations – a fact not accounted for in the framework of our current model. This leads to an appreciable error between model prediction and IR thermography similar to the case of the supported overhang (Part 6).

4.6. Conclusion

In this study, a three-dimensional heat transfer model for MEX capable of directly parsing machine tool-pathing command (i.e., g-code) has been developed. The model has been utilized to predict the temperature evolution of various benchmark geometries representing features that are commonly encountered in the practical applications of MEX.

Through a rigorous comparison with IR thermography, our results highlighted that the model’s simulated temperature profiles generally align well with the experimental IR thermography for MEX printing process that employ active fan cooling, which is the most prevalent scenario in practice. Minor prediction errors were noted in cases involving parts with support structures or loose infills, though these were within acceptable limits. However, much more significant prediction errors were observed when simulating printing processes without active fan cooling, especially in parts with varying dimensions or those incorporating support/infill structures.

Examining these results, we identified two critical challenges that significantly impact the model's ability to accurately predict temperature profiles. These challenges, which have not been thoroughly addressed in prior literatures, are as follows:
The first challenge lies in selecting an appropriate convection heat transfer coefficient, a factor pivotal to the accuracy of the model. Existing modeling studies often overlook the intricacies involved in determining this coefficient. In scenarios without active cooling, while empirical equations may suffice for simple geometries, they sometimes fall short in ensuring accurate predictions. This issue is further compounded in practical MEX applications where part geometries can be exceedingly complex, rendering suitable empirical equations nonexistent. In cases with active cooling, the unknown airflow speeds out of the fan duct causing the empirical equations for forced convection ineffective. Overall, these limitations often necessitate an iterative trial and error process against actual thermography data to identify the convection coefficient that yields the most accurate predictions.

The second challenge involves determining appropriate boundary conditions for different surfaces, which is significantly influenced by the part's size and the presence of support structures or sparse infill. These factors can sometimes create a limited air temperature gradient localized to certain surfaces of the part, which impedes the local convective cooling efficiency. Accurately identifying these surfaces within the model and assigning the correct boundary conditions presents a significant challenge. While using active fan cooling mitigates this problem significantly, some minor errors might still be present.

In conclusion, modeling the temperature profile for MEX printing process of a 3D geometry is challenging, as underscored by the findings of this study. Addressing these challenges is essential not just for enhancing the precision and reliability of current MEX model applications, but also for unlocking new possibilities in advanced manufacturing, where the ability to predict and control thermal properties may open up opportunities for the tuning of localized material properties.
4.7. Appendix

4.7.1. Evidence to ignore heat generated by crystallization in the model

To validate the assumption that heat generated by PET crystallization can be effectively ignored in the model, the IR temperature profiles of Part 3 printed with PET (highly crystallized as indicated by the opaqueness in Fig. 58) and ABS (amorphous in nature, i.e., does not crystallize) are recorded and compared in Fig. 66. The complete overlap between the two curves confirms that the crystallization of PET has a negligible impact on the temperature profile during printing, thereby justifying that this term can be effectively ignored in the model.

4.7.2. Determination of natural convection coefficient

Natural convection heat transfer coefficient is estimated with Eq. 15:

\[ h = \frac{Nu \times k_{air}}{D} \]

\[ Eq. 15 \]

where \( Nu \) is the Nusselt number, \( k_{air} \) is the thermal conductivity of the air, and \( D \) is the characteristic dimension. For part 1 and 2, \( D \) equals the vertical height of the specimen, for part 5, \( D \) equals the bottom radius of the cone geometry.

For Part 1 and 2, Nusselt number is estimated by Eq. 16 [271, 307]:

![Comparison of IR Temperature profiles of part 3 printed with PET and ABS](image)
\[ Nu = 0.56 \cdot Ra^{1/4} \]

\textit{Eq. 16}

Where \( Ra \) is the Rayleigh number, estimated by Eq. 17:

\[ Ra = Gr \times Pr \]

\textit{Eq. 17}

\( Gr \) is the Grashof number, estimated by Eq. 18:

\[ Gr = \frac{D^3 \times \rho^2 \times g \times \Delta T \times \beta}{\mu^2} \]

\textit{Eq. 18}

\( \Delta T \) is the difference in temperature between the specimen (\( T_{\text{specimen}} \)) and the environment (\( T_{\text{env}} \)). \( \rho \) is the fluid's (i.e., air in this work) density, based on the air film temperature (\( T_{\text{film}} = (T_{\text{specimen}} + T_{\text{env}})/2 \)), \( g \) is the gravitational acceleration. \( \mu \) is the viscosity of the air, also based on the air film temperature. \( \beta \) is the volume expansion coefficient, for ideal gas, \( \beta = 1/ T_{\text{film}} \).

\( Pr \) is the Prandtl number, estimated by Eq. 19:

\[ Pr = \frac{\mu \times C_p}{k} \]

\textit{Eq. 19}

Where \( C_p \) is the heat capacity of the air based on the air film temperature.

For Part 5, Nusselt number is estimated by Eq. 20 [306]:

\[ Nu = 1.68 \cdot \Phi^{1/4} \cdot Ra^{1/4} \]

\textit{Eq. 20}

The parameter \( \Phi \) is determined by solving Eq. 21:

\[
\begin{align*}
\Phi &= F \frac{\cos \varphi}{72} + \frac{\sin \varphi}{40} \\
F(F \frac{\cos \varphi}{72} + \frac{\sin \varphi}{40})^{1/4} &= 3.778 \frac{Ra^{1/4}}{40}
\end{align*}
\]

\textit{Eq. 21}

Where \( \varphi \) is the inclination angle of the cone, and \( F \) is a coefficient defining to the velocity of the boundary layer growth.

The values of all parameters are summarized in Table 13:
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D) (part 1 and 2)</td>
<td>0.02</td>
<td>m</td>
</tr>
<tr>
<td>(D) (part 5)</td>
<td>0.015</td>
<td>m</td>
</tr>
<tr>
<td>(g)</td>
<td>9.81</td>
<td>m/s²</td>
</tr>
<tr>
<td>(T_{\text{specimen}})</td>
<td>543.15</td>
<td>K</td>
</tr>
<tr>
<td>(T_{\text{env}})</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td>(T_{\text{film}})</td>
<td>420.65</td>
<td>K</td>
</tr>
<tr>
<td>(\rho)</td>
<td>0.839</td>
<td>Kg/m³</td>
</tr>
<tr>
<td>(\beta)</td>
<td>0.0024</td>
<td>1/K</td>
</tr>
<tr>
<td>(\mu)</td>
<td>23.7×10⁻⁶</td>
<td>Pa·s</td>
</tr>
<tr>
<td>(C_p)</td>
<td>1.017×10³</td>
<td>J/kg·K</td>
</tr>
<tr>
<td>(k_{\text{air}})</td>
<td>34.84×10⁻³</td>
<td>W/m·K</td>
</tr>
<tr>
<td>(\varphi)</td>
<td>40</td>
<td>degree</td>
</tr>
<tr>
<td>(F)</td>
<td>0.685</td>
<td>N/A</td>
</tr>
<tr>
<td>(\Phi)</td>
<td>0.023</td>
<td>N/A</td>
</tr>
</tbody>
</table>

For Part 1 and 2, the natural convection coefficient is determined to be 13.8 W/m²K, and for Part 5, the natural convection coefficient is determined to be 17.3 W/m²K.

4.7.3. Rationale for different boundary conditions

In the simulation for benchmark Part 3, 4 and 5, we opted for a different boundary condition for the top surface, guided by two key rationales.

First, it is important to note that the efficiency of both convective and radiational cooling is influenced by the temperature of the surrounding environment. In the case of Part 3 and 4, the dimensions of the top surface are similar to those of the hot end. This results in the hot end staying in close proximity to the entire top surface throughout the infilling process. Such consistent proximity increases the air temperature in the narrow space between the top surface and the hot end, thereby significantly reducing the efficiency of both convective and radiational cooling on the top surface. Moreover, the top surface continuously absorbs radiation energy from the hot end. These combined effects lead to a significantly reduced cooling efficiency on the top surface during the printing process. Therefore, to accurately capture this scenario, a different boundary condition is required, as illustrated in Fig. 67.
Second, our simulation results indicated that merely adjusting the natural convection coefficient \( h \) does not suffice to improve the prediction accuracy. For benchmark Part 3, treating the top surface in the same manner as the other side surfaces, i.e., without applying a distinct boundary condition, resulted in significant underprediction of the temperature profile, as shown in Fig. 68. In attempts to refine the prediction, we experimented with reducing \( h \) values, even to as low as 0.1 W/m²·K. However, as demonstrated in Fig. 69, these adjustments were not effective in aligning the model predictions with the observed data.
In Fig. 69, a gradual reduction in prediction error as the value of h decreases is observed. However, even at $h = 0.1 \text{ W/m}^2\cdot\text{K}$ – highly improbable for natural convection in MEX printing as per literature values [270, 271] – a significant prediction error remains. As evidenced in Fig. 69d, this observation suggests that an excessively large natural convection coefficient is unlikely to be the primary cause of the prediction error. Consequently, it becomes apparent that a different boundary condition for the top surface is necessary for more accurate simulation results.

For simplicity, we tested applying an adiabatic boundary condition to the top surface for benchmark Part 3 and 4. This adjustment resulted in good match between the simulation and the in-situ IR thermography (Fig. 59 and Fig. 60). However, it is important to note that Parts 3 and 4 represent a specific scenario where the parts are uniform from bottom to top, with cross-sectional dimensions similar to those of a MEX printer’s hot end. Given these specific conditions, the effectiveness of the adiabatic top surface boundary condition could be coincidental. Nonetheless, it is reasonable to consider that some parts might require more complex boundary conditions. This could involve modified convection and radiation cooling parameters, rather than a completely adiabatic surface.
The cone-shaped Part 5 serves as an illustrative example of the aforementioned complexities. In our simulation, we applied an adiabatic boundary condition only to the top surface. Yet, as illustrated in Fig. 70, a considerable portion of the side surfaces is also exposed to the influence of the hot end. These side surfaces, being slightly further from the hot end compared to the top surface, likely require a boundary condition that allows for limited convection and radiation cooling, rather than being completely adiabatic. However, accurately determining the extent of these surfaces and the precise degree to which convection and radiation cooling should be limited presents a significant challenge. This complexity underscores the intricacies involved in modeling realistic 3D printing scenarios, particularly for parts with non-uniform geometries.

![Fig. 70. Illustration of layers affected by hot end during (a) simulation and (b) printing](image)

### 4.7.4. Build envelope discretization & element construction

Generally, the framework of this 3D model follows the reported finite element, discrete event approach [296, 298, 301], with the printing road discretized into individual elements and activated chronologically to simulate the actual MEX printing process.

To start, the Cura software serves as the slicer for generating the printing g-code. A custom-constructed g-code parser created using Python 3.8 is implemented in the model to discretize the entire build envelope and recognize elements activated at each time step. A more detailed illustration of this process follows:

a) **Build envelope recognition:**

As depicted in Fig. 71, the g-code parser recognizes the dimensions of the build envelope occupied by a specific part (in this example, a truncated cone geometry). This is achieved by searching for the minimum and maximum XYZ coordinates within the header section of the corresponding g-code file.
Upon obtaining this information, the entire build envelope is mathematically discretized into small voxels (0.2 mm × 0.2 mm × 0.2 mm). This is achieved by constructing three arrays ranged from the minimum values of X, Y and Z coordinates to the maximum. For simplicity, the X_{min}, Y_{min}, Z_{min} values are assumed to be 0 in this example. Additionally, the indexing of each axial value in the array is used for labeling each corresponding voxel, as illustrated in Fig. 72.

**Z axis array:**
\[ Z_{\text{min}} = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, ... , Z_{\text{max}} \]

**Z label:**
\[ [0, 1, 2, 3, 4, 5, 6, ... , k, ...] \]

**Y axis array:**
\[ Y_{\text{min}} = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, ... , Y_{\text{max}} \]

**Y label:**
\[ [0, 1, 2, 3, 4, 5, 6, ... , j, ...] \]

**X axis array:**
\[ X_{\text{min}} = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, ... , X_{\text{max}} \]

**X label:**
\[ [0, 1, 2, 3, 4, 5, 6, ... , i, ...] \]

**b) g-code analysis:**
Following the build envelope discretization, the g-code parser proceeds to analyze each subsequent line of the g-code file, gathering details such as the nozzle movement speed, extrusion state, starting and ending coordinates for each movement, etc. The nozzle coordinate during the printing process at each time can be calculated based on the collected information about nozzle movement speed and nozzle movement target coordinates.

As illustrated in Fig. 73, if a given line of g-code involves both nozzle movement and material extrusion, then all voxels situated within 0.2 mm distance (nozzle diameter = 0.4 mm) to the toolpathing line are going to be “activated” by this toolpath. In contrast, voxels farther than 0.2 mm from the toolpathing line remain “inactivated”.

![Fig. 73. Activation of voxels based on the g-code toolpath](image)

**c) Toolpathing line segmentation and element formation**

Following the aspects previously mentioned, a time step parameter (denoted as $t_{step}$) is manually defined ($t_{step} = 0.5s$, for example). The g-code specified toolpathing line is further divided into individual segments, each representing the nozzle’s movement distance within the time scale of $t_{step}$ based on the nozzle movement speed, as illustrated in Fig. 74. Finally, every voxel activated within the time interval of $t_{step}$ is grouped into an element. This approach is to reduces the computational demand for the model. By grouping the voxels into elements, the number of nodes requiring computation is significantly reduced.
In the Python program, each element is a class object with corresponding attributes storing information such as the element’s activation time and labels of consisting voxels, etc.

To simulate and track the MEX printing process within the program, two lists are also created, the first list stores all the elements consisting the part, while the second list only stores the activated elements at the current time, as illustrated in Fig. 75:

**List of all elements:**
[element₁, element₂, element₃, ..., elementₙ]

**List of activated elements:**
[element₁] - Simulation starts
[element₁, element₂] - Current time = activation time of element₂
[element₁, element₂, element₃] - Current time = activation time of element₃
...

**Fig. 75. List of all element and list of activated elements**

### 4.7.5. Determination of corresponding boundary conditions

Before any heat transfer calculation, the corresponding boundary conditions for each activated element need to be determined. This part of the process is as illustrated in Fig. 76:
For every activated element, based on the labels of its consisting voxels, it is identified whether or not there is a neighboring element in contact at this moment. Using the case shown in Fig. 76 as an example, a random voxel \((i, j, k)\) belongs to element 1, its six neighboring voxels \((i \pm 1, j \pm 1, k \pm 1)\) are searched among the consisting voxels of all currently activated elements. At any arbitrary time, if a neighboring voxel is found, but belongs to a different activated element, that means the two activated elements are in contact, thus the corresponding surface is assigned with a conduction boundary condition. On the contrary, if no neighboring voxel is found, it means the surface is currently exposed to the environment, thus assigned with a convective and radiational boundary condition.

These specific assignments ensure that the heat transfer mechanisms within the model are accurately represented, whether it involves heat conduction between adjoining elements or convection and radiation with the external environment.

4.7.6. Heat transfer calculation for each element

The numerical calculation of heat transfer in this study is based on a finite difference approach. As noted in the previous section, there are three heat transfer mechanisms considered in the calculation, namely, the conductive heat transfer, the convective heat transfer, and the radiational heat transfer.
For an arbitrary element, considering the net heat flux through all three mechanism with heat from crystallization ignored, the governing heat transfer equation can be expressed as Eq. 22:

\[ V_{\text{tot}} \cdot \rho \cdot C \cdot \frac{\partial T}{\partial t} = -[q_{\text{cond}} + q_{\text{conv}} + q_{\text{rad}}] \]

\[ \text{Eq. 22} \]

Where \( V_{\text{tot}} \) is the total volume of this element, equals the volume of a cubic voxel \( (V_{\text{voxel}}) \) multiplied by the number of voxels that consist of this element \( (n_{\text{voxel}}) \), i.e., \( V_{\text{tot}} = V_{\text{voxel}} \cdot n_{\text{voxel}} \). \( \rho, c \) and \( k \) represent the density, the specific heat capacity and the thermal conductivity of the material, respectively. For simplification, these parameters are treated as constant (for PET, \( \rho = 1380 \text{ kg/m}^3, c = 1030 \text{ J/kg}^\circ \text{C}, k = 0.15 \text{ W/mK} \)).

Heat flux through surfaces with conductive heat transfer boundary condition is governed by Fourier’s law, with a forward finite difference numerical method, it is expressed as Eq. 23:

\[ q_{\text{cond}} = k \cdot A \cdot \frac{\left(T_{\text{elm}} - T_{\text{neighbor}}\right)}{x} \cdot n_{\text{contact}} \]

\[ \text{Eq. 23} \]

Where \( x \) is the center to center distance between two voxels (equals 0.2 mm in this work), and \( A \) is the surface area of each side of a voxel (equals 0.2 × 0.2 mm²). \( n_{\text{contact}} \) denotes the number of voxel surfaces in contact between the two elements. For example, in Fig. 76, element 1 and 2 has 2 voxel surfaces in contact, thus \( n_{\text{contact}} \) equals 2. \( T_{\text{elm}} \) is the temperature of the specific element, with an initial value set to \( T_{\text{melt}} \) (equals 270\(^\circ\) C), representing the temperature of freshly deposited molten material. \( T_{\text{neighbor}} \) is the temperature of its neighboring element in contact.

Specifically, for elements in the first layer, conduction to the build plate is calculated with Eq. 24:

\[ V_{\text{tot}} \rho c \frac{dT}{dt} = h_{\text{plate}} \cdot A \cdot \left(T_{\text{elm}} - T_{\text{plate}}\right) \cdot n_{\text{contact–plate}} \]

\[ \text{Eq. 24} \]

Where \( h_{\text{plate}} \) is the thermal contact conductance between the material and the build plate, set to 1000 W/m²K in this work.

Heat flux through surfaces with convective heat transfer boundary condition is calculated with Newton’s law, expressed as Eq. 25:

\[ q_{\text{conv}} = h \cdot A \cdot (T_{\text{elm}} - T_{\text{env}}) \cdot n_{\text{convective}} \]

\[ \text{Eq. 25} \]
Where \( h \) is the convective heat transfer coefficient. The value of \( h \) varies based on different part geometry or cooling fan power applied to the printing process. \( n_{\text{convective}} \) refers to the number of voxel surfaces exposed to the open environment, and \( T_{\text{env}} \) refers to the environment temperature.

Heat flux through surfaces with radiation heat transfer boundary condition is governed by Stefan-Boltzmann’s law, expressed as Eq. 26:

\[
q_{\text{radi}} = \varepsilon \cdot \sigma \cdot A \cdot [(T_{\text{elm}} + 273.15)^4 - (T_{\text{env}} + 273.15)^4] \cdot n_{\text{convective}}
\]

\[\text{Eq. 26}\]

Where \( \varepsilon \) is the emissivity of the material (\( \varepsilon = 0.8 \) in this work), \( \sigma \) is the Stefan-Boltzmann constant (equals to \( 5.67 \times 10^{-8} \text{ W/m}^2\cdot\text{K}^4 \)). Since convection and radiation cooling occurs on the same surfaces (which are exposed to the open environment), \( n_{\text{convective}} \) is directly used here in Eq. 26 for representing the number of voxel surfaces with radiation cooling.

In the program, the temperature of each element is calculated through Eq. 27:

\[
T_{\text{elm}}^{c+dt} = T_{\text{elm}}^c + dT
\]

\[\text{Eq. 27}\]

Where \( T_{\text{elm}}^{c+dt} \) denotes the element’s future temperature after time \( dt \), and \( T_{\text{elm}}^c \) denotes the element’s current temperature, with \( dT \) being the change in temperature within \( dt \).

To calculate \( dT \), Eq. 23 to Eq. 26 are substituted into Eq. 22, and re-arranged to the vector dot product form (Eq. 28), with the first vector compiles all the corresponding boundary conditions for each element:

\[
V_{\text{tot}} \rho c \, dT = \begin{bmatrix}
    h \\
    \varepsilon \cdot \sigma \\
    k \\
    k \\
    \ldots
\end{bmatrix}^T \cdot \begin{bmatrix}
    A \cdot n_{\text{convective}} \cdot (T_{\text{elm}1} - T_{\text{env}}) \cdot dt \\
    A \cdot n_{\text{convective}} \cdot [(T_{\text{elm}1} + 273.15)^4 - (T_{\text{env}} + 273.15)^4] \cdot dt \\
    A \cdot n_{\text{contact}1} \frac{T_{\text{elm}} - T_{\text{neighbor}1}}{x} \cdot dt \\
    A \cdot n_{\text{contact}2} \frac{T_{\text{elm}} - T_{\text{neighbor}2}}{x} \cdot dt \\
    \ldots
\end{bmatrix}
\]

\[\text{Eq. 28}\]

With Eq. 27 and Eq. 28, the program calculates \( dT \) for every activated element through every time step \( dt \) (equals 0.1s for this work). And after every heat transfer calculation, the boundary conditions in the first vector is updated through the method described in the previous Section 4.7.5. Eventually, the simulated temperature profile is obtained.
4.7.7. Parameters used in the model

Table 14. Parameters used in the model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Physical meaning</th>
<th>value</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>Dimension of cubic in the discretization step</td>
<td>0.2</td>
<td>mm</td>
</tr>
<tr>
<td>$A$</td>
<td>surface area of each side of a voxel</td>
<td>0.04</td>
<td>mm$^2$</td>
</tr>
<tr>
<td>$T_{\text{melt}}$</td>
<td>Temperature of molten material extruded from the nozzle</td>
<td>270</td>
<td>°C</td>
</tr>
<tr>
<td>$\rho_{\text{PET}}$</td>
<td>Density of PET</td>
<td>1380</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$C_{\text{PET}}$</td>
<td>Heat capacity of PET</td>
<td>1030</td>
<td>J/kgK</td>
</tr>
<tr>
<td>$k_{\text{PET}}$</td>
<td>Thermal conductivity of PET</td>
<td>0.15</td>
<td>W/mK</td>
</tr>
<tr>
<td>$h$</td>
<td>Convective heat transfer coefficient</td>
<td>Varies</td>
<td>W/m$^2$K</td>
</tr>
<tr>
<td>$T_{\text{env}}$</td>
<td>Environment temperature</td>
<td>30</td>
<td>°C</td>
</tr>
<tr>
<td>$T_{\text{plate}}$</td>
<td>Build plate temperature</td>
<td>30</td>
<td>°C</td>
</tr>
<tr>
<td>$h_{\text{plate}}$</td>
<td>Thermal contact conductance between material and build plate</td>
<td>1000</td>
<td>W/m$^2$K</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
<td>$5.67 \times 10^{-8}$</td>
<td>W/m$^2$K$^4$</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Material emissivity</td>
<td>0.8</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Evaluation of Nakamura Model on Predicting Crystallinity of Semi-Crystalline Polymers Printed via Material Extrusion Additive Manufacturing

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5.1. Abstract

The growing application of Material Extrusion Additive Manufacturing (MEX) in producing high performance, semi-crystalline polymer parts necessitate the need for a better understanding of material crystallization during the printing process. Accurate crystallization modeling is essential not only for optimizing the material properties of printed parts but also for reducing the reliance on extensive experimental work. Although the Nakamura non-isothermal crystallization model is widely used and validated in non-isothermal processes controlled by Differential Scanning Calorimetry (DSC), its application to MEX has not been thoroughly examined. The significantly higher cooling rates and periodic re-heating due to subsequent material layers in MEX differ significantly from controlled DSC cooling, potentially challenging the Nakamura model's applicability. This study, therefore, evaluates the Nakamura model's ability to predict crystallinity in semi-crystalline polymer parts produced via MEX, using in-situ IR thermography for temperature profiling. Our results indicate a notable underestimation of final crystallinity by the Nakamura model, primarily due to its failure to account for shear-induced crystallization prevalent in MEX. This discrepancy, further validated by DSC, highlights the necessity for models that incorporate the effects of shear history. This research advocates for the development of advanced models that fully capture the complex dynamics of MEX processes, thereby significantly improving the accuracy of crystallinity predictions in semi-crystalline polymers.

5.2. Introduction

Traditionally, material extrusion additive manufacturing (MEX) has been predominantly utilized for prototyping, primarily employing amorphous polymers. However, in recent years, driven by a growing demand for customized, generatively designed components, MEX is rapidly evolving towards the direct fabrication of end-use parts across diverse applications. Due to this transition, there has been greater need for the ability to print high-performance, often semi-crystalline, polymers.

However, this need introduces additional complexities in MEX process/structure/property (P/S/P) relationships as the crystallization process during printing can significantly vary the part’s final crystallinity, which further results in different mechanical properties [24, 308, 309]. Studies by Lee et al. [310], Trimini et al. [311] and Yang et al. [84] have demonstrated significant variations in crystallinity levels in PEEK (polyetheretherketone, a high performance engineering semi-crystalline polymer in MEX), attributed to differing print parameters.

The consistent production of MEX-printed semi-crystalline parts with uniform quality and properties is currently challenged by a limited understanding of the P/S/P relationships. This is particularly true in comprehending how crystallinity develops across various MEX printing processes. Traditional approaches to bridge this knowledge gap involve extensive experimental work. For instance, Vaes et al. [285] employed IR thermography and fast-scanning calorimetry to investigate crystallinity development in single-walled geometries printed with PA6/66...
random copolymer. Their findings indicated that while print speed and nozzle temperature exerted minimal influence on the final crystallinity, the bed temperature has a significant impact on it.

However, the applicability of experimental findings is often constrained and not universally transferable across different part designs. Given the extensive effort required, testing each design through varied parameter sets is impractical. Here, numerical modeling for crystallization emerges as a more efficient alternative, offering rapid iterations with minimal effort and significantly enhancing the efficiency of MEX process optimization. The Nakamura non-isothermal crystallization model, an extension of the Avrami model proposed by Nakamura et al. [312, 313], exemplifies this approach. It has been used to estimate crystallinity development under diverse thermal conditions [102, 314-318], and has been validated against the differential scanning calorimetry (DSC) data under controlled cooling rates. However, its applicability to actual MEX printed parts remains unverified. The MEX process involves cooling rates significantly higher than those in controlled DSC environments, and the material experiences complex shearing prior to deposition, these factors all alter the crystallization kinetics, thus presenting a potential challenge to existing crystallization models.

In response to this gap, our study evaluates the Nakamura model’s predictions on several benchmark parts fabricated via MEX. We employed in-situ temperature profiles from IR thermography as inputs for the Nakamura non-isothermal crystallization model to predict the crystallinity development during the MEX printing process. This assessment aims to evaluate the model's effectiveness and suitability for predicting crystallinity in MEX-manufactured components. Our findings reveal that the Nakamura model does not adequately predict the crystallinity developed in the MEX printing process, likely owing to the shear flow inherent in the MEX process that induced and accelerated the crystallization. This discrepancy highlights the need for utilizing more specialized models or adapting existing ones to better suit the MEX process.

### 5.3. Material, Method, and Experiment

#### 5.3.1. Material selection

PolyQuest080 PET is selected as the benchmark material for this study due to several reasons. First, MEX printing of semi-crystalline polymers is known to be more challenging than amorphous polymers. PET, as a typical semi-crystalline polymer, has been reported to exhibit good printability in MEX [186]. Second, PET exhibit a suitable crystallization rate for this research. To effectively validate the crystallinity predictions of the Nakamura model, it is advantageous to use benchmark parts that display a broad spectrum of crystallinities. This variability provides a comprehensive range of reference values for different MEX scenarios. In MEX processes involving PET, manipulating process parameters can yield a wide range of crystallinities, making PET an exemplary candidate for validating crystallization models. In contrast, other semi-crystalline polymers reported in MEX, such as PP or HDPE, crystallize too
rapidly, while polymers like PLA crystallize too slowly. Consequently, parts printed with these materials tend to exhibit extreme crystallinity values—either very high or very low—regardless of the printing parameters and part design. This makes them less suitable for providing a nuanced series of reference values for model validation.

5.3.2. Design of benchmark parts

In this study, four benchmark specimens were utilized. Illustrations of these specimens, along with images of the actual printed parts, are presented in Fig. 77.

These benchmark parts are designed to exhibit varying thermal histories during the printing process, resulting in different levels of crystallinity. This variation in thermal history is primarily achieved through two mechanisms: altering the specific surface area of the parts and varying the layer deposition rate.

Part 1 to 3 are designed with varying specific areas. In terms of heat transfer, particularly in convection, the cooling rate of an object is significantly influenced by its surface area. Parts with larger specific surface areas have a greater interface for heat exchange with the environment, promoting more efficient heat dissipation. This leads to a lower temperature during the printing process and, consequently, a reduced degree of crystallinity. Part 4, featuring a conical geometry, demonstrates a change in layer deposition rate due to its gradually decreasing diameter towards the top. This results in a varied thermal history from the bottom to the top of the part, closely resembling the scenarios encountered in MEX printing of actual components, where most 3D parts have varying cross-sectional areas.

5.3.3. Fabrication of benchmark specimens & assessment of crystallinity

For this study, PolyQuest080© PET pellets were initially dried in a vacuum oven at 130° C for 24 hours, then extruded into ~2.5 mm filament for MEX printing using a Filabot EX2 desktop filament extruder. All the benchmark parts were printed on an Ultimaker3 MEX printer with a 0.4mm nozzle, the corresponding print parameters are summarized in Table 15.
Table 15. Printing parameters for the benchmark specimens

<table>
<thead>
<tr>
<th>Nozzle temperature (°C)</th>
<th>Bed temperature (°C)</th>
<th>Print speed (mm/s)</th>
<th>Layer Thickness (mm)</th>
<th>Infill density</th>
<th>Fan cooling</th>
<th>Infill pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>Non-heated</td>
<td>40</td>
<td>0.2</td>
<td>100%</td>
<td>0%</td>
<td>concentric</td>
</tr>
</tbody>
</table>

During printing, an IR camera (Micro-Epsilon/TIM640) was securely mounted to the print bed using a custom-designed camera mount. The entire arrangement, including the printer and camera setup, is depicted in Fig. 78. The stationary positioning of the camera on the print bed ensured consistent focus on the target spot for the duration of printing. Notably, the focus spot of the IR camera corresponded to the DSC sampling site, as indicated in Fig. 77.

Fig. 78. Recording the in-situ temperature profile with IR camera

Upon completion of the printing process, samples around 5-10mg are collected from the sampling site, as marked in the drawings in Fig. 77. The crystallinity of these samples was analyzed using a DSC (TA Instrument DSC Q2000) with a heating ramp rate of 10° C/min, spanning a range from 0 to 280° C.

The crystallinity is calculated based on Eq. 29:

$$X\% = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f}$$

Eq. 29
Where $\Delta H_m$ and $\Delta H_{cc}$ represent the area of the melting peak and cold crystallization peak, respectively, and $\Delta H_f$ is the heat of fusion for 100% crystallized PET. For this study, $\Delta H_f = 120$ J/g is used [228].

**5.3.4. The Nakamura non-isothermal crystallization model**

The Nakamura non-isothermal crystallization model is an extension to the well-known Avrami model, which describes the isothermal crystallization kinetics of polymeric materials. This extension accommodates for scenarios characterized by non-isothermal conditions.

The classical form of the Avrami equation (Eq. 30), and the commonly employed double logarithm form are given by Eq. 31.

$$\alpha(t) = 1 - \exp(-kt^n)$$

*Eq. 30*

$$\ln(-\ln(1-\alpha(t))) = \ln k + n \ln t$$

*Eq. 31*

Where $k$ is the Avrami rate constant that encompasses the effect of nucleation and growth rates. The Avrami exponent, $n$, is indicative of the nucleation mechanism and growth geometry (i.e., one dimensional, two dimensional or three dimensional). The variable $t$ represents the crystallization time. Most importantly, $\alpha(t)$ signifies the relative degree of crystallinity or degree of space filling, defined as the ratio of crystallized volume at a given time to the total crystallizable volume. Utilizing the data from DSC isothermal crystallization tests, the relatively crystallinity $\alpha(t)$ can be calculated using Eq. 32:

$$\alpha(t) = \frac{\int_{t_0}^{t} H(t)dt}{\int_{t_0}^{\infty} H(t)dt}$$

*Eq. 32*

Where $t_0$ and $t_\infty$ indicates the start and end time of the crystallization process, respectively. $H(t)$ is the heat flow rate at time $t$ as measured by the DSC.

To adapt the Avrami equation for non-isothermal processes, Nakamura et al. proposed a temperature dependent integral form (Eq. 33) of the Avrami equation [312, 313]:

$$\alpha(t) = 1 - \exp\left(-\left[\int_{0}^{t} K(T(\tau))d\tau\right]^n\right)$$

*Eq. 33*

A time differential form of Eq. 34, proposed by Patel et.al [102, 319], offers a more practical application for numerical modeling:
\[ \frac{d\alpha(t)}{dt} = nK(T)[1 - \alpha(t)][\ln\left(\frac{1}{1 - \alpha(t)}\right)]^{n-1} \]

*Eq. 34*

In both Eq. 33 and Eq. 34, \( K(T) \) represents the Nakamura non-isothermal crystallization rate, which links to the Avrami rate constant as follows:

\[ K(T) = k(T)\left(\frac{1}{n}\right) = \ln(2)\left(\frac{1}{t_{1/2}(T)}\right) \]

*Eq. 35*

Where \( t_{1/2} \) denotes the isothermal crystallization half time (the time when \( \alpha(t) \) reached 50%) at a given temperature, which can be further expressed by Eq. 36 according to Hoffman-Lauritzen theory [102]:

\[ \frac{1}{t_{1/2}} = \left(\frac{1}{t_{1/2}}\right)_0 \exp\left(\frac{-U}{R(T - T_\infty)}\right) \exp\left(-C_3\frac{T}{T\Delta T f}\right) \]

*Eq. 36*

In Eq. 36, \( U \) is the activation energy of the crystallization transport, which usually takes the universal value of 6270 J/mol. \( R \) is the universal gas constant, equals to 8.314 J/mol·K. \( T_\infty = T_g - 30 \). \( \Delta T \) is the degree of supercooling, equals \( T_m^0 - T \), where \( T_m^0 \) is the equilibrium melting temperature. Correction factor \( f \) approximately equals to \( 2T/(T + T_m^0) \).

The value of \( t_{1/2} \) at each temperature is determined with the isothermal crystallization experiment. Then, by linear fit \( \ln\left(\frac{1}{t_{1/2}}\right)_0 + \frac{U}{R(T - T_\infty)} \) against \( \frac{1}{T\Delta T f} \), the value of \( \ln\left(\frac{1}{t_{1/2}}\right)_0 \) and \(-C_3\) can be obtained from the intercept and slope, respectively.

Finally, with the parameter \( K(T) \) and \( n \) determined, the relative crystallinity \( \alpha(t) \) is obtained and further correlated to the actual crystal fraction \( X(t) \) (measured through DSC) via Eq. 37:

\[ X(t) = \alpha(t) \times X_{max} \]

*Eq. 37*

Where \( X_{max} \) is the maximum attainable crystallinity in the polymer. For this study, \( X_{max} = 50\% \) is adopted [320].

Eventually, the crystallinity predicted by the Nakamura model will be compared with the crystallinity measured by DSC to evaluate the model's predictive accuracy.

5.3.5. Isothermal crystallization test

The determination of the Avrami rate constant, \( k(T) \) and Avrami index, \( n \), for the Nakamura model was accomplished through a series of isothermal crystallization tests. In detail, a piece of
sample was collected from the extruded PET filament. The tests were conducted using a TA Instrument DSC Q2000, with the isothermal crystallization temperatures ranging from 110° C to 230° C in increments of 5° C. The test begins with heating the sample to 280° C, followed by a holding period for 5 min. This was then rapidly cooled to the predetermined isothermal crystallization temperature at the instrument’s maximum cooling rate, approximately 60° C/min. The sample was maintained at this temperature isothermally for 50 minutes to record the complete exotherm over time. Following this isothermal hold, the sample was reheated to 280° C for 5 min to erase the residual thermal history. This procedure was repeated sequentially for each temperature setting in the isothermal crystallization series.

5.3.6. Stress relaxation test

The relaxation of PET after extrusion was qualitatively assessed with a TA instrument HR1 Discovery Hybrid rheometer using 25 mm parallel plates and 1 mm gap. The tests were conducted at 260° C, which is slightly lower than the nozzle’s set temperature (270° C) to account for the temperature drop experienced by the material upon extrusion [283, 321].

The true strain of the extrusion process, denoted as Eq. 38, is calculated by the natural logarithm of the extrusion ratio $A_0/A_f$ [322]:

$$
\gamma = \ln\left(\frac{A_0}{A_f}\right)
$$

Eq. 38

Where $A_0$ stands for the filament’s cross-sectional area, and $A_f$ stands for the area of the nozzle orifice. With 2.5 mm filament and 0.4 mm nozzle, the extrusion strain $\gamma$ is calculated to be approximately 336%. This strain value is then used as the initial strain in the rheometer, with the relaxation modulus monitored over time to evaluate the material's stress relaxation.

5.4. Results and Discussion

5.4.1. Determination of model parameters

As outlined in Section 5.3.5, DSC isothermal crystallization tests on the PET filament were conducted over a temperature ranged from 110° C to 230° C, increasing in 5° C increments. It was observed that discernible exothermic peaks occurred only within certain temperatures. Specifically, below 130° C and above 200° C, the crystallization process was too slow to produce exothermic peaks detectable by the DSC. Conversely, between 145° C and 165° C, the crystallization happened so swiftly that the DSC failed to register any exothermic peaks. The exothermic peaks that were successfully recorded are presented in Fig. 79. Analysis of these data, particularly evident in Fig. 79a, shows that crystallization initiates earlier at higher temperatures, while Fig. 79b indicates the opposite trend, with crystallization starting later at higher temperatures. These findings suggest that the highest crystallization rate for PET lies within the range of 165 to 145° C.
Fig. 79. DSC exothermic curves of various isothermal crystallization test (a). from 140 to 135°C, (b). from 190 to 170°C

Fig. 80a plots the relative crystallinity data for each isothermal temperature against crystallization time. Remarkably, all curve exhibit a sigmoidal shape, a characteristic feature of polymer crystallization well-documented in literatures [314, 323]. Initially, the transformation from the amorphous to the crystalline state is primarily constrained by the rate of nucleation process. This early stage is followed by a period of rapid crystal growth, where the crystals progressively replace the amorphous regions, leading to a linear increase in relative crystallinity over time. As the material approaches its maximum crystallinity, the crystallization rate begins to slow down due to limited polymer chain mobility and the impingement of already formed crystals. Thus, overall the observed relationship between relative crystallinity and time embodies a sigmoidal shape.

For analyzing the crystallization kinetics, Eq. 31 (Section 5.3.4) is commonly employed. By applying a double logarithm transformation to both side of Eq. 30, a linear relationship between $\ln(-\ln(1-\alpha(t)))$ and $\ln(t)$, known as the Avrami plot, is established. This allows for the determination of the Avrami index $n$ and rate constant $k$ from the slope and intercept of the fitted line, respectively. To construct this plot, relative crystallinity values within the range of 10% to 90% were utilized. The estimated Avrami indices $n$, for each crystallization temperature, are summarized in Table 16.
In the case of the PET material studied in this work, values of the Avrami index $n$ vary around 2 for most of the isothermal temperatures. An exception was noted at 195°C, where $n$ sharply increased to 2.78. This kind of increase in $n$ at higher temperatures has also been observed in other study [324]. Nevertheless, considering that the average value of the Avrami index $n$ is approximately 2 for the range of temperatures studied, this average value will be adopted in the subsequent numerical calculations within the Nakamura model.

As the next step, to determine the Nakamura crystallization rate $K(T)$, the expression

$$\ln \left( \frac{1}{t_{1/2}} \right) + \frac{\nu}{R(T-T_\infty)}$$

was linear fitted against $\frac{1}{T\Delta T_f}$, as described in Section 5.3.4. The fitting results displayed a strong linear correlation, as highlighted in Fig. 81a. The value of $(\frac{1}{t_{1/2}})_0$ and $C_3$ in Eq. 36 are consequently derived from the intercept and slope of the fitted line, respectively.
Finally, the values of all parameters utilized in the Nakamura model for this study of PET are summarized in Table 17.

**Table 17. Parameters and the corresponding values used in the Nakamura model**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>2</td>
</tr>
<tr>
<td>$(\frac{1}{t_{1/2}})_0$</td>
<td>21247.6</td>
</tr>
<tr>
<td>$C_3$</td>
<td>-426630.7</td>
</tr>
<tr>
<td>$X_{\text{max}}$</td>
<td>50%</td>
</tr>
<tr>
<td>$U$</td>
<td>6270 J/mol</td>
</tr>
<tr>
<td>$R$</td>
<td>8.314 J/mol·K</td>
</tr>
<tr>
<td>$T_g$</td>
<td>75° C</td>
</tr>
<tr>
<td>$T_m^0$</td>
<td>279° C</td>
</tr>
</tbody>
</table>

**5.4.2. Model prediction assessment**

Having determined the necessary parameters for the Nakamura model, the IR temperature profile for each benchmark part are imported into the Nakamura model to estimate the crystallinity development during the MEX printing process.
Interestingly, as highlighted in Fig. 82 and Fig. 83, when applying the Nakamura model, all the prediction consistently indicated a negligible degree of crystallinity. This was particularly noteworthy for Parts 1, 2 (Fig. 82 a and b) and layer 57 of Part 4 (Fig. 83 c), where both DSC measurements and visual observations suggested a substantial increase in crystallinity, contrasting with the model’s prediction. The differences between the crystallinities predicted by the Nakamura model and those determined from DSC are detailed in Table 18.
Typically, the Nakamura model under-predicted the crystallinity approximately by 10% to 30%. As discussed in Section 5.3.4, the Nakamura model relies on parameters determined from isothermal crystallization experiments. Results from these experiments suggested that the PolyQuest080® PET utilized in this study crystallizes relatively slowly, with a crystallization half time ranging from around 6 minutes to over than 10 minutes.

However, when compared with the IR thermography data presented in both Fig. 82 and Fig. 83, it is obvious that the deposited material cools rapidly, remaining within the temperature range favorable for crystallization (155-175° C) less than a minute. Moreover, the majority of the temperature profile is even observed to fall below 140° C, a range where isothermal crystallization tests indicate a crystallization half-time of more than 10 minutes. Therefore, given these conditions, it is understandable why the Nakamura model, based on parameters from isothermal crystallization tests, would predict a minimal amount of crystallinity.

Such substantial discrepancy underscores that the original Nakamura model does not adequately predict the crystallinity development during the MEX process of semi-crystalline polymers. Upon examining the framework of Nakamura model, it is hypothesized that shear induced crystallization – a phenomenon not accounted for in the Nakamura model – could be the source of this considerable error. A more detailed explanation is provided as follows:

In this study, neat PET is used, leading to the assumption that the crystallization process initiates with homogeneous nucleation. Furthermore, the Avrami index n equals to 2, indicating a rod-like crystal growth. According to the Avrami theory, the crystallization rate constant $k$ for rod-like crystal growth can be written as [325]:

$$k = \frac{\pi}{2} r^2 G \hat{N}$$

*Eq. 39*

Where $r$ is the radius of the crystal rods.
Fundamentally, MEX involves extrusion, during which the molten material experiences significant shearing inside the nozzle before being deposited. This shearing effect leads to the stretching and orientation of polymer chains, accompanied by simultaneous chain relaxation [326]. Post-deposition, any unrelaxed residual stretching and orientation of the chains can significantly accelerate both the crystal growth rate ($G$) and the nucleation rate ($\dot{N}$), [327], with the latter experiencing a more pronounced increase [326, 328, 329]. Literature suggests that un-relaxed shear-induced stretching can increase the rate of nucleation by several orders of magnitudes [326]. Considering Eq. 39, it becomes evident that any increase in either $\dot{N}$ or $G$ would consequently raise the Avrami crystallization rate constant $k$. This, in turn, leads to a more rapid crystallization process during the MEX printing, ultimately resulting in a higher in final crystallinity.

The residual stretching of the polymer chain can be substantiated by the result of the stress relaxation test, as depicted in Fig. 84. It is clear that at a temperature of $260^\circ$ C, the relaxation of the initial strain takes around 6 to 8 seconds. However, during the actual MEX printing, the extruded material cools down to below $180^\circ$ C well within this same timeframe, as evident in both Fig. 82 and Fig. 83. Given that the chain relaxation process is slower at lower temperatures, it can be inferred that a portion of the chain stretching remains unrelaxed before crystallization.
Fig. 85. Nakamura model prediction with adjusted rate constant k

Fig. 85 highlights the critical role of the rate constant by manually adjusting it to align with the DSC crystallinity results. Notably, to attain a satisfactory prediction, the rate constant for different samples required varying degrees of amplification, ranging from a factor as low as 80 for Part 1 to as high as 40000 for Part 3. This variation theoretically correlates with the relaxation of the polymer chain: parts that maintain higher temperatures during printing are likely to experience more relaxation of the shear-induced stretching in the deposited material. Consequently, shear-induced crystallization is less pronounced in these parts, resulting in a smaller required magnification of the rate constant. However, it's important to note that these manually modified rate constants serve solely to demonstrate the Nakamura model's limitations and are not intended as a definitive solution. To enhance model predictions of crystallinity, a more comprehensive model that incorporates the effects of shearing and relaxation should be considered, such as the one proposed by McIlroy et al [326, 330]. Although this falls outside the scope of the current study, it suggests a promising direction for the future research.

5.5. Conclusion

This study aimed to test the suitability of the Nakamura non-isothermal crystallization model on predicting the resultant degree of crystallinity in semi-crystalline polymer parts produced by the MEX printing process. An experimental technique for evaluating crystallization models using both in-situ IR thermography and benchmark geometries that can alter crystallinity is employed. The model's parameters were determined through a series of isothermal crystallization tests. The temperature profile from in-situ IR thermography was directly used as the model’s input.
Results revealed that the original Nakamura model significantly underpredicted the final crystallinity of the printed parts. This discrepancy indicates that the model, in its current form, is not fully equipped for direct application in MEX processes. A key factor contributing to this prediction error is hypothesized to be an underestimated crystallization rate constant, likely stemming from shear-induced crystallization effects inherent in the MEX process. Recognizing this limitation, future research should focus on employing a more sophisticated model accounting for the complexities of shear history and its impact on crystallization, thereby enhancing the prediction accuracy of crystallinity in semi-crystalline polymer parts produced through MEX printing. A better predictive tool not only aims to significantly improve the prediction accuracy of crystallinity in semi-crystalline polymer parts fabricated via MEX printing, but also opens up new possibilities for precisely controlling the crystallinity at specific locations within a part, thereby tailoring its properties and performance to meet exacting requirements.
6. Chapter 6

Summary, Contributions and Future work
6.1. Summary of key findings


This chapter reviewed the MEX printing of various semi-crystalline polymers. It was highlighted that different semi-crystalline polymers in MEX exhibits different levels of challenge, the faster the crystallization rate, usually the more difficult to be printed via MEX.

For semi-crystalline polymers with fast crystallization rate:

- High crystallinity causes significant shrinkage, potential infill gaps, and residual stress. Warpage frequently encountered if print bed adhesion is insufficient.
- High crystallinity also hinders polymer chain entanglement and co-crystallization across the layer interface, resulting in poor interlayer adhesion.
- Achieving sufficient interlayer adhesion requires an interface temperature near or above the polymer’s melting temperature ($T_m$). Usually realized with a high temperature printing chamber, or high temperature nozzle, or both.

For semi-crystalline polymers with intermediate crystallization rate:

- Heated environment is not critical for good interlayer adhesion.
- Proper parameters can maintain low crystallinity, reducing warpage and facilitating better chain diffusion.
- More sensitivity to printing parameters; print speed and layer time can substantially affect crystallization and, consequently, the mechanical properties.

For semi-crystalline polymers with slow crystallization rate:

- Crystallization process is usually too slow to cause any significant impact on their MEX process.
- Generally possess great printability and interlayer adhesion.


This chapter studied the impact of GF reinforcement on MEX printed rPET’s resultant crystallinity and mechanical properties. Overall it was demonstrated that rPET and its composite possess excellent printability in MEX, key findings include:

- GF significantly increased rPET’s viscosity but did not hinder its printability, even at a high GF loading of 20 wt.%.
- GF filler size decreased during multiple processing and extrusions steps, thus the increase in ultimate tensile strength is less significant compared to modulus.
- Higher GF loadings led to increased anisotropy.
- GF filler slightly decreased crystallinity of printed parts.
6.1.3. Chapter 3. Material Extrusion Additive Manufacturing of Semi-crystalline Polymers: Exploring the Effects of Specific Area and Layer Time on Crystallinity and Mechanical Properties

This chapter explored the process/structure/property relationships of semi-crystalline polymers in MEX, using PET as the benchmark material. Key findings include:

- Part specific area and print layer time have significant impact on resultant thermal history.
- Resultant crystallinity of the MEX printed part can be tuned by adjusting the corresponding values of specific area and print layer time.
- Crystallization impedes the development of interlayer adhesion. Efficient cooling or extremely short layer time is necessary to deposit material before crystallization of the underlying layer.


This chapter developed a 3D heat transfer model for MEX that directly parse the machine toolpathing commands (g-code) to predict temperature evolution. The model predictions are validated against experimental IR thermography. The key findings and challenges identified are:

- Proper selection of convection heat transfer coefficient presents as a challenge, empirical equations might not satisfy the accuracy requirement for an actual applicable prediction performance.
- Without active cooling applied in the MEX printing process, boundary conditions become complex. Different boundary conditions may need to be applied depending on the part’s size, support, or infill structures.
- Active cooling eliminates the issue of local limited temperature gradients. Without having to assign different boundary conditions to different surfaces, the simulation process is simplified with improved prediction accuracy.

6.1.5. Chapter 5. Evaluation of Nakamura Model on Predicting Crystallinity of Semi-Crystalline Polymers Printed via Material Extrusion Additive Manufacturing

This chapter evaluated the Nakamura non-isothermal crystallization model on predicting the crystallinity of MEX printed parts. The key observations and findings are as follows:

- The Nakamura model significantly under-predicted the crystallinity of MEX printed parts.
- The impact from shear induced crystallization, which is not accounted for in the Nakamura model, could be a potential source of error.
6.2. Contributions

- Specifically highlighted that the common impression about semi-crystalline polymers being incompatible in MEX is an over-simplification of a more nuanced fact.
- It is clearly shown that processability of semi-crystalline polymers in MEX is related to their rate of crystallization, with faster crystallizing polymers being more challenging to be printed via MEX.
- Underscored the existing research gaps for various semi-crystalline polymers in MEX.

- Demonstrated the excellent printability of both neat rPET and its GF reinforced composites, showcasing their capability for direct fabrication of end-use ready components.
- Highlighted the impact of a varying tool pathing time on the crystallinity of printed part. Emphasized a gap in understanding and control over this localized crystallinity.

6.2.3. Chapter 3. Material Extrusion Additive Manufacturing of Semi-crystalline Polymers: Exploring the Effects of Specific Area and Layer Time on Crystallinity and Mechanical Properties
- Advanced the current understanding of process/structure/property relationship of semi-crystalline polymers in MEX through the incorporation of impact from both part design and print parameter, depicted a more complete picture of how different thermal histories in MEX can be induced by varying these factors, thus subsequently affect the resultant crystallinity.
- Showcased the development of crystallinity during the layer deposition process, it was highlighted that the layer deposition should occur before the crystallization of underlying layer to improve interlayer adhesion. This serves as a reference knowledge for optimization of MEX parameters.

6.2.4. Chapter 4. Validating a 3D Heat Transfer Model for Material Extrusion Additive Manufacturing: A Comparative Analysis with In-situ Thermography
- Rigorously validated the 3D heat transfer model for MEX against experimental data from various benchmark geometries, highlighting the actual performance of the 3D heat transfer model in different MEX scenarios beyond the commonly utilized single-walled geometry.
• Un-reported challenges affecting the prediction accuracy of 3D heat transfer model in MEX were addressed, clearly indicated the research gap in current MEX heat transfer modeling.

6.2.5. Chapter 5. Evaluation of Nakamura Model on Predicting Crystallinity of Semi-Crystalline Polymers Printed via Material Extrusion Additive Manufacturing

• Showcased the incompatibility of Nakamura non-isothermal crystallization model in predicting the crystallinity of MEX printed semi-crystalline polymer parts, encouraging the development and utilization of more complex and accurate models.

6.3. Future work

Building upon the insights and contributions of this thesis, several prospective research paths have emerged. These directions not only aim to augment our comprehension of the complex mechanisms involved in the MEX process, but also seek to refine and advance the practical application of this technology in both industrial and innovative contexts. Key areas identified for future exploration include:

• Advanced materials and composites:

  The continued exploration into feedstock materials such as other type of fillers and even continuous fiber reinforcement is of considerable interest. Investigating the synergy between different materials and their influence on printability and mechanical properties could lead to the creation of novel products with superior qualities for a broader range of applications.

• Customization of crystallinity at specific location:

  It is established that various thermal history can be achieved through altering the part design and the layer deposition rate, thus eventually resulting in different crystallinity and mechanical properties. However, this technique only offers control over vertical direction, and currently crystallinity tuning has only been achieved for the entire parts and only with simple geometries.

  It is of specific interest for subsequent research to develop techniques that enables the possibility of a customized crystallinity at specific locations of each part, which would enable in-situ tuning of mechanical properties during the MEX printing process.

• Advanced modeling techniques:

  (1). MEX heat transfer modeling

  Future work addressing the limitations observed in the current MEX heat transfer modeling framework, particularly concerning identification of surfaces which requires
different boundary conditions, would enable a more accurate prediction against geometries with complex shapes.

(2). MEX crystallization modeling

A more advanced crystallization model which accounts for the effect of shear induced crystallization should be employed in the future research to describe the crystallinity development during MEX printing process.

(3). Combining heat transfer and crystallization modeling

With heat transfer and crystallization modeling combined, the development of crystallinity during the entire printing process can be simulated. This serves as a powerful tool for studying and optimizing the MEX printing process.
Reference


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