Process-structure-properties of additively manufactured continuous carbon fiber reinforced thermoplastic composite

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**PROCESS-STRUCTURE-PROPERTIES OF ADDITIVELY MANUFACTURED
CONTINUOUS CARBON FIBER REINFORCED THERMOPLASTIC
COMPOSITE**

GOH GUO DONG

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2019

PROCESS-STRUCTURE-PROPERTIES OF ADDITIVELY MANUFACTURED
CONTINUOUS CARBON FIBER REINFORCED THERMOPLASTIC
COMPOSITE

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School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University in partial fulfillment of
the requirements for the degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Yeong Wai Yee

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as **G. D. Goh**, Y. L. Yap, S. Agarwala, W. Y. Yeong, “Recent progress in Additive Manufacturing of Fiber Reinforced Polymer Composite: A Review”, *Advanced Material Technologies*, 4, 1800271, 2019.

The contributions of the co-authors are as follows:

- Prof. Yeong provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Ms. Yap Yee Ling, Dr. Shweta, and Prof. Yeong.

and **G. D. Goh**, Y. L. Yap, H. K. J. Tan, S. L. Sing, G. L. Goh, W. Y. Yeong, “Process-structure-properties in Polymer Additive Manufacturing via Material Extrusion: A review”, *Critical Reviews in Solid State and Materials Sciences*, 2019.

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- I performed all the mechanical tests, collected CT-scan images, conducted Raman spectroscopy, and conducted data evaluation.
- Mr. Goh Guo Liang collected SEM images of the fracture surface of the tested specimens.
- Dr. Vishwesh helped me with the high-speed camera for the flexural test.
- Mr. Arun Nagalingam collected data evaluation on the indentation tests.

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4. **G. D. Goh**, V. Dikshit, A. P. Nagalingam, G. L. Goh, S. Agarwala, S. L. Sing, J. Wei, W. Y. Yeong, “Characterization of mechanical properties of additively manufactured carbon fibre and glass fiber reinforced thermoplastics”, *Material & Design*, 2017.
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Abstract

Fiber-reinforced polymer (FRP) composites have been widely used in various applications such as aircraft structures due to their high strength-to-weight ratios and excellent corrosion resistance. The fused filament fabrication (FFF) has become one of the well-received additive manufacturing (AM) techniques to fabricate FRP composites due to its ability to align continuous fibers at tow level. It takes advantage of the fibers' directional strength to distribute loads throughout a structure and allows more design flexibility for novel composite structures to be developed.

The extrusion of continuous FRP composites presents a new research topic on the improvement of interlaminar properties of FRP composites. This research investigates the extrusion process of continuous FRP composites and the mode I interlaminar fracture toughness (ILFT) of FRP composites, which dictates the delamination resistance of composites. In this thesis, the prior arts of using various AM techniques to fabricate discontinuous and continuous FRP composites are analyzed. The anisotropic thermal behavior of the AM continuous carbon fiber-reinforced thermoplastic (CFRTP) renders more in-depth investigation into the temperature history of the AM CFRTP. A numerical heat transfer model is developed to study the temperature profile of the extruded composite filament in the extrusion process. The model will advance the field of extrusion of continuous FRP composites by allowing the prediction of the process parameters for the development of new continuous FRP composite filament.

In the process-structure-property study, the formation of groove, the flatness of the top surface, the waviness of extruded composite filament, and the shearing of matrix from the fiber surface are among the factors that are found to have contributed to porosity of

the printed composite parts which have direct impact on the mode I ILFT. The occurrences of these phenomena are very much related to the rheological properties of the AM CFRTP. Process parameters such as print speed, nozzle and bed temperatures would be able to control the porosity by changing the viscosity and shear rate. Nonetheless, interdiffusion of polymer chains at the interlayer boundary is found to be playing the major role in providing the mode I ILFT. It is found that the highest attainable mode I ILFT is 943 J/m^2 and is achieved by using low print speed (7 mm/s), high nozzle temperature (265 °C), and high bed temperature (70 °C).

Mechanical properties and the failure modes of AM CFRTP are evaluated. The anisotropic nature of the AM CFRTP is apparent in the tensile, compression, and shear modes, which is attributed to the nature of the carbon fibers. It is found that z-direction tensile strength (5.3 MPa) is lower compared to x- (808 MPa) and y- directions (39 MPa). The huge difference in mechanical properties in two transverse directions (y and z directions) was likely due to the difference in the effective contact surface of the intralayer and inter layer boundaries as evidenced in the fracture analysis. Lastly, the ability of the extrusion process to fabricate a geometrically complex structure is demonstrated by printing a quadcopter structure.

These findings contributed to the scientific knowledge on how printing parameters would affect the mode I ILFT through systematic investigation of material science of the AM CFRTP and heat transfer of the extrusion process.

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List of Abbreviation

Abbreviations	Full terms
AM	Additive manufacturing
AM CFRTTP	Additive manufactured carbon fiber reinforced thermoplastic
ASTM	American Society for Testing and Materials
CAD	Computer-aided design
CBAM	Composite-based additive manufacturing method
FDM	Fused deposition modeling
FFF	Fused filament fabrication
FRP	Fiber-reinforced polymer
FRTTP	Fiber-reinforced thermoplastic
FWHM	Full width at half maximum
ILFT	Interlaminar fracture toughness
LOM	Laminated object manufacturing
PSP	Process-structure-property
SLA	Stereolithography
SLS	Selective laser sintering
UAV	Unmanned Aerial Vehicle
T_r	Reptation time
ρ	Density
c	Specific heat capacity
$k_{\parallel}, k_{\perp}$	Thermal conductivity along the fiber direction and in transverse directions respectively
ϕ_f, ϕ_m	Volume fractions of fiber and matrix respectively

1. Introduction

The carbon fiber reinforced polymer (CFRP) material is known for high specific strength-to-weight ratio owing to its unique structure, consisting of high strength load-bearing fiber and load transmitting resin material [1, 2]. Commercial carbon fibers normally come in tow form. Each tow of carbon fibers consists of a few thousands of strands of fine carbon fibers. Each of these strands of carbon fibers is a long thin tube with a diameter of 5-8 microns [3], which consists of layers of flat sheets of carbon atoms arranged in turbostratic crystalline structure leading to high-strength fiber [4]. The strength of the carbon fibers comes in the axial direction. Hence, the fibers need to be aligned in such a way to impart their strength by distributing loads throughout a structure. Using CFRP as the major material to fabricate high-performance structures has become the current trend of various industries [5].

Although different conventional manufacturing techniques have been developed to manufacture FRP composites, there remain some fundamental technological barriers. One common issue with traditional manufacturing techniques is the need for molds which are expensive to manufacture and limiting the formability of the composite parts. As a result, customization of composite parts, which is much anticipated by many industries including aerospace, sports [6] and biomedical industries [7], becomes very costly and uncommon.

The needs to have a mold-free automated fabrication process and more design flexibility have spurred the development of AM, such as material extrusion technique, for FRP composites. AM refers to a group of fabrication techniques in which parts are fabricated layer by layer directly from CAD file [8]. The ability to turn digital files into

physical objects allows people to design, scan, share and send digital representations of physical objects. The disruptive technology of AM, which does not require expensive molds, has simplified the way complex parts are designed. Moreover, the fabrication costs and lead time are significantly reduced, which are ideal for high-performance components that normally have low production volume[9]. Another advantage of using AM to produce FRP composites is the ability to create functionally graded structures[10]. The added flexibility of changing fiber volume fraction and the ability to have locally changing fiber orientations along the projected stress lines, enabling more efficient higher-performance structures to be manufactured, would certainly make AM a lead technology in the composite industry.

The adoption of AM FRP composite in the high-performance structures warrants the need to have a detailed knowledge of the mechanical behavior of the composites under various loading conditions [11]. Delamination is one of the common failure mechanisms that lead to stiffness degradation and the breakdown of composite structures. Other effects of delamination include premature buckling of the laminate, excessive vibration, intrusion of moisture, and loss of fatigue life[12]. Apart from that, delamination is hard to be spotted by means of conventional non-destructive inspection techniques. Delamination is induced by high interlaminar stresses along with the relatively poor out-of-plane strength [13]. This is due to the fact that the fibers within the plane of a laminate do not contribute to out-of-plane reinforcement, thus the composite depends on the relatively low-strength matrix to bear loads in that direction [14].

The resistance to delamination is characterized by the fracture toughness. There are in total of three basic modes of fracture toughness. Mode I is the tensile/peeling mode, whereas mode II and III are shearing modes [15]. The fracture toughness at which the delamination occurs is greatly dependent on the mode of loading. Mode I ILFT is generally lower compared to mode II ILFT [16-18], due to lesser mechanical interlock to impede the propagation of a crack in the peeling mode than in shearing mode [19].

1.1 Motivation

The literature reviewed shows the limitations of the conventional fabrication techniques to fabricate FRP composites. Various AM techniques have been explored to produce FRP composites. They are fused filament fabrication (FFF), ink deposition, stereolithography (SLA), laminated object manufacturing (LOM), computer-based additive manufacturing (CBAM), and selective laser sintering (SLS). Most of the research focused on short fiber reinforcement with only a few on continuous fiber reinforcements, which exhibit superior tensile properties. Thus far, only the material extrusion process possesses the highest ability to selectively align the continuous fiber-reinforced polymer composite. As this technology is still in its infancy, it requires more understanding of its mechanical properties and failure modes of the fabricated composite parts as well as the limitations of these techniques. Detailed analysis of the printing capability and the mechanical performance of fabricated parts would certainly advance the field of AM material extrusion process.

Moreover, AM takes advantage of the fibers' directional strength to distribute loads throughout a structure and allows more design flexibility for novel composite structures to be developed. It enables the creation of a complex higher-performance structure in

one go, which not only does save time and materials but most importantly saves weight by eliminating the need for welding, bolting and riveting individual components. However, the creation of consolidated single structure poses more stringent requirements to the design as well as the materials aspects, especially on the interlaminar properties of the AM CFRTP, which are found to be the weakest link that affects the mechanical performance of the AM composite parts. It is understood that the interlaminar strength of pure thermoplastic is generally affected by process parameters such as nozzle temperature and print speed. However, there is no systematic investigation of the process parameters on the interlaminar properties of the AM continuous composite that look into the PSP relationship. The improvement to the interlaminar properties can be achieved by a more in-depth study of the printing process such as the influence of the printing parameters with fiber alignment and porosity which in turn affect the interlaminar properties.

1.2 Aim and objectives

The main objectives of the project are to achieve good interlaminar properties in FFF-fabricated composites for Unmanned aerial vehicle (UAV) applications through the detailed study of the material extrusion process. Through this research, the understanding of the relationship between the material extrusion process and the behavior of the composite will improve the capability of manufacturing CFRTP parts with good interlaminar properties. In particular, the objectives of this research are:

1. To investigate the thermal profiles of the extrusion process, which affect the polymer fusion process at the interlayer boundaries, through simulations. To investigate the fusion of polymer composite via the heat-press method.

2. To study the effect of printing process parameters on the microstructural changes of composite filament through single filament study.
3. To study the effect of printing process parameters on the mode I ILFT of the continuous FRP composites fabricated using the extrusion-based technique.
4. To characterize the anisotropic mechanical properties and fracture modes of the AM CF RTP.
5. Fabricate 3D printed technology demonstrator using the CF RTP via the extrusion-based technique. The limits and feasibility of material extrusion technique in 3D printed technology demonstrator fabrication will be discovered. To characterize the anisotropic mechanical properties and fracture modes of the AM CF RTP and identify the weakest link in the mechanical properties.

The approach to achieve the objectives and scope of the research is summarized in Figure 1.

Figure 1 Research overview

1.3 Contribution to knowledge

1. A 2D numerical heat transfer model was developed to estimate the thermal profiles of the extruded composite filament. Coupled with formulas with predict the thermal conductivities in the longitudinal and transverse directions, the 2D heat transfer model is able to predict the temperature profile of the composite filament. The model is more accurate than the existing lump-sum analytical model, especially in the first 0.3s of the extrusion process, which is critical in understanding the bond development during the extrusion process. Using this numerical method, the thermal profile of the extrusion of multi-material is also understood.
2. This research presents a systematic approach to investigate the interlaminar properties of the AM CFRTP. The material properties of the AM CFRTP feedstock is first studied to understand its processability. Numerical simulation is used to understand how process parameters affects the temperature profile and the bond development. Single filament extrusion is carried out to study how process parameters influence the microstructure of the extruded composite filament. Lastly, the double cantilever beam method proves to be an effective way to gauge the mode I ILFT of the AM CFRTP.
3. Fracture behaviors of the AM CFRTP under various loading conditions are studied using high-speed camera and computer tomography (CT) images. The understanding of the mechanical properties as well as the fracture behaviors lays the foundation towards having a set of design guidelines for AM CFRTP parts.

1.4 Organization of report

This report comprises of nine chapters. The first chapter is the introduction, in which the need to use AM to produce FRTP composites have been explained, highlighting the objectives and scope. It is then followed by the literature review section, in which the limitation of conventional techniques is explained. In addition, the mechanical properties and the formability of the FRP composites produced using different AM techniques are analyzed to identify the research gap. The research methodology will be presented at chapter 3.

Chapter 4 focuses on the numerical investigation of temperature variation of AM process using finite difference method. The effect of material composition and process parameters on thermal histories of the extruded composite filament are explored. It also gives details of the thermal properties and polymer fusion of AM composites, while the anisotropy and the temperature dependence of the thermal properties are investigated.

In chapter 5, process-structure relationship of the single composite filament is studied, particularly on the fiber alignment, fiber-matrix interface.

Chapter 6 focuses on the process-structure-properties (PSP) of the AM FRTP. Building from the knowledge obtained in chapter 5, the relationships between the material extrusion processing parameters on the fiber alignment, porosity and mode I interlaminar fracture toughness are characterized.

Chapter 7 focuses on the characterization of the mechanical properties of additively manufactured carbon FRP composites components. The anisotropic mechanical properties and failure modes of standardized samples are investigated. Building from

the understanding derived in chapter 7, a 3D printed technology demonstrator part will be presented in Chapter 8 to showcase the capability of the AM material extrusion technique in manufacturing high-performance composite parts by applying the knowledge of material properties derived from previous chapters.

Conclusion and possible future work of the research will be mentioned in Chapter 9.

2. Literature Review

Although there have been review articles highlighting various aspects in additive manufacturing of composite materials, there are still important aspects that are worth discussing which the author included in this thesis. **Table 1** is the list of review papers related to this additive manufacturing of composite materials and their strengths and weaknesses.

Table 1 Recent literature reviews on composites

No	Title	Strengths	Weaknesses
1.	Composites by rapid prototyping technology, <i>Materials & Design</i> , 2010 [20]	<ul style="list-style-type: none"> Discussed different techniques used for composite materials Discussed the use of AM for composite materials in bio-medical applications 	Lack of newest trend in AM for composites since it has been 8 years.
2.	Additive manufacturing of multi-directional preforms for composites: opportunities and challenges, <i>Materials Today</i> , 2015 [21]	Discussed the opportunity and challenges of additive manufacturing of multi-directional preforms for composites	Lack the list of mechanical properties to provide insight to readers as to how the AM composites performs
3.	3D printing of polymer matrix composites: A review and prospective, <i>Composites Part B: Engineering</i> , 2016 [22]	List of mechanical properties available in the literature	The list of mechanical properties is not comprehensive
4.	Recent developments in 3D printable composite materials, <i>RSC Advances</i> , 2016 [23]	Discussion on 3D printable composite materials with different properties such as optical, thermal, mechanical, and electrical	Although provided a long list of composites materials developed by various groups, it lacked the discussion of mechanical properties
5.	A review on composite materials and process parameters optimisation for the fused deposition modelling process,	Detailed discussion on how each printing parameters affects the mechanical properties	Only focused on one technique which is the fused deposition modeling

	<i>Virtual and Physical Prototyping</i> , 2017 [24]		
6.	State-of-the-art of fiber-reinforced polymers in additive manufacturing technologies, <i>Journal of Reinforced Plastics and Composites</i> , 2017 [25]	<ul style="list-style-type: none"> • Briefly touched on fiber and matrix. • Applications in aerospace, injection molding, racing and train technologies 	Did not discuss the fiber-matrix interface and interlayer properties
7.	A review on additive manufacturing of polymer-fiber composites, <i>Composite Structures</i> , 2017 [26]	4D printing of active polymer-fiber composites, and modeling of	Lack of comparison with conventional composite materials
8.	Automated manufacturing and processing of fiber-reinforced polymer (FRP) composites: An additive review of contemporary and modern techniques for advanced materials manufacturing, <i>Additive Manufacturing</i> , 2018 [27]	Provided a quite comprehensive list of composite materials together with the mechanical properties	<ul style="list-style-type: none"> • Did not make comparison with conventional composite materials • Lack discussion on fiber-matrix interfacial properties and interlayer properties.
9.	Printing polymer nanocomposites and composites in three dimensions, <i>Advanced Engineering Materials</i> , 2018 [28]	3d printing of nano composite materials	Focus is on nano materials, Lack of discussion on the continuous carbon fiber composite
10.	Fused filament fabrication of fiber-reinforced polymers: A review <i>Additive Manufacturing</i> , 2018 [29]	Physics involved in the fused filament fabrication	Only focused on one technique.

The literature review of this thesis will focus on the high performance continuous fiber composite and as well as discontinuous fiber composite and will include the discussion on all techniques used for composite materials and a comprehensive list of composite materials developed together with their composition and mechanical

properties. It also touches on important aspects such as interlayer properties, fiber-matrix properties, fiber alignment. In this chapter, recent literature reviews along with their pros and cons are first discussed. It is followed by the limitation of the conventional fabrication techniques for composite parts is first discussed. Then, a set of requirements needed for AM of composites is discussed. It is then followed by the introduction of the techniques that have been used to fabricate composites. A comparison of techniques using a set of requirements introduced will be made and the most suitable candidate for fabrication of continuous FRP composites is identified based on the requirements. Lastly, the parameters that influence the selected fabrication process are identified and discussed.

2.1 Limitation of conventional fabrication techniques for composite parts

Conventional technologies take a complex route and require a mold for printing CRFP materials. Fiber and resin have to be laid out manually in an alternate fashion and cured under high pressure to achieve the desired strength [30] (Figure 2). Apart from the high tooling cost for mold, conventional manufacturing processes such as manual layup [31-34] and resin transfer molding [33, 35-37] use fibers in the form of mats which have poor drape properties making them difficult to form complex parts [38]. Although new laminate designs have been developed such as the non-crimp fiber sheet, which has a better conformability making them more suitable for doubly curved surface, the improvement in formability comes at the expense of lower in-plane performance [39]. Spray up technique, on the other hand, is capable of producing complex parts due to the short fiber nature [40-42]. However, the process is highly dependent on the operator's skill and it is difficult to control the deposition of material accurately. This leads to local

variations in fiber fraction and molding thickness causing reproducibility issue [43]. The needs to reduce the reliance on the human operator and to increase productivity have led to the invention of automated layup processes, namely, automated tape laying (ATL) and automated fiber placement (AFP).

The advantage of ATL is that it can minimize layup errors and material wastage, which brings about better material utilization [44]. However, ATL, due to the wider prepreg tape used, is only suitable to produce parts with simple geometries. On the other hand, AFP is capable of producing more reliable layup over complex geometries and producing locally varying fiber alignments due to smaller individual tape widths that are used, allowing possible enhancements in mechanical performance. Despite all the advantages that ATL and AFP have, the automated processes come at the expense of high initial capital investiture [44] and they are still not mature enough to replace manual layup of complex geometry [45]. There are other techniques that have been developed to fabricate parts with certain design characteristics, such as filament winding and pultrusion [46, 47]. These techniques are specifically developed to produce parts in specific forms at high production rates. However, there are certain constraints on these techniques. For instance, filament winding can only produce cylindrical parts and it cannot align fibers in the longitudinal direction [48]. The pultrusion has also got limitation in terms of design flexibility as it only allows uniform cross-section parts to be produced [48]. The constraint in design flexibility has limited its use to only long and slender parts. All these limitations have led to the search for alternatives in manufacturing composite parts.

Figure 2 Various conventional fabrication techniques and their limitations

2.2 Requirement for additive manufacturing of composites

Researchers have turned to AM to fabricate composite parts due to its flexibility in manufacturing. However, this field is still in its infancy and there are a lot of aspects that need consideration for manufacturing composite parts using AM technologies. For instance, there are certain requirements that FRP composite material needs to fulfill in order to be processed by AM (Figure 3). Fiber reinforcement of appropriate size, shape, and length needs to be selected to suit the intended purpose of the part. Both matrix material, which holds the fibers in place, and reinforcement, need to be compatible with the selected AM technique. A good fiber-to-matrix bonding is required at the fiber-matrix interface to allow loads to be transferred efficiently from the matrix, thus resulting in composites that follow the ‘rule of mixture’ [49]. Fiber loading should also

be optimized in order to obtain the best mechanical properties for AM composites as tensile strength will not increase indefinitely with fiber loading [50]. Homogeneity in fiber distribution is needed to ensure consistent properties throughout the printed part. Added ability to control fiber distribution and alignment in a predefined location and direction respectively also allows strengthening sections of an object. A good inter-layer fusion is required to avoid delamination. Unwanted voids that would affect the mechanical properties of FRP composites should be minimized [51]. Lastly, Rheology of a composite material needs to be taken into account as it affects the printability.

Figure 3 Flow chart illustrating the how the composition of materials affects the meso-level material properties, feedstock material properties and subsequently the resulting part properties

2.3 State-of-the-art in the fabrication of composites using different AM techniques

In this section, different AM techniques for FRP composites are classified into four processes such as material extrusion, vat polymerization, powder bed fusion, and sheet lamination as per ASTM/ISO standard (Figure 4). Each of the processes will be discussed in detail using the requirements introduced at the beginning of this chapter.

Figure 4 Classification of different AM processes for FRP composites

2.3.1 Material extrusion

Material extrusion process selectively deposits the composite material in the solid filament form or paste form, through a nozzle (Figure 5). The technique used to melt and extrude the filament is called fused filament fabrication (FFF) [52] whereas the one in which paste or fluid-like feedstock is printed is called liquid deposition modeling (LDM) [53].

Fused Filament Fabrication

This section focuses on various research carried out on developing new FRP composite materials, ranging from nano-scale discontinuous to continuous fibers using the FFF technique.

Figure 5 Material extrusion process: (a) fused filament fabrication, (b) liquid deposition modelling.

Discontinuous fibers

Discontinuous fibers in varying sizes have been used for the FFF techniques. Among them are nano-scale single-walled carbon nanotube (SWNT) [54, 55], multi-walled carbon nanotube (MWNT) [56], vapor-grown carbon fiber (VGCF) [54, 55] and graphene [57, 58]; micron-sized metal powders, copper [10] and iron [10,11]; and

millimeter long chopped fibers such as thermotropic liquid crystalline polymers (TLCPs) [59, 60], glass [61], and carbon [62, 63]. The commonly used matrix materials are thermoplastics with low melting temperatures like Acrylonitrile Butadiene Styrene (ABS) [54, 55, 57, 58, 61-65], nylon [66], polylactic acid (PLA) [56, 58] and polypropylene (PP) [59, 60], and Ultem® with high melting point [67].

Initially, the fibers are not fully aligned in the composite filament, but shearing force between fibers and nozzle walls give rise to alignment during the AM process [54, 55]. Long fibers generally provide improved mechanical properties [64]. Adding millimeter-sized carbon fiber reinforcement [62] has noted a greater improvement in the in-plane tensile strength and modulus by 250% and 400%, respectively, than that with nano-scale SWNT reinforcement [54]. The improvement is attributed to the larger surface area that permits higher shear at the fiber-matrix interface, thus allowing longer fibers to bear significantly higher load. However, the mechanical properties of the discontinuous FRP composites (Table 1) still remain inferior to composites fabricated by manual layup processes (Figure 10). Effect of fiber loading is another area that has been studied and it is found to be dependent on the reinforcement-matrix combination. Mechanical properties tend to increase with fiber loading at low loading ratio but deteriorate after reaching an optimum value [66]. This phenomenon generally occurs due to poor wettability of fiber with thermoplastic which leads to a poor fiber-matrix interface. Moreover, higher loading causes viscosity to increase, thus causing processability issues such as nozzle clogging [57, 58, 63]. Surfactants and plasticizers can be added to improve fiber-to-matrix bonding. For instance, linear low-density polyethylene (LLDPE) and hydrogenated Buna-N were added as toughening and compatibilizer agent with reinforcement in ABS [61].

The addition of fibers weakens the inter-layer fusion, contrary to what was expected. The out-of-plane tensile strength of the composites was found to be lower than that of the unreinforced thermoplastics [62]. This could be due to the low conformity of the fibers to the previous layer, thus reducing the contact area between layers.

Short FRP composites are relatively easier to be processed by FFF as they are extruded in normal filament from without the need for extra fiber laying mechanism. FFF, however, suffers from limitations like porosity and voids. Voids have been observed to form in between the extruded filaments, thus leading to delamination and reducing the tensile strength [14]. Reinforcement is also more effective along the direction of the filament as compared to across the layer direction as fibers tend to align along the extrusion direction resulting in high anisotropy in mechanical properties [57].

Continuous fibers

Much work has been done to fabricate continuous FRP composites using PLA [68, 69], ABS [70-74], nylon [75, 76] and Ultem® as the matrix, and carbon [69, 76], glass [74], and Kevlar fibers [75] as the reinforcement. AM processing of continuous fiber can be done by simply modifying the print head. Different approaches to print continuous fiber FRP composites have been demonstrated (Figure 5a), such as i) in-situ fusion of thermoplastic liquid resin before extrusion [74]; ii) in-situ fusion of molten thermoplastic with fibers at the nozzle [68-73] and iii) extrusion of pre-impregnated fibers [75-78]. In (i), glass fibers pass through the solution containing dissolved ABS [74]. It is discovered that viscosity would affect both the resin content and the traction force to pull the fibers impregnated within the resin. In (ii), fibers are fused into molten thermoplastic filament at the nozzle [68-73]. The fibers are extruded automatically,

without any feeding device as they tend to be drawn into the nozzle by the movement of melted thermoplastic. In (iii), continuous fiber bundle pre-impregnated with thermoplastics such as nylon and Ultem® are directly fed and extruded from the nozzle. Mechanisms like mechanical cutting [76], laser cutting and resistive heating [77, 78], are needed to cut the fibers at the end of each layer. Comparing to unreinforced specimens, reinforcement by continuous fibers brings about significant improvement in the tensile properties [21, 22, 27].

However, like discontinuous fiber, higher loading of continuous fibers also leads to nozzle clogging. Nozzle clogging issue could be potentially solved by having a separated laying mechanism for fiber, such that the fiber is directly encapsulated by the extruded thermoplastic [79]. Moreover, high fiber loading weakens inter-layer fusion, resulting in low inter-laminar shear strength [70]. In addition to inter-layer fusion, fiber-matrix interface also needs to be improved for printing continuous FRP composites. It was found out that higher temperature during extrusion and post-process like thermal bonding can help to reduce the viscosity and improve impregnation [72, 73].

Liquid Deposition Modeling

For composite feedstock in the form of paste or fluid, the materials are selectively deposited from a syringe that is attached to the computerized numerical control (CNC) machine (Figure 5b). To date, reinforcements only exist in the form of discontinuous fibers in the composite feedstock.

Discontinuous fibers

Thermoplastics such as PLA [80] and thermosets such as acrylic-based and epoxy-based resins have been used as the matrix material [81, 82]. So far, the reinforcement exists only in form of discontinuous fibers like silicon carbide (SiC) whiskers [10], carbon fibers [10, 36, 37], glass fibers [36] and carbon nanotubes (CNT) [38, 39]. Reinforcement materials are mixed homogeneously with liquid resin to form paste-like composite feedstock. Some reinforcements especially CNTs generally suffer from the problem of agglomeration, it is hence essential to do surface treatment with acid to ionize the CNTs or to use suitable solvent mediums such as polyvinylpyrrolidone to uniformly disperse them [83].

Being in liquid form at room temperature, it is generally easier to process thermoset resins than the thermoplastics using LDM technique. Epoxy resin ink, however, requires specific rheological and viscoelastic properties to be extruded smoothly from the nozzle. It should be noted that most ink dispersions formed using these materials exhibit a shear-thinning behavior characterized by the increasing shear rate with decreasing viscosity [83].

In another variation, photo-curable and thermo-curable components are added to form dual-cure composites, where the former allows fast curing to maintain the shape while the latter helps to complete the crosslinking to achieve good mechanical properties [81, 82]. Imidazole-based ionic liquids have been explored to use as a curing agent to prolong the printing window to up to 30 days under ambient conditions [53]. It has been shown that the use of volatile solvents for dissolving thermoplastics lowers the processing temperature [10].

The work on epoxy-based resins is of significance as it demonstrates how fibers can be aligned by controlling parameters like aspect ratio and nozzle diameter [53]. Although only discontinuous FRPCs have been printed so far, the efforts mark an important step in designing engineering materials and can be manipulated to print continuous fibers in the future.

2.3.2 Vat photopolymerization

Vat photopolymerization selectively cures photopolymer in a vat using ultraviolet (UV) light. Stereolithography (SLA) is a commonly used vat photopolymerization technique to print FRP composites (Figure 6).

Figure 6 Vat-photopolymerization process and the schematic representation of the cross-sectional view of the UV curing of FRP composites in SLA.

Stereolithography

To date, reinforcements in the forms of discontinuous fibers, continuous fibers, and fiber mat have been used in SLA to create FRP composites. SLA is known to produce parts with low porosity (0-5%) [84-86].

Discontinuous fibers

Various types of discontinuous reinforcements ranging from nano-scale fibers, for example, silicate dioxide (SiO_2) nanoparticles [87] and carbon black [88], micron-scale fibers, for example, alpha-alumina powder [89], ferromagnetic fibers [86, 90], titanium carbide (TiC) [91], bioglass [85] and SiC [92], and to milli-scale glass fiber [84, 93, 94] have been used to create FRP composites in SLA. Matrix materials used are generally photosensitive polyacrylate resin [84, 85, 87, 94, 95], although polyester resin [96] and epoxy resin [97] have also been attempted.

There are mainly two methods to prepare the composite materials, i.e. i) by premixing the reinforcement and resin [84-88, 91, 92, 95, 97, 98] and ii) dispersing the fiber on the surface of resin [94]. Additives may be added into the composite for various reasons, namely to facilitate polymerization, reduce the viscosity of the resin, stabilize the suspension, and to act as a coupling agent between the fiber and matrix. In another variation, a new layer of composite resin is added onto the build tray at the start of each layer to avoid sedimentation of fiber in the resin [99-103]. The fiber surfaces are treated in order to decrease the viscosity of resin to permit higher fiber concentration. The highest tensile strength reported so far is 72 MPa with the addition of 16 vol% of glass fiber [101], implying that SLA fabricated FRP composite is, nevertheless, still inferior to the conventional FRP composites.

As the composite materials are normally premixed, fibers are randomly oriented and uniformly dispersed, resulting in the need for an extra mechanism to align the fibers [84, 87]. Although fiber loading up to 60 vol% has been attempted, it was found that higher loading would generally lead to a poorer fiber dispersion [92]. In addition, the entanglement of fibers is noticed at higher loading, which weakens the fiber-matrix bonding.

Improvement in tensile strength [84, 88], Young's Modulus [87], flexural strength [92], fracture toughness [87, 92], and hardness [97] have been observed upon adding reinforcement. However, these mechanical properties are influenced by the shape, density, and size of the reinforcement. Unlike the aforementioned cases, the addition of microsphere was found to have a negative effect on the tensile strength [94, 95]. The drop in tensile strength were probably due to the use of low density hollow microsphere. Lu *et al.* varied the carbon fiber length and found out that the fracture toughness was enhanced using 2 mm fibers while the flexural strength was higher with 1 mm fibers [92]. Apart from that, adding reinforcement minimizes the shrinkage and thus improving the printing quality [87].

However, there are several issues associated with the addition of reinforcement into the photo-curable resin. Firstly, the viscosity of the resin increases with the addition of the reinforcement, which may affect processability [87]. The light scattering caused by the particles in the suspension reduces the UV penetration depth and lateral resolution so longer irradiation [89] or higher laser power [84] is required to achieve the same polymerized depth. The issue can be circumvented by using materials that are transparent to the UV radiation, such as the aluminum-based quasicrystalline [97].

Continuous fibers

Research has been carried out on continuous FRP composites using glass [94] and carbon fiber bundles [104, 105] and e-glass and carbon fiber mats [106, 107] as reinforcement. Continuous fiber AM in SLA has been done by manual laying [94, 106, 107] or incorporating fiber laying mechanisms [104, 105].

The addition of continuous fiber has shown improvement in the tensile strength of the pure resin by 2-3 times [105]. In another work, E-glass, carbon, and aramid nonwoven mats are used to reinforce acrylic- and epoxy-based resins [107]. It is found that E-glass and carbon in acrylic-based resin could bring about 50% improvement in both elastic modulus and tensile strength. However, the reinforcement loading achievable is low (<20%) due to the lack of consolidation process [94]. Although tensile strength between 83.5-143 MPa is obtainable, it still is short of the predicted strength due to poor fiber-matrix bonding [105]. The poor bonding is a result of incomplete curing in the interior due to the scattering of UV radiation caused by the fiber tows. In order to improve the fiber-matrix interface, thermal treatment [104] and post UV curing [106] are used to post-cure the resin. Hence, the use of fibers that is transparent to UV radiation could be a potential solution to the problem. Placement of the continuous fiber or fiber mat is a problem, which may cause air entrapment [106] and cause uneven surface in printed part [105], thus weakening the inter-layer bonding.

2.3.3 Sheet lamination

In sheet lamination, sheets of material are bonded to form an object. There are two techniques under this, namely laminated object manufacturing (LOM) and composite-based additive manufacturing method (CBAM).

Laminated Object Manufacturing (LOM)

LOM is a process that combines additive and subtractive techniques to build a part layer-by-layer from a stack of fiber sheets [108]. A laser is used to cut the shape of each layer and the layers are then bonded together by adhesive or by pressure and heat to reduce the void content (Figure 7a).

Sheet Lamination

(a) Laminated Object Manufacturing

(b) Composite-based Additive Manufacturing

Figure 7 Sheet lamination process: (a) laminated object manufacturing (LOM) and (b) composite-based additive manufacturing.

Mat/sheets

The feedstock to the LOM is in the form of sheet material, which can be commercial prepreg sheets or any fiber preform. Using prepreg sheets containing 55 vol% unidirectional E-glass fibers with epoxy matrix, tensile strength and flexural strength of the LOM fabricated FRP composites are found out to be 716 MPa and 1.19 GPa

respectively indicating good fiber-matrix and inter-layer bonding [109]. The LOM process is further improved by integrating a curved layer building mechanism, which eradicated the stair-step effect, minimized wastage, and provided the capability to keep continuous fibers in the direction of curvature [110].

Composite-based additive manufacturing method (CBAM)

Mat/Sheet

CBAM utilizes an aqueous-based solution to be deposited first on each layer of fiber sheet using inkjet technique (Figure 7b). Subsequently, the fiber sheet is covered with the thermoplastic powder matrix, which adheres only to the aqueous solution. After removing the excess powder, the fiber sheets are stacked, compressed, and heated in the oven to fuse the matrix for consolidation. Finally, the part is sandblasted to remove the excess fibers, revealing the final product. The highest tensile strength achievable so far is 165 MPa [111]. Low strength of CBAM printed part, when compared to LOM, is due to the use of randomly oriented discontinuous fiber sheets [112].

The ability to produce high strength parts compared to conventional methods is one of the advantages of the sheet lamination technique. In addition, this technique does not require any support structure as the sheets can act as the support. However, unlike other AM processes where the support structures are generated for overhanging features, the fiber sheets are needed in every layer. This leads to material wastage, as the used sheets are not reusable. Moreover, this technique does not allow complex internal features to be fabricated as the removal of unwanted materials would be difficult [108].

2.3.4 Powder bed fusion

Powder bed fusion makes use of thermal energy to selectively fuse regions of a powder bed. A commonly known powder bed fusion process for polymers is selective laser sintering (SLS) (Figure 8).

Selective Laser Sintering

To date, reinforcements for SLS-fabricated FRP composites are mostly found in the form of discontinuous fibers.

Figure 8 Schematic representation of powder bed fusion and the composite powder used.

Discontinuous fibers

Many attempts to improve mechanical and physical properties by reinforcing raw powder with nano-scale and micro-scale fibers such as CNT [113, 114], carbon black [115], carbon nanofiber [116], yttrium stabilized zirconia (YSZ) [117], glass beads [118-120], SiC [121, 122], and nano-silica [123] have been carried out. Various composite

PA-12 powder are available commercially, namely glass-filled PA-12 (Duraform GF, PA3200 GF), carbon-fiber-filled PA-12 (Duraform HST, CarbonMide, Windform XT) and aluminum-filled PA-12 (Alumide). Matrix materials used are typically the thermoplastics like polyamide, with PA-12 being most widely used in SLS [116, 117]. Instead of modifying the manufacturing process, research is targeted at homogeneously mixing the composite powder. This is achieved by using either mechanical [118, 122] and melt mixing [116] of the materials or by coating the fibers by dissolution-precipitation [123, 124] and surfactant-facilitated latex methods [113]. Recently, Zhu, et al. [125] developed short carbon fiber (CF) reinforced thermosetting composite by infiltrating the porous SLS manufactured PA-12/CF with epoxy resin under high temperature and pressure. Unlike other methods, the composite powder is prepared by coating a thin layer of PA-12 on the CF surfaces to produce a porous green-part before infiltration.

Although adding reinforcement leads to enhancement in tensile modulus; weak interface as a result of poor adhesion and voids is also observed [116]. Though SLS fabricated pure PA-12 parts are generally stronger than those made by extrusion and injection molding, the SLS fabricated FRP composite has significantly lower elastic modulus and strength than the ones made by conventional methods [115]. This was found to be due to poor dispersion of fibers in the powder feedstock and higher internal porosity predominantly present in the fiber-rich domains. SLS is also restricted to developing discontinuous FRP composites due to its fabrication nature [112]. If SLS is to be explored for laying continuous fibers, additional devices would be required to lay fibers and this would complicate the entire manufacturing process.

Table 2 Summary of various AM techniques for FRP composites

Techniques	Advantages	Disadvantages	Types of fiber		Fiber/ matrix composition	Mechanical Properties			Ref
						UTS (MPa)	Young's Modulus (GPa)	Other Properties	
Material Extrusion									
FFF	<ul style="list-style-type: none">• Easy fabrication• Able to modify print-head for laying fibers• Multi-material capability	<ul style="list-style-type: none">• Nozzle degradation• Nozzle clogging at high fiber volume	Disconti	Nano	SWCNTs (5%)/ Carbon fiber (5%)/	30	1.75	High	[54,
					MAGNUM 213 ABS			reinforcement and	55]
								better strength.	
					Graphene (5.6 wt%) /ABS/PLA	-	-	High mechanical	[58]
								strength	
					MWCNTs (0.2%)/ PLA	55	3	47% increase in	[56]
								tensile strength	
					Graphene nanoplatelets (4 wt%)/ ABS	35.5	2.8	Higher tensile	[57]
								modulus	

FFF

Discontinuous	Micro	Fe ₃ O ₄ (30–80 μm) (30-40%)/ P301	4	0.054	Improved	[66]
		Nylon			stiffness and	
					thermal properties	
		Cu (10 or 45μm)/ Fe (45 μm)/ ABS	15	0.23	Tensile modulus: 54 MPa with 30% Fe	[65]
		Short fiber (15%)/ ABS	42	2.5	Toughness: 6.3 Jm ⁻³ 10 ³	[64]
Milli		Vectra A950 TLCP (60 mm) (28%)/ Amoco polypropylene	45	4	High tensile modulus	[59, 60]
		Glass fiber (18%)/ ABS	58.6	-	Improved ductility and flexibility	[61]
		Carbon fiber (0.2-0.4 mm) (40%)/ ABS	65	14	115% higher tensile strength	[63]

FFF

Discontinuous	Milli	Carbon fiber (3.2 mm)/ ABS	70	8.91	Increased strength and stiffness	[62]
Continuous		Carbon fiber (34.5%)/nylon	475	35.7	High tensile modulus	[76]
		Carbon fiber bundle/ ABS	-	-	Increased strength	[72]
		Carbon fiber bundle/PLA	90	5.8	Tensile modulus: 294 GPa	[69]
		CNT yarn/ Ultem® 1010	117	2.4	Tensile strength: 317 MPa	[77, 78]
		1000-carbon fiber bundle/ ABS	150	4	Flexural strength: 125 MPa Flexural modulus: 7.8 GPa	[70, 71]

FFF		Continuous					Interlaminar shear strength: 2.81 MPa			
		Kevlar (10%) / Nylon					90	9	Elastic modulus: 1767 MPa	[75]
		Carbon fiber / PLA					91	-	Flexural strength: 156 MPa	[68]
<hr/>										
Liquid deposition modeling	<ul style="list-style-type: none">• Laying continuous fiber• Epoxy-based resin	<ul style="list-style-type: none">• Need for fresh resin	Discontinuous	Micro	SiC whiskers/epoxy using an Epon 826 epoxy resin, nano-clay platelets, and dimethyl methyl phosphonate (DMMP)	Longitudinal: 96.6	Transverse: 10.61	Young's modulus nearly equivalent to wood cell walls	[53]	
						Transverse: 69.8	Longitudinal: 16.10			
<hr/>										

Liquid deposition modeling	Disconti nuous	Micro	SiC whiskers-carbon fibers/ epoxy (Epon 826), nano-clay platelets, and dimethyl methyl phosphonate (DMMP)	Longitu dinal: 66.2 Transv erse: 43.9	Transver se: 8.06 Longitud inal: 24.5		
			Carbon Fibers (length 100-150 mm)/ Bisphenol A ethoxylate diacrylate/Bisphenol A diglycidyl ether/2,4,6- trimethylbenzoylphenyl phosphinate (Irgacure TPO-L)	40	3.6	Using dual-cure technique	[81, 82]
		Nano	A-MWNT (7 wt%)/ PVP (17 wt%)	-	-	Electrical Conducting	[83]
			MWCNTs (1 wt%) and PLA (30 wt%)	-	-	Electrical Conducting	[80]

Vat photopolymerization									
SLA	<ul style="list-style-type: none">• Random alignment of discontinuous fibers for isotropic mechanical property• Adding fiber increases viscosity, thus making handling difficult• Fiber sedimentation in resin• Need for additional feeding device for deposition• UV penetration issue• Bubble formation causing pores to form and leading to crack initiation	Discontinuous	Nano	SiO ₂ nanoparticles (20 nm)/ acrylate functionalized oligomers Genomer 4302 (G4302)/ Sartomer CN922 with the monomer tris(2-hydroxyethyl)isocyanurate triacrylate (SR368)	-	1.7	Fracture Toughness K _{IC} : 0.38 MPa m ^{-1/2}	[87]	
				Nano-carbon black (30 nm)/ Visible light curing polymer	0.24	-	Hardness: 81 mm	[88]	
							Decomposition temperature: increased to 359.23°C		
			Micro	Hollow microsphere (55 μm)/ polyacrylate resin	-	-	Reduced tensile stress by using low-density microsphere	[94]	

SLA	Discontinuous	Micro	Alpha-alumina powder (P172SB, Pechiney)/ photocurable monomer	-	-	Improved vertical resolution	[89]
			Ferromagnetic fibers (γ Fe ₂ O ₃)/ photopolymer	-	-	Magnetic alignment	[86, 90]
			Electrical conductive whisker (TiC) (50 μ m)/photopolymer	-	-	Electric alignment	[91]
			Bioglass (5-30 μ m)/ Acrylate-based monomer	-	-	Biaxial strength: 40 MPa	[85]
			Al ₅₉ Cu _{25.5} Fe _{12.5} B ₃ (25 μ m)/ Accura Si40 resin	-	-	Improvement in shrinkage improves by 90%	[97]
			Irregular SiC powders(40-53%)/ DSM Somos 19120 resin	-	-	Flexural Strength: 325 MPa	[92]

SLA

Discontinuous

Micro

Fracture

toughness: 4.5

MPa m^{1/2}

Milli

e-glass fiber (10-15 mm)/ polyacrylate resin

26

-

Provide better mechanical improvement compared to the microsphere

[94]

e-glass epoxy (80%)/ SLA 250 photopolymer

24.13

5.8

Functionally graded materials with thermal and electrical conductivities can be created

[93]

Glass fiber (20%)/ DeSolute SCR310 (SCR-310, 1995), a urethane acrylic based photo-polymer

29

3

Improved shrinkage

[84]

SLA

Discontinuous	Milli	Glass fiber (17.9%)/Ciba-Geigy SL5170 resin	72	2.49	60 percent increase in the modulus for the (riveted) composite specimens	[99, 100, 102, 103]
Continuous		800 e-glass fibers (4.6%)/ Somos 3100 resin	87.2	3	twofold improvement of resin strength and stiffness	[126]
		Thornel T-300 tow of 3000 fibers (5%)/ XB5081 Ciba Geigy	46.3	-	30% improvement in tensile strength	[104]
		Nonwoven fiber mat (e-Glass, PAN-based carbon, Aramid)/ Acrylic based matrix (AlliedSignal Exactomer 2202SF) or Epoxy based matrix (DSM Somos 7110)	30-55	1.81-2.85	increase of 36% in ultimate tensile strength	[106, 107]

Sheet Lamination								
LOM	<ul style="list-style-type: none"> • High-strength parts can be produced • Low cost, • No post-processing • No need for support structures 	<ul style="list-style-type: none"> • High material wastage • Difficult to build complex internal cavities [108] 	Mat/ Sheet	Aerospace-grade prepreg containing e-glass fibers (52–55 vol%) / epoxy	713	-	Compression 896 MPa Flexure: 1190 MPa Interlaminar shear strength: 42.6 MPa	[109]
CBAM	<ul style="list-style-type: none"> • No need for support structures 	<ul style="list-style-type: none"> • Difficult to build complex internal cavities • Cannot align fibers in a plane • Involves multiple steps • Manual mechanism 	Mat/sheet with randomly oriented short fibers [112]	Carbon fiber/ Kevlar/ fiberglass/ high-density polyethylene	165	-	-	[111]

Powder Bed Fusion									
SLS	<ul style="list-style-type: none"> • Easy to remove support material • Unused powder can be reused • High loading of reinforcement 	<ul style="list-style-type: none"> • Long and continuous fiber reinforcement not possible • Rough surface finish 	Discontinuous	Nano	CNT (0.5 wt %)/PA-12 & PU Carbon black (4 wt%)/PA-12 Carbon nanofiber (3 wt %)/PA-12	- 26 -	- 1.0 -	Thermal conductivity: up to 16.9 W m ⁻¹ K ⁻¹ Flexural modulus: 1.4 GPa Flexural strength at 5% strain: 65 MPa Impact strength: 12 J/m Storage modulus at room temperature: 1.2 GPa	[113] [116]

SLS	Discontinuous	Micro	YSZ (5 wt%)/ PA-6	25	-	-	[117]
			Glass beads (30 vol%)/PA-11	-	1.7	Near full density of 99%	[118]
						Compressive modulus: 2.6 GPa	
			SiC (10,25,50 wt %)/PA-12	34-40.5		Reduced strength with higher loading	[122]
						High porosity: >20%	
			Nanosilica (3 wt%)/PA-12	20.83	1.98	Impact strength=40.2KJ/m ²	[123]

2.4 Comparison of different AM techniques

Table shows the comparison among different AM techniques on a set of requirements that have been introduced at the beginning of the literature review. Information is filled in when available for each technique.

Thus far, only FFF [68-72, 75-78], LOM [109], SLA [104, 106, 107, 126] techniques have been used to produce continuous fiber-reinforced composites. In LOM, continuous fibers woven in sheet form can be used to fabricate continuous FRP composites. Fabrication of continuous FRP in SLA is made possible with the addition of fiber laying mechanism whereas fabrication of continuous FRP in FFF is made possible by a simple modification of existing print head. Although no attempts have been made for ink deposition, it is thought that ink deposition technique has the potential to fabricate continuous FRP composites by applying an in-situ coating of continuous fiber technique that is used in FFF technique.

For alignment of fibers in a layer, most of the AM techniques are capable of doing alignment of fibers to a certain degree except for SLS, which is only able to produce randomly oriented short fibers composites [113, 116-118, 122]. LOM provides slightly more freedom as fibers are oriented in the same direction in a layer of fiber sheet and fibers direction can be varied at different layers by changing the stacking orientation of fiber sheets. SLA, FFF, and ink deposition, on the other hand, have the flexibility to control and change the fiber direction in the same layer. FFF and ink deposition have a slight advantage over SLA as they do not require an additional mechanism to align the

fiber. This is because fibers can be automatically aligned by shearing against the nozzle wall when they are extruded from the nozzle [127]. SLA requires additional mechanisms such as electric field [91] or magnetic field [86] to align the short fibers and requires laying mechanism for laying continuous fibers (Figure 9).

Figure 9 Various fiber alignment mechanisms for various AM techniques

In fiber loading aspect, SLA [92], SLS [122], and LOM [109] are able to process composite materials with more than 50 vol % of fiber loading (Figure 10). On the other hand, extrusion processes such as FFF and ink deposition can only achieve up to 40 vol% and 30 vol% respectively [66]. Nozzle clogging issue was the limiting factor for

the fiber loadings of FFF and ink deposition [57, 58, 63]. Modeling of the extrusion process for short fiber has been attempted to simulate the alignment of fibers and nozzle clogging [127]. Optimum fiber-matrix composition can be obtained to avoid nozzle clogging through modeling and simulation. However, the modeling of the extrusion process for continuous fiber has not been attempted in which the nature of the process is distinctly different from that of the short fiber. For instance, buckling of continuous fiber in the nozzle at high temperature is a phenomenon that is absent in short fiber extrusion process.

Figure 10 Tensile strength vs fiber volume ratio of parts manufactured via various conventional and AM techniques

The matrix used for each technique is different from one another. For instance, thermoset resin is normally used for ink deposition. Thermoplastics, which has better

impact resistance than thermoset resin [128], are used in filament form and powder form for FFF and SLS respectively. These AM-fabricated thermoplastics have similar characteristics as injection-molded thermoplastics and are relatively stable. SLA, on the other hand, uses photocurable resins which are less stable and would creep under constant load [129]. This renders SLA not suitable for high-performance engineering applications.

Interlayer bonding of pure thermoplastics in AM has been researched [130], where parameters such as z -direction tensile strength, mode-I interlaminar fracture toughness [131] and interlaminar shear strength [132, 133] have been used to gauge the interlayer properties. In general, the z -direction tensile properties are weaker than those in in-plane as observed in various AM techniques of FFF [132], SLS [134], and inkjet [135]. In polyjet, the ultimate tensile strength in the z -direction is only 60% of that in x and y -directions [135]. In SLS, the fracture strain in the z -direction is found to be lower compared to the x -direction, indicating that the interlayer fracture is more brittle than intralayer fracture [134]. Direct comparison of the interlayer bonding among the AM techniques cannot be made as different methods were used, however, the results point out that it is imperative to put efforts in the direction to improve interlayer bonding of AM materials.

Porosity information is not available for every technique. Thus far, only the porosity for the FFF and SLA fabricated composite parts have been reported. FFF generally produces parts with higher porosity. This is due to the extrusion nature of the FFF technique whereby patterns are filled lines by lines which results in voids in between

the lines [14]. The voids can be reduced by changing the printing parameter to make the two adjacent lines overlap thus avoiding gaps.

Table 3 *Comparison of different AM techniques*

	FFF	SLA	SLS	LOM	Ink deposition
Alignment in a layer	yes	Yes- with an additional mechanism	No	Yes –uni-directional in a layer	yes
Fiber loading	Up to 40 vol%	Up to 60 vol%	50 vol%	55 vol%	30 vol%
Continuity of fiber	continuous	continuous	Nano-discontinuous	Continuous or discontinuous depending on a fiber sheet	Potential to be continuous
Matrix	-Thermoplastics -Relatively stable	-photocurable resin -Not stable, Creep would occur	-thermoplastics in powder form	-epoxy	-thermoset resin
Porosity	10-25%	<5%	-	-	-
Inter-layer bonding	-Tensile strength and shear strength Reduced with the addition of fiber. (compared to pure thermoplastic) -Increases with fiber content	-	-inter-layer fracture is a more brittle and intra-layer fracture	-	-

In summary, although parts with porosity is an inherent nature of extrusion process, the extrusion processes, namely the FFF and ink deposition, seem to be more the promising candidates for additive manufacturing of high-performance composites. This is due to their abilities to lay continuous fiber, to align the fiber direction in a layer

and achieve decent fiber loading. Between the two extrusion-based techniques, FFF is seen to be the better process for producing high-performance FRP composites due to its ability to process high impact resistance thermoplastics.

2.5 PSP relationship and process optimization in AM

PSP relationships for materials are useful to design parts with the intended properties. The investigation of PSP relationship of a material enables the understanding of the cause and effect of the process on the material, which in turn allows the creation of the performance-tailored microstructures based on the objectives and goals of the design [136]. PSP relationships are obtained through experimental characterization of the microstructure and properties of the materials as well as through numerical simulation based on the understanding of the science involved during the fabrication process (**Figure 11**). The structure of the AM parts are categorized into 3 levels: the microstructure, mesostructure and macrostructure[137]. Microstructure in AM materials involves phase and grain size distributions as well as pores in the microscale. Mesostructures involves periodic arrangement of microstructure as a result of printing strategies, lattice structures and open-cell foams. Macrostructure involves the overall design of the parts and the dimensional accuracy of the AM parts, which is normally inspected using optical microscope or other length measuring tools. To study the PSP relationship, the effect of the process parameters on the microstructure is normally investigated from the most fundamental unit, which is a single road of filament in the case of FFF or a single laser track in the case of SLA and SLS. The dimensions of the single road or a single laser track can be characterized using optical or SEM images.

The grain and phase distributions are analyzed using TEM, XRD, EDX[138]. The mechanical properties of the AM parts are evaluated through various standard mechanical tests. The mechanical response and the failure behavior of the AM parts in various part orientations are normally investigated in detail due to the anisotropic nature of the AM parts.

The PSP relationships of materials can be further understood through numerical simulations. Yan et al. developed a multiscale modelling framework to investigate the driving mechanisms of the direct energy deposition AM technique through a bottom-up approach [139]. In this approach, the source was modeled at microscales to study the laser-particle interaction to obtain laser penetration trajectories and energy transfer. Mesoscale powder spreading model and hydrodynamic model were incorporated to study the particle colliding and melting and cooling of the molten pool at the powder scale. Cellular automata coupled finite element (CAFE) and kinetic Monte Carlo (KMC) methods were used to simulate the grain nucleation/growth and subsequent coarsening due to the repeated reheating and cooling process. Using the PSP relationship, it allows the data driven material design through the use of machine learning algorithm.

Apart from mechanical properties, PSP relationship for other properties have also been performed. For instance, Ravoori et al. investigated the PSP relationship on the thermal conductivity of the FFF-fabricated PLA samples. High speed camera and optical microscope were used to understand the effect of printing parameters such as layer thickness, raster orientation and extruder speed on the microstructure of the FFF-fabricated samples. The thermal conductivity of the samples printed with various

printing parameters were measured using Fox50 thermal conductivity measurement instrument to complete the PSP relationship.

Figure 11 PSP relationship of AM combining efforts from experimental characterization and numerical modelling [140].

As optimal process windows of the AM processes are material specific, process optimization is normally carried out for every new material developed for an AM process. Also, the optimal process window of a single material varies depending on the targeted material properties to achieve. Design of experiment (DoE) method is normally

used to study the effect of process parameters on the microstructure as well as the mechanical properties of the AM materials. For instance, Abbott et al. used DoE to study the effect of FFF print parameters on extrudate cooling profiles, road-to-road contact lengths, and transverse tensile strength of ABS [141]. Parameters that were investigated were nozzle temperature, print speed, layer height, and part orientation. Two levels were selected for each print parameter. Analysis of variance (ANOVA) revealed that the main effects (i.e. the nozzle temperature, print speed, layer height, and part orientation) do have significant effects on the transverse tensile strength. Print speed is found to be inversely related to the transverse tensile strength, whereas increasing the nozzle temperature increases the transverse tensile strength.

Lee et al. used Taguchi approach to study the effect of the print parameters on the throwing distance of the FFF-printed catapult[142]. 4 print parameters (air gap, raster width, raster angle, and layer thickness) were selected for the study and 3 levels were chosen for each print parameters. ANOVA was then carried out to study the significance of each print parameter on the throwing distance of the catapult. Study revealed that air gap, raster angle, and layer thickness played major roles in the quality of the printed catapult whereas the effect of raster width is the most insignificant.

In short, there is not a universal set of print parameters that will produce optimal properties for all possible build orientations. Therefore, detailed PSP relationships are required for every material and process. Engineers should wisely choose the part orientation and print parameters based on the PSP relationships obtained from the experiments. Design and manufacturing judgments must depend on anticipated usage of

the printed parts and the possible loading conditions, like the magnitudes and directions of mechanical stresses.

2.6 Process and printing parameters of FFF

Many factors affect the quality of the FFF-fabricated parts and they are illustrated in Figure 12. Proper control of the associated factors is required in order to build products with high quality. Recently, there has been a lot of research in FFF process optimization as well as the development of new materials for FFF technology. In process optimization, extruder temperature [143], raster angle [143-148], layer thickness [144, 147, 148], raster gap [143, 144, 147, 148], raster width [143, 144, 147, 148], contour width [147], and specimen orientation [144, 148, 149] are the process parameters that have been studied extensively to obtain the highest possible mechanical properties. Other factors such as filament quality and environmental factors such as oxygen content [150], temperature [151] and humidity [151, 152] are known to have an effect on part quality and mechanical properties. For instance, Lederle *et al.* observed an increase in elongation at break for amorphous material like ABS and a 30% improvement in tensile strength for polyamide under the absence of oxygen [150]. Halidi and Abdullah noticed that the diameters of the ABS filament feedstock would increase as it absorbs moisture [152]. However, the effect of change in diameters as a result of an increase in moisture content on the print quality or mechanical properties were not determined. Chuang *et al.* argued that entrapped moisture in the filament will undergo expansion at elevated temperature and thus increases the porosity within the filament which results in lower mechanical properties [153]. Kim *et al.* noted that FFF-fabricated samples generally

absorb more moisture (5-8%) as compared to injection molded samples (0.34%) and samples with more moisture content perform poorer by as much as 10% in terms of tensile strength [151]. In the same study, they found out that the tensile strength is reduced by about 27% whereas the strain increases when the specimens are at 60 °C as compared to room temperature. Materials used for FFF technology are normally pure thermoplastics such as ABS, PC, Ultem, Nylon, PEEK, etc. Composite materials have also been developed to be used in the FFF technology by adding short fibers into the thermoplastics to obtain better mechanical strength. Various static and dynamic mechanical tests have been conducted to assess the suitability of the FFF-printed materials for end-product applications.

Figure 12 Factors affecting the part quality and mechanical properties of the FFF-fabricated thermoplastic parts

2.6.1 Process parameters of FFF

In this section, the definitions of the process parameters will be introduced with the help of illustration as shown in Figure 13 [148, 154].

Layer thickness [mm]: Is the height of each slice of the 3D printed part

Raster angle [degree]: Is the angle at which the nozzle deposits molten thermoplastics line-by-line for each layer and it ranges from 0° to 180°.

Contours/shell perimeters: are the outermost shells to use for the exterior skin and internal hole of the part. The number of the contours/shell perimeters and the contour's width can be used to vary the shell thickness.

Raster/bead width [mm]: refers to the width of the extruded filament.

Air/raster gap [mm]: refers to the opening between two adjacent extruded filaments, and, a negative air gap means there is overlapping between two adjacent filaments.

Deposition speed [mm/min]: It is the speed at which the nozzle moves. This is directly related to printing speed.

Fill Density [%]: The amount of material within the part. The higher the percentage of fill, the better the mechanical properties of the part, however, the printing time will be longer and more material will be needed.

Platform/bed Temperature [°C]: It is the temperature of the build platform. This parameter determines the cooling rate of the extruded filament especially on the first

layer and is an important parameter for good adhesion of the first layer and the prevention of warping effect.

Nozzle Temperature [°C]: This is the temperature at which the material is being extruded. The temperature is normally a few degrees Celsius higher than the melting point of the materials.

Chamber Temperature [°C]: Some FFF printers have a controlled temperature environment to have a more consistent printing result. This refers to the ambient temperature inside the building environment.

Specimen/Build orientation denotes the direction of the printed part on the build platform, about the x , y , and z -axes.

Figure 13 *Printing parameters of FFF technique*

2.6.2 Mechanical properties of additively manufactured polymeric materials

Review of the literature shows that a significant amount of the published work has concentrated on tension and flexural testing. In Table 4 and Table 5, the effects of specimen orientation and printing parameters such as raster angles and layer thickness on various mechanical properties are reported. The X, Y, Z labels used for the specimen orientation shown in Figure 14 are in accordance with the standard (ISO/ASTM 5291:2013 Standard Terminology for Additive Manufacturing – Coordinate Systems and Test Methodologies) and have been used by Lewandowski *et al.* to systematically discuss the mechanical properties of the AM metal parts [155].

Figure 14 Definition of the specimen orientations

As stated in the standard, Z denotes the build direction. The X-axis is parallel to the front of the machine and is at right angle to Z. The Y-axis is normal to both the Z and X axes, with a positive direction defined to make a right-hand set coordinates. For rectangular and unsymmetrical test specimens, three letters (X, Y, Z) are needed to define the orientation. The first letter denotes the axis in the direction of the longest

overall dimensions. The second letter denotes the second-longest overall dimension, while the third letter denotes the shortest dimension of the coupon. As an illustration, a specimen with XYZ designation means that its longest dimension is aligned to X-axis, its second-longest dimension is aligned to Y-axis, and its shortest overall dimension is aligned to Z-axis.

Quasi-static properties: tensile and flexural

Thus far, various tests have been used to determine the tensile and flexural properties of the polymer materials. Tensile properties are the most commonly used properties by researchers to determine the material properties. Hence, in this section, tensile properties of different materials produced using FFF technique will be discussed in depth. Based on available information, other mechanical properties will also be discussed.

Tensile properties

Table 4 is a compilation of published tensile properties for various materials fabricated using FFF along with literature references.

Dependence of mechanical properties such as ultimate tensile strength (UTS), elastic modulus, and elongation to failure on printing parameters such as raster angle and specimen orientation is observed. Generally, 0 ° raster angle gives the highest UTS and elastic modulus [146, 156-159]. The UTS and elastic modulus drop as the raster angle increases until 90 °. This is because changing raster angles affect how the load is transferred within the specimens. When the raster angle increases, the bonding between

adjacent filaments (intra-layer bond (Figure 15a)) play a bigger role in carrying the load [160]. The variation with respect to raster angle suggests that bonding of polymer between the adjacent filament is not as strong as the bonding of polymer within the filament. The poorer bonding could be attributed to the inadequate fusion of polymer chains at the boundary between the adjacent filaments as a result of the fast cooling nature of the printing technique. Due to the inadequate fusion at the boundary, each extruded filament can be treated as a fiber which can take higher stress in the fiber direction and lowest stress perpendicular to the fiber direction.

The effect of the raster width on the tensile properties is divisive. Onwubolu and Rayegani [148] found that smaller raster width would result in higher tensile strength. However, the results are the opposite in the studies by Sood *et al.* [144] and Alhubail [147] in which higher tensile strength is obtained with larger raster width. More in-depth research would be needed to conclusively determine the effect of raster width on the tensile properties.

Apart from that, the anisotropy of mechanical properties is affected by specimen orientation. Specimen printed in XYZ and XYZ orientations generally provides better mechanical strength compared to ZXY orientation [156, 161, 162]. The tensile strength and the elongation in the ZXY orientation is normally 40-50% of the tensile strength and elongation respectively in XYZ and YXZ orientations. The reason for the deviation was due to the different failure modes that specimens of different orientations exhibit. For the ZXY orientation, the specimens are pulled in the across-the-layer direction and

the load is normal to the direction of the fibers, leading to inter-layer fusion bond (ILFB) failure.

In the ZXY orientation, interlayer or fiber-to-fiber bond (Figure 15a) greatly influences the tensile strength. This is because the fibers do not take the applied load, instead, ILFBs between adjoining layers bears the majority of the pulling force. As far as the YXZ and XYZ orientations printed tensile coupons are concerned, they are pulled in the in-plane directions and the fibers are stressed, leading to trans-layer failure. Here, the fibers bear the majority of the pulling force and fiber breakage would normally be observed. Interestingly, the elastic modulus is least affected by the specimen orientation. The maximum percentage deviation of the elastic modulus in the three orientations is only about 18% [162].

Figure 15 Illustration of the cross-sectional view of (a) polymer chains, and the inter- and intra-layer bonds; (b) the presence of reinforcement affecting the interlayer bonds

Table 4 Tensile properties

Process	Material	Standard	Sample design	Strain rate/ test setting	Specimen orientation/ raster angle	Layer thickness/ crystallinity	E (GPa)	Yield strength (MPa)	UTS (MPa)	Elongation (%)	Ref.
FDM, Printed with heating plate, 100% in-fill	ABS	ASTM D638	Type 1, 0.125"	5 mm/min	XYZ/ 0°		1.2	24	27.6	4.2	[156]
FDM, 100 in- fill,	ABS	ASTM D638	Type V	10 mm/min	XYZ/ 0° and 90° alternating ZXY/ 0° and 90° alternating		NA NA	NA NA	33.96±1.74 17.73±2.52	8.64±3.3 2.08±0.55	[163]
FDM, 100% infill, raster angle: 0°, extrusion temperature 340 °C, platform temperature: 230 °C	PEEK	ASTM D638	Dogbone 165x19x3mm	5 mm/min	XYZ/ 0° XYZ/ 0° and 90° XYZ/ 90°		2.871 2.732 2.846	34.68 40.40 45.93	71.36 67.75 53.91	5.01 3.93 2.29	[164]
FDM, 100% infill,	PLA	ASTM D638	Dogbone 165x19x3mm	50 mm/min	XYZ/ 0° YXZ/ 90°		1.538 1.246	NA NA	38.7 31.1	NA NA	[157]

					XYZ/ 45°	1.350	NA	33.6	NA	
FDM, 100%	ABS P400	ASTM	Dogbone	4.46	XYZ/0°	1.486	24.18	25.15	NA	[158]
infill		D638	165.1x19.1x2.5 mm	mm/min	XYZ/45°	1.042	9.4	10.11	NA	
					XYZ/90°	1.041	8.55	9.16	NA	
					XYZ/45°/-45 °	1.282	15.34	16.9	NA	
FDM, 100%	PLA	ASTM	Dogbone	5	XYZ/0°	3.33	NA	58.45	2.02	
infill		D638	136.6x19x6mm	mm/min	XYZ/45°	3.60	NA	64.03	2.50	[159]
					XYZ/90°	3.49	NA	54.01	4.14	
FDM, 100%	ABS	ASTM	Rectangular	NA	XYZ/ (0°)	1.549	34.2	38.1	NA	[146]
infill		D3039	slabs		XYZ/ (45°)	1.250	221.3	25.7	NA	
Air gap 0.0 mm			190.5 x 12.7 x		XYZ/ (90°)	1.270	20.8	23.3	NA	
Nozzle T12			2.6 mm		XYZ/ (+45°/-	1.439	26.5	32.2	NA	
Road width 0.3048 mm										
Slice height 0.1778 mm										

Nozzle temperature 320 °C					45°)						
Envelope temperature 80 °C											
FDM,	PLA	ASTM	Dogbone	2	XYZ/0°	0.06 mm	4.409	NA	88.2	NA	[162]
		D638-10		mm/min							
Air gap			165x20x4 mm			0.12 mm	3.892	NA	68.6	NA	
0.0mm						0.24 mm	3.622	NA	64.6	NA	
Nozzle temperature					YXZ/0°	0.06 mm	4.040	NA	83.4	NA	
210 °C						0.12 mm	3.976	NA	65.4	NA	
						0.24 mm	3.934	NA	71.9	NA	
					ZXY/0°	0.06 mm	3.266	NA	22.4	NA	
						0.12 mm	3.796	NA	27.5	NA	
						0.24 mm	3.468	NA	39.5	NA	
	PC		-		XYZ/45°/-45°		2.10	45.9	NA	4.35	[161]

FDM, 100%		ASTM	1	YXZ/45°/-45 °		2.41	54.6	NA	4.22
infill		D638	mm/min	ZXY/45°/-45 °		2.26	45.6	NA	2.90
				X+45 ° Y+45 °		2.13	45.5		3.58
				Z/45°/-45 °					
				Y+45 ° X+45 °		2.32	53.3		3.35
				Z/45°/-45 °					
				Z+45 ° X+45 °		2.18	36		2.05
		Y/45°/-45 °							
FDM, 100% infill	PLA	ASTM	NA	ZXY/ 0° and 90° alternating	Crystallinity: 0.93%	NA	52.47	57.16	2.35
	natural	638							
	black				Crystallinity: 2.62%	NA	49.23	52.81	2.02
	Gray				Crystallinity: 4.79%	NA	46.08	50.84	1.98
	Blue				Crystallinity: 4.85%	NA	50.10	54.11	2.13
	White				Crystallinity: 5.05%	NA	50.51	53.97	2.22

nozzle temperature: 200 °C					Crystallinity: 4.6%	NA	NA	52.6	NA		
nozzle temperature: 210 °C					Crystallinity: 13.9%	NA	NA	57.2	NA		
nozzle temperature: 215 °C					Crystallinity: 5.9%	NA	NA	58.3	NA		
FDM, 100%	ABS	ASTM	5	XYZ	0.2 mm	1.839	29.7	NA	2.01	[166]	
infill		638	mm/min		0.3 mm	1.736	27.6	NA	2.31		
					0.4 mm	1.875	28.2	NA	1.97		
	PLA				0.2 mm	3.48	60.4	NA	1.96		
					0.3 mm	3.34	48.5	NA	1.71		
					0.4 mm	3.286	54.9	NA	1.94		

Layer thickness (Lt) is a highly disputed parameter due to variation in the results from different research groups. Rankouhi *et al.* [167] stated that even though layer thickness has been investigated widely, more detailed investigations should be carried out owing to the discrepancy of results. For instance, Sood *et al.* [144] found out that tensile strength first dropped and eventually rose with increasing layer thickness from 0.127 mm to 0.178 mm, and to 0.254 mm. Another research group compared two layer thicknesses (0.2mm and 0.4mm) of acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) specimens and concluded that lower thickness produced higher tensile strength [166]. However, PLA specimens exhibited larger variability between parameters. Similar results have been shown by Vaezi and Chua [168] in which a decrease in layer thickness would favor the enhancement of tensile properties. It was found that an increasing number of shell perimeters would lead to a higher disparity of tensile strength with layer thickness [154]. Onwubolue *et al.* concluded that maximum tensile stress is achieved by using minimum layer thickness [148]. A more detailed study on the effect on layer thickness on the mechanical properties of the FFF printed parts at different specimen orientations revealed that the effect of layer thickness and the specimen orientation are coupled in determining the tensile properties of FFF-printed parts [162]. It was found that the tensile strength increases for the specimens in XYZ direction as the layer thickness decreases. The opposite trend is observed for the specimens in ZXY orientation.

The feed rate/ printing speed is an important parameter as it is associated with printing time, and therefore, to production cost. The higher feed rate allows parts to be

printed faster and thus increasing productivity. However, the feed rate cannot be increased indefinitely as it also has an effect on the tensile properties. For instance, the studies of Ning *et al.* [169] and Christiyana *et al.* [170] have revealed that tensile strength dropped as the feed rate increased. It was also found that the significance of the feed rate is dependent on the specimen orientation. Feed rate plays an important role when the specimen is in ZXY orientation. Tensile strength increases when the feed rate decreases. However, the effect of feed rate on the tensile strength is not significant in the XYZ and XYZ orientations.

In FFF, when the layer thickness is larger or printing speed is higher, the lesser the overall degree of cooling on the deposited filaments [171]. The higher average temperature of the deposited filament is essential for interdiffusion of polymer chain at the boundary between the layers which in turn gives rise to higher mechanical properties in across-the-layer direction. Due to this, higher layer thickness, which usually has lower cooling rate due to the higher heat capacity of the extruded filament (due to higher mass of the extruded filament), usually associates to higher mechanical performance in across the layer direction [172]. Inter-layer cooling time is found to be inversely related to tensile properties of FFF-printed parts [173], i.e., the lower the printing speed, the longer the inter-layer cooling time. A longer interlayer cooling time allows the just-deposited material to be cooled down to the chamber temperature, which normally is lower than the glass transition temperature of the material. This lower temperature disfavors the fusion of the thermoplastics at the interlayers. As the samples in ZXY orientation are loaded in the across-the-layer direction, and hence their strength and ductility are

affected by the interlayer cooling time. The XYZ specimens, contrarily, are not loaded in the across-the-layer direction, and hence are not directly influenced by interlayer cooling time.

Infill pattern and infill percentage are two parameters that are available in the FFF technique to save materials [174]. The lower the infill percentage, the lesser the material is used, thus saving cost and reducing the weight of the part. However, at the same time, the mechanical properties will be compromised as lowering the infill percentage also means introducing voids inside a part. Numerous studies have been conducted in relation to the infill pattern and infill percentage of the printed parts[175]. It was found out that the fill pattern has a negligible effect on the mechanical properties of the FFF-printed parts.

Apart from printing parameters and choice of materials, there are other factors that would affect the resulting mechanical properties. For instance, the mechanical properties of the AM materials are dependent on the how fast the load is applied in the tensile test, i.e. the measured UTS and elastic modulus are found to be higher at lower strain rate. It should be noted, however, that due to the variation in gauge length used by different researchers, direct comparison of elongation to failure should be avoided. In addition to that, variation in the type and quality of the polymer filament is found to affect the resulting mechanical properties. Tymrak *et al.* noticed that the filaments of different colors would give different extrusion characteristics, even though they are from the same manufacturer[166]. In general, the reported tensile properties of the AM polymeric materials are found to be slightly lower than those conventionally manufactured

polymers. The lower mechanical properties are attributed to the presence of voids in the additively manufactured specimens (Figure 16). Voids can be reduced by applying negative raster gap and thus better mechanical properties can be achieved [176].

Figure 16 *micro-CT images showing the presence of voids in between the adjacent filaments in an FFF-printed specimen.*

In-situ processing processes such as infrared preheating [177] and laser-assisted heating [178] were introduced to improve the mechanical performance of the parts. Post-treatment process such as thermal treatment could help improve the tensile properties by improving bonds between adjacent filaments (for FFF) [179]. Improvement in tensile properties after the thermal treatment has been reported. But most importantly, precise

control of FFF process parameters like printing speed and particularly build platform and the chamber temperatures can prevent such problem during the fabrication process.

Flexural properties

The flexural test is the second most common quasi-static mechanical test conducted to get the knowledge of how the materials behave under bending loads. The available information on the flexural properties is significantly lesser as compared to the tensile properties. The FFF-printed materials that have been tested for flexural properties are ABS, PEEK, Nylon, and PLA (Table 5). Thus far, the three-point bending test is the only method to get the flexural data and ASTM D790 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials is the most commonly used standard for the three-point bending test although ISO 178:2001 Plastics - Determination of flexural properties has also been used to test the flexural properties. It is interesting to note that another standard test method, ASTM6272 - Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials by Four-Point Bending – has not been used to determine the flexural properties of FFF-printed materials to the author's knowledge. The reason for not using the four-point bending test could be due to the need for an extra instrument to determine the maximum deflection at the center of the test coupon. Although the researchers used the same standard for the flexural test, the specimen dimensions and the strain rates differ resulting in deviation in the data obtained from the flexural test. It is evident in [162] and [159] that although both groups

used PLA as the material of study, the differences in specimen dimensions and strain rates resulted in the disparity in the results.

Similar to tensile properties, it was found that printing parameters such as specimen orientations, raster angle, and layer thickness affect the flexural properties of FFF-printed materials. Anisotropy in flexural properties was observed in FFF-printed materials. The maximum flexural strength and stiffness were observed in YXZ orientation and were followed by XYZ orientation and then ZXY orientation. Specimens in the YXZ are the strongest because the load is acting across the intralayer bond between the adjacent filament in the YXZ specimens. On the other hand, the load is acting across the interlayer bond between adjacent layers in the XYZ specimens. As noted in the tensile section, the intralayer bond would be stronger than the interlayer bond due to the better fusion of the adjacent filament as a result of the lower temperature drop of the deposited filament. The ZXY specimens exhibit the lowest flexural strength as the load is applied in the direction such that the fibers do not bear the load, instead, interlayer fusion bonds between adjacent layers or fibers bear the majority of the pulling force.

Raster angle also plays a part in determining the flexural properties of the FFF-printed parts. In general, 0° raster angle is the strongest and the strength decreases as the raster angles increases to 90°. The effect of raster angle on flexural properties can be explained from the failure mode of the flexural specimens. When a flexural specimen is loaded, one side will experience compression while the other side will experience tension. As observed in Table 1 and Table 4, the tensile strengths of the thermoplastic

materials are lower than their compressive strength. This means that the tensile side of the specimen will fail first and thus the tensile properties are the determining factors of the flexural properties. As the UTS of the thermoplastics is affected by the raster angle, and thus the flexural properties are also a function of raster angle.

Layer thickness has a dominant, statistically significant effect on flexural force [180]. However, the layer thickness has a different effect on specimens of different orientations. For XYZ specimens, flexural strength is the highest when the layer thickness is the lowest. For ZXY specimens, the flexural strength is the highest when the layer thickness is highest.

In general, the flexural properties are strongly influenced by the printing parameters such as specimen orientations, raster angles, and layer thickness. However, the effect of infill pattern on the flexural properties has not been extensively studied.

Table 5 Flexural properties

Technique	Sample design	Material	Strain rate	Specimen orientation/ raster angle	Layer thickness	E (GPa)	Yield strength (MPa)	UTS (MPa)	Elongation (%)	Ref.
FDM, raster angle: 0°, extrusion temperature: 340 °C, platform temperature: 230 °C	100% infill, 12.7*64*3.2	PEEK	In accordance to ASTM D790	XYZ/ 0°		1.972	86.26	114	10.6	[164]
				XYZ/ 90°		1.954	65.90	83.59	5.81	
			0.01 mm/mm.min	XYZ/ 0° and 90°		2.146	66.50	88.70	6.58	
			6.8 mm/min							
FDM, raster angle: 0°	100% infill, 124*12.7*3.2	ABS	1.4 mm/min	XYZ		1.75	38	60	3	[64]
			Support span: 51.2 mm							

FDM, 100% infill, extrusion temperature: 200 °C, layer height 0.3 mm	Nylon	10 mm/min	XYZ/0°/45°/90°/-45°	1.050	-	46	-	[181]	
FDM, 65x13x4	PLA	2 mm/min	XYZ/0°	0.06 mm	1.596	NA	56	NA	[162]
Air gap 0.0mm				0.12 mm	1.434	NA	49	NA	
Nozzle temperature 210 °C				0.24 mm	1.246	NA	46.2	NA	
			YXZ/°	0.06 mm	1.852	NA	65	NA	
				0.12 mm	1.729	NA	61.3	NA	
				0.24 mm	1.886	NA	64.2	NA	
			ZXY/0°	0.06 mm	1.318	NA	14.3	NA	
				0.12 mm	1.392	NA	23.8	NA	

					0.24 mm	1.414	NA	28.4	NA	
FDM, 100% infill,	127x12.7x3.2	PLA	10 mm/min	XYZ/0°		3.187	NA	102.203	10.6	[159]
230 °C, platform				XYZ/45°		2.985	NA	90.649	7.8	
temperature 65 °C,				XYZ/90°		3.000	NA	86.136	4.5	
extrusion speed 100										
mm/s										
FDM, nozzle	In accordance	PA-12	10 mm/min			1376.14	61.27	-	>25	[181]
temperature: 200 °C,	to	ASTM								
printing speed: 20	D790									
mm/s, layer height: 0.3										
mm,										

2.7 Interlaminar properties of FFF composites

Thus far, three different properties have been used to gauge the interlayer properties of the FFF-fabricated polymer parts, they are the z-direction tensile [62], interlayer fracture toughness [182] and interlaminar shear properties [70] (Table 6). The interlayer properties have been compared with that of the polymers fabricated using conventional processes. The mode I interlayer fracture toughness was found to be lower than that of the compression-molded polymer parts [182]. Apart from that, the effect of the addition of reinforcements to the polymers on the interlayer properties has been investigated. All studies have shown that the interlayer properties drop with the addition of the fiber reinforcements. For instance, the z-direction tensile properties of the carbon fiber-filled ABS is only 42% of that of the pure ABS [62]. Apart from that, another study has shown that the interlayer fracture toughness of the carbon fiber-filled ABS is about 5 times lower than that of the pure ABS [182]. Another study showed that the interlaminar shear strength of the reinforced ABS is 8.5 times lower than that of the pure ABS [70]. This suggests that the addition of reinforcement weakens interlayer properties. The reason for the weakening effect can be found from the microstructure analysis. This is due to the uneven surface created at the previous layer by the fibers which makes the next layer of fiber unable to properly fused with the previous one resulting in a drop in strength [70]. The poor interlaminar properties are undesirable as it means that a larger surface area and hence more material is needed to make up for the lower interlaminar properties. It would affect the design flexibility and even the adoption of this technique for producing parts high-performance applications.

Table 6 Interlaminar properties

Materials	Sample design	Strain rate/ test setting	Specimen orientation/ raster angle	Interlayer properties	Ref.
ABS	152x22.5x4 mm	2 mm/min	XYZ/ 0°	Interlayer fracture toughness (kJ/m ²)	1.57 [183]
ABS with fiber	Crack length: 76 mm	1 mm/min			0.33
ABS	ISO 14130:1998	NA	XYZ/ 0°	Interlaminar shear (MPa)	24 [184]
ABS with fiber	80x10x4 mm Span length:64mm				2.81
ABS	ASTM D638 Type V specimens	NA	ZXY	z-direction tensile	16.75±4.56 [62]
ABS with 13% carbon fiber			ZXY		7.00+2.59

Existing methods to improve the interlaminar properties of the FFF-fabricated parts include adding CNT between the layers, using microwave irradiation [185] and controlling the chamber temperature [186]. A recent attempt has been made to use infrared to preheat the previous layer before laying the new layer [177]. However, the improvements were not significant. For instance, the tensile properties improved 40% after 60 seconds of microwave irradiation [185]. This warrants further investigations on the effect of printing conditions on the interlaminar properties.

2.8 Modelling of the temperature profile of deposited materials in the extrusion process

Temperature history of the material during the cooling after leaving the nozzle has a direct impact on the interlayer bonding strength [187], residual stress [188], rheological behaviour [189], crystallinity of the polymer [190], deformation of the component and therefore the mechanical properties of the final part [191]. Although attempts have been made to acquire temperature measurement, the experimental results are still inadequate up to now. For instance, Sun *et al.* measured the temperature of the bottom layer of the deposited material using a 0.0118 mm diameter thermocouple [187]. The effect of nozzle temperature, chamber temperature, layer thickness, specimen orientation and geometry on temperature profile was investigated in order to associate the printing parameters with the quality of bond formation. Lately, Kousiatza and Karalekas [192] used fiber Bragg grating sensor and thermocouples to study local temperature change relative to time, however, the measurable range of temperature was limited to be around the glass transition temperature of the polymer. Zhou *et al.* used a non-intrusive infrared sensor to acquire temperature readings of the extruded material [193]. The fast response of the infrared sensor-enabled them to capture the sharp temperature drop in the scale in the first 0.3s. However, this method is only able to capture the top surface temperature of the deposited filament and gives no insight on the temperature at the interface at the bottom layer [193]. The use of thermocouple, on the other hand, is an intrusive method which require suitable opening for the insertion which would in turn affects the way heat is transferred. Apart from that, as the deposited material has a dimension in the range of 100-300 microns, which is about the same size

as the normal thermocouple, the presence of thermocouple would have some impact on the heat transfer to some extent.

Analytical and/or numerical investigation is another solution to obtaining the temperature history and distribution. The development of predictive models would enable the prediction material properties that are dependent on the thermal history during the extrusion process and allow optimization and control of the process. Several analytical models have been developed to predict the temperature history of a filament under extrusion. Few analytical models have been established to predict the thermal history of a filament under extrusion. Rodriguez and Thomas did a 2D transient heat transfer analysis of a single-road-width solidification process [194]. They assumed that filaments have a rectangular cross-section, the effects of conduction to the platform can be neglected and any contact resistances between filaments are negligible. The eigenfunction expansion solution averaged over the width, is given by:

$$T_{ave}(x, y, t) = T_E + \frac{2T_E}{W} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \left(\frac{a_{mn}}{\beta_n} \sin(\lambda_m y) \cos\left(\frac{\beta_n W}{2}\right) \right) e^{-\alpha^2(\lambda_m^2 + \beta_n^2)t} \quad (1)$$

Where

$$a_{mn} = \frac{4T_L^*}{E_m^2 F_n^2 \lambda_m \beta_n} \sin\left(\frac{9\lambda_m H}{2}\right) \sin\left(\frac{\lambda_m H}{2}\right) \sin\left(\frac{\beta_n W}{2}\right) \quad (2)$$

$$\alpha^2 = \frac{k}{C_p \rho} \quad (3)$$

$$E_m^2 = \frac{1}{2} \left(5H - \frac{\sin(10\lambda_m H)}{2\lambda_m} \right) \quad \text{and} \quad F_n^2 = \frac{1}{2} \left(W - \frac{\sin(\beta_n W)}{\beta_n} \right) \quad (4)$$

And λ_m and β_n are obtained by solving

$$\lambda_m \cot(5\lambda_m H) = \frac{-h}{k} \quad \text{and} \quad \beta_n \tan\left(\frac{\beta_n W}{2}\right) = \frac{h}{k} \quad (5)$$

Using eq. (1), they found out that the temperature histories at the interfacial boundaries are almost identical for the second layer and above. Also, the temperature difference between the center of the filament and the edge would be greater when the heat convection is higher.

Bellehumeur *et al.* further proposed a lumped capacity model that assumed uniform temperature distribution on the cross-sectional areas of filaments, semi-infinite filament length, and constant heat transfer and convection coefficients [195]. The analytical solution is as follows

$$T = T_\infty + (T_0 - T_\infty)e^{-mx} \quad (6)$$

$$\text{with } m = \frac{\sqrt{1 + 4\alpha\beta} - 1}{2\alpha} \text{ and } x = vt \quad (7)$$

where $\alpha = \frac{k}{\rho C_p v}$, and $\beta = \frac{hP}{\rho C_p A v}$.

It should be noted that this analytical solution is obtained under the three assumption: (1) uniform temperature distribution of the cross-sectional area of the filament; (2) semi-infinite filament length; and (3) constant heat transfer/convection coefficients. Also, they excluded heat generation/loss due to phase change and crystallization in their heat transfer model.

Although analytical models provide an indication as to how the process parameters such as nozzle temperature, chamber temperature, and print speed, they do not predict the temperature accurate enough to allow process optimization. This is because the

process is simplified, and a lot of factors are excluded. On the other hand, the numerical study enables the process to be considered in greater details through finite element analysis and/or finite difference method. The numerical simulation of the thermal behavior of the deposition process in FFF for pure thermoplastics with isotropic thermal properties has been done by a few groups [171, 193, 196-198].

Zhou *et al.* used finite element analysis for 3D space discretization coupled with a Chernoff strategy for processing time discretization to obtain the temperature profile of the extruded filament [198]. ANSYS SHELL281 element was used to mesh the base material and the extruded filament with mid nodes at the edges for accuracy. Also, the 3D finite element SOLID90 with 20-node is applied to the meshing of the platform and ABS filament. APDL (ANSYS Parametric Design Language) strategy, the ABS material ‘birth’ during depositing processing is simulated using APDL program to provide the parameter input of ABS filament and heat reservoir at different time and position. In the simulation, enthalpy of the ABS material, variable thermal properties, heat convection, and radiation are taken into consideration. They found out that thermal properties of the materials have a significant effect on the thermal histories of the extruded filament.

Zhou *et al.* also used a three-dimensional uncoupled thermal–structural finite element model to study the thermal-structure relationship of the extruded filament [193]. The 3D thermal element SOLID70 and the structural element SOLID45 were used to mesh the domain with the element dimension of 1×1 mm by layer thickness in the thermal and structural analyses, respectively. In their study, they found that the time is taken for the temperature of the extruded filament to drop from deposition temperature

to glass transition temperature is in the order of 0.1s, which agreed well with the experimental results.

Zhang *et al.* used the finite difference method to create an adaptable three-dimensional transient mathematical model of temperature variation in relation to space and time, during and after the fused filament fabrication process [171]. They found that nozzle and ambient temperatures, print speed, and layer thickness had an influence on the thermal history of the extruded filament as well as on the reheating of the previously-deposited layers.

The above-mentioned models are meant only for isotropic materials and did not take into consideration of the anisotropic thermal properties of composite materials, especially continuous FRP composite in which the in-plane thermal conductivity can 10 times higher than the across-the-thickness thermal conductivity [199]. Apart from that, there is no numerical heat transfer study on the multi-material extrusion to investigate the effect of different material properties on the temperature history of the deposited material. Additionally, 3D heat transfer models are computationally expensive because small time-step and element size are needed due to the small size scale of the filament.

2.9 Summary

With the advancement in AM technologies, it is now possible to fabricate fully functional composite parts directly. In particular, material extrusion technique stands out from the rest due to its ability to produce parts with intricate geometries using continuous fiber-reinforced thermoplastics.

To sum up, above-mentioned studies demonstrate the potential of material extrusion technique in producing composite parts with generally better mechanical properties as compared to the pure thermoplastics. However, there are still research challenges that need to be overcome, especially in:

1. Understanding of Thermal history of the composite material in the extrusion printing process

Current heat transfer models developed to study thermal history are meant for isotropic materials. Continuous FRTP which are highly anisotropic in material properties would require additional heat transfer model to accurately predict the temperature profile of the extrusion process. Moreover, the thermal transport properties of the AM composites are rarely reported in the literature. Characterization of thermal transport properties would be useful for the heat transfer model.

2. Understanding the process window of the extrusion-based printing technique

The addition of fibers to the polymer filament introduces new research area especially in the fiber-matrix interaction during the extrusion printing process. Although commercially available composite printers have been around for quite some time, the in-depth investigation of the process-structure relationship of the single composite filament is still not available. The knowledge of the process window and the process-structure relationship would enable a better understanding of the extrusion process and its effect on the microstructural properties of the AM CFRTP parts.

3. Study of interlaminar properties of 3D printed composite materials

Although the interlaminar properties of AM composites have been investigated by several research groups, most studies have been focused on short fiber reinforced thermoplastics composites. There is a need to study the interlaminar properties of the continuous FRTP composites. The improvement to the interlaminar properties can be achieved by a more in-depth study of the printing process such as the influence of the printing parameters with fiber alignment and porosity which in turn affect the interlaminar properties. Scientific discussions on the possible mechanisms that result in the phenomena observed are provided.

4. Investigation of mechanical properties and fracture modes of AM composite materials

The additive manufacturing of the continuous FRTP is still new and a full list of mechanical properties required for structural simulation of geometrically complicated models is still lacking. Moreover, the understanding of the fracture modes would enable us to understand how AM composites behave under different loading conditions. The understanding of mechanical properties enables the identification of the weakest link in the mechanical performance of the AM composite, which is the interlaminar properties.

3. Research methodologies

The research overview of this research can be found in Figure 1. In this research, the extrusion process of continuous FRP composite filament will be examined in detail, particularly, thermal properties of the composite materials and heat transfer principles will be used to model the temperature variation of the extrusion process, which is critical to the interlaminar bonding. Carbon fiber-reinforced composite chosen to be evaluated due to superior mechanical properties. Carbon fibers are known for their high stiffness-to-weight ratio and are used in industries that are very particular about weight such as the aerospace industry.

The interlaminar property (mode I interlaminar fracture toughness) of the composite part fabricated using extrusion process will be characterized. Effects of parameters such as printing speed, extrusion temperature, and bed temperature on the mode I interlaminar fracture toughness will be examined. To understand the effect of the process parameters on the microstructure and interlaminar properties, the PSP relationship is investigated.

The mechanical properties and the fracture mechanisms of the AM CFRTP fabricated using the commercially available Markforged composite printer will be investigated. Anisotropic mechanical properties (such as tensile, compressive, shear, flexural properties), which are needed for the design and structural finite element analysis of the UAV and are rarely reported in the available literature, will be reported for the first time.

Lastly, the main body of a quadcopter is used as a proof of concept part to demonstrate the capability of the extrusion-based printing technique to fabricate geometrically complex high-performance UAV structure. Static finite element stress analysis is conducted and the performance is compared with the conventional design. Static bending test and actual flight test is then conducted to evaluate the actual performance.

3.1 Materials

The material used in this research is the continuous carbon fiber reinforced nylon produced by Markforged, United States. The materials are composed of multiple strands of carbon fibers coated with nylon matrix and come in spools [200]. The carbon fibers have diameters of about 9 microns as shown in Figure 17.

Figure 17 Illustration of the extrusion-based AM technique

3.2 Manufacturing process

Two extrusion-based 3D printers are used in this study, they are the Markforged composite printer and the low-cost Hello BeePrusa desktop FFF open-source 3D printer. In the extrusion-based AM technique, the thermoplastic matrix of the composite filament is melted in the nozzle before being extruded out (Figure 17). The molten composite material is selectively deposited according to the pattern generated in each layer. Upon extrusion, the molten thermoplastic matrix will fuse with the previously-deposited layer as it cools. The extrusion and selective deposition process are repeated every layer until the designed part is formed.

The Hello BeePrusa is a low-cost dual-extruder open-source FFF 3D printer. Being an open-source printer, it provides higher control flexibility over the printing parameters. As such, nozzle temperature, bed temperature, print speed, and layer thickness are a few printing parameters that can be adjusted. The maximum nozzle temperature of the extruder is about 265 °C which is limited by the maximum service temperature of the Polytetrafluoroethylene (PTFE) tubing inside the nozzle. In addition to that, this open-source printer has a temperature-controlled build plate which can be stably heated up to 70 °C. This printer is used to investigate the microstructural changes of the single filament at various process parameters as well as the fabrication of mode I ILFT specimens.

The Markforged composite printer has a fixed nozzle temperature of 250 °C and does not regulate the bed and chamber temperatures. It is capable of depositing composite filament freely in any required direction in the x-y plane at a fixed layer thickness (0.125mm). This printer is used to study the anisotropic mechanical properties of the AM CFRTP. The tensile, compression, shear, flexural, and indentation specimens are fabricated using this printer. The 3D technology demonstrator is also fabricated using this printer.

3.3 Investigation of process window of the extrusion printing process and its effect on a single filament of AM CFRTP

The thermal properties of the CFRTP composite are characterized to obtain the decomposition temperature and glass transition temperature.

3.3.1 Decomposition temperature

The decomposition temperature is performed according to ASTM E1131-08 (Standard Test Method for Compositional Analysis by Thermogravimetry). TA Instrument's TGA Q500 (**Figure 18**) was used to obtain the thermal decomposition profile of the carbon fiber reinforced nylon. The composite sample with a weight of 11.68 mg was used.

Figure 18 TGA Q500 for measuring decomposition temperature

3.3.2 Glass transition temperature

The Glass transition temperature is estimated using Differential Scanning Calorimetry (DSC, Q200, TA Instrument) (**Figure 19a**) according to ASTM E1269-11 (Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry). 10 mg samples are prepared and tested at a heating rate of 10 °C/min. Dynamic Mechanical Analysis (DMA) test is performed in accordance to ASTM D7028 - 07 (Standard Test Method for Glass Transition Temperature (DMA Tg) of Polymer Matrix Composites by Dynamic Mechanical Analysis (DMA)) on the AM CFRTP to confirm the results. Single cantilever beam test is conducted for the DMA using DMA Q800, TA Instrument (**Figure 19b**). The dimension of the specimen is 40x15x2 mm. The test is performed from 30°C to 150°C at 1 Hz.

Figure 19 Thermal Analysers. a) DSC b) DMA

3.3.3 Single filament study

The composite filament is extruded at various layer thicknesses (0.1 mm, 0.2 mm, and 0.3 mm) using the Hello beePrusa printer to characterize the overall dimensions and top surface profile of the extruded composite filament. The print speed is then varied (7 mm/s, 10 mm/s, and 14 mm/s) while fixing the layer thickness at 0.1 mm. Lastly, the composite filament is printed at two different nozzle temperatures (250 °C and 265 °C) to study the crystallinity of the nylon matrix. At least 3 samples of straight lines were printed for each process parameter conditions. The microstructures of the composite filament in the single filament study were characterized using SEM (JSM-IT300LV, JEOL (Japan Electro Optics, Ltd.), USA). To investigate the fiber alignment and surface profile of the continuous FRTP, laser scanning confocal microscope (VK-X250, Keyence, Japan) was used. An Image analyzing software (ImageJ) was used to obtain the directionality of the extruded fibers [201]. The OrientationJ plugin was used to obtain the distribution of the fibers [202], using the cubic spline method to compute the gradient with a local window of 2 pixels. In order to quantify the directionality of the fibers, a measure called the full width at half maximum (FWHM) was used [203, 204].

The FWHM can be obtained by taking the total length of a straight line that cuts through the normalized distribution curve at half of the highest amplitude (Figure 38b). In this case, half of the highest amplitude is 0.5. To study the crystallinity of the nylon matrix of the composite filament, X-ray diffraction (XRD) and Raman tests are conducted. XRD spectra are obtained using the Malvern Panalytical's Chi-Phi-z-stage configuration from 10° - 90° with the step size of 0.1° . Raman tests is conducted using the Renishaw inVia Raman Microscope (1800 l/mm grating and 633 nm of wavelength) with an exposure time of 20 s.

3.4 PSP Relationship of Additively Manufactured Continuous

CFRTP: An Investigation of Mode I Interlaminar Fracture

Toughness

To characterize the effect of printing parameters on microstructure (fiber directionality and porosity) and ILFT, the double cantilever beam (DCB) test specimens were designed and printed using Hello bee Prusa printer according to ASTM D5528-13 (standard test method for mode I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites). The dimensions are 20 x 125 x 4 (in mm) with an initial crack length: 50 mm (Figure 20a). 25 microns Kapton tape was used to create the initial crack. Slic3r slicing software was used to generate the g code for the print. There are 32 layers with the layer thickness of 0.125mm. Eight process conditions are set up to study the effect of printing parameters such as nozzle temperature, print speed, and bed temperature as shown in Table . As the DCB test specimens require more print material and print time, therefore, only two levels are considered for each print parameter to save time and materials. Two levels of print speed (7 and 12 mm/s) with

reasonable print duration and good printability were selected in this study. Print speed of 12mm/s is selected for the high level instead of 14 mm/s because the print quality of the 14mm/s is poor, causing by poor adhesion to the base layer. The poor adhesion at higher speed could be attributed to the higher tension on the fiber as well as poorer interlaminar bonding due to faster cooling as high print speed. Similarly, two levels of nozzle temperature (250 °C and 265 °C) and bed temperature (30 °C and 70 °C) were also selected in this study. The low level of nozzle temperature (250 °C) is the extruding temperature of the Markforged composite printer. The high level of nozzle temperature (265 °C) was limited by the thermal stability of the PTFE tubing in the heated nozzle. 70 °C bed temperature was selected because it is the highest temperature that the open-source printer can stably heat up to whereas 30 °C bed temperature is selected to represent room temperature and no significant bed heating.

Table 7 Printing parameters

No	Print speed (mm/s)	Nozzle temperature (°C)	Bed temperature (°C)
1	7	250	70
2	12	250	70
3	7	265	70
4	12	265	70
5	7	250	30
6	12	250	30
7	7	265	30
8	12	265	30

Three specimens are prepared and printed for each process condition using a 1.0 mm nozzle diameter and 0.1 mm layer thickness. The fiber was laid unidirectionally in 0°

(Figure 20b). The mode I ILFT test was conducted with a universal testing machine (10kN, Shimadzu Co., Japan). The double cantilever beam test was video recorded to capture the crack length, force, and displacement simultaneously for the convenience in data collection. The crosshead speed was set to be 5 mm/min in accordance to the standard.

Figure 20 Double cantilever beam (DCB) test specimen. a) The dimension of DCB test specimen b) a layer of the 0° unidirectional print pattern of the specimen.

The mode I ILFT at the onset of nonlinearity (NL) (Figure 21a) is used as a standard throughout the whole experiment. It is calculated as follows:

$$G_I = \frac{nP\delta}{ba} \quad (8)$$

Where P is the load, δ is the load point displacement, b is the specimen width, a is the delamination length, and $n = \Delta y / \Delta x$, where Δy and Δx are defined in (Figure 21b) [205].

Figure 21 Obtaining nonlinearity (NL) point and Δ from experiment data. a) Load, P vs load point displacement, δ b) $\text{Log}(\delta/P)$ vs $\text{Log}(a)$.

After the mode I DCB tests, various measuring instruments were used for process quality measurement and fracture analysis. The porosities of the printed specimens were obtained using the micro-computed tomography (μ CT)-scan (Skyscan 1173, Bruker Co., United States) image analysis. The μ CT-scan machine is equipped with a CCD sensor, which has 2240 by 2240 pixels, with each having pixel size of 50 μm . 1x1 camera binning mode was used and the resulting image pixel size was 7.9 μm . Source voltage, source current and the exposure time were set to 40 kV, 200 μA , and 1200 ms, respectively. SEM images of the fracture surfaces were observed using SEM (JSM-IT300LV, JEOL (Japan Electro Optics, Ltd.), USA).

3.5 Characterization of the mechanical properties of the CF RTP

The mechanical properties of the AM CF RTP fabricated using Markforged composite are first characterized. The specimens were fabricated with the continuous CF RTP filament using the print speed of 15 mm/s, the nozzle temperature of 250 $^{\circ}\text{C}$ and no heating of build plate. The methods to obtain the mechanical properties are discussed below. The convention of the direction used in the discussion is shown in Figure 22a.

3.5.1 Tensile properties

The tensile test specimens were designed and printed according to ASTM D3039/D3039M-14 (Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials) [206]. The dimension of the specimen is 25 x 250 x 2.5 mm. Three specimens are prepared for each direction (Figure 22b). The fiber was laid unidirectionally at 0°. The tensile test was conducted with a universal testing machine (100kN, Shimadzu Co., Japan). The crosshead speed was set to be 1.5 mm/min.

Figure 22 Sign convention and specimens orientation. (a) the sign convention used in this study. (b) Orientations and dimensions of tensile test specimens. (c) Orientations and dimensions of compression test specimens. (d) Orientations and dimensions of shear test specimens.

3.5.2 Compression properties

The compression test specimens were designed and printed according to ASTM D695-15 (Standard Test Method for Compressive Properties of Rigid Plastics) [206]. The dimension of the specimen is 12.7 x 12.7 x 50.4 mm. Three specimens are prepared for x-, y-, and z-directions (Figure 22c). The fiber was laid unidirectionally at 0°. The compression test was conducted with a universal testing machine (10kN, Shimadzu Co., Japan). The crosshead speed was set to be 1.3 mm/min.

3.5.3 Shear properties

The orthotropic shear properties of the composite material are measured in accordance with ASTM D7078-12 (Standard Test Method for Shear Properties of Composite Materials by V-notched Rail Shear Method). 15 specimens are printed in 3 orientations (5 each) as shown in **Error! Reference source not found.** to get the shear properties that are essential for finite element structural analysis. Shear tests were conducted with a universal testing machine (50kN, Shimadzu Co., Japan). Shear tests were video-recorded so that shear strain could be obtained via Differential Image Correlation (DIC) technique using GOM Correlate.

Figure 23 Orientations and fiber directions of specimens (1 represents the direction of fibers, 3 represents through-the-thickness direction, and 2 is perpendicular to both 1 and 3 and is in the direction that completes the left-hand rule).

3.5.4 Flexural properties

The flexural test specimens were designed and printed according to ASTM D790-15e2 (Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials) [207]. The dimension of the specimen is set to be 13 x 154 x 4 mm such that the support span-to-depth ratio is 32:1. The support span was set to be 128 mm. Three specimens are prepared for each type of fiber. The fiber was laid unidirectionally at 0°. The flexural test was conducted with a universal testing

machine 10kN, Shimadzu Co (10kN, Shimadzu Co., Japan). The loading and supports noses have a diameter of 5 mm. The crosshead speed was set to be 6.82 mm/min such that the strain rate is 0.01 mm/mm.min.

3.5.5 Quasi-static indentation properties

Indentation test specimens were designed and printed according to ASTM D6264/D6264M-12(Standard Test Method for Measuring the Damage Resistance of a Fiber-Reinforced Polymer-Matrix Composite to a Concentrated Quasi-Static Indentation Force) [208] with slight modification in specimens' dimensions. The dimension of the specimens is 100 x 100 x 1.6 mm. Three specimens are prepared for each type of fiber. Quasi-isotropic fiber layup was used in which fiber direction is changed by 45° from one layer to the next [0/45/90/-45] for 14 layers. Quasi-static indentation tests were conducted with a universal testing machine (10kN, Shimadzu Co., Japan). Standard indenter geometry which has a blunt, hemispherical tip with a diameter of 13 mm was used. The specimens were tested in an edge supported condition (circular boundary with a diameter of 78 mm) so that the deflection of the specimen and stiffness effect can be considered [209]. The test specimens were supported over a circular opening. The crosshead speed was 1.25 mm/min. The maximum indentation energy during quasi-static indentation was defined as the area under the loading curve.

3.5.6 Microstructural analysis

After the tests, μ CT-scan (Skyscan 1173, Bruker Co., United States) images of the fractured specimen were taken to observe the fracture mode and porosity. The μ CT-scan machine has a CCD sensor with 2240x2240 pixels, each with the pixel size of 50 μ m. 1x1 camera binning mode was used and the resulting image pixel size was 16.404 μ m

when the object was placed 119.318 mm from the source. Source voltage, source current and the exposure time were set to 40 kV, 200 μ A, and 1200 ms, respectively. To investigate the interfacial and inter-layer properties of the continuous FRTP, the microstructure of the additive manufactured FRTP was observed using SEM (JSM-IT300LV, JEOL (Japan Electro Optics, Ltd.), USA).

3.6 3D printed demonstrator

The main body structure of a quadcopter is used as a 3D printed technology demonstrator part to demonstrate the ability of the extrusion printing technique for CFRTP to fabricate high-performance structures.

The initial design of the main quadcopter is slightly modified to take into account the fiber steering ability and the creation of honeycomb infill structure by the extrusion printing technique. The modified structure, which has got hollow structures to reduce weight, are evaluated and compared with the initial design, which would undergo the conventional manufacturing process for thermoplastics, using finite element analysis. The stress and fracture analyses are conducted using Ansys Workbench 19.2 and static structure module. Tetrahedral meshes are used for finite element analysis. The mechanical properties of AM CFRTP needed for the analysis were taken from the tests discussed in chapters 6 and 7.

In the fracture analysis, critical strain energy release rate is used as the fracture criterion to evaluate the structural performance. For orthotropic materials, it has been shown that the stress intensity factors under pure mode I and mode II loadings are related to the respective energy release rates according to the equations below.

$$G_I = \left(\frac{1}{2E_1E_2} \right)^{1/2} \left[\sqrt{\frac{E_1}{E_2} + \frac{E_1}{2\mu_{12}} - v_{12}} \right]^{1/2} K_I^2 \quad (9)$$

$$G_{II} = \frac{1}{\sqrt{2}E_1} \left[\sqrt{\frac{E_1}{E_2} + \frac{E_1}{2\mu_{12}} - v_{12}} \right]^{1/2} K_{II}^2 \quad (10)$$

Where E_1, E_2 are the Young's moduli in the fiber and transverse directions respectively, μ_{12} is the shear modulus in the 1-2 plane or the axial shear modulus, v_{12} is the Poisson's ratio for uniaxial tension in the fiber direction. G_I is mode I ILFT for the AM CFRTP (Appendix G), G_{II} is the mode II ILFT for the AM CFRTP (Appendix H).

Using equations 9 and 10, the critical stress can be determined using the strain energy release rate criterion if the loading and crack size are known.

Static bending test is conducted before the flight test to evaluate the actual structural performance. The flight test is also conducted to evaluate the flight performance.

4. Numerical investigation of the effect of printing parameters and material compositions on the temperature history and degree of bonding in extrusion-based technique

4.1 Background

The literature review section has highlighted the need for numerical simulation for the AM extrusion technique of composite materials. Therefore, the objective of this chapter is to introduce a numerical simulation model suitable for continuous FRP composite and multi-material to simulate the effect of printing settings on the temperature change at the interface in FFF using finite difference method [171]. A less computational expensive 2D transient numerical model describing the FFF technique is introduced. The effect of nozzle temperature, environment temperature, layer thickness, print speed, nozzle size of FFF printer as well as material composition on the temperature profile with space and time are shown and explained. Numerical results are cross-checked with available reported experimental results. The temperature history coupled with the non-isothermal healing model of the AM CFRTP is used to predict the degree of bonding at the interlayer boundary of the AM CFRTP. The numerical results may be useful in the study of fusion bonding at the interlayer boundaries, residual stress caused by fast cooling, crystallization of polymer, and other applications of FFF.

4.2 Model

4.2.1 2D Heat transfer model

Assumptions

Assumptions used in developing the mathematical heat transfer model to obtain temperature change in relation to time and space are listed below.

1. As there is no sideways/lateral heat transfer in the normal 2D model, the heat conduction in the through-the-thickness direction is multiplied by 2 to take into consideration the sideways heat loss that happens in the actual 3D model (Figure 24).
2. The heat released/absorbed due to melting/crystallization of polymer is neglected.
3. The effect of heat radiation is ignored.
4. Thermal expansion and friction in micro viscous flow are ignored.
5. Contact resistance at the interlayer boundaries is assumed to be zero.
6. Ideal bond and thermal contact between the matrix and fiber phases.
7. Porosity is assumed to be zero.

Governing equation and boundaries

A numerical model is developed using the finite difference method to predict the temperature change in relation to space and time during the extrusion process of composite material. Figure 24a below shows how nodes are defined in the finite difference method.

Assuming there is no internal heat generation, the energy balance at node (a,b) (Figure 24b) is shown in the equation below.

$$\begin{aligned} \rho c \Delta x \Delta y \frac{T_{(a,b)}^{i+1} - T_{(a,b)}^i}{\Delta t} = & k_{\parallel} \Delta y \left(\frac{T_{(a+1,b)}^i - T_{(a,b)}^i}{\Delta x} \right) + k_{\parallel} \Delta y \left(\frac{T_{(a-1,b)}^i - T_{(a,b)}^i}{\Delta x} \right) \\ & + 2k_{\perp} \Delta x \left(\frac{T_{(a,b-1)}^i - T_{(a,b)}^i}{\Delta y} \right) + 2k_{\perp} \Delta x \left(\frac{T_{(a,b+1)}^i - T_{(a,b)}^i}{\Delta y} \right) \end{aligned} \quad (11)$$

Where $k_{\parallel}$ and $k_{\perp}$ are along-the-fiber and through-the-thickness thermal conductivities, ρ and c are density and specific heat capacity of composite material respectively, Δx and Δy are the distance between the nodes with the length, L .

The density of the composite can be calculated as

$$\rho = (1 - \phi_f) \rho_m + \phi_f \rho_f \quad (12)$$

Where ϕ_f is the fiber volume fraction, ρ_m is the density of matrix, and ρ_f is the density of fiber.

Specific heat capacity of the composite can be calculated as

$$c = \frac{\phi_f \rho_f}{\phi_f \rho_f + \phi_m \rho_m} c_f + \frac{\phi_m \rho_m}{\phi_f \rho_f + \phi_m \rho_m} c_m \quad (13)$$

Where c_f and c_m are specific heat capacity of fiber and matrix respectively.

In this study, $k_{\parallel}$ for continuous FRP composite is defined according to Rayleigh's formula [210] as,

$$k_{\parallel} = k_m + (k_f - k_m) \phi_f \quad (14)$$

Where k_f is the thermal conductivity of fiber, k_m is the thermal conductivity of the matrix.

The $k_{\perp}$ is determined using the model developed by Torquato for a random dispersion of equi-sized fully impenetrable cylinders as given by the fourth-order bound model[211].

$$\frac{k_{\perp}}{k_m} = \frac{1 + 2\phi_f\beta_{fm} - 2\phi_m\xi_f\beta_{fm}^2}{1 - \phi_f\beta_{fm} - 2\phi_m\xi_f\beta_{fm}^2} \quad (15)$$

Where β_{fm} is a scalar quantity involving the phase conductivities k_f and k_m and is calculated using the expression below

$$\beta_{fm} = \frac{k_f - k_m}{k_f + (d - 1)k_m} \quad (16)$$

Where d is the number of dimensions and has a value of 2 for long oriented fibers in the polymer matrix. ξ_f can be obtained using the model by Torquato and Lado [211],

$$\xi_f = \frac{\phi_f}{3} - 0.05707\phi_f^2 \quad (17)$$

This model can give an accurate approximate expression for the $k_{\perp}$ for various fiber volume fraction ranging up to $\phi = 0.7$.

For any single material middle node, the temperature at the next instance ($t + \Delta t$) becomes,

$$T_{(a,b)}^{i+1} = \left(1 - 2\tau - 2\frac{2\tau}{r}\right) T_{(a,b)}^i + \tau \left(T_{(a-1,b)}^i + T_{(a+1,b)}^i + \frac{2T_{(a,b+1)}^i}{r} + \frac{2T_{(a,b-1)}^i}{r} \right) \quad (18)$$

Where $r = k_{\parallel}/k_{\perp}$ and $\tau = k_{\parallel}\Delta t / \rho c L^2$.

As the topmost layer is exposed to the environment, convection at the top layer must be taken into consideration. The energy balance at the nodes (c,d) experiencing convection is shown in the equation below.

$$\begin{aligned} \rho c \Delta x \frac{\Delta y}{2} \frac{T_{(c,d)}^{i+1} - T_{(c,d)}^i}{\Delta t} = & k_{\parallel} \frac{\Delta y}{2} \left(\frac{T_{(c+1,d)}^i - T_{(c,d)}^i}{\Delta x} \right) + k_{\parallel} \frac{\Delta y}{2} \left(\frac{T_{(c-1,d)}^i - T_{(c,d)}^i}{\Delta x} \right) \\ & + 2k_{\perp} \Delta x \left(\frac{T_{(c,d+1)}^i - T_{(c,d)}^i}{\Delta y} \right) + h \Delta x (T_{env} - T_{(c,d)}^i) \end{aligned} \quad (19)$$

Where h is the heat convection coefficient typically in the range between 30-100 W/m²K for FFF printing process [195, 212]. For nodes at the top surface (Figure 24b) where heat convection takes place, the temperature at the next instance ($t + \Delta t$) becomes,

$$\begin{aligned} T_{(c,d)}^{i+1} = & \left(1 - 2\tau - 2\frac{2\tau}{r} - \frac{2\tau hL}{k_1} \right) T_{(c,d)}^i \\ & + \tau \left(T_{(c-1,d)}^i + T_{(c+1,d)}^i + 2\frac{2T_{(c,d+1)}^i}{r} + \frac{2hL}{k_1} T_{env} \right) \end{aligned} \quad (20)$$

The energy balance for nodes at the boundary between two materials can be obtained in a similar manner. It is left for the readers to work out the equation. The temperature at the next instance ($t + \Delta t$) for nodes at the boundary between two materials (Figure 24b) is shown below,

$$\begin{aligned} T_{(e,f)}^{i+1} = & \left(1 - \tau_2 \left(1 + \frac{k_{b\parallel}}{k_{a\parallel}} \right) - \tau_2 \frac{2k_{a\perp}}{k_{a\parallel}} - \tau_2 \frac{2k_{b\perp}}{k_{a\parallel}} \right) T_{(e,f)}^i \\ & + \tau_2 \left[\frac{1}{2} \left(1 + \frac{k_{b\parallel}}{k_{a\parallel}} \right) (T_{(e-1,f)}^i + T_{(e+1,f)}^i) + \frac{2k_{a\perp}}{k_{a\parallel}} T_{(e,f-1)}^i + \frac{2k_{b\perp}}{k_{a\parallel}} T_{(e,f+1)}^i \right] \end{aligned} \quad (21)$$

Where $k_{a\parallel}$ and $k_{a\perp}$ are thermal conductivities of material A in fiber direction and through-the-thickness direction, respectively; $k_{b\parallel}$ and $k_{b\perp}$ are thermal conductivities of material B in fiber direction and through-the-thickness direction, respectively; and

$\tau_2 = \frac{k_{a\parallel} \Delta t}{(\rho_b c_a + \rho_b c_b) L^2}$. If the material used has isotropic material properties, then $k_{a\parallel} = k_{a\perp}$.

Figure 24 Illustration showing (a) the heat transfer in a normal 3D mode and. (b) the 2D heat transfer model used in this study and element boundaries for each type of nodes.

To simulate the addition of material during the deposition process, new nodes are assumed to be at nozzle temperature at every time, t . For a moving nozzle at a velocity, v , the time for the new nodes staying at the nozzle temperature is $\frac{L}{v}$, where L is the distance between the adjacent nodes, after which the nodes will undergo normal heat transfer and their respective temperature at the next instance will be calculated as described in the equation mentioned above.

Validation of model

In order to assess the validity of the 2D heat transfer model, the prediction of the model is compared with experimental data collected for the cooling profile of a single deposited ABS filament by Sun et al [187]. The thermal properties of ABS were

obtained from the material supplier (Stratasys Inc. USA) as reported by Rodríguez [213]. Since pure ABS thermoplastic is used, isotropic material properties assumption is made, which means thermal conductivity in all directions is assumed to be the same. The material properties and printing parameters used can be found in Table 8.

Table 8 material properties and printing parameters for validation

Parameters	Values	Ref.
Thermal conductivity, k (W/mK)	0.177	[213]
Specific heat capacity, C_p (J/kg K)	2080	[213]
Density, ρ (kg/m ³)	1050	[213]
Print speed (mm/s)	40	[187]
Heat convection coefficient (W/m ² K)	75	[187]

From Figure 25, the model prediction is plotted against the experimentally data obtained from [187]. It should be noted that the lower initial temperature and lower temperature gradient in the first 0.5s of the experimentally obtained data were likely due to the slow response time of the thermocouple. Nonetheless, the prediction of the model is generally in agreement with the experimentally obtained data (average percentage error within 11%) in the longer run. A comparison with the lump capacity analytical model is also made in the same figure. The lump capacity analytical model, which assumes uniform temperature distribution on the cross-sectional areas of filaments, semi-infinite filament length, and constant heat transfer and convection coefficients, is not able to capture the fast temperature drop in the first 0.3s as it assumes heat is dissipated from the deposited filament through convection which is a slower mode of heat transfer compared to conduction. Using the 2D numerical model, the temperature profile of the deposited filament is predicted at a much higher accuracy. The higher accuracy is due to ability of

the numerical model to take into account the non-uniform temperature distribution on the cross-sectional areas and the different heat transfer and convection coefficients.

Figure 25 Comparison of the temperature history of the newly deposited material.

4.2.2 The non-isothermal healing model

When two thermoplastic surfaces come into contact at a temperature higher than the glass transition temperature, interdiffusion of polymer chains happen at the interlayer boundary. Interlaminar bonding is formed when the two surfaces join. In order to predict the interlaminar bonding of the AM CFRTP fabricated using the extrusion printing process, it is necessary to understand how the bonds are developed with respect to temperature and time. In this section, the non-isothermal bond development model of the AM CFRTP at the interface is explained.

For non-isothermal healing condition, it has been shown that using the failure criterion that states that fracture stress is proportional to interpenetration distance, the degree of healing can be estimated using the equation below [214, 215].

$$\frac{\sigma}{\sigma^{max}} = \sum_{t=0}^t \frac{t_{i+1}^{1/4} - t_i^{1/4}}{T_r^{1/4}} \quad (22)$$

Where σ^{max} is the fracture stress of the fully healed interface and T_r is the reptation time which is temperature-dependent. In order to use the model, σ^{max} and T_r needs to be determined experimentally. The σ^{max} are determined through lap shear testing on fully welded AM CFRTP samples. Fully welded samples are prepared by welding the lap shear samples for a time longer than T_r . T_r is obtained by conducting a few isothermal welding experiments for various temperatures and durations (Appendix B). For each temperature condition, the non-dimensional strength is then plotted against $t^{1/4}$. The gradient of the best fit line is $(T_r^{-1/4})$. The T_r values at the different temperatures can then be related using Arrhenius relationship as shown below [214].

$$T_r = Ae^{B/T} \quad (23)$$

The constants A and B in the Arrhenius equation are found to be $-38.686 \text{ s}^{1/4}$ and 21579 K^{-1} respectively for the AM CFRTP.

Equations 22 and 23 can be used to predict the degree of bonding at the interlayer boundary of the AM CFRTP fabricated using extrusion printing process, which is non-isothermal in nature.

Validation of model

The model is validated by crosschecking with the experimental results from the lap shear specimens printed using the Markforged composite printer. The printing parameters of the Markforged composite printer are as shown in Table 9. The degree of bonding estimated by the non-isothermal model is compared with the experimental data as shown in Figure 26. It is observed that the non-isothermal healing model tend to underestimate the degree of bonding at the interlayer boundary. The discrepancy could be due to the fact that single filament extrusion is considered in the numerical simulation and reheating effect by the adjacent filament and the top layers are not considered. The r Nonetheless, the model enables the understanding of the evolution of the bond strength over the period of fabrication. For instance, the effect of various printing strategies on the bond strength can be predicted using the model.

Table 9 *Printing parameters of Markforged composite printer*

Nozzle temperature	Bed temperature	Print speed	Layer thickness
250 °C	30 °C	15 mm/s	0.125 mm

Figure 26 *Degree of bonding validation with experimental data. Degree of bonding development at the interlayer boundary over time after the extrusion process.*

4.3 Results and discussion

4.3.1 Temperature distribution and temperature history

With the 2D heat transfer model, the effect of the deposition process on the temperature of the deposited material with respect to space and time $T_{(a,b)}^t$ will be captured. For instance, the temperature history of any point (say node (1,2)) can be obtained by plotting the temperature variation of that point $T_{(1,2)}(t)$ with respect to time. In the temperature history of a particular position, information such as cooling rate can be drawn which is particularly useful for fusion and crystallization studies. The cooling rate is mathematically defined as $\beta(t) = \frac{dT(t)}{dt}$ and can be obtained numerically using $\beta(t) = \frac{T(t+\Delta t) - T(t)}{\Delta t}$. The cooling rate in the first 0.1s when the material is newly deposited is the highest and is estimated to be in the order of 1000 °C/s. The cooling rate at the latter stage (~3s) is found to be about 170 °C/min. This is an order of magnitude larger compared to the result by Zhang et al [171]. The difference could be due to the different layer thickness used in the study which would have an effect on the cooling rate, which will be discussed in detail in the following section. Nonetheless, this shows the importance of the first 0.1s as the majority of the bonds are formed in this period. The fast drop in temperature was due to heat dissipation to the previously deposited material as well as to the environment, which are at much lower temperatures. Due to this, the polymer at the interlayer boundary may not have sufficient energy to fuse and coalesce, leading to poor interlaminar properties which have been reported in several studies. Printing parameters such as nozzle temperature, bed temperature, chamber temperature, print speed, and layer thickness are found to have an effect on the cooling rate, which will be discussed in the next section.

Spatial temperature distribution at any instance t_n is another characteristic that is worth studying, especially for anisotropic material and multi-material extrusion. From the spatial temperature distribution, information such as temperature gradient can be obtained. The temperature gradient is believed to be playing a part in the mechanics of thermo-elasticity and is the reason that causes warping of the fabricated parts in FFF. Temperature gradient $\nabla T = [T_x, T_y]$ at any position can be approximated as $T_x(a, b) \approx \frac{T_{(a+1,b)}^{t_n} - T_{(a,b)}^{t_n}}{L}$ and $T_y(a, b) \approx \frac{T_{(a,b+1)}^{t_n} - T_{(a,b)}^{t_n}}{L}$, where T_x and T_y are the component of the temperature gradient vector. The intensity of the temperature gradient as the vector sum of each component, $|\nabla T| = (T_x^2 + T_y^2)^{\frac{1}{2}}$. In the following section, the temperature distribution of the anisotropic material and multi-material extrusion will be discussed.

4.3.2 Effect of material properties on the temperature history

Since the inception of FFF, various materials have been developed as the feedstock of FFF. In the past, the trial-and-error method was normally used to obtain a set of processing window that a material can be successfully extruded from the nozzle without fully understanding the physics behind it. Later on, heat transfer models were developed to study the effect of processing condition of extrusion. However, almost all studies have focused on a single material and did not investigate the effect of material properties on the temperature variation. As more composite materials are being developed, it becomes necessary to study the effect of material composition on the thermal history of the extrusion process. In this section, the effect of material composition and multi-material extrusion on thermal history will be discussed in detail.

In the study of material composition, the continuous carbon fibers are assumed to be used as the reinforcement material and the nylon is assumed to be used as the matrix

material. The thermal properties of the reinforcement and matrix materials are shown in Table 10. The continuous carbon fiber composite is assumed to be processed at the nozzle and ambient temperatures of 265 °C and 70 °C, respectively and a print speed of 7 mm/s.

Table 10 *Material properties of the constituent materials*

	Pure nylon	Continuous Carbon fiber
Density (g/cm ³)	1.14 [104]	1.78
Specific heat capacity (J/kg/K)	1.67 [216]	0.795
Thermal conductivity (W/m/K)	0.33 [216]	8.5

The variation of the effective thermal conductivities in the fiber direction and the through-the-thickness direction calculated using equations (13) and (14) are shown in Figure 27a. The effective thermal conductivity in the fiber direction changes drastically as fiber content increases. This is because the continuous carbon fibers conduct heat 25 times faster than the pure nylon. On the other hand, the fibers are discontinuous in the through-the-thickness direction, which results in lower increment in the effective thermal conductivity in the through-the-thickness direction. The temperature histories of various material compositions are shown in Figure 27b.

The temperature variation of the Nth top layer at the interface is illustrated in Figure 27b. It is observed that carbon fiber composite with higher ϕ_f cools faster. This is due to the lower specific heat capacity and higher thermal conductivity of the carbon fiber composite with higher ϕ_f , which results in high thermal diffusivity. This causes the heat to be dissipated away from the just deposited material more quickly, resulting in higher cooling rate.

Figure 27 Numerical simulation results showing (a) Thermal conductivity variations with fiber volume fraction (b) Temperature variation of composite materials of different fiber volume fraction at various interlayer boundaries. Materials with higher fiber content cool faster. Reheating effect is most obvious at (N-1)th layer and becomes less significant as it goes further down.

The temperature variations further below the top surface are shown in the same Figure 27. It is observed that the (N-1)th layer which is just below the top surface experience the most reheating effect for the composite materials of different ϕ_f but to a different extent. The reheating effect is less prominent in (N-2)th layer and it becomes weaker as it goes further down. The carbon fiber composite with higher ϕ_f heats up faster and to

a higher temperature but also cools down faster. The more prominent reheating effect in the composite material with higher ϕ_f is due to the higher thermal conductivity and lower specific heat capacity.

It is interesting to note the temperature gradient variation at the top layer (newly-deposited layer) (Figure 28). It is observed that the magnitude of the temperature gradient at the bottom surface of the newly-deposited layer is an order higher compared to the top surface. This shows that the top surface of the newly-deposited layer cools much slower as compared to the bottom surface which is in contact with the previously-deposited layers. This is due to the higher heat transfer rate via conduction towards the bottom layers as compared to convection at the top surface of the layer. This also shows that it is important to capture the temperature variation at the bottom surface instead of the top surface, especially when studying the polymer bonding at the interlayer boundary. The effect of material composition on the temperature gradient is also studied. It is found that the temperature gradient, ∇T at the bottom surface of the newly-deposited material with ϕ_f : 0% is higher as compared to that of the material with ϕ_f : 40%. This is likely due to the lower thermal diffusivity of the ϕ_f : 0% material which makes the heat to be transferred more slowly to the base material, resulting in the higher average temperature at the bottom surface of the newly-deposited material.

The higher cooling rate of the composite filament is thought to be one of the factors for the poorer interlaminar properties of the composite materials compared to the pure thermoplastic counterparts. The higher cooling rate reduces the available time for bond fusion and hence the poorer interlaminar properties. Hence, it is necessary to tune the printing parameters for different compositions of fiber-reinforced thermoplastic

composites so as to achieve an optimum overall cooling time for bond formation by either increasing the nozzle and/or ambient temperature or lowering the print speed.

Figure 28 Temperature gradient at the top and bottom surfaces of the newly-deposited material.

4.3.3 Effect of nozzle temperature and ambient temperature

Nozzle temperature is the temperature at which the polymer is extruded from the nozzle; it is assumed as the initial temperature of the material right after coming out of the nozzle and being deposited onto the previous layer. The nozzle temperature must be above the melting point of the polymer so that the polymer is in the molten state and is able to be extruded out from the nozzle when squeezed. However, there is a limit as to how high the nozzle temperature can go as polymer would start to decompose when decomposition temperature is reached. Figure 29a below shows the temperature variation of the top-most layer with different nozzle temperatures. It is observed that the higher the nozzle temperature, the higher the initial cooling rate. This is due to the higher temperature difference from the ambient temperature at the initial stage. Nonetheless, the time taken to cool to ambient temperature is still longer for the higher nozzle temperature. Apart from that, nozzle temperature also influences the magnitude of the reheating at the previously deposited (N-1)th layer as shown in Figure 29b. It is noticed,

however, that the reheating at the (N-1)th layer did not give rise to significant improvement on the degree of bonding.

Figure 29 Numerical simulation result showing (a) temperature variation and degree of bonding of N^{th} layer (the top-most layer) with different nozzle temperature (b) temperature variation and degree of bonding at the (N-1)th layer with different nozzle temperature.

When the ambient temperature is changed from a higher temperature to a low temperature, the overall cooling rate and temperature gradient increase (Figure 30). The degree of bonding improves as the ambient temperature increases. These results indicate that in order to have a longer dwell time above the glass transition temperature, where

bond formation occurs, higher nozzle temperature and ambient temperature is preferable to achieve a lower overall cooling rate.

Figure 30 Temperature variation and degree of bonding of N^{th} layer (the top-most layer) with different ambient temperatures.

4.3.4 Effect of print speed and layer thickness

Print speed and layer thickness are two non-temperature-related printing parameters that affect the temperature history of the deposited material. The effect of the print speed and layer thickness on the temperature history are simulated using the heat transfer model.

In the study of print speed, it is found that the lower the print speed, the lower the overall cooling rate (Figure 31a). This is because, at a lower print speed, the material has a longer time staying at nozzle temperature leading to more heat being transferred to the previously deposited material which results in higher average temperature. As a result, the degree of bonding is higher at lower print speed. Apart from that, print speed also has the same effect on the previously-deposited layers, i.e. the lower the print speed, the lower the overall cooling rate.

Figure 31 Numerical simulation results showing (a) temperature variation with different print speeds (solid line: 7 mm/s, dash line: 14 mm/s, dash-dot line: 28 mm/s) (b) temperature variation with different layer thicknesses (solid line: 0.3 mm, dash line: 0.2 mm, dash-dot line: 0.1 mm)

Layer thickness, on the other hand, is inversely related to the overall cooling rate (Figure 31b). This is because the larger the layer thickness, the larger amount of material are deposited. The larger amount of material corresponds to higher heat content which explains the lower cooling rate at the top-most layer (N^{th} layer). The reheating effect on the $(N-1)^{\text{th}}$ layer diminishes as layer thickness increases. This is probably due to the fact

the interlayer boundary of the $(N-1)^{\text{th}}$ layer is further away from the heat source for large layer thickness, resulting in a lesser amount of heat being absorbed. Another deduction can be drawn from this result, which is the effect of nozzle size on the overall cooling rate. With a larger nozzle size, more material will be extruded at any single time, which leads to lower overall cooling rate. When the cooling rate is low, the polymer crystallization and thermomechanical effect should be taken care of. On the contrary, when the nozzle size is small, the overall cooling rate is too high and the time for interlayer bonding is too short, leading to insufficient bonding between layers. Thus, temperature management becomes very important for the small nozzle size to compensate for the high cooling rate. Inter-layer cooling rate was found to be inversely associated with the tensile strength of FFF fabricated parts [173].

4.3.5 Multi-material extrusion

Further investigation of multi-material extrusion is also conducted. Two scenarios are set up to investigate the effect of the deposition of two distinctly different materials on temperature variation and temperature gradient. In the first scenario, carbon fiber composite material with ϕ_f : 40% (high thermal conductivity and low specific heat capacity) is deposited onto pure nylon (ϕ_f : 0%) (low thermal conductivity and high specific heat capacity), whereas in the second scenario, pure nylon (ϕ_f : 0%) is deposited onto carbon fiber composite material with ϕ_f : 40 %. The simulation results are shown in Figure 32. In the first scenario, although it is carbon fiber composite being deposited, the cooling rate is not as drastic as compared to deposition onto carbon fiber composite base layers shown in Figure 32.

Figure 32 Numerical simulation results. (a) Temperature variations of extrusion of two materials with distinctive thermal properties. (i) dashed line- based material having higher thermal conductivity. (ii) solid line- base material having lower thermal conductivity (b) schematic and temperature distribution of the extrusion of two materials with distinctive thermal properties.

Similarly, in the second scenario, although nylon is being deposited, the cooling rate is significantly greater as compared to deposition onto pure nylon. This shows the overall

cooling rate is largely dependent on the base material. On the reheating, it can be seen that the heat-affected zone is much larger for the carbon fiber composite base as compared to the nylon base. This means that the heat is transferred more quickly in the carbon fiber composite base leading to material further down to experience the reheating effect. The two scenarios suggest that for multi-material deposition, the temperature history of the deposited material will depend on the material properties of both the extruded material and base material. Thus, it is important to tune the print speed, nozzle temperature or bed temperature for each deposition condition especially for materials with distinctive thermal properties so that there is sufficient time for the materials to fuse together.

4.4 Summary

A 2D heat transfer model capable of predicting the effect of the extrusion of material onto another material with distinctly different thermal properties have been developed to study the effect of printing condition on the temperature variation. For the first time, the governing equations for estimating the material and thermal properties of continuous fiber-reinforced thermoplastics were added to the heat transfer model for the extrusion printing process. Using this model, the FFF process for continuous fiber-reinforced thermoplastics in terms of energy balance is understood, via the investigation of each existing controlling parameter. Some conclusions can be drawn from the deposition heat transfer analysis,

- The cooling rate of the newly-deposited layer is extremely high at the first 0.3s due to the small feature size of the extrudate. A suitable measuring technique

with response time shorter than 0.1s should be used to accurately capture the temperature variation.

- Reheating effect at the bottom layers by a freshly deposited layer is a common occurrence of heat transfer. The reheating effect is more significant at the high-temperature difference between the newly deposited layer and the bottom layer, low print speed, thin layer thickness, and the use of high thermal conductivity and low heat capacity material.
- Temperature settings (nozzle temperature, ambient temperature) are important factors that determine temperature changes with space and time. Choosing a suitable nozzle temperature and chamber temperature could assist in decreasing the temperature gradient and regulating the overall cooling rate, in order to minimize residual stress inside the printed part or to improve interlayer properties.
- From the temperature gradient variation in the top layer, it is concluded that it is important to capture the temperature variation at the bottom surface instead of the top surface especially in the study of polymer bonding between the interlayer boundary.
- Thermal properties of the material play an important role in the cooling after the extrusion. Material with high thermal conductivity and low heat capacity would cool much faster. Hence, proper control of the printing speed is necessary to achieve the required cooling rate.
- If fibers have higher thermal conductivities than the polymer matrix, increasing the fiber content the composite filament increases the effective thermal conductivities, thus resulting in extruded filament having a higher cooling rate.

- On the multi-material extrusion, the overall cooling rate is largely dependent on the base material. Careful control of the printing parameters is required, especially for the extrusion of two distinctly different materials.

This numerical study about the effect of printing settings and material composition on the temperature change in relation to space and time in FFF could be served as a guideline to fine-tune the process of FFF. Properties like polymer interdiffusion at the interlayer boundaries as well as internal residual stress may be investigated from the viewpoint of heat transfer using this numerical model, particularly when it is tricky to measure the actual temperature history. Moreover, understanding the temperature change is essential to comprehending the working principle of the FFF.

5. Investigations of process window of the extrusion printing process and its effect on a single filament of AM CFRTP

5.1 Background

In order to understand the influence of printing parameters on the overall mechanical properties of the AM CFRTP parts, it is critical to understand how the extrusion printing parameters affect the AM CFRTP in its most basic form, that is the single composite filament. In this chapter, the geometrical shape and the thermal properties of the materials are first characterized to get an insight into the range of suitable processing window for the extrusion printing. Then, the effect of the extrusion process on the constituent materials (fibers and matrix) is investigated.

5.2 Result and discussion

5.2.1 Thermal properties of the raw AM CFRTP

Thermogravimetric analysis (TGA) is first conducted to determine the decomposition temperature of the nylon matrix. It is then followed by the differential scanning calorimetry (DSC) to determine the melting temperature of the AM CFRTP.

Decomposition Temperature

The TGA result is shown in Figure 33. It is observed that there is a slight drop (about 3%) in weight when the CFRTP is heated from room temperature to 160 °C. The weight loss could be due to the moisture as well as the degradation of the additive present in the CFRTP. The second step with the weight loss of about 43 % at the temperature range 300-482 °C. represents the degradation of the nylon matrix of the CFRTP. The onset

temperature for the degradation of nylon was found to be 300 °C, and the nylon loses 50 % of its weight at 450 °C. The remaining 54.55 % represents the carbon fibers content and the residue of the nylon matrix. From this result, it is found that the maximum processing temperature for the CFRTP is 300 °C to avoid any degradation of the nylon matrix.

Figure 33 TGA of AM continuous CFRTP

Glass Transition Temperature

The DSC results of the AM CFRTP are shown in Figure 34. On the first heating, it is noticed an endothermic peak at 60 °C. The presence of the peak could be due to the presence of the additive in the raw composite material as well as the manufacturing process condition of the composite feedstock material. To eliminate the effect manufacturing process condition, the composite material was cooled and reheated.

The glass transition temperature can be observed from the cooling curve. On the cooling curve, a small transition is observed to occur at 124 °C, which corresponds to the glass transition temperature [217].

DMA results are used to confirm the glass transition temperature of the AM CFRTP. In Figure 35, the peaks of the tan delta, which corresponds to the glass transition temperature, are located at 123°C, above which the mobility of the polymer chains increases significantly.

Figure 34 DSC results showing heating and cooling of the AM CFRTP raw material.

Figure 35 Graph of loss factor against temperature showing glass transition temperature of the AM CFRTP.

As the polymer chains break free from their position, the mobility of the polymer increases, and the composite becomes softer. The rheology properties come into play when the temperature of the material is above the glass transition temperature. It is known that viscosities of the polymer composites reduce temperature increases. Apart from that, fiber reinforced nylon composite is known to exhibit shear-thinning behavior [218], where viscosity reduces shear rate increases. Hence, a proper study on the effect of extrusion printing process parameters on the matrix and fibers of the extruded composite filament is warranted.

5.2.2 Single filament study

This section discusses the effect of extrusion on the microstructures of the composite filament. SEM images of the pre-extruded and extruded composite filament were taken in order to investigate the change in shape after the extrusion process. Both the pre-extruded and extruded composite filaments were broken at room temperature to capture the SEM images of the cross-section of the filaments. Figure 36a shows a composite filament before undergoing extrusion whereas Figure 36b shows a composite filament after extrusion. The initial diameter of the composite filament is 460 μm . It is observed that the composite filament gets flattened after the extrusion process. Due to the flattening nature, the base is considerably wide ($\sim 1.0\text{ mm}$) making it impossible to create thin wall structures.

In the investigation of the process parameters on the single extruded filament, the process parameters such as layer thickness, print speed, as well as nozzle and bed temperatures are investigated.

Figure 36 SEM image of (a) a single raw carbon fiber composite filament (b) the two overlapping extruded composite filaments.

Effect of layer thickness

The AM continuous CFRTP was printed in different layer thicknesses while keeping other process parameters constant. Three layer thicknesses (0.1 mm, 0.2mm, and 0.3mm) were selected for this study. The profiles (width and height) of the extruded composite filament are characterized as shown in Figure 37. The actual heights of the extruded composite filament are found to be $65.5 \pm 8.5 \mu\text{m}$, $152.3 \pm 3.6 \mu\text{m}$, and $217 \pm 9.5 \mu\text{m}$, slightly lesser than the design values 0.1 mm, 0.2 mm, and 0.3 mm respectively. The discrepancy of the heights from the design values was likely due to the improper bed calibration. The discrepancy could be potentially prevented by performing a proper z-offset calibration for the build plate. Apart from that, the top surfaces of the extruded composite filament are uneven for all layer thicknesses. Despite that, the surface profile of the 0.1 mm layer thickness appears to be flatter in general compared to that of the 0.2 mm and 0.3 mm layer thicknesses. This is likely because the material is being squashed more at 0.1 mm layer thickness. Flatter surface is preferable for the next layer of composite filament to conform to. The width of the extruded composite filament reduces as layer thickness increases. This trend is expected as the cross-sectional area should

remain constant as the material deposition rate is unchanged. This implies that distance between adjacent filament should be adjusted accordingly such that no gap exists in between the adjacent filaments.

Figure 37 Typical top surface profiles of the extruded composite filaments showing the respective actual layer heights and width at design values (a) 0.1 mm (b) 0.2 mm (c) 0.3 mm for layer thickness.

Effect of print speed

The relationship between the print speed and fiber directionality is investigated by fixing other printing process parameters constant. Although the extruded lines of different print speeds appear straight in general, the lines exhibit some amount of in-plane waviness (Figure 38a). The waviness of extrusion lines is not ideal as it can cause porosity and it usually indicates that the printing conditions are not optimal. The waviness in the

extruded line causes the fibers to deviate from the intended direction. Lower FWHM indicates higher directionality and means that the fibers are more aligned with the intended direction.

Figure 38 Fiber directionality of the extruded single road of filament. (a) laser microscopy image of single filament at different print speed showing some amount of waviness (b) normalized fiber distribution curve illustrating the directionality of the fibers. (c) FWHM (mean $\pm$ standard error) at different print speeds (repeated measures one-way ANOVA: $n=4$, $p=0.047$ (Appendix C)).

It is found that the FWHM increases from 7° to 8.9° and then to 9.1° when print speed increases from 7 mm/s to 10 mm/s and then marginally to 14 mm/s (Figure 38b, c). Rheological properties of the AM CFRTP could be playing an important role in the difference in fiber directionality at different print speeds. It is known that fiber reinforced nylon exhibits shear-thinning behavior [218]. As the print speed increases, the AM CFRTP gets sheared against the nozzle wall at a higher shear rate. The composite material becomes less viscous at higher print speed due to the shear-thinning behavior. As a result, the AM CFRTP is less stiff and more susceptible to small perturbation during the printing that causes the waviness of the composite filament.

It is observed that there is a tendency for groove formation at the top surface of the extruded filament at higher print speed (14 mm/s) (Figure 39a). A comparison between the microstructure at two print speeds (7mm/s and 14 mm/s) shows that fibers tend to be more well-arranged and matrix are more uniform at 7 mm/s (Figure 39b). The matrix is more uneven at print speed of 14 mm/s which is the sign that matrix polymer being stretched or thinned, exposing carbon fibers near the surface of the filament (Figure 39c). This is again due to the shear-thinning effect of the composite materials, where the viscosity reduces as shear rate increases. As the viscosity reduces, the material can get sheared off more easily from the carbon fibers, thus reducing the uniformity of the nylon matrix on the carbon fiber surface. The shearing of the nylon matrix from the carbon fibers creates small perturbation that causes the separation of carbon fibers during the extrusion process which may cause the formation of grooves. The reduced viscosity at higher print speed, which makes the composite materials to be more flexible and able to move more freely, increases the likelihood of the groove formation. The formation of groove would lead to the reduced effective contact area to form bonds with the next layer of filament resulting in poorer interlaminar properties. Additionally, the presence of groove would lead to the formation of pores and would significantly increase the porosity of the FFF-fabricated parts.

A small amount of fiber breakage is observed at the top surface of the extruded composite filament at higher print speed (14 mm/s) (Figure 40). The higher occurrence of the fiber breakage at the top surface of the extruded composite filament is due to the fact that the radius of curvature at the top surface is smaller during the extrusion process. As a result of that, each individual strand of fibers at the top surface experienced higher bending stress. Additionally, the tensile stress existing in the fibers as a result of pulling

Figure 39 Laser-optical image of (a) formation of grooves at high print speed (14 mm/s) in the single filament study. (b) smooth and more aligned fibers and uniform matrix at 7 mm/s. (c) more chaotic and random of carbon fiber and matrix at 14 mm/s. (d) SEM image of smooth and aligned fibers covered with matrix at 7 mm/s (e) sign of matrix polymer being sheared and thinned at 14 mm/s, exposing the carbon fiber surfaces.

of the composite filament from the spool is higher at a higher print speed, causing them to have a higher tendency to break. Fiber breakage will result in poorer mechanical properties as fewer continuous fibers are available to bear the loads.

Figure 40 *Laser-optical microscopy image showing fiber breakage observed at higher print speed (14 m/s)*

Effect of nozzle temperature

The FWHMs with respect to bed temperature at two nozzle temperatures are shown in Figure 41a. At 30 °C bed temperature, it is found that the FWHM at nozzle temperature 250 °C (14.0°) is slightly higher as compared to that of 265 °C (12.0°), whereas, at 70 °C bed temperature, the FWHM at nozzle temperature 250 °C (15.1°) is marginally higher as compared to that of 265 °C (14.8°) and is considered statistically insignificant.

In the same figure, it can be observed that the FWHM at bed temperatures 30 °C is lower compared to that of at 70 °C for both nozzle temperatures. This shows that process temperature has minimal influence on the waviness or directionality of the fibers. This waviness indicates non-optimal print conditions.

Figure 41 Bar charts showing (a) FWHMs (mean $\pm$ standard error) at different bed and nozzle temperatures.

DSC results show the response curves for the 250 °C and 265 °C nozzle temperatures in comparison with the raw composite material. It is observed that the raw composite material exhibits some degree of crystallinity as indicated by the drop in the enthalpy in the temperature between 60 °C and 175 °C. The samples extruded at 250 °C and 265 °C nozzle temperatures show a much smaller drop in the enthalpy with a relatively flat response curve. The absence of melting peak indicates that the nylon matrix of the extruded composite material is amorphous or with a very low degree of crystallinity.

Figure 42 DSC results AM CF RTP printed at 250 °C and 265 °C nozzle temperatures.

The difference in the crystallinity can be explained through the mobility of polymer chains. As the nylon matrix initially exists in the semi-crystalline form before extrusion printing process, a higher temperature is required to provide sufficient energy for the polymer chains to break free from its semi-crystalline form. Due to the fast cooling nature of the extrusion printing process, the polymer chains did not have enough time to rearrange themselves to the semi-crystalline form, thus retaining the amorphous structure. The process parameters, however, do not seem to influence the nylon polymer arrangement.

Raman Spectra of the AM CFRTP are shown in Figure 43. The peak at 1000 cm^{-1} is characteristic of the stretching of the C-C skeletal backbone structure [219-221]. The peak at 1300 cm^{-1} represents the CH_2 twisting, while the peak at 1440 cm^{-1} represents the CH_2 bending. The peak at 1640 is associated with the amide I ($\text{C}=\text{O}$) group stretching. The peaks at 2854 and 2925 cm^{-1} are attributable to the CH_2 stretching.

Figure 43 Raman spectra of AM CFRTP printed at 250 °C and 265 °C nozzle temperatures.

A comparison of Raman spectra between 250 °C and 265 °C nozzle temperatures show no significant difference in relative intensity of the peaks, an indication that the AM CF RTP fabricated at 250 °C and 265 °C nozzle temperatures exhibit a similar degree of crystallinity.

XRD results confirm that the nylon matrix of the composite filament exists in an amorphous state as no characteristic diffraction peaks for α (at 19.8° and 23.7°) and γ -form (at 21°) nylon crystallites are observed [222], Figure 44. The broad C (002) diffraction peak ($2\theta = 15\text{-}30^\circ$) corresponds to the amorphous carbon structures. The weak and broad C (101) diffraction peak ($2\theta = 40\text{-}50^\circ$) is attributed to the a -axis of the graphite structure [223]. Additionally, there is no obvious variation in the XRD patterns between 250 °C and 265 °C, signifying that the extrusion printing process does not have a significant effect on the crystallinity of the composite materials.

Figure 44 XRD patterns of extruded composite filament printed at 250 °C and 265 °C nozzle temperature.

Effect of turning radius of printability

In addition, the design window of the laying of the carbon fibers is investigated. A single layer benchmark part with various turning radii (1, 1.5, 2, 2.5 and 3 mm) was printed and put under the optical microscope to observe the microstructures of the printed part. Carbon fiber breakage was observed for turning radii smaller than 1 mm (Figure 45). The fiber breakage is likely due to the excessive stress induced during the small turns. It is also noticed that the composite filament is twisted at the start of the turn, where the fibers initially at the bottom surface of the extruded composite filament get to the top surface after the turn.

Figure 45 Fiber breakage at a turning radius of about 1 mm

5.3 Summary

In this chapter, the process window of the extrusion-based printing technique is discussed through the characterizing the thermal properties of the AM CFRTP and the single filament study. The process window of the extrusion process for AM CFRTP is

thoroughly investigated. Figure 46 shows the factors affecting the resulting microstructures of the extruded composite filament.

Figure 46 Schematic showing the factors that result in the microstructure of the extruded composite filament

Due to the flattening nature, the base is considerably wide making it impossible to create thin wall structures. The thinnest possible wall thickness is approximately 900 microns by using 0.3 mm layer thickness setting.

The formation of groove, the flatness of the top surface, the waviness of extruded composite filament, and the shearing of the matrix from the fiber surface are some of the phenomena observed through the single filament study. These phenomena are very much related to the rheological properties of the composite filament, in which viscosity reduces as temperature and shear rate increase. Process parameters can be adjusted to improve the quality of the extrusion. For instance, a lower print speed would result in fibers with higher directionality. A smaller layer thickness would result in flatter top surface profile. Also, the nozzle temperature does not have a significant effect on the crystallinity of the nylon matrix.

6. PSP Relationship of Additively Manufactured Continuous CF RTP: An Investigation of Mode I Interlaminar Fracture Toughness

6.1 Background

Mode I and mode II ILFT has been widely used to characterize the interlaminar bonding of composite materials [224-226]. Mode I ILFT, which is governed by peel forces, is generally lower compared to mode II ILFT, which is governed by shear stress, due to smaller amount of mechanical interlock to impede the propagation of a crack in the peeling mode than in shearing mode [19]. In a recent review article, Hu *et al.* highlighted that more research is needed to improve the bonding strength between neighboring layers and reduce the porosity [227]. Hence, it is the author's motivation to investigate and improve the mode I ILFT of the FFF-fabricated continuous FRTP composites through optimizing the printing parameters.

This chapter aims to provide an in-depth study to develop the PSP relationship of the FFF-fabricated continuous carbon FRP composite with mode I ILFT. Print speed is an important parameter that influences the build time of a part which in turn influences the productivity and cost-effectiveness of the fabrication process [193]. However, the effect of print speed on the microstructure and ILFT of the FFF-fabricated continuous FRP composite has still not been investigated. On the other hand, nozzle temperature plays an important role in the bond formation at the interlayer boundaries [228]. In this study, the effect of print speed and nozzle temperature on the microstructure and ILFT will be discussed in detail. Microstructures such as fiber directionality and porosity as well as bond formation will be studied to draw a relationship between the printing parameters and the resulting ILFT. The interlaminar fracture surfaces will also be investigated to

study the fracture mechanism. This study will be useful for the growing additive manufacturing and composite communities in further understanding the process and improving the current technique in manufacturing continuous FRTP composites.

6.2 Results and discussion

6.2.1 Effect of process parameters on microstructure

In the μ CT-scan porosity analysis, the main effects of the print parameters as shown in Figure 47. ANOVA analysis reveals that print speed exhibits the most significant effect on porosity ($p = 0.016$) whereas nozzle temperature exhibits less significant effects ($p = 0.27$). The bed temperature exhibits insignificant effect on the porosity ($p=0.95$). The interactions between the process parameters are found to be insignificant ($p=0.46-0.87$).

Figure 47 Effect of process parameters on porosity from ANOVA a) print speed b) nozzle temperature c) bed temperature

The composite parts printed at higher speed (12 mm/s) exhibit higher porosity (3.8-4.9%) as compared to the ones printed at a lower speed (7mm/s) which has a porosity between 1.7-2.1% (Figure 48a). Plus, the average pore size for the 12 mm/s is higher compared to the 7 mm/s (Figure 48b).

Figure 48 Porosity results and reconstructed images from μ CT-scan for different print speeds. (a) Average porosity (mean $\pm$ standard error) at different print speeds (ANOVA: print speed effect is significant ($p=0.013$)) (Appendix D). (b) pore size distribution for different print speeds. (c) graph of sphericity against pore volume (1 represents pores with a perfect sphere, low sphericity represents long and slender pores). (d) Gap due to the waviness of the extruded filament. (e) CT-scan 3D reconstruction of the pores showing small and scatter pores (in yellow) and long and slender pores (in green and blue).

Upon examination, it is found that there are two types of pores. The first type is the small and scattered pores and the second type is the thin and long pores. Figure 48c shows that most of the pores are small and exist in a wide range of sphericity, whereas the large pores are fewer and only exhibit low sphericity. Low sphericity is an indication

of long and slender pores. Parts printed at 12 mm/s exhibit a lot more small and scattered pores as compared to that of the parts printed at 7 mm/s (Figure 48e, f). The presence of the thin and long pores is likely due to the formation of the groove within the surface of the filament (Figure 39a) and as well as the formation of the voids between the adjacent filament due to the nature of the extrusion process (Figure 17). Also, it is found that some gaps formed are due to the waviness of the extruded filament (Figure 48d). It is therefore deduced that the waviness of the extruded filament contributes to the porosity of the printed parts. The lower porosity at lower print speed is likely due to the higher fiber directionality (lower FWHM) and together with fewer groove formations.

It can also be seen that nozzle temperature has the same influence on the porosity as with on the fiber directionality (Figure 41b). It is found that the porosity can be further reduced by having higher nozzle temperature (Figure 47b). Higher nozzle temperature reduces the viscosity of the composite material. As such, the composite material is able to flow or deform more easily when extruded out from the nozzle and conform better to surface of the previously deposited layers, which are irregular and not entirely flat as shown in Figure 39a. As a result, a high nozzle temperature can help reduce porosity slightly. It is observed that the reduction in porosity due to lower print speed (1.1-2.8%) is greater than the reduction in porosity due to the change in temperature (by 0.4-1.2%).

The first order fitted response surface of process parameters on porosity is shown in Figure 49. Equation can be used to describe the model the effect of process parameters on porosity.

$$\text{Porosity} = -9.242 + 3.485A + 0.014B - 0.037C - 0.010AB - 0.006AC \quad (24)$$

where A is the print speed, B is the nozzle temperature, and C is the bed temperature in their respective units.

Figure 49 Response surfaces of the process parameters on porosity. a) at print speed of 12 mm/s b) at print speed of 7 mm/s.

6.2.2 Effect of print parameters on mode I ILFT

Further analysis reveals that increasing the nozzle temperature from 250 °C to 265 °C would significantly improve the mode I ILFT, whereas increasing print speed would lower the mode I ILFT (Figure 50a). The improvement in mode I ILFT due to the higher nozzle and bed temperatures and lower print speed is in good agreement with the simulation results where the degree of bonding increases with the higher nozzle and bed temperature and lower print speed. The highest mode I ILFT obtained is 943 J/m² and it is achieved with a print speed of 7 mm/s, a bed temperature of 70 °C and a nozzle temperature of 265 °C. On the other hand, the lowest mode I ILFT obtained is 200 J/m² and it is achieved by having the print speed, bed and nozzle temperatures set to 7 mm/s 30 °C and 250 °C, respectively. It is noted that increasing nozzle temperature, the improvement in the mode I ILFT is more than 200% (from 475 J/m² to 943 J/m² for 7 mm/s print speed). From Figure 50b, it is noticed that bed temperature has a positive effect on the mode I ILFT at low print speed (from 599 J/m² to 943 J/m² for 7 mm/s print

speed) but the effect is reduced at high print speed (from 586 J/m² to 685 J/m² for 12 mm/s print speed).

Figure 50 Bar charts showing a) Mode I ILFT (mean $\pm$ standard deviation) for various printing process parameters. b) effect of bed temperature on Mode I ILFT. (Appendix F).

ANOVA was conducted to check the significant level of each process parameter. ANOVA results show all three process parameters have significant effects on the Mode I ILFT, with all having p-value lesser than 0.05 (Appendix F). The nozzle temperature has the most significant effect on Mode I ILFT at $\alpha=0.05$ (with f-statistic value = 208.86 and p-value < 0.0001). The effect of bed temperature is also significant at $\alpha=0.05$ (with f-statistic value = 57.97 and p-value < 0.0001). The print speed is the least significant at $\alpha=0.05$ (with f-statistic value = 13.18 and p-value = 0.0021). It is also noted that the interaction between print speed and bed temperature is significant. It is noted that the increase in the mode I ILFT is higher as print speed increases at high bed temperature

as compared to that of at low bed temperature. Response surface analysis (Figure 51) using linear fitting enables the mode I ILFT to be predicted based on the process parameters used. Equation below can be used as a model to predict the Mode I ILFT.

$$\text{Mode I ILFT} = -8306 + 288A + 32B - 1.9C - AB - 0.98AC + 0.06BC \quad (25)$$

where A is the print speed, B is the nozzle temperature and C is the bed temperature in their respective units. The signal to noise ratio value of 20.507 for the Adeq precision, indicates that an adequate signal and the model can be used to navigate the design space.

Figure 51 Response surface modelling of the mode I ILFT.

A comparison with conventional CFRTP showed that the mode I ILFT of the additively manufactured CFRTP was about 2 times higher than that of the conventionally manufactured epoxy matrix CFRP (200-300 J/m² [229-231]) (Figure 52). However, it is still considerably lower (about 3 times) compared to the thermoplastics matrix CFRTP (1500-2500 J/m² [232, 233]), indicating poorer interlayer adhesion in comparison with the conventionally manufactured ones which normally undergo consolidation process such as vacuum bagging and autoclaving.

A comparison is also made with the Markforged fabricated specimens. It is also found that the highest mode I ILFT obtained in this study is equivalent to that of the Markforged-fabricated specimens. ANOVA was conducted to check the statistical variance between the two data sets. ANOVA results show that the difference between the two data sets are insignificant at $\alpha=0.05$ (with f-statistic value = 0.36012 and p-value = 0.58078) (Appendix G). This shows that low-cost printers with well-tuned printing parameters can achieve equivalent, if not better, mode I ILFT than the commercially available high-end Markforged composite printer.

Figure 52 Box and whiskers chart showing a) Mode I ILFT (mean $\pm$ standard deviation) for conventionally manufactured epoxy matrix, thermoplastic matrix, Markforged fabricated composite and the best print parameters in this study.

6.2.3 Fracture analysis

The interlaminar fracture surfaces of the mode I ILFT test specimens are investigated. Randomly aligned discontinuous fibers are observed at fracture surface of the mode I ILFT test specimen (Figure 53a, b). The randomly aligned discontinuous fibers indicate that fibers pullout occurred during the test. Figure 53c clearly shows fiber pullout on the fracture surface of the mode I ILFT test specimen. The fiber pullout is an indication of good fiber-matrix adhesion.

Figure 53 Laser-optical microscopic images of (a) fracture surface of the carbon FRP composite specimen at lower magnification (b) fracture surface of the carbon FRP composite specimen at higher magnification (c) fiber pullout at the fracture surface of the carbon FRP composite specimen.

Fiber pullout is significant in the specimen printed using low print speed and high nozzle temperature (Figure 54b) whereas a noticeable decrease in the amount of fiber pullout is noted in specimen printed using high print speed and low bed and nozzle temperatures (Figure 54a). The fiber pullout is an indication that fiber bridging occurred during the crack propagation which is a typical behavior for the unidirectional FRP composites (Figure 53c). The smaller amount of fiber pullout at lower nozzle temperature and higher print speed suggests that the main failure mechanism is interlayer matrix failure as that interlayer bonding between the layers is not strong enough to cause fiber pullout and elucidates the lower mode I ILFT as compared to that of the higher nozzle temperature and lower print speed.

Figure 54 Optical microscopic image showing (a) reduced amount of fiber pullout observed in specimen printed with low nozzle and bed temperatures and high print speed. (b) a significant amount of fiber pullout observed in specimen printed with high nozzle and bed temperatures and low print speed.

SEM images of the fracture surfaces are shown in Figure 55 to show the amount of matrix attached to the fiber surface. The SEM examination suggests that the fracture happens both in the matrix as well as along the fiber/matrix interface. It is evidenced in Figure 55a and Figure 55b that some carbon fiber surfaces are clean whereas some carbon fibers have got some matrix adhered to its surface. The occurrence of both matrix fracture and fiber/matrix interface debonding indicates that the interfacial shear strength is adequate in enhancing the fracture toughness of the composite [234].

Figure 55 SEM micrographs of fracture surfaces showing (a) the presence of both matrix fracture and fiber/matrix debonding. (b) matrix adhering to the fiber surface. (c) clean matrix fracture indicating brittle fracture for specimen printed at 250 °C. nozzle temperature (d) presence of hackles for specimens printed at 265 °C nozzle temperature indicating a slightly more ductile behavior.

Figure 55c and Figure 55d show the matrix fracture surfaces for specimen extruded at 250 °C and 265 °C . Clean matrix fracture at some areas as shown in Figure 55c is an indication of brittle fracture of matrix [234, 235]. The hackle marks in the matrix material shown in Figure 55d suggests a slightly more ductile fracture of the matrix. The hackle marks are likely due to yielding that originates from the edge of the individual fibers during fiber pull-out [236, 237].

Figure 56 summarizes the effects of print speed, nozzle temperature, bed temperature on the microstructure and degree of thermoplastic bonding at the interlayer boundary, which in turns affect the mode I ILFT.

The reduction in mode I ILFT as print speed increases can be explained by the higher porosity level at high print speed. The higher porosity reduces the contact area between the adjacent layers that polymers can inter-diffuse, thereby reducing the mode I ILFT (Figure 56a,b). Additionally, the higher print speed would cause a faster drop in temperature as illustrated in Figure 31a, which shortens the available time for bond formation resulting in a lower degree of bonding.

It is noted that although increasing nozzle temperature does not significantly reduce the porosity, the improvement in mode I ILFT is more than 200%. It can hence be deduced that the improvement in mode I ILFT is partly due to the reduction in porosity as a result of lower print speed and predominantly due to better interdiffusion of polymer chains between the adjacent layers as a result of higher nozzle temperature (Figure 56c). The better fusion is due to the longer dwell time above the glass transition temperature as discussed previously. Likewise, bed temperature can be used to improve the mode I ILFT.

It is noted that although the porosity is slightly higher at higher bed temperature, the mode I ILFT at higher bed temperature is still higher compared to lower bed temperature. Again, the same deduction can be made that the improvement in interdiffusion of polymer chains between the adjacent layers outweighs the reduction in properties due to the higher porosity. Process parameters either promote or inhibit defects formation

(pores). The ideal porosity should be 0 to have maximum interdiffusion of polymer chains at the interlayer boundary.

Figure 56 Illustration of the microstructure and degree of bonding of the FFF-fabricated CFRTP. (a) the waviness of the roads of filament due to print speed would cause gaps between the adjacent filament. (b) formation of groove and degree of bonding due to print speed. (c) degree of bonding due to the effect of nozzle and bed temperatures.

6.3 Summary

The PSP relationship of the additively manufactured continuous carbon FRP with mode I ILFT is investigated in this study. The effect of parameters such as print speed, nozzle temperature and bed temperature on the porosity are investigated to obtain a good mode I ILFT of the printed composite parts. The mechanism that leads to the porosity is found to be related to the waviness of fibers, groove formation, which has been extensively discussed in the previous chapter. Mode I ILFT is found to be affected by the porosity as well as the time for bond formation between the layers. The single filament study showed that higher print speed would cause more waviness and groove formation to the extruded composite filament thus leading to higher porosity and hence lower mode I ILFT. Higher nozzle temperature allows the extruded material to have longer dwell time to stay in the temperature range for bond formation, thus leading to higher mode I ILFT.

Mode I ILFT as high as 943 J/m^2 is achievable by using low print speed (7 mm/s), high nozzle temperature (265 °C), and high bed temperature (70 °C). It should be noted that the highest nozzle temperature achievable in this study was limited to 265 °C. This study has shown that low-cost printers with well-tuned printing parameters can achieve equivalent, if not better, mode I ILFT than the commercially available high-end Markforged composite printer. Fracture analysis reveals the fiber bridging plays an important role in providing the ILFT as evidenced in specimens printed with low print speed, high nozzle and bed temperature. Future work can be on finding optimal print conditions and re-designing a nozzle that extrudes smooth lines with minimal waviness and reduces the porosity.

7. Characterization of the fracture mechanics of FFF-fabricated continuous FRP composites

7.1 Background

The fabrication of continuous fibers reinforced thermoplastics is relatively new and there is only one commercially available composite printer that is capable of fabricating continuous FRP composite in recent two years. The detailed characterization of mechanical properties and the failure mode of the FFF-fabricated continuous fibers reinforced thermoplastics are not yet available. Hence, this section discusses the characterization of the mechanical properties, microstructures, and the failure behaviors of the continuous fibers reinforced thermoplastics composites fabricated using the Markforged composite printer.

Various mechanical properties that are relevant to sports and aerospace industries, such as tensile, compression, shear, flexural, and indentation resistance of additively manufactured continuous carbon FRTP are evaluated by conducting mechanical testing. The anisotropic mechanical properties are reported which has led to the motivation of this research to improve the interlaminar properties. In addition to that, scanning electron microscopy (SEM) and micro-computerized tomography (μ CT) -scan is also used to observe the microstructures and fracture mechanism of the composites.

7.2 Results and discussion

In this section, the tensile, compression, shear, flexural, indentation resistance, and mode I ILFT properties of the additive manufactured carbon FRTP are reported. Three specimens were tested per material for each type of test. The anisotropic mechanical properties of the carbon FRTP is shown in Table 11. The failure mode of each test is also observed and evaluated. The larger discrepancy of Young's modulus and the

flexural modulus from the manufacturer's data could be due to the difference in the method in obtaining the strain values.

Table 11 Mechanical properties of FFF-fabricated CFRTP (average value $\pm$ standard deviation).

		FFF CFRTP (V _f : 41 _{vol} %)		Manufac- turer's data (CFRTP)	Conven-tional carbon fiber composites
Tensile test	Tensile Strength (MPa)	x	808 ± 89	800	408 ^a
		y	38.9 ± 1.21	NA	NA
		z	5.34 ± 0.16	NA	10-35 ^b
	Young's Modulus (GPa)	x	70.0 ± 3.9	60	71.4 ^a
		y	4.32 ± 0.37	NA	NA
		z	1.02 ± 0.09	NA	2-3 ^b
Compression test	Compressive Strength (MPa)	x	276 ± 20	320	270-370 ^c 600 ^d
		y	72 ± 6	NA	NA
		z	80 ± 10	NA	NA
	Compressive Modulus (GPa)	x	20.8 ± 1.9	54	100 ^d
		y	1.36 ± 0.11	NA	NA
		z	1.55 ± 1.84	NA	NA
Shear test	Shear Strength (MPa)	XY	45.0 ± 6.85	NA	78 ^e
		XZ	9.51 ± 1.39	NA	57 ^e
		ZY	12.8 ± 2.12	NA	NA
	Shear Modulus (GPa)	XY	1.86 ± 0.24	NA	4.4 ^e
		XZ	0.49 ± 0.07	NA	4.4 ^e
		ZY	1.06 ± 0.17	NA	NA
Flexural test	Flexural Strength (MPa)	x	430 ± 13	470	750 ^f
	Flexural Modulus (GPa)	x	38.1 ± 1.0	51	47 ^f

Quasi-static	Maximum Force, $F_{\max}$	1080 ± 123	NA	1580 ^g
Indentation	(N)			
test	Displacement at	3.54 ± 0.20	NA	NA
	maximum force (mm)			
	Displacement at $0.2 \cdot F_{\max}$	10.6 ± 0.3	NA	NA
	(mm)			
	Maximum Energy (J)	6.26 ± 0.67	NA	NA

^a $V_f=40\%$ unidirectional carbon fiber/ PA 6/6 composites, hot compression molded at 270 °c and 2 MPa for 80 mins [238]

^b $V_f=40\text{-}70\%$ unidirectional carbon fiber/ PA 6/6 composites, autoclaved at 80°C for 2 h at a constant pressure of 80 psi, post curing in oven for 2 h at 160°C [239]

^c $V_f=40\text{-}60\%$ unidirectional carbon fiber/PA 6 composites , hot compression molded at 250 °c and 2 MPa for 80 min [238]

^d $V_f=55\%$ unidirection carbon/epoxy composite, vacuum-infusion at room temperature, followed by a postcuring in an oven at 80 °C for 12 h [240]

^e $V_v=55\text{-}57\%$ carbon fiber in the warp direction and glass fiber in the weft direction/ polyamide [241]

^f $V_f=47.5\%$ unidirectional carbon fiber/epoxy composites, autoclave at 120 °C with five different magnitudes of compressive pressure (0.25–1.25 MPa) and holding time (20–40 min) [242]

^g CFRP with a 0/90 configuration[243]

Since the AM CFRTP parts were fabricated without any heat treatment and consolidation process, its mechanical properties are in generally lower to that of the hot compression molded and the autoclaved counterparts of similar fiber loadings. The effect of the lack of consolidation process of the AM CFRTP is more pronounce in the y and z-directions due to the lack of reinforcing effect of the fibers.

7.2.1 Tensile properties

Figure 57a shows typical tensile stress vs strain graph of the additively manufactured carbon fiber tensile coupons. The maximum tensile strength and modulus are achieved in the x-direction, registering 808 MPa and 70.05 GPa, respectively (Figure 57b,c). The tensile strength and modulus in the y-direction are 38.88 MPa and 4.32 GPa, whereas the tensile strength and modulus in the z-direction are the lowest, registering 5.34 MPa and 1.02 GPa respectively. For all the directions, it is observed that the stress increased almost linearly with the strain before breaking abruptly at 1.15%, 1.30%, and 0.83% strain for x-, y-, and z-direction respectively (Figure 57d), indicating brittle nature of the composite.

A slight increase in X-direction tensile modulus is observed which is likely due to the straightening of the fibers as tensile stress is applied. This non-linear behavior has also been observed by various groups [73, 75]. The tensile strength and modulus in the x-direction are significantly higher as compared to the other two directions because the fibers are unidirectionally laid in the x-direction. The carbon fibers, which exhibit superior tensile properties, bear the load transferred from the thermoplastic matrix resulting in significantly improved load-bearing capability of the composite. As there are no fibers laid in the y- and z-directions, it results in anisotropy in the material properties. The lower tensile strength and modulus in the z-direction as compared to that of the y-direction is a common phenomenon in the FFF technique and can be explained by the polymer interdiffusion at the interlayer and intralayer boundaries.

Figure 57 Tensile properties of AM CFRTP in different directions. (a) Typical tensile stress-strain curves. (b) Tensile strength. (c) Tensile modulus. (d) tensile strain. (mean $\pm$ standard deviation)

The intralayer diffusion strength is normally stronger than the interlayer diffusion strength because the heated nozzle tends to be closer to the adjacent filament at the top layer than to the bottom layer. Hence, the adjacent filament heats up more resulting in a better interdiffusion of polymer chains at the intralayer boundaries. Another reason for the difference in tensile strength can be explained through the way the composite filaments are extruded. As the adjacent filaments are made to overlap, the interlayer boundary exists in the jagged form rather than a flat one like the interlayer boundary (Figure 58). Due to this, the intralayer boundary tends to be larger compared to the interlayer boundary for the same length.

Figure 58 Schematics of extruded composite filament showing the intralayer and interlayer boundaries.

Figure 59a shows the fracture mode of the additively manufactured x-direction tensile CFRTP specimen. Figure 59b illustrates failure mechanisms occurred in the tensile specimen in the tensile test. Tensile rupture and shear rupture are observed in all the x-direction CFRTP specimens. Shear rupture is regarded as shear damage along the fiber direction whereas tensile rupture is regarded as damage in perpendicular to the loading direction. A horizontal crack formed without necking as shown in Figure 59c is a result of tensile rupture, which indicates the brittle nature of the composite. Additionally, specimens of both materials showed severe delamination after the tensile test. Also, de-bonding between two adjacent fiber filaments in the same layer is also noticed (Figure 59a). Delamination and de-bonding (as observed in Figure 59c) are a result of the sheer rupture. As the fiber layers and the fiber bundles are held together by the matrix, the delamination and de-bonding between fiber bundles indicate that weak bonding exists between the layers. The weak bonding between layers is attributed to the lack of consolidation process in the FFF technique.

Figure 59 Images of the fracture surfaces of the x-direction tensile specimen. (a) Fracture mode that consists of cracking and delamination of a x-direction tensile CFRTP specimen (b) illustration of x-direction tensile fracture mechanism of additively manufactured CFRTP (c) matrix crack due to shear rupture and fibre breakage due to tensile rupture (d) SEM image showing fibre pull-out at the fractured surface (e) SEM image showing fibre breakage and matrix adhering to fibre.

The micro-scale fracture mechanism can be observed using SEM. A large amount of fiber breakage is observed in Figure 59d,e. Extensive fiber breakage suggests that the failure mode of additively manufactured CFRTP specimens subjected to tension are fiber dominant, indicating loads are effectively transferred from matrix to fibers. Figure 59e shows that matrix adheres onto the pulled-out fiber which indicates good interfacial bonding between matrix and fiber. Although the printed composite part generally has a

good fiber-matrix interfacial bonding, a small number of holes observed (Figure 59d) suggests that only a very small amount of fiber pull-out occurred in the tensile test. The small amount of pull-out could be due to the improper coating of nylon matrix onto the fiber surface during the fabrication of composite filament. That said, the fiber pull-out is generally insignificant in comparison to a large number of fiber breakages.

The fracture modes of the y- and z-directions tensile specimens are similar, in which horizontal cracks are observed (Figure 60a). Upon examining the fracture surfaces, it is observed that y-direction tensile specimens have uneven surfaces with larger undulation (Figure 60b) whereas z-direction tensile specimens have smoother surfaces with smaller undulations (Figure 60d). The larger undulation of the fracture surface may be the reason for the higher tensile strength in the y-direction as compared to that of the z-direction. The difference in fracture surface is likely due to the printing manner as discussed earlier.

Figure 60 Fracture surfaces of y- and z-directions specimens obtained from confocal laser-optical microscope. (a) Horizontal cracks observed in y- and z-directions specimens. (b) the surface profile of the fracture surface of the y-direction specimens. (c) laser-optical image of the fracture surface of the y-direction specimen. (d) the surface profile of the fracture surface of the z-direction specimens. (e) laser-optical image of the fracture surface of the z-direction specimen.

7.2.2 Compressive properties

The compressive properties of the CFRTP in x-, y- and z-directions are shown in Figure 61. The compressive strength and compressive modulus showed similar trends, in which the compressive strength and modulus in the x-direction are the highest, achieving 129.16 MPa and 4.275 GPa respectively.

Figure 61 Compressive properties of the AM CFRTP in x-, y-, and z-directions. (a) typical compressive stress-strain curves. (b) Compressive strengths and moduli (mean $\pm$ standard deviation).

The compressive strength and modulus in the z-direction are 80.50 MPa and 1.546 GPa respectively whereas the compressive strength and modulus in the y-direction are the lowest, achieving only 72.06 MPa and 1.362 GPa respectively. The better compressive properties in the x-direction are likely because the fibers, which are in the same direction, strengthen and stiffen the matrix in that direction. The compressive properties in the y- and z-directions, which are not in the fiber direction, are lower because they did not exhibit the strengthening and stiffening effect of the fibers.

The fracture mode of the compression specimens in the x-, y-, and z-directions are shown in Figure 62. In the x-direction compression specimens, kink band and fiber breakage are observed. The formation of kink bands is a result of the instability of equilibrium against the compressive stress [244]. The fibers are broken at the kink band boundary. Interestingly, axial splitting is not observed as would normally be found in carbon/epoxy composites [245]. This is probably due to the better interlaminar fracture toughness of the thermoplastic as compared to the epoxy matrix.

Figure 62 Compression test failure modes of the AM CF RTP. (a) x-direction specimen showing kink bands and fiber breakage. (b) y-direction specimen showing matrix shear failure. (c) z-direction specimen showing multiple modes of failures, including intralayer boundary crack, transverse cracks.

Shear fracture is observed for the y-direction specimens (Figure 62b). There are several fracture modes observed in the z-direction compression specimens as shown in Figure 62c. It can be seen that shear fracture and axial splitting are coupled [246]. The shear fracture occurs at the plane 45° to the loading axis where the shear stress is maximum. Two types of axial splitting are observed. The first type of axial splitting is a single long crack happens within the road of the extruded filament. The second type of axial splitting is multiple short cracks which happen at the boundaries between the adjacent roads of extruded filament. Transverse failure mode due to the specimen buckling is also observed. The shear fracture, axial splitting, and transverse failure are all matrix failures, indicating fibers play a minimal role in the compressive properties in the y- and z-directions. This explains why compressive strength in the y- and z-directions is significantly lower as compared to that of the x-direction.

7.2.3 Shear properties

The shear properties of the AM CFRTP in XY, XZ, and ZY directions are shown in Figure 63.

The shear stress-strain curves show that the shear stresses for XY and XZ orientations increases to non-linearity and keep increasing after 15% shear strain. ZY specimen showed linear response up until 1% shear strain before breaking catastrophically. The shear strength in XY direction is the highest recording 45.0 ± 6.8 MPa whereas the shear strength in XZ and ZY directions are 9.5 ± 1.4 MPa and 12.8 ± 2.1 MPa respectively. The shear modulus in XY direction is found to be the highest registering 1.86 ± 0.24 GPa whereas the shear modulus in XZ is the lowest recording 0.495 ± 0.07 GPa. The anisotropic characteristic in the shear properties of the AM CFRTP is typical of the

unidirectional fiber-reinforced composite. However, unlike conventional unidirectional fiber-reinforced composites [241], the difference between G_{xy} and G_{xz} is huge, with G_{xz} being only one-fifth of the value of G_{xy} . Similar magnitude of reduction is observed in the shear strength. This is likely due to the fact that the degree of interdiffusion of the polymer at the interlayer boundary is lower than that of the intralayer boundary. This is because of the higher average temperature history at the intralayer boundary which favors the interdiffusion of polymers.

Figure 63 Shear properties of the AM CFRTP in different orientations. (a) shear stress-strain curves. (b) Shear strengths and shear moduli (mean $\pm$ standard deviation).

In the fracture analysis of the shear specimens (Figure 64), it is noticed that the axial splitting occurred at the notch tips of the XY and XZ specimens. The crack is initiated due to the shear stress concentration at the tip and propagates along the fiber direction. The fibers appeared to be slightly bent and no crack is observed in the principal stress plane as it is prevented by the aligned fibers [247].

Figure 64 Fracture modes of the AM CFRTP in the shear test (from left to right: XY, XZ, and ZY specimens).

On the other hand, the horizontal crack is observed at the interlayer boundary of the ZY specimen instead of at the boundary at the adjacent filaments. The failure initiation not occurring within the vicinity between the tips of the notches suggests that there are manufacturing defects at the interlayer boundary which has caused shear stress concentration to occur. This again suggests that interlayer bonding is much weaker than that of the intralayer bonding.

7.2.4 Flexural properties

The flexural stress of carbon CFRTP is linear up to 1.0% flexural strain (Figure 65). At 1.0% strain, a slight drop in flexural stress is observed. The reason for the drop could be due to localized fiber breakage on the tensile side of the specimen. The flexural stress continues to rise after the slight drop. The flexural specimens broke abruptly upon reaching the maximum flexural strength with a corresponding strain of 1.5%. The

maximum flexural strength and flexural modulus recorded for carbon fiber were 430 MPa and 38.1 GPa respectively.

Figure 65 Typical 3-point bending test response of AM carbon and glass FRTP composite specimens

In fracture analysis of carbon fiber specimens, a high-speed camera (Fastcam SA4, Photron, Japan) was used to observe the fracture mechanism of the carbon fiber specimens at 5000 frames per second. Crack initiation at the top-most surface of the compression side was first observed (Figure 66d-ii). The crack was likely formed as a result of the crushing of fibers due to the high compressive stress at the top-most surface. The crack continued to propagate towards the neutral axis while the specimen still remained in one piece under the bending load (Figure 66 d-iii). This behavior is similar to most of the conventional CFRP in which failure in compression is normally observed due to the poor compressive strength of carbon fibers [248, 249].

The sudden drop in flexural stress at 1.57% strain is because the flexural specimens fail catastrophically when the fibers at the tensile side break. When the outermost fiber layers at the tensile side break (Figure 66d-iv), the bending load will have to be distributed among the remaining intact layers. However, the fewer number of layers that remains intact will not be able to take up more loads and would break eventually causing the catastrophic failure (Figure 66d-v).

Figure 66 Fracture analysis of the flexural test. (a) schematics illustrating fracture mode of carbon FRP undergone flexural test (b) fibers breakage occurred at the outer most layers which are in tensile (c) cross-section view of the fracture surface (d) image sequence of the flexural test captured using highspeed camera.

7.2.5 Indentation test

Figure 67 shows the typical results of the indentation test for carbon and glass fiber specimens. For carbon fiber, the indentation force increases to a maximum before dropping abruptly at 3.8 mm indentation when the quasi-isotropic carbon fiber sheets break. The force continues to rise initially after the sudden drop until a local maximum and begins to drop thereafter. The maximum indentation force recorded for the carbon fiber specimens was 1078 N and the indentation energy calculated up to 10.62 mm displacement (20% maximum force) was 6.53 J. The sudden drop in indentation force is very similar to what happened in flexural test and could be due to the catastrophic failure at the tensile side of the carbon fiber flexural specimens.

Figure 67 Force-indentation curves for carbon FRTP.

The typical fracture mode of additively manufactured carbon fiber specimen and the illustrations are shown in Figure 68. During the test, a dent at the top layers is first observed and followed by fiber breakages at the bottom layers and eventually in all layers as the indenter perforates the specimens (Figure 68a). Delamination will also occur as a result of indentation.

The fractured area is evaluated after the test. No fiber breakage or delamination occurred in a region far away from the indentation center (Figure 69a-i). Voids observed in Figure 69(a-i) are results of the extrusion-based fabrication method. Fiber breakage is observed in the middle where the indenter acted on and the maximum damage diameter (viewed from outside without considering internal damage) was 21 mm (Figure 69a-iii).

The average damaged area is found to be 201.5 mm^2 or 4.4% of the total area. In addition to that, delamination is observed around the perforated region (Figure 69a-iii for carbon FRP and beyond the perforated region (Figure 69a-ii, a-iv) for carbon FRP in which black gaps between the layers are observed. This suggests that the delamination would propagate from the middle where indenter is acting on towards the side of the specimen and the affected area is often larger than the damaged area observed from outside.

Figure 68 Illustration of fracture modes of the indentation test. (a) Deformation and delamination of fiber laminate before fiber breakage (b) fiber breakage of different fiber layup orientation after the indentation (c) failure mode of single fiber layup orientation which consists of fiber breakage and de-bonding between adjacent filament (d) cross-section view which consists of delamination and fiber breakage in the indentation specimen

Figure 69 CT-scan image of (a) the side view and (b) bottom view of the fractured area of carbon fiber specimen.

7.3 Summary

AM CFRTPs are fabricated using Markforged composite printer and are characterized and reported in this chapter. Mechanical tests such as tensile, compression, shear, flexural, and indentation are conducted and compared with the conventional composite materials. The mechanical properties of the AM CFRTP are generally poorer as compared to the compression molded and autoclaved composites of similar fiber loadings. The poorer mechanical properties were attributed to the lack of consolidation of the extrusion-based AM process. Also, the detailed fracture behaviors of the AM CFRTP have been evaluated and discussed. Similar to conventional composites, the properties of the AM CFRTP are anisotropic. The properties in the x-direction are the highest due to the reinforcing effect of the fiber. Interestingly, unlike conventional composites, the mechanical properties in the y- and z-directions are different, with y-direction achieving higher strengths as compared to the z-direction. It is attributed to the difference in the interlayer and intralayer bonding. The interlayer bonding is significantly weaker compared to the intralayer bonding. This warrants further thorough investigation into the process-material interaction to further improve the interlayer bonding.

The data obtained from a series of mechanical tests can be useful for performing finite element structural simulation of CAD models before the actual fabrication of the parts. It is particularly useful as it can save time and materials during the iterative design process. Iteration of designs can be performed virtually in the structural simulation to find the most optimum design for a specific application. Allowable stress design approach [250] could be used in the design process applying the mechanical properties obtained from this study. A factor of safety is used to account for the uncertainty in the

fabrication process, material properties, and loading conditions. The allowable stresses were estimated by dividing the failure stress by a factor of safety, which has a value greater than unity. The failure stress is normally the yield stress or the proportional limit of the material. Using this approach, finite element structural simulation can be done to estimate the stresses at various modes of loads, which are then verified alongside the specified allowable stresses. This approach, however, assumes stresses and deformations are maintained at low levels, thus non-linearity of the materials could be ignored and only the linear elastic regions of the material properties are used in the analysis.

Another approach of the design process is the limit state design approach [250]. In this design approach, the structures should be able to bear all the loads and deformations that they will be possibly incurred during the fabrication process, and in the normal service life. The limit states are categorized into two groups: the ultimate and serviceability limit states. The ultimate state refers to the complete failure of the structure which include loss of static equilibrium whereas the serviceability limit state refers to the interruption from the normal use of the structure which include excessive deformations that disrupt the appearance and usefulness of the structure. The serviceability limit state criterion is more difficult to determine as it takes into account of characteristic, frequency, and quasi-permanent of the loadings and it should be lower than the yield strength of the material.

In short, this study, in which the anisotropic mechanical properties are characterized, will be helpful to product designers wanting to attempt using FFF technique to fabricate continuous fiber composite parts.

8. 3D-Printed Technology Demonstrator

8.1 Background

One important characteristic of the CFRTP is the highly anisotropic mechanical properties where the strength comes in the fiber direction. Extrusion-based printing technique enables the creation of more optimized high-performance structures through fiber steering.

This section covers the design, analysis, fabrication, and load test of a UAV structure, the frame of the quadcopter's main body that holds the motor arms taking advantage of the extrusion-based printing technique.

8.2 Quadcopter main body structure

A strong yet light quadcopter structure would increase the amount of payload, flight endurance, and range. Mass reduction of the structural weight is therefore critical.

Figure 70a shows the main body structure of a quadcopter that is to be fabricated with the CFRTP to reduce weight and have a better structural performance. To take advantage of the fiber alignment ability of the AM technique and the high directional strength of the CFRTP, the fibers are laid along the contour of the outer and inner walls of the CAD model (Figure 70b). Honeycomb structures are used as the infill pattern to reduce the overall weight of the main body structure. The composite main body structure should have a better or equivalent mechanical performance at a much lighter weight as compared to the one manufactured using PC-ABS via a conventional method, which would have solid infill.

Figure 70 Design of quadcopter. (a) The CAD model of a quadcopter main body. (b) illustration of concentric carbon fiber pattern and hollow quadcopter main body. (c) initial part design for injection molding with full solid infill (d) modified the part design for extrusion printing technique with hollow structure.

8.2.1 Stress and fracture analyses

The design and structural analysis are performed using the allowable stress design method. A factor of safety of 1.5 is used in this study. The maximum allowable stress for the AM CFRTP is 533 MPa. The main body has to be stiff and strong enough to sustain the loading requirement of a quadcopter in different phases of flight. Takeoff and landing conditions, which normally have the most extreme loading conditions, are considered in the simulation. The maximum load applied to the structure was about 80 N (equivalent to 3g's of the design mass) and are equally distributed among the four remote forces, which represent the thrust force generated by the four motors. The fixed supports are defined at the four holes as shown in Figure 71 where the screws are used

to hold the main body of the quadcopter to the lower bay in which most of the mass, including the battery and other electronic components, are located. To evaluate the performance of the AM CFRTP parts, the static stress analyses are performed on the modified design for AM CFRTP and the conventional design for injection-molded PC-ABS. The results are shown in Figure 72.

Figure 71 Loading and support conditions.

From the static analysis, it is found out that the maximum deflection of the AM CFRTP part is 0.015 mm which is only 50% of the maximum deflection of the PC-ABS part. The amount of deflection at the four corners is the largest. It should be noted that the deflection is considered small (only a few percents of the height of the main body) considering the large force exerted. The small deflection generated is important to the flight characteristic as it means that the motor arms would get deflected in a smaller magnitude, retaining the lift force of the quadcopter. The maximum stress in the main body is 99.4 MPa which is well below the maximum allowable stress of the CFRTP.

Figure 72 Maximum deflection at the corners. a) AM CFRTP b) PC-ABS

As discussed in chapter 6, it is the nature of AM CFRTP to have voids. Presence of voids may induce stress concentration which may cause crack propagation. Also, the use of lattice structures would inevitably introduce sharp corners or edges that cause stress concentration as shown in Figure 73. Hence, it is also necessary to check whether crack would propagate if voids or pre-cracks are present in the regions where stress concentration occurs.

In the fracture analysis, cracks are introduced in the regions 1 and 2 highlighted in Figure 73 where stress concentration occurs. Figure 74 shows the modes I and II stress intensity factors at the crack introduced in region 1. The negative values of the mode I stress intensity factors indicate that the crack is being closed as the compressive stress is dominant in the region. It also means that crack will not propagate in mode I as there is no peeling force on the crack front. The negative mode II stress intensity factor is attributed to the direction of the tangential component (shear) of the applied load. The highest mode II stress intensity factor is $9.99 \times 10^5 \text{ Pa} \cdot \text{m}^{0.5}$ which is well below the critical mode II stress intensity factor of $6.48 \times 10^6 \text{ Pa} \cdot \text{m}^{0.5}$, indicating that crack propagation will not happen in region 1.

Figure 73 Stress distribution of the main body of the quadcopter.

Figure 74 Modes I and II stress intensity factors distributions at the crack in region 1.

The fracture analysis is also conducted in region 2. Figure 59 shows the stress distribution across the crack front in region 2. The positive mode I stress intensity factor in the middle of the crack indicates that the crack front is experiencing peeling force. The maximum mode I stress intensity factor ($2.0 \times 10^6 \text{ Pa.m}^{0.5}$) occurred at the middle of

the crack front is just within the critical mode I stress intensity factor ($2.1 \times 10^6 \text{ Pa.m}^{0.5}$), indicating crack will not propagate. The maximum mode II stress intensity factor is found to be $1.78 \times 10^6 \text{ Pa.m}^{0.5}$ which is well within the critical mode II stress intensity factor ($6.48 \times 10^6 \text{ Pa.m}^{0.5}$), which means crack will not propagate. Hence, from the fracture analysis, it can be concluded that the main body of the quadcopter should be able to function properly under the most extreme working condition.

Figure 75 Modes I and II stress intensity factors distributions at the crack in region 2.

8.2.2 Manufacturing of quadcopter frame

After the stress analysis, the main body of the quadcopter was fabricated using the Markforged composite printer. The print parameters were 15 mm/s, 250°C, and 30°C for the print speed, nozzle and bed temperature, respectively. The fabricated main body is shown in Figure 76. The main body structure has 188 layers and the total print time was about 10 hours. It should be noted that it would have taken a few weeks if the injection molding technique was used. The final weight of the AM CF RTP part is 31

grams and is about 11 grams lighter compared to the injection-molded PC-ABS part (Table 12).

Table 12 Comparison between AM CFRTP and conventional injection molded PC-ABS part

	AM CFRTP	Injection molded PC-ABS(density = 1.2 g/cm ³)
Weight	31 grams	42 grams
Manufacturing time	10 hours	2-4 weeks

The weight reduction of the modified part printed using CFRTP shows high weight efficiency of the structure.

Figure 76 Main body of quadcopter fabricated using the extrusion-based 3d printing technique.

8.2.3 Static bending test

The printed main body of the quadcopter is assembled with glass fiber rods to form a complete quadcopter structure. A static bending test is performed on the quadcopter structure to examine the mechanical performance of the structure before performing flight test. The setup of the bending test is shown in Figure 77. The quadcopter structure, which has fixed supports 4 cm away from the ends of the main body, are loaded up to 140 N, which is equally distributed at four loading positions as shown in Figure 77. Figure 78 shows the force-displacement curve of the static bending test. The quadcopter structure is able to withstand loads up to 140 N without breaking. A typical 3kg quadcopter having an acceleration of 3 times its weight will experience about 90 N. This means that the quadcopter will be able to perform well within the normal operating flight loads.

Figure 77 Experimental setup of the static bending test.

Figure 78 Force-deflection curve of the bending test showing that quadcopter is able to sustain load up to 140 N without noticeable loss in strength.

8.3 Summary

In this chapter, the use of the extrusion-based technique to fabricate UAV structure is demonstrated. The ability of the extrusion-based printing technique to align fibers has enabled the creation of geometrically complexed composite parts, which are otherwise hard to manufacture. Finite element structural and fracture analyses are conducted applying the knowledge gained from the mechanical characterization of the AM CFRTP. The static bending test is conducted on the printed UAV structure to evaluate its performance. Finite element analysis and static bending test confirmed that the 3D printed UAV structure is able to perform well under the most extreme flight condition. This study did not study how PSP relationship could be applied to the design and fabrication of the UAV structure. Future study could consider applying the PSP relationship to the design and fabrication of UAVs. Limited state design approach could be applied to ensure the structure does not exceed the ultimate limit state and the serviceability limit state. Design structures are considered safe when the ultimate limit

state criterion under factored loadings (with a magnification factor greater than unity) such as tensile, compressive, shear, and bending loading are lower than the relevant “reduced resistance”. The reduction factor on the reduced resistance is to account for the variability in the quality of the fabrication, and the consistency of the material which normally has a factor smaller than one, typically between 0.75 and 0.9[251]. The loading factor depends on the types of loadings, which would factor in dead load, live loads as well the frequency of the loadings [251]. Generally, the ratio of the factored loading to reduced resistance should be lower than 1.0 for permanent loads and 1.2 for temporary loads [252].

Tensile, compressive, and shear, properties are the fundamental input parameters for the static structural finite element analysis. To satisfy the serviceability limit state, the stresses in the design part must be within the elastic zone and the structure behaves elastically to ensure the structure remain functional when subjected to routine loading.

After the static structural analysis, Mode I ILFT can be used to gage if the composite material would fail or crack propagation would occur under the presence of micro-cracks at high stress level regions. Similarly, the serviceable state limit approach could be applied here to ensure the loads are within material limit under normal loading conditions.

Having determined the routine loading, uncharacteristic loading such as impact loading can then be studied to understand the dynamic performance of the structure. Indentation resistance could be used to study the behavior of the structures under unexpected loading such as impact. Permanent deformation of the structure as a result of the impact can be understood through this dynamic analysis.

Having considered all the normal and uncharacteristic loading conditions and known the stress distribution of the design part, the optimal process parameters and the microstructures can be selected using the models obtained experimentally or numerically to minimize the fabrication time and at the same time ensure the microstructure of the printed materials can serve the intended function. To achieve that, finite element software must be improved by adding composite simulation capabilities with multiscale modelling and inverse design capabilities to facilitate the search in the complex PSP relationships. Data-driven models could potentially speed up the search by having a hybrid approach, combining experimental data and numerical data [140]. Figure 7 below shows an integrated approach to designing structural parts[253]. In short, coming up with a predictive model to determine the structural integrity or properties of an FFF-printed parts require a collective effort from several science and engineering disciplines.

Figure 79 Integrated approach to designing structural parts [253].

9. Conclusion and future work

This chapter summarizes the research work carried out for the completion of this thesis.

Limitations and feasible future work are proposed.

9.1 Conclusion

Firstly, the anisotropic mechanical properties of the AM CFRTP and their respective failure modes have been explored. The need to investigate the interlaminar properties has been established. Secondly, a 2d heat transfer model has been developed to investigate the temperature history of the AM CFRTP with respect to material composition printing parameters such as nozzle and bed temperatures, print speed and layer thickness. Thirdly, PSP relationship on mode I ILFT are presented. Lastly, the feasibility of AM CFRTP for UAV structures is studied.

Heat transfer simulation of the extrusion process for composite materials.

For the first time, a heat transfer model capable of predicting the temperature history of the AM CFRTP for the multi-material extrusion process is developed. The extrusion process is understood in detail in terms of energy balance, through the investigation of each existing controlling parameter and material composition. It is found that if fibers have higher thermal conductivities than the polymer matrix, increasing fiber content in the composite filament increases the effective thermal conductivities, thus resulting in extruded filament having a higher cooling rate. Hence, proper control of the printing speed is necessary to achieve the required cooling rate. On the multi-material extrusion, the overall cooling rate is largely dependent on the base material. Careful control of the printing parameters is required especially for the extrusion of two distinctly different materials. The model is useful to study properties like fusion bonding at the interlayer

boundaries, the crystallinity of semi-crystalline polymers as well as internal residual stress, particularly when the actual temperature history is hard to measure.

Investigation of thermal properties and polymer chains interdiffusion of AM CFRTP.

The thermal properties that are required for the 2D heat transfer model have been investigated. The dependence of thermal conductivity on direction and temperature has been identified. Additionally, the polymer chains interdiffusion with respect to time and temperature is investigated.

Single filament study

The effect of process parameters on the microstructures of the AM CFRTP has been studied through the single filament study. The formation of grooves, the waviness of the fibers, and the shearing of the matrix are a few phenomena observed on the extruded composite filaments. These phenomena are related to the rheological properties of AM CFRTP. Smaller layer thickness can result in flatter surface for the next layer, at the expense of broader width of the composite filament. A lower print speed would result in a lower shear rate which in turn favors a higher fiber directionality. A smaller layer thickness would result in flatter top surface profile. Also, the nozzle temperature does not have a significant effect on the crystallinity of the nylon matrix. The understanding of the extrusion of a single composite filament lays the foundation to the knowledge of the overall microstructures and mechanical properties of the AM CFRTP parts.

Investigation of Mode I ILFT

The PSP relationship of the extrusion of AM CFRTP on Mode I ILFT is investigated using a low-cost FFF printer. Lower print speed is found to increase the fiber

directionality and hence reduce the porosity of the printed CFRTP. Nozzle and bed temperatures, on the other hand, do not have a significant effect on porosity but has a great effect on the temperature history of the deposited material, which in turn affect the interdiffusion of the polymers at the interlayer boundary. The highest mode I ILFT achieved in this study is found to be 943 J/m^2 and is achieved by using low print speed (7 mm/s), high nozzle temperature (265 °C), and high bed temperature (70 °C). This study has shown that low-cost printers with well-tuned printing parameters can achieve equivalent, if not better, mode I ILFT than the commercially available high-end Markforged composite printer.

Characterization of mechanical properties and failure modes

Tensile, compression, shear, flexural, and indentation tests have been conducted to understand the anisotropic mechanical performance of the AM CFRTP which are critical for the design of UAV structures. The failure modes of each test are also identified. The higher tensile strength in the y-direction as compared to the z-direction tensile strength are explained through the difference in the boundaries, which is evident in the fracture surfaces of the specimens. The understanding of the anisotropic material properties and the fracture mechanisms enable a set of design rules to be formulated as a guideline for the design and fabrication of the AM CFRTP parts.

Proof of concept part

The extrusion-based method was used to fabricate the geometrically complex structures, which are otherwise hard to manufacture. Finite element structural and fracture analyses are conducted applying the knowledge gained from the mechanical characterization of the AM CFRTP. The static bending test was performed on the printed UAV structure to

evaluate its performance. Finite element analysis and static bending test confirmed that the 3D printed UAV structure should be able to resist the loadings experienced under the most extreme flight condition.

9.2 Limitations

There may be some possible limitations in this study. Firstly, the Markforged composite printer's process parameters setting cannot be modified. Therefore, an open source Hello BeePrusa printer was used to study the effect of print parameters on the Mode I ILFT. The Hello BeePrusa has its own limitations as well. For instance, the highest temperature it can heat up is just 265 °C, making it impossible to further investigate the effect of higher temperature on the mode I ILFT. Also, due to the long print time of the mode I ILFT specimens, only two levels for each print parameter were investigated. Hence, the information between the two levels is not available.

The mode I ILFT and the other mechanical properties of the AM CFRTP produced using this technique are still low in comparison to that of the conventional thermoplastic composites. The lower mode ILFT of the AM CFRTP could be attributed to the lack of consolidation during the printing process. The material used is a proprietary composite filament which has a fixed fiber loading of about 40%, which is restricted by the extrusion process. New type of extrusion process with consolidation process could be developed in the future to improve the mechanical properties of the AM CFRTP.

Also, only static mechanical properties are investigated in this study. Dynamic properties should be investigated in the future.

In the numerical simulation part, only thermal effect is considered. Thermo-mechanical simulation could be performed to study the extrusion process in-depth.

In the 3D printed demonstrator, critical strain release fracture criterion was used to demonstrate the use of the mechanical properties data to predict the mechanical performance of the printed UAV structures without going into detail how to apply the PSP relationship in the design. Future work should focus more on the application of the PSP relationship.

9.3 Future work

The following research directions are recommended:

1. Investigation of the fatigue and creep properties of the AM CFRTP
 - Thus far, focus has been on the static mechanical properties of the AM CFRTP [76, 254]. Dynamic mechanical properties such as fatigue and creep properties should also be investigated in the future.
2. Investigation of the change in material properties due to the extrusion printing process through thermal analysis.
3. New in-situ or post-processing method to improve interlaminar properties
 - Conventional compression molding is found to be effective in improving the interlaminar properties. However, it will cause deformation of the parts due to the uneven pressure applied to the parts. New in-situ technique that can improve the interlaminar properties without compromising the dimensional accuracy of the parts is required. Although efforts have been made to improve interlaminar properties of FFF-fabricated materials through in-process pre-deposition laser heating [255], adding CNTs, microwave irradiation [185] and control of chamber temperature [186], not much enhancement has been achieved. This can be attributed to lack of

consolidation process that stimulates the mobility and diffusion of the polymer chains. Parandoush *et al.* incorporated compaction roller and a laser source in an attempt to enhance the interlaminar lap shear strength through pressure and heat [256]. The research concluded that by using a laser power of 26 W and roller speed of 1~2 mm/s, the lap shear strength obtained is 96% of that of compression molded specimen (9.87 MPa). However, the effect of the compaction force is not investigated in their study.

4. Identify new electrical and thermal applications for AM CFRTTP taking advantage of the 3D printing techniques.
 - The addition of carbon fibers to the thermoplastics changes the electrical and thermal properties. The ability of the extrusion-based technique to align fibers would enable the creations of new and novel applications. Research can be done to identify new applications which previously were not possible through conventional fabrication technique. Multifunctional composites could be developed for application such as de-icing of wing structures[257], where the printed composite structures has self-heating ability [258] and energy storing structure [259].
5. Use proposed relationship to specific components or products in terms of the tensile, compression, shear, flexural, indentation resistance, and mode I ILFT properties in details.
 - Data-driven models could be developed to apply the PSP relationship in the real-world applications [140].

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Appendix A

Specific Heat Capacity

Specific heat capacity of the composite material is measured using Differential Scanning Calorimetry (DSC, Q200, TA Instrument) according to ASTM E1269-11 (Standard Test Method for Determining Specific Heat Capacity by Differential Scanning Calorimetry). Sapphire with the weight of 25.4 mg was used as the reference sample. Three runs were conducted at the ramp rate of 20 °C/min. Empty pans were used in the first run to obtain the baseline value. The second run was performed with Sapphire reference sample to obtain reference data. The third run was performed with the composite sample (10 mg) to obtain the sample data. The specific heat capacity was calculated using the following equation:

$$C_p(s) = C_p(st) \frac{D_s \cdot W_{st}}{D_{st} \cdot W_s} \quad (26)$$

where: $C_p(s)$ = specific heat capacity of the specimen, J/(g*K), $C_p(st)$ = specific heat capacity of the sapphire standard, J/(g*K), D_s = vertical displacement between the specimen holder and the specimen DSC thermal curves at a given temperature, mW (**Figure 80**), D_{st} = vertical displacement between the specimen holder and the sapphire DSC thermal curves at a given temperature, mW, and W_s = mass of the specimen, mg, W_{st} = mass of sapphire standard, mg.

Figure 80 Specific heat capacity thermal curves of standard Sapphire, and test samples

The specific heat capacities of the AM CFRTP and its constituent materials are measured using the DSC (**Figure 81**). It is found that the variation with temperature of the AM CFRTP is mostly dependent on the nylon matrix as the specific heat capacity of the carbon fibers changes slightly with temperature. The specific heat capacity of the AM CFRTP at room temperature is about 1.1 J/g/°C and keeps increasing until 110 °C to 2.25 J/g/°C before dropping to and stabilizing at 1.8 J/g/°C beyond 190 °C. The huge variation of specific heat capacity within the temperature range of the cooling process of the extrusion of AM CFRTP makes it necessary to consider the variation with temperature in the simulation.

Figure 81 specific heat capacity of AM CFRTP and its constituent materials

Appendix B

Isothermal data results for obtaining T_r

Steps for preparing the lap shear specimens are shown in **Figure 82**. The halves of the lap shear specimens are printed. The two halves are then hot pressed to form a complete lap shear specimen at isothermal conditions (140 °C, 180 °C, and 190 °C) and for various hot press durations. The lap shear specimens are then tested at a strain rate of 1 mm/min using the universal testing machine.

Figure 82 Steps for preparing and testing the lap shear specimens.

The results of the lap shear test are shown in **Table 13**. The $\sigma^{\max}$ used in this study (45 MPa) has been determined by welding the AM CFRTP at 190°C for 60 minutes. The measured interlaminar shear strength was converted to the degree of healing by scaling with respect to $\sigma^{\max}$. The non-dimensional strength is then plotted against $t^{1/4}$. It can be seen that the non-dimensional strength has a linear relationship with $t^{1/4}$ which follows the isothermal reptation theory. **Figure 83** Degree of healing at various temperatures. a) 140oC b) 180oC c) 190oC shows the non-dimensional strength, which relates to the degree of bonding, at various processing conditions. The dotted line, which passes through the origin, represents the best fit line for each temperature. The reptation time for each temperature condition is derived from the gradient of the best fit line, which

equals $T_r^{-1/4}$. The relationship between the T_r and temperature is then related using the Arrhenius equation.

$$T_r = Ae^{B/T} \quad (27)$$

The constants A and B in the Arrhenius equation are obtained by plotting $\ln(T_r)$ against the inverse of temperature, $(1/T)$ (**Figure 84**), where A and B are by definition the y-intercept and the slope of the best fit line, and are found to be $-38.686 \text{ s}^{1/4}$ and 21579 K^{-1} respectively.

Table 13 Hotpress welded lap shear strength of AM CFRTP samples

Temperature (°C)	t (s)	Average strength (MPa)	Standard deviation (MPa)
140	300	4.65	1.58
140	600	8.16	0.85
140	1200	9.13	2.01
140	1800	10.08	3.49
180	300	22.35	1.70
180	600	23.76	6.32
180	1200	28.39	4.41
190	120	25.32	1.57
190	300	29.82	2.53
190	600	35.63	5.31

Figure 83 Degree of healing at various temperatures. a) 140°C b) 180°C c) 190°C

Figure 84 Graph of $\ln(Tr)$ vs $1/T$

Appendix C

Repeated measure one way ANOVA (effect of print speeds on fiber directionality)

Data set:

FWHM values for different print speeds			
No.	7 mm/s	10 mm/s	14 mm/s
1	6.3964	9.7155	9.0145
2	8.2012	8.4025	8.2827
3	6.5666	9.831	10.4982
4	7.0676	7.6676	9.26

Output:

Source	SS	df	MS	F	P
Between	11.2	2	5.6	5.289	0.04741
Subject	1.5	3	0.5		
Error	6.4	6	1.1		

Conclusion:

The compared groups differ significantly, F-ratio value is 5.289, the p-value is 0.047. Hence, the result is significant at $p < 0.05$.

Appendix D

ANOVA on the effect of print speed on porosity

Data set:

No.		1	2	3	4	5	6
Porosity	Group 1:	1.28	2.22	1.45	2.23	1.37	2.65
(%)	7 mm/s						
	Group 2:	1.78	4.08	5.29	6.34	3.41	
	12 mm/s						

Summary of Data			
	<i>Groups</i>		
	1	2	Total
N	6	5	11
$\sum X$	11.2	20.9	32.1
Mean	1.8667	4.18	2.918
$\sum X^2$	22.5416	99.6226	122.1642
Std.Dev.	0.5718	1.7508	1.6879
Result Details			
<i>Source</i>	<i>SS</i>	<i>df</i>	<i>MS</i>
Between-treatments	14.595	1	14.595 <i>F</i> = 9.45306
Within-treatments	13.8955	9	1.5439
Total	28.4906	10	

The *f*-ratio value is 9.45306. The *p*-value is .013255. The result is significant at *p* < .05.

Appendix E

No	Process parameters			Porosity (%)				
	Print speed (mm/s)	Nozzle temperature (°C)	Bed temperature (°C)	1	2	3	average	Standard deviation
1	7	250	70	2.23	2.65	1.37	2.08	0.65
2	12	250	70	3.41	6.34	5.01	4.92	1.47
3	7	265	70	1.45	2.22	1.28	1.65	0.50
4	12	265	70	4.08	1.78	5.59	3.82	1.92
5	7	250	30	1.32	2.00	1.30	1.54	0.40
6	12	250	30	5.40	3.45	7.84	5.56	2.20
7	7	265	30	0.49	0.50	1.59	0.86	0.63
8	12	265	30	4.49	4.77	3.21	4.16	0.83

ANOVA for selected factorial model

Response 2: porosity

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	55.58	6	9.26	5.28	0.0058	significant
A-printing speed	27.82	1	27.82	15.86	0.0016	
B-nozzle temperature	2.25	1	2.25	1.28	0.2779	
C-bed temperature	0.0067	1	0.0067	0.0038	0.9518	
AB	0.3504	1	0.3504	0.1999	0.6622	
AC	1.01	1	1.01	0.5768	0.4611	
BC	0.0450	1	0.0450	0.0257	0.8752	
Pure Error	22.79	13	1.75			
Cor Total	78.38	19				

The **Model F-value** of 5.28 implies the model is significant. There is only a 0.58% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Appendix F

Process parameters				Mode I Interlaminar fracture toughness (J/m2)				
No	Print speed (mm/s)	Nozzle temperature (°C)	Bed temperature (°C)	1	2	3	average	Standard deviation
1	7	250	70	472	450	506	476	28
2	12	250	70	379	402	251	344	81
3	7	265	70	877	893	1062	944	102
4	12	265	70	720	650	690	687	35
5	7	250	30	247	193	216	218	27
6	12	250	30	290	209	197	232	51
7	7	265	30	707	550	540	599	93
8	12	265	30	538	571	651	587	58

ANOVA for Mode I interlaminar fracture toughness

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1.269E+06	6	2.115E+05	49.31	< 0.0001	significant
A-printing speed	56551.04	1	56551.04	13.18	0.0021	
B-nozzle temperature	8.959E+05	1	8.959E+05	208.86	< 0.0001	
C-bed temperature	2.487E+05	1	2.487E+05	57.97	< 0.0001	
AB	8550.38	1	8550.38	1.99	0.1760	
AC	57135.04	1	57135.04	13.32	0.0020	
BC	2147.04	1	2147.04	0.5005	0.4889	
Residual	72921.04	17	4289.47			
Lack of Fit	3725.04	1	3725.04	0.8613	0.3672	not significant
Pure Error	69196.00	16	4324.75			
Cor Total	1.342E+06	23				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 49.31 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 0.86 implies the Lack of Fit is not significant relative to the pure error. There is a 36.72% chance that a Lack of Fit F-value this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Appendix G

Analysis of Variance Results

F-statistic value = 0.36012

P-value = 0.58078

Data set

No.		1	2	3
Mode I ILFT (J/m²)	Group 1: Markforged	919	722	1006
	Group 2: This study	877	893	1062

Data Summary				
Groups	N	Mean	STD. DEV.	STD. ERR.
Group 1	3	882.3333	145.5072	84.0086
Group 2	3	944	102.5037	59.1805

ANOVA Summary					
Source	Degrees of Freedom DF	Sum of Squares SS	Mean Square MS	F-Stat	P-Value
Between Groups	1	5704.1728	5704.1728	0.3601	0.5808
Within Groups	4	63358.7075	15839.6769		
Total:	5	69062.8804			

The f-ratio value is 0.36012. The p-value is 0.58078 and is larger than the significance level of 0.05. The result is not significant at $\alpha < 0.05$. This means that there is no significant difference between the two data sets.

Appendix H

Mode II interlaminar fracture toughness (ILFT) of AM CFRTP

End notched flexure (ENF) test was used to determine the mode II ILFT of the unidirectional AM CFRTP. The dimensions of the ENF specimens are 140mm long, 20 mm wide, and 4 mm thick. The test was conducted using a three-point flexure test fixture with a span length of 100 mm. The crosshead speed is set to 0.5 mm/min. A total of 2 specimens were tested. Fig. shows a typical response curve of the ENF test. The Mode II ILFT is calculated as follows [260];

$$G_{II} = \frac{9P_c \delta a^2}{2b(2L^3 + 3a^3)} \quad (28)$$

Where P_c is the highest bending load, δ is the corresponding load displacement, a is the crack length, b is the width of the specimen, and L is the span length.

Figure 85 Load-displacement curve for the end-notched flexure test.

Data set for the mode II ILFT:

	1	2	average	Std. dev.
Mode II ILFT (J/m ²)	1982	2062	2022	56