3D printing materials for large-scale insulation and support matrices

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Muhammad Harris

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Abstract

Additive manufacturing (AM) techniques have promising applications in daily life due to their superiority over conventional manufacturing techniques in terms of complexity and ease of use. However, current applications of polymer-based 3D printing (3DP) are limited to small scale only due to the high cost of materials, print times, and physical sizes of the available machines. In addition, the applications of 3DP are yet to be explored for insulation of different large-scale mechanical structures. For example, milk vats are large structures with complex assemblies (like pipes, joints, couplings, valves, ladders, vessel doors) that requires insulation to store the milk at a low temperature of 6 °C as per the NZCP1 regulations in New Zealand. Generally, milk vats lack any kind of proper insulation around them and require additional cooling systems to keep the milk at a prescribed temperature. Any variations in the temperature can lead to deterioration in the quality of milk. Therefore, there exists a research gap that can not only help to solve an industrial issue but also can be a first step towards real large-scale 3DP applications that can potentially lead to many others in future. For example, pipe insulation, food storage tanks, chemical storage tanks, water treatment.

This research explores new and inexpensive materials for large-scale 3DP. For this purpose, the current state of the 3DP materials is analyzed and based upon this analysis two distinct approaches are devised: 1) in-process approach to improve the mechanical properties of the existing materials like polylactic acid (PLA), and 2) modification of inexpensive materials (like materials used in injection, rotational, and blow moulding) to make them printable. In the first approach, by controlling the process parameters, mechanical properties are studied. While in the second approach, blends of high density polyethylene (HDPE) and polypropylene (PP) with different thermoplastics (acrylonitrile butadiene styrene, ABS and polylactic acid, PLA) are investigated to achieve printability. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) are used to analyze the proposed materials.

The overall objective of this research is to devise low-cost materials comparable to the conventional processes that are capable of providing good mechanical properties (tensile, compressive and flexural) along with high resistance to thermal, moisture, and soil degradation.

The results present significant enhancement, up to 30%, in tensile strength of PLA through in-process heat treatment. However, the softness induced during printing above 70 °C directs to the second approach of developing the novel blends of HDPE and PP. In this regard, the research develops three novel blend materials: 1) PLA/HDPE, 2) ABS/HDPE, and 3) ABS/PP. These materials are compatibilized by a common compatibilizer, polyethylene graft maleic anhydride (PE-g-MAH). PLA/HDPE/PE-g-MAH provides highest tensile strength among all existing FDM blends (73.0 MPa) with superior resistance to thermal, moisture and soil degradation. ABS/HDPE and ABS/PP provide one of the highest mechanical properties (tensile, compressive, and flexural) in ABS based FDM blends with superior thermal resistance to six days aging.

The chemical characterization of aforementioned novel FDM blends shows partial miscibility with sufficient signs of chemical grafting. The significant intermolecular interactions are noted in FTIR that shows the grafting through compatibilizer (PE-g-MAH). The DSC analysis shows visible enhancement in different thermal parameters like glass transition, melt crystallization and degradation along with signs of partial miscibility. Furthermore, TGA analysis confirms the partial miscibility along with the enhanced onset of degradation temperature. The increase in onset temperatures of each of the three blends proves the thermal stability to high temperatures. Hence, each of the developed blends is capable of resisting any material deterioration during routine cleaning operation at 70 °C of milk vats.

This research has resulted in 5 journal publication (four published and one submitted), two conference proceedings and a number of posters presented at local conferences.

This research is the part of food industry and enabling technologies (FIET) research program funded by the ministry of business, innovation and employment (MBIE), New Zealand in collaboration with Massey University, Auckland.

Authors Declaration

This thesis was produced with five journal and two conference publications according to Massey University's "PhD thesis by publication" guidelines. This thesis is based on research that has been published, or is currently under review, or in process of submission. Two publications are published in Taylor & Francis and two in MDPI journals. In accordance with Taylor & Francis's and MDPI's copyright policy, this thesis contains the accepted version of each published manuscript, rather than the corresponding final versions. Moreover, as the content is identical to the published versions, there are formatting differences between the registered work, and the published versions to maintain the uniformity in this thesis. The fifth publication is submitted to Springer and is in process of review. The two conference papers are published in peer reviewed IEEE conference.

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Abbreviations

Abbreviations used in the report are given below in alphabetic order,

Alphabet	Abbreviation	Full form
A	ABS	Acrylo nitrile butadiene styrene
	AM	Additive manufacturing
	ANOVA	Analysis of variance
	ASTM	American Society for Testing and Materials
B	BADGE	Bisphenol A diglycidyl ether
	BSQM	Bead surface quenching mechanism
C	CAD	Computer aided design
	CF	Carbon fiber
	CGHTM	Continuous gradual heat transfer mechanism
	CPP	Conventional polymer process
D	DFMA	Design for manufacturing and assembly
	DMLS	Direct metal laser sintering
	DoE	Design of experiment
	DSC	Differential scanning calorimetry
E	EPDM	Ethylene–propylene–diene terpolymer
F	FDM	Fused deposition modeling
	FFF	Fused filament fabrication
	FIET	Food industry and enabling technology
	FTIR	Fourier transform infrared spectroscopy
G	GF	Glass fiber
	GTR	Ground tyre rubber
H	HDM	Hybrid deposition manufacturing
	HHMPA	Hexahydro-4-methylphthalic anhydride
	HPDE	Hi density polyethylene
I	IM	Injection moulding
L	LDPE	Low density polyethylene

	LLDPE	Linear low density polyethylene
M	MFI	Melt flow index
O	OMMT	Organic montmorillonite
P	PC	Polycarbonate
	PE	Polyethylene
	PET	Poly ethylene terephthalate
	PEEK	Polyether ether ketone
	PLA	Polylactic acid
	PMMA	Poly meth methacrylate
	PP	Polypropylene
	PS	Polystyrene
	PVC	Polyvinyl chloride
R	RCPE	Recycled polyethylene
	RM	Rotational moulding
	RUL	Remaining useful life
S	SCARA	Selective compliance assembly robotic arm
	SEM	Scanning electron microscopy
	SEBS-g-MA	Styrene ethylene butylene styrene-grafted- maleic anhydride
	SiC	Silicon carbide
	SLA	Stereolithography
	SS	Stainless steel
T	TGA	Thermogravimetric analysis
	TiAl	Titanium aluminium
U	UHMWPE	Ultra-high molecular weight polyethylene
	UV	Ultraviolet
W	w.r.t.	With respect to
Mix	3D	3-dimensional
	3DP	3-dimensional printing

Chapter 1. Introduction

3D printing (3DP) has proven its prominence in manufacturing through its innovative process of fabrication in layers. It has been known for generating complex structures with precision. Wide variety of materials are fabricated through different 3D printing techniques, most of which are polymer-based materials. The polymer materials of 3DP have good mechanical properties like ultimate tensile strength (UTS), modulus, stiffness etc. Besides the diversity of 3DP to have the complexity, precision and variety of materials. The polymer-based applications in 3DP are yet to be reported for large-scale application. Meanwhile, the insulation of various mechanical structures of different scales are also yet to report in 3DP. Another important factor that heavily concerns the existence of 3DP in global market is the total cost of fabrication as compare to conventional polymer processes. The major part of the total cost of 3DP is of material. Hence there is a research gap to explore the new polymer materials for insulation of large-scale applications.

Milk vats are large stainless-steel structures that generally consists up to 30,000 liters of raw milk and need good refrigeration system to preserve milk at 6 °C for at least 12 hours a day according to the law (NZCP1) in New Zealand. The ambient conditions raise the temperature of stored milk due to insufficient insulation and hence the milk goes through various low to high temperature cycles that influence the quality of the milk. This emphasize for these structures to have good thermal insulation to maintain the temperature of milk by reducing the frequency of variations in the temperature.

This research aims to investigate the current and to explore the new polymer materials for 3D printing of insulation and support matrices of milk vats. The research sets the objectives of low cost, reasonable strength, good life and good printability for new 3D printing materials.

First, this research highlights the requirements of milk vat insulation and provides a detailed infeasibility of current 3DP materials, like acrylonitrile butadiene styrene (ABS) and

Polylactic acid (PLA). Based on the infeasibility, the conventional injectional moulding (IM) materials are proposed for developing novel insulation materials. In this regard, the experimentation is performed in two parts: 1) in-process thermal treatment of contemporary material (PLA), and 2) melt blending of conventional polymer materials with polyolefins (polyethylene and polypropylene). The first part includes a detailed design of experiment (DoE) accompanied with ANOVA analysis to investigate the mechanical and thermal properties of commercial polylactic acid (PLA) filament. In the second part, the research implements the approach of exploring new materials along with the investigation of their structural behavior to thermo-mechanical properties. The key properties aimed in this research to investigate are: 1) tensile, compressive and flexural strength and ductility on Instron testing machine, 2) thermal degradation through thermogravimetric analysis (TGA), 3) compositional analysis through Fourier transform infrared spectroscopy (FTIR), 4) analysis of thermal transitions (glass, melting, degradation) through differential scanning calorimetry (DSC), and 5) fractographic and phase separation analysis by scanning electron microscopy (SEM).

This research is funded by Food industry and enabling technology (FIET) New Zealand and it proposes novel 3D printing materials of thermal insulation for milk vats. The research aims to develop and analyze novel and existing polymer materials that are suitable for a milk vat insulation.

1.1. Avenue for large-scale printing

Large-sale application in conventional polymer process includes big structures with least to no complexities and thin walls. Few applications are polyvinyl chloride (PVC) plastic pipes, polyethylene (PE) liquid containers, water treatment tanks, dock floats, docking fenders, dash boards and bumpers. Most of the large-scale products are made by rotational moulding (RM). The products in RM are fabricated with least number of intricate details

because RM is not capable to fabricate complex designs [1]. On the other hand, the additive manufacturing is promisingly capable of fabricating extreme complexities with ease due to its layer by layer manufacturing technique [2]. Therefore, the ability of printing complexities with ease makes the large-scale applications a research-worthy avenue for 3DP.

1.1.1. Milk vats

Milk vats are large stainless steel (SS) tanks with refrigeration system used to store raw milk at a specific cooling temperature. These are also known as bulk milk tanks or bulk tanks. The milk vats include various parts like manhole, vents, cooling system, pipes, adjustable legs, etc. Cooling system is the most important of all parts [3, 4]. There are two general types of cooling systems that are installed, i.e., direct expansion and ice bank cooling systems [3, 4].

Direct expansion includes pipes surrounding the milk storage chamber. The pipes are circulated with refrigerant. The pipes are further covered with insulation, which are shielded by outer metal shell. Direct expansion uses a combination of large compressors, condenser and radiators to cool the milk rapidly as it is poured into the bulk tank [5, 6]. Afterwards it maintains the temperature during preservation time (12 hours normally) through gradual cooling. Direct expansion cooling systems requires high electrical energy to operate, i.e., three phase electric power.

Ice bank cooling includes the bottom of the milk chamber immersed in a water bath with refrigerant contained pipes. The refrigerant keeps on circulating into the pipes to build an ice layer of specific thickness (2-3 inches normally). After achieving the desired ice layer thickness, the cooling system stops working and the preserved energy of water bath and ice is used to cool the stored milk. This process is repeated after the melting of ice up to a specific thickness. Ice bank cooling system requires low energy to operate, i.e., single phase electric power [3, 4].

The milk vats pass through low to high temperature cycles during cleaning each day. The cleaning criteria for milk vats includes the washing at 70 °C each day. Therefore, the storing temperature of as low as 6 °C to cleaning temperature of 70 °C requires good thermal endurance.

1.2. NZCP1 2017 refrigeration requirements

Under the clause 5.15 of "new milk cooling standards" in NZCP1, the storing temperature of raw milk must be

- 10 °C within 4 hours after the commencement of milking
- 6 °C within 6 hours after the commencement of milking or 2 hours from completion of milking in non-freeze state [7].

1.3. Required properties for milk vat insulation

There are various properties that are presented in literature for insulation of vats, e.g., resistance to corrosion, thermal stability, strength, aging, durability, cost etc. [8, 9]. Meanwhile considering the polymers of 3D printing to be used as insulation in this research, the considerable factors are cost, time, printability, moisture resistance, resistance to aging, strength (tensile, compressive and flexural) [10]. However, the scope of this PhD is established around few of the prime properties that are as follow,

1. Cost
2. Time
3. Thermally insulative (low thermal conductivity)
4. Printability
5. Strength

1.4. 3D printing (3DP)

Manufacturing of complex products with ease is one of the challenges for any conventional polymer process [11]. 3D printing, also known as additive manufacturing (AM) or Rapid prototyping (RP) [12], comprehensively solves this challenge by its breakthrough ability to manufacture complexity with precision through fabrication in layers [11, 13]. Stereolithography (SLA) is the first AM technique invented by Chuck hull in 80's that implemented the layer by layer fabrication process to build the product [11, 14]. A photosensitive resin is cured into a product in SLA through UV light in layers [12, 15]. SLA is followed by the Fused deposition modeling (FDM), also known as Fused filament fabrication (FFF), that extrude thermoplastic polymer in layers to build a part in 3D [11]. AM techniques also 3D print the metals through direct metal laser sintering (DMLS) that sintered the powder metal in layers, one above the other [16]. Hence, each evolutionary AM technique brings in different materials along with the unique and innovative capability to build complexity with ease.

1.5. Materials available for 3DP and their cost

Different kinds of materials are available for different 3D printing techniques. Generally, FDM deals with thermoplastic and elastomer [17], SLA deals with thermoset [18] and DMLS have metal alloys [16] as main materials. Although the literature reports many other materials in each of these techniques. However, the commercial materials are limited and expensive as shown in Table 1 for FDM.

Table 1. 3D printing materials and pertinent data updated in 2018.

Domain	Materials	Supplier	3D printer	Cost
FDM	Acrylo nitrile butadiene styrene (ABS) + Polycarbonate (PC)	Tier Time	UP02, UPBOX	$90 per 500 grams
	Polylactic acid (PLA)	Tier Time	UP02, UPBOX	$90 per 500 grams
	ABS plus	Stratasys	Fortus MC250	$600 per cartridge (920 cm^3)
	Kevlar CFF Spool	Mark one	Mark one	$401 per 150 cm^3
	Fiber glass CFF Spool	Mark one	Mark one	$303 per 150 cm^3
	Nylon Filament Spool	Mark one	Mark one	$228 per 800 cm^3

1.6. Importance for considering 3DP insulation

There are three reasons for considering the 3D printing for making an insulation for milk vats in this PhD as given below.

1.6.1. Reason 1: Conventional polymer processes

Conventional polymer processes (CPP) are feasible only in mass production of low scale (small size) products due to the large monetary gains [19, 20]. However, large products with complex designs in low quantity and low profits make the CPP infeasible. Injection moulding (IM) is considered in this research as the main process to study the feasibility for fabricating large-scale product in low quantity. IM is analyzed in the light of three factors i.e., cost, time and complexity.

1.6.1.1. Cost

The factor of cost is unfolded in three types of concealed sub-costs that are normally ignored while estimating the total production cost of small-scale products in masses by IM. They are as follow

1) IM process requires a die to manufacture any product. More complex the product, more complex will be the die and hence more will be the designing cost for the die [21].

2) The injection moulding dies require maintenance after a specific number of moulding [21]. The maintenance can be performed by any one of the two common techniques, i.e., melting [22] or remanufacturing [23]. In melting technique, a localized damaged portion of a die is melted [22] and in remanufacturing, the whole die is melted and forge from scratch [23]. Both techniques add an extra cost to hire the skills of maintenance personals.

3) The working life of dies is an indirect measure of their returns. The life of dies is calculated by remaining useful life (RUL) estimation. Estimation of RUL requires expert people from manufacturing background [24, 25]. This is added as another cost to the total expenses to hire the skills for calculating the satisfactory working life of a die.

Therefore, the analysis of cost regarding IM explains that it is not feasible to make such a large structure with any IM either in parts or as a complete unit.

1.6.1.2. Time

Lesser lead times for the products to reach markets helps to gain competitive advantage as well as high profits. Design for manufacturing and assembly (DFMA) is normally applied to reduce the lead times, which it proficiently achieved. The significant applications for DFMA to reduce the lead times are associated with high profits from mass production as depicted in Figure 1 for small-scale application in literature [26]. However, high profits from large-scale products in low quantities will not be able to satisfy the application of DFMA due to expected low returns.

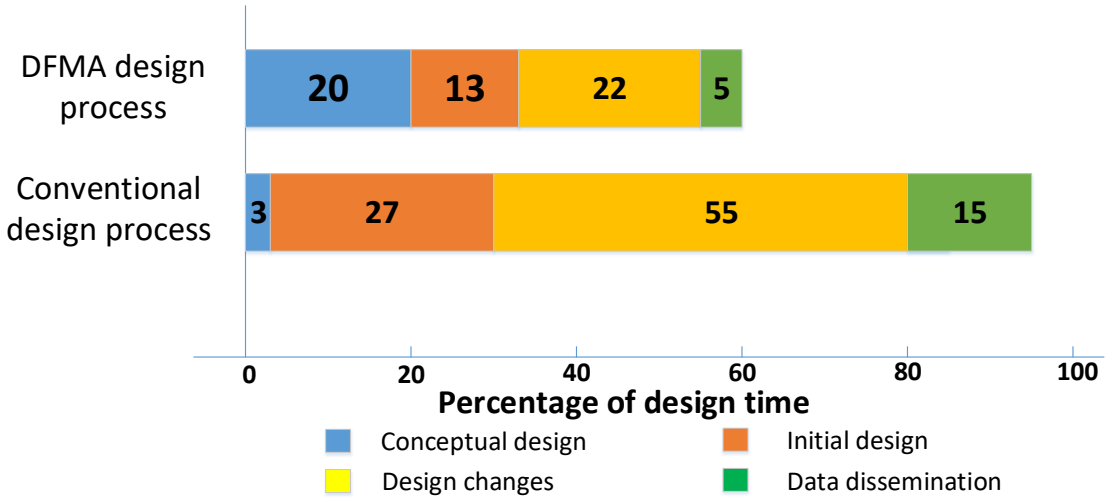

Figure 1. DFMA comparison with conventional management processes [26].

1.6.1.3. Complexity

As shown in Figure 2, numerous technical factors must be considered for making product of any design level (complex or simple) [27]. IM die is designed to fabricate number of small products in each run. Hence, an error in one fabricated part due to technical discrepancies in any specific element of a die will not probably lead to the rejection of the whole batch. The mass production of one type of small products reduces the probability of rejection due to the gains obtained from remaining correct parts. However, the process susceptibility towards non-conformed large-scale parts is expected to increase manifolds because even a minor error in anyone of the mentioned technical element in Figure 2 will lead to rejection of whole product. Hence, the process of IM becomes more complex and prone to errors in case of large-scale products in low quantities.

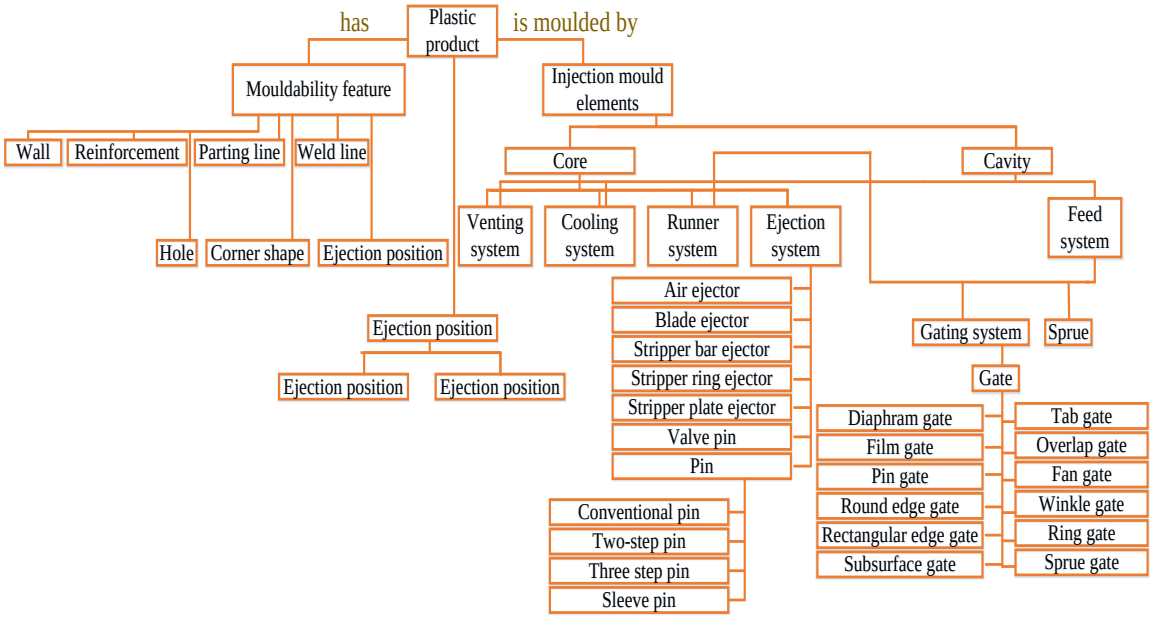

Figure 2. Manufacturing model for injection moulding as a guide [27].

Therefore, it is concluded on basis of cost, time and complexity that injection moulding process is infeasible for fabricating large-scale product in low quantities.

1.6.2. Reason 2: Current industrial efforts

RX plastics, New Zealand, has been working on fabricating an insulation for milk vats that is made of polyethylene. The consideration of polyethylene is due to the ease of availability and wide operation window that provides ease of processing and manufacturing. However, according to my research, polyethylene has the highest thermal conductivity among all polymers [28-30]. This makes polyethylene a least acceptable option among the existing polymers for insulation.

The insulation made as a prototype by RX Plastics is built by gluing polyethylene sheets manually around the stainless-steel vat. It is also noticed that the large water or chemical storage tanks are normally made by rotational moulding in one day as shown in Figure 3, but it is yet impossible to rotationally mould an insulation around the stainless-steel vats. This takes more time to build a single unit of milk vat insulation.

Therefore, lack of high thermal insulation capability, limited material choice, more time to make a single insulation and absence of automated manufacturing process are the main drawbacks. These drawbacks provide a solid reason to shift to additive manufacturing (AM).

Figure 3. Rotational moulding setup.

1.6.3. Reason 3: Novelty in large-scale polymer 3DP

3D printing has been reported in various applications of variable size or scale range from nanoscale [31] followed by micrometer [32-34] to meters [35] as shown in Figure 4. Although the large-scale 3D printing for concrete houses is reported [35] but it is not yet been reported for large-scale polymer based application. Therefore, this novelty is another reason for 3D printing the insulation.

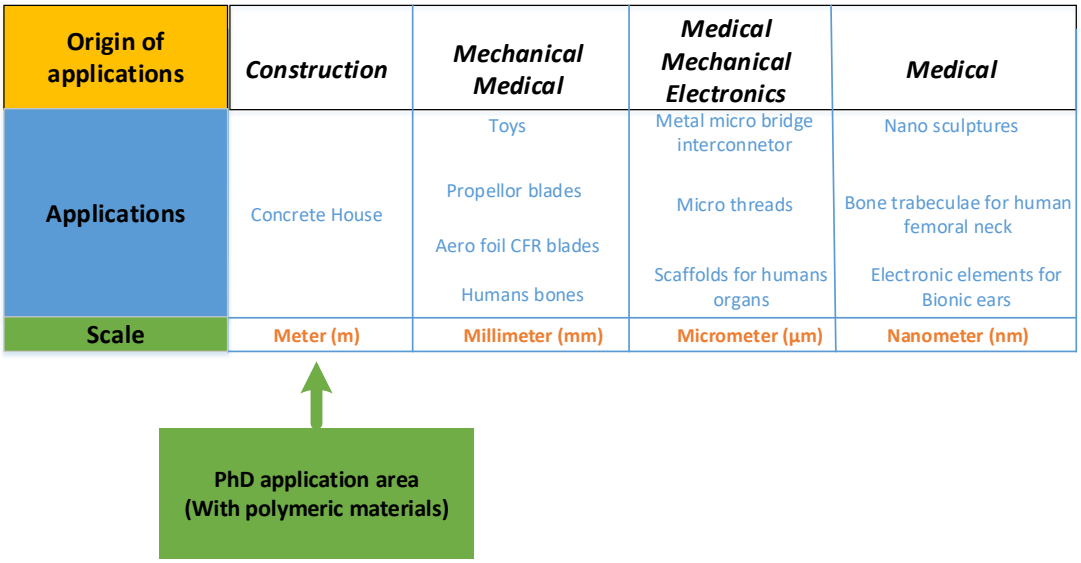

Figure 4. Comparison of scale.

1.7. Research objective

The objective of this research is to develop novel materials for 3D printing insulation of a milk vat. The research is further aimed to achieve following goals in the 3DP polymers

1. Low cost
2. Printability in less time
3. Good thermal insulation (low thermal conductivity)
4. Strength
5. Resistant to aging.

1.8. Thesis layout

The contents in the subsequent chapters are based on the development of 3DP materials for milk vat insulation. The feasibility of using AM or 3DP is provided with reasons in this chapter, which is published in IEEE conference (attached in Appendix).

Chapter 2 includes the literature review and the analysis among different 3DP techniques. It explains the reasons for the selection of FDM and further requirements for the

materials through cause and effect (fish bone) diagram. The contents related with literature review in chapter 2 are published in the MDPI journal of “Materials”.

Chapter 3 includes the first experimental approach that is associated with the enhancement in mechanical properties of polylactic acid through in-process heat treatment. However, the softness observed above 70 °C after printing leads to the second experimental approach for the development of novel materials, i.e., melt blending. The contents of chapter 3 are published in journal of “Materials and Manufacturing Processes, Taylor & Francis”.

Chapter 4 comprises the reasons of blending polyolefins (high density polyethylene, HDPE and polypropylene, PP) with printable materials (ABS and PLA).

Chapter 5 reports the first novel blend material of PLA with high density polyethylene (HDPE). The contents of chapter 5 is in process of review under “International journal of advanced manufacturing technology, Wiley”.

Chapter 6 reports the second novel blend material of ABS with high density polyethylene (HDPE). The contents of chapter 6 are published in journal of “Materials and Manufacturing Processes, Taylor & Francis”.

Chapter 7 reports the third novel blend material of ABS with polypropylene (PP). The contents of chapter 7 are published in the MDPI journal of “Materials”.

Chapter 8 includes the overall conclusion of PhD research work along with directions for future work.

Chapter 2. Effect of Material and Process Specific Factors on the Strength of Printed Parts in Fused Filament Fabrication: A Review of Recent Developments

Chapter 2 includes the following article, “Effect of material and process specific factors on the strength of printed parts in fused filament fabrication: A review of recent developments” published in the MDPI journal of “Materials”. This article is open access and has been republished in this thesis under the Creative Commons Attribution License.

The full text is included in the thesis without any modifications. However, there are formatting differences to keep the formatting same for the thesis. The formatting modifications involve page setup, font style, referencing style, reference citation style and bibliography style.

Effect of Material and Process Specific Factors on the Strength of Printed Parts in Fused Filament Fabrication: A Review of Recent Developments

Muhammad Harris [1], Johan Potgieter [2], Richard Archer [3] and Khalid Mahmood Arif [1,*]

[1] School of Food and Advanced Technology, Massey University, Auckland 0632, New Zealand; m.harris@massey.ac.nz
[2] Massey Agritech Partnership Research Centre, Massey University, Palmerston North 4442, New Zealand; j.potgieter@massey.ac.nz
[3] School of Food and Advanced Technology, Massey University, Palmerston North 4442, New Zealand; r.h.archer@massey.ac.nz
***** Correspondence: k.arif@massey.ac.nz

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2.1. Abstract

Additive manufacturing (AM) is rapidly evolving as the most comprehensive tool to manufacture products ranging from prototypes to various end-user applications. Fused filament fabrication (FFF) is the most widely used AM technique due to its ability to manufacture complex and relatively high strength parts from many low-cost materials. Generally, the high strength of the printed parts in FFF is attributed to the research in materials and respective process factors (process variables, physical setup, and ambient temperature). However, these factors have not been rigorously reviewed for analyzing their effects on the strength and ductility of different classes of materials. This review systematically elaborates the relationship between materials and the corresponding process factors. The main focus is on the strength and ductility. A hierarchical approach is used to analyze the materials, process parameters, and void control before identifying existing research gaps and future research directions.

2.2. Introduction

Additive manufacturing (AM) or 3D printing [36-40] is the next generation manufacturing technology that allows manufacturing of complex parts without requiring specialized tooling [2, 41]. Therefore, AM is currently being used in a wide range of applications such as high value consumer products [42], food [43], electronics [44-46], machinery [47], aerospace industry [48, 49], automobiles [49, 50], medical and dental applications [51-55], textile [56-58], construction [35, 59-61], education [62], and architecture [63-72]. AM has various forms that share the same concept of layer-by-layer manufacturing [72-76]. The most common among all the AM technologies is fused filament fabrication (FFF), also known as fused deposition modeling (FDM). In FFF, melt thermoplastic polymers are extruded to make the layers for fabricating the design provided in one of the following formats: STL (stereolithography), AMF (additive manufacturing file), Step (standard for exchange of product model data), Voxel, 3MF (3D manufacturing format), or JT (Jupiter tessellation) [11, 77-79]. The simple extrusion process that can be applied to a large variety of materials makes FFF an affordable technology for research institutes, industries and domestic users.

Despite the technical simplicity, geometric accuracy, ability to build complex shapes with no waste of material and commercial success [80], the FFF structure is composed of voids that contribute to the vulnerability of the product to lack mechanical properties[81]. In the recent growing market, structural integrity is represented by numerous characteristics like strength, fatigue resistance, resistance to aging, resistance to chemical and moisture erosion, etc. Major research in FFF encompasses numerous facets that aim to improve strength (tensile, compressive, and flexural), ductility, and modulus (elastic and flexural) [81-87]. Since the invention of FFF/FDM in the 20th century, researchers have adopted different ways to improve the strength of parts. However, for a long time, FFF research remained limited to the process parameters/variables (feed rate, speed, layer thickness, etc.) and single materials [88]. In this regard, a recent review by Cuan-Urquizo et al. [89] presents a comprehensive overview of the effect of process parameters on the mechanical properties of FFF parts.

It has been observed that the advancements in the form of customized physical setups, ambient temperature control, and different forms of new materials (composites and blends) have become the main research topics to enhance strength in the last decade or so. Therefore, the strength of printed parts is not only a result of process parameters but is also affected by the material construct (not just the material strength), in addition to process specific strategies

and factors. In Figure 5, the vertices of the equilateral triangle identify the three most important factors: (1) process variables, (2) physical setup, and (3) ambient temperature control. The triangle is also divided into three equal sections, each one showing material construct that is related to the vertices on the line touching the particular section. The factors on the vertices for the section of the triangle and the circle together impact the strength of the printed parts. For example, for a single material, process variables and ambient temperature are governing factors to achieve high strength. Similarly, for blends the governing factors are process variables and physical setup.

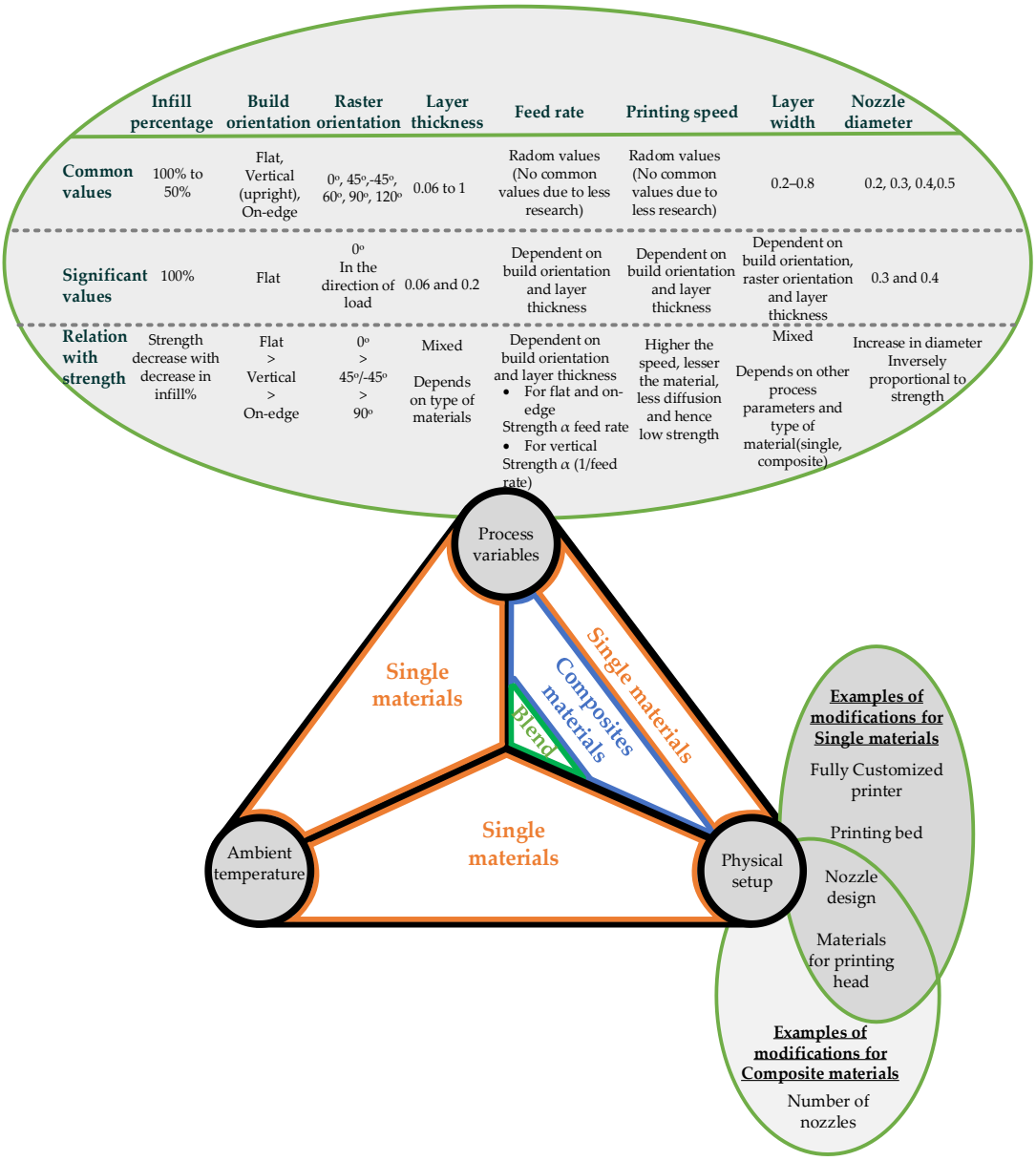


Figure 5. Summary of fused filament fabrication (FFF) materials and corresponding process factors (process variables, physical setup modifications, and controlled ambient temperature) based on the overall understanding of literature [28, 36, 88-102].

It is important to mention that there are other types of in-process and post-printing processes performed on the FFF materials. For example, humidity exposure (water absorption) [103, 104], chemical treatment (acetone, ethyl acetate, tetrahydrofuran, dichloromethane, chloroform) [105-108], plasma treatment and epoxy infiltration [109], aluminium coating, metal coating [110, 111], physical vapor deposition (PVD) [112], etc. However, apart from humidity [104], these processing techniques are mostly applied for decreasing the surface roughness or to achieve higher dimensional accuracy. Moreover, the before-mentioned post processing techniques are not intended for enhanced tensile strength and ductility. For example, the humidity decreases the strength instead of increasing it. On the contrary, thermal processing (pre-printing, in-process, and post-printing) can result in significant enhancement in tensile strength and ductility [113, 114].

This review is focused on the combined effect of materials and process factors on the optimal strength of printed parts. The materials are categorized into three groups: single materials, reinforced composites, and blends. A comprehensive review of each category is provided by dividing the main material category into subcategories in a hierarchical manner (see Figure 6). The approach taken for grouping (subcategorization) is based on the way they are presented in the literature, e.g., commercial and non-commercial materials, partial or fully biodegradable, or continuous and discontinuous materials, etc. Since all the material groups differ from each other, the subcategorization is not the same for each material. For example, single materials are subcategorized into commercial and non-commercial categories. On the other hand, blends are presented as multi-layered subcategories to capture the correct terminology and relevance in the context of FFF.

2.3. FFF materials

Various materials are researched in Fused filament fabrication (FFF), however, not all materials are researched for tensile strength and ductility. In this regard, different materials are experimented and applied in different applications. A brief detail is provided in Table 2.

Table 2. Fused filament fabrication (FFF) materials for different applications that are not generally investigated for tensile properties.

Domain	Applications	Materials
Medical	Scaffolds, Organs and Tissues	Poly caprolactone (PCL)[115], Poly(Ethylene Glycol) Terephthalate Poly(Butylene Terephthalate)(PEGT/PBT) [116], Chitosan/hydroxyapatite, Polyurethane [117], Poly l-lactide (L-PLA) [118], Corn starch/dextran/gelatin [119], Polylactic acid/Poly caprolactone [115], Chitosan/Hydroxyapatite (HA) [120], Chitosan/PLA/Keratine [121], Polyurethanes (PURs), Diisocyanate/Methylene diphenyl diisocyanate (MDI) [122], Polyols-polyether/PCL, Chain extender/Butanediol (BDO) [123].
Aerospace	Ceramic and metal filled parts	Zirconia/Wax [124], Polypropylene (PP)/Tricalcium phosphate (TCP), Polylactic acid/Hydroxyapatite (HA)/ceramic particles [125], Iron/nylon, Copper/Acrylonitrile butadiene styrene (ABS) , Nylon 6/Al-Al_2O_3 [126, 127], PC-ABS/Graphene
Electrical	Conducting products	ABS/Steel, PLA/Graphene/MWCNT [128], Polyurethane/MWCNT [129]
Unmanned air vehicle	Aero foil, frame	Polyether imide (PEI) or ULTEM, Acrylonitrile styrene acrylate (ASA), Acrylonitrile butadiene styrene (ABS), Carbon fiber reinforced nylon [130].
Electronics	Sensors	Polylactic acid (PLA) [131], ABS, Wax blend, Nylon [113, 132]

For example, the materials shown in Table 2 have not been specifically investigated for the tensile strength or ductility, e.g., the porous ceramic materials are mostly investigated in terms of compression strength [125, 133]. The focus of this review is limited to the materials that are analyzed in terms of tensile strength and elastic modulus. FFF materials are found in three main categories (Figure 6), i.e., single materials, reinforced composites, and blends.

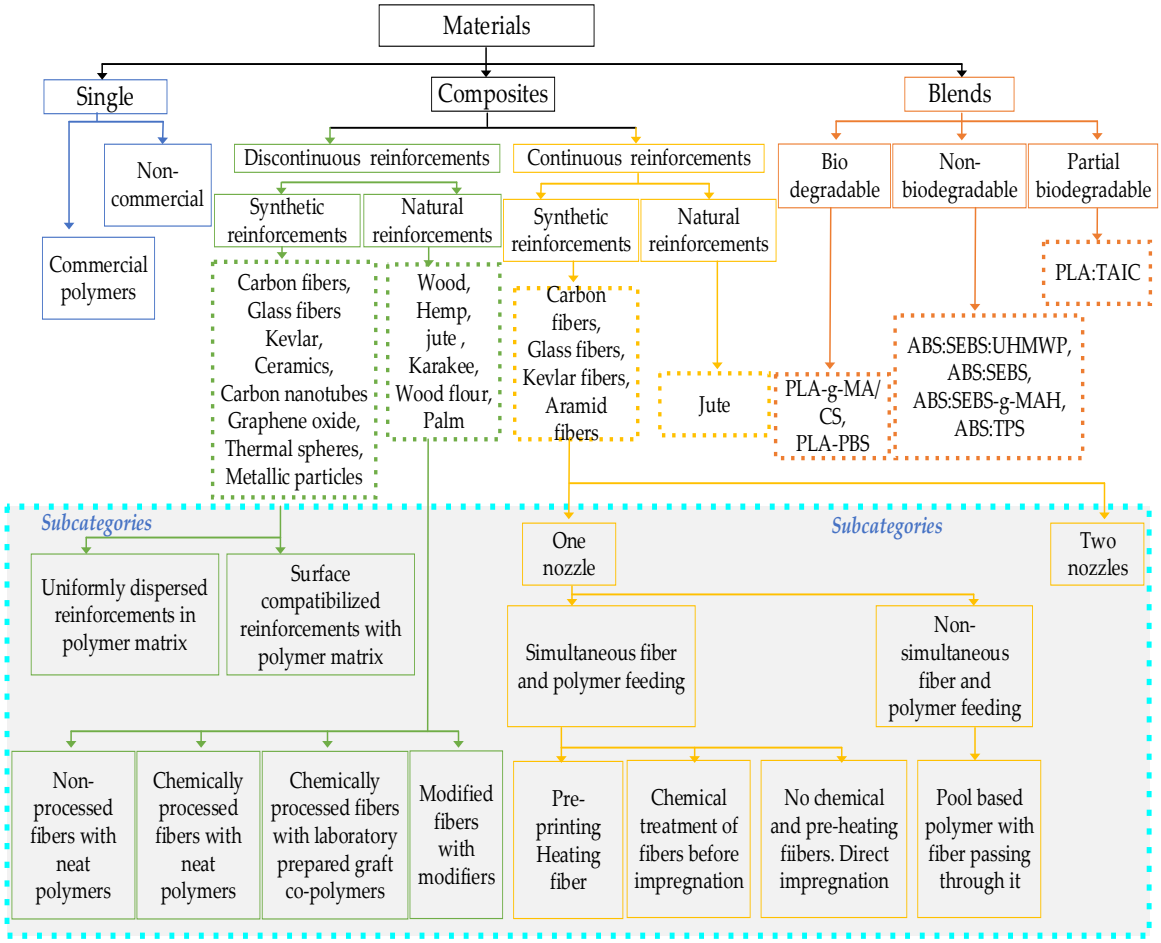


Figure 6. Materials for fused filament fabrication.

2.3.1. Single Materials

Single materials are highly significant for FFF as they are commonly available for domestic users. Specifically, the entry level printers (Tiertime [113], Makerbot, Reprap [95], etc.) come with single material filament spools. The single materials presented in the literature include either commercial 3D printing filaments [134] or research-based filaments prepared from polymers by extrusion or injection molding [135]. However, it is noticed that the commercial filaments are used in the majority of research as shown in Figure 7. The reason for this can be the excessive processing requirements and chemistry involved in the filament-making process. Another reason for less research on laboratory-prepared filaments (non-commercial) can be the nature of research that aims for quality of parts only through parametric optimization instead of improvements in the printing materials.

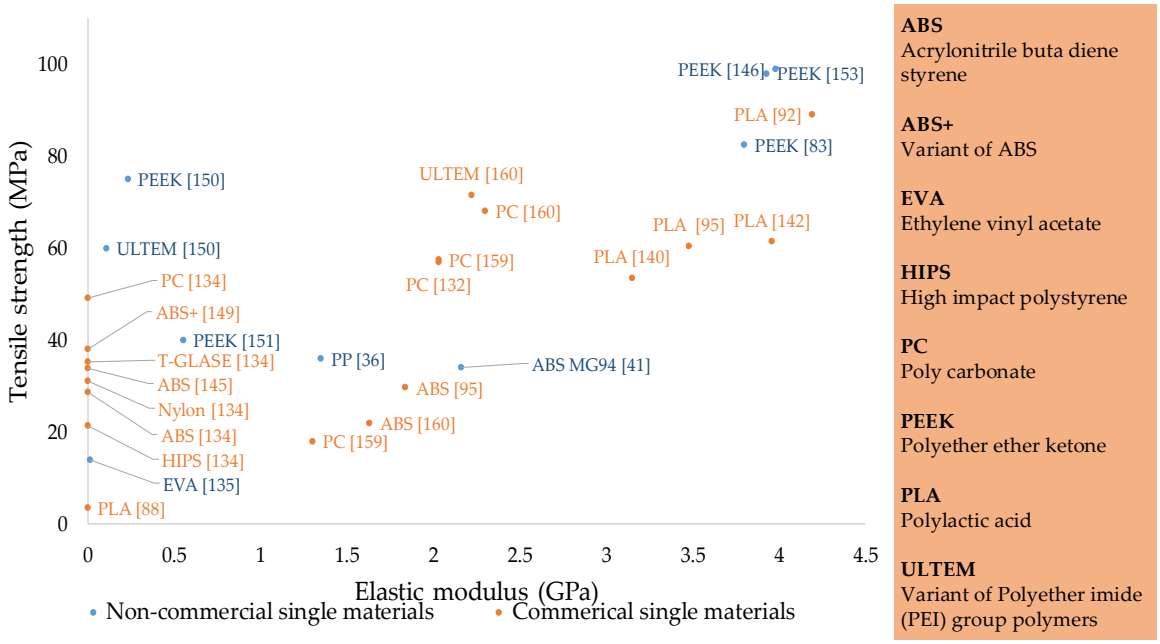


Figure 7. Tensile strength and elastic modulus of single materials of fused deposition modeling.

Various single materials have been researched since the invention of FFF as shown in Table 3 and Figure 7. Significant enhancements have been made in mechanical properties like tensile strength, ductility, and elastic modulus of these materials, specifically in the last couple of years. The enhancements in properties of single materials have been achieved through advancements made in physical setups, optimal process parameters, or controlled environmental conditions. Figure 7 includes the materials that show prominent tensile strength. However, there are other FFF single materials in the literature like high impact polystyrene (HIPS), polycaprolactone (PCL) [122, 135], polyvinyl alcohol (PVA) [136], and Polyurethane (TPU) [122], that have been mostly reported for medical applications and exhibit low tensile strength [122]. This section highlights the tensile capability of various potential FFF single materials along with the special measures (e.g., Orientation in Figure 4) taken to achieve enhanced mechanical properties.

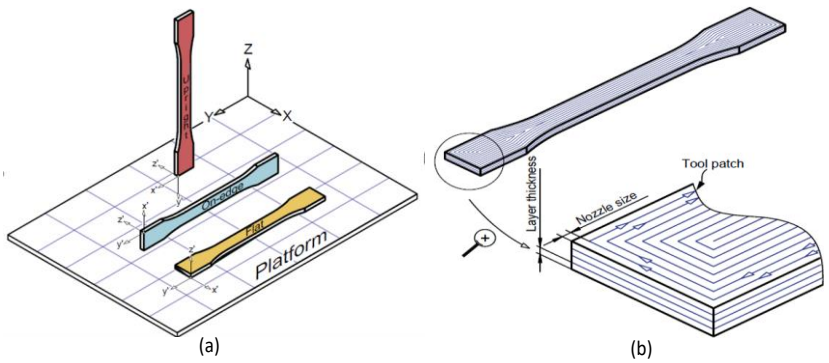


*Figure 8. Process parameters: (**a**) build orientation; and (**b**) raster orientation. Adapted from [92], with permission from © 2017 Elsevier.*

Polylactic acid (PLA) is a renewable, low cost, low melting temperature, and commonly available FFF polymer. It is a biodegradable polymer made by lactic acid or dimers of D-lactides or L-lactides produced by fermentation of starch obtained from natural sources such as plants. It inherits a problem of low crystallization even with the optimal contents of D-lactide (0.5% to 12%) that deprives PLA of achieving good mechanical properties. Various techniques including the addition of additives and post-process thermal treatments have been employed to improve the mechanical properties. The tensile strength gained from PLA structures ranges from 15.5 MPa to 89.1 MPa [73, 94, 102, 137-141]. The highest value of 89.1 MPa, reported in the literature, was achieved with a commercial filament on a small open source 3D printer through an optimal combination of feed rate, layer thickness, and build orientation (Figure 7 and Table 3). This research employed an optimal method of load application in the direction of tool path as shown in Figure 8. The reported reasons for fracture are the inter-layer fusion and trans-layer failure that brought significant difference in strength with the change in build orientation. Inter layer fusion is the fusion bond of lower layer with extruded one and the trans-layer fusion bond is the fusion between beads (roads) of the same layer. In upright (vertical) samples, the breakage of the inter-layer fusion bond occurred due to the applied load parallel to the deposited layer. The deposited layer withstood the whole force instead of individual beads leading to low strength and hence the failure occurred between layers (interlayer). On the contrary, the load applied perpendicular to the deposited layer, in flat and on-edge samples, making the beads bear the applied load, resulted in high strength [28].

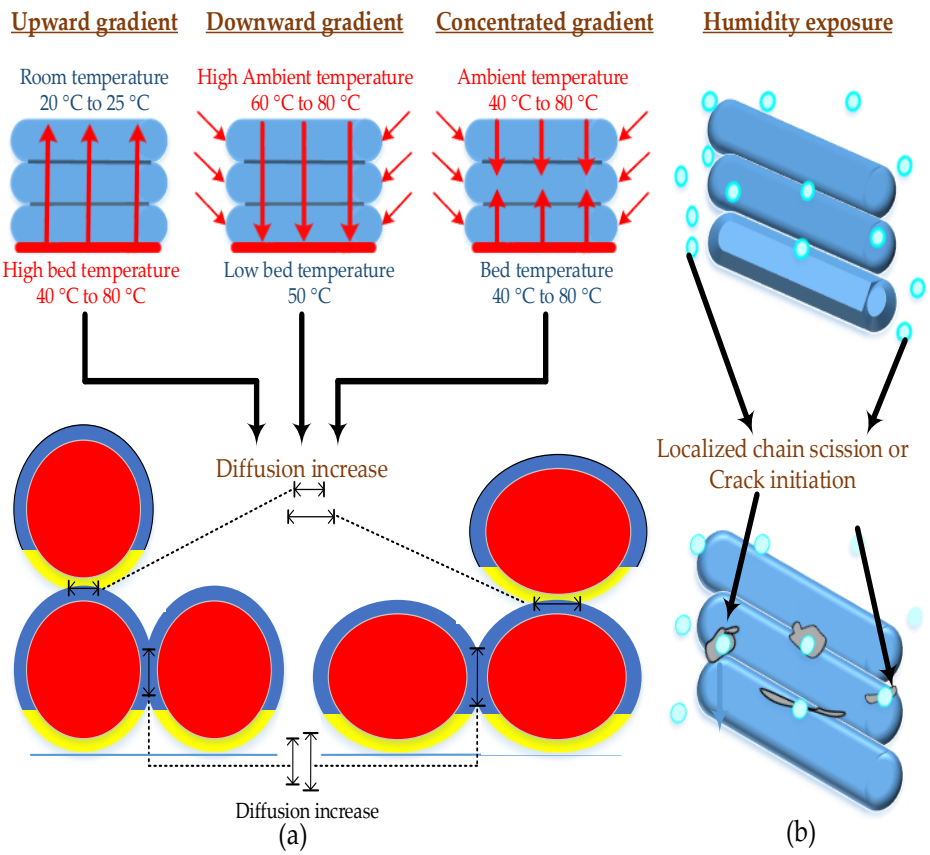


Figure 9. Illustration of in-process and post-process processing on printed structure of PLA: (a) in-process thermal treatment at different types of heat gradients; and (b) effect of moisture on localized areas.

Another research reports optimal values of strain rate (2.5×10^{-4} s^{-1}) and raster angle (45°) to achieve 61.4 MPa of tensile strength [142]. PLA is also reported with in-process [113] and post-printing (annealing) thermal treatments. However, it is noted that the annealing does not result in any improvement in tensile properties [142, 143]. The in-process thermal treatment reports enhancement in either tensile strength or ductility based on the direction of the heat gradient [113]. However, as shown in Figure 9a, the chemical degradation of PLA has not been reported. Another important aspect researched for PLA is the resistance to humidity. There is a limited literature on behavior of FFF-printed PLA against humidity that reports chain scission (or material separation) at localized areas exposed to moisture (Figure 9b). The increase in percentage humidity causes the tensile load to decrease significantly [103]. The brief aforementioned literature concludes that the optimal process parameters are more in trend to gain high strength for PLA as compared to the

controlled environmental conditions or precise physical setups as shown in Table 3. However, the significant degradation of mechanical properties points towards the importance of considering humidity in future PLA 3D printing.

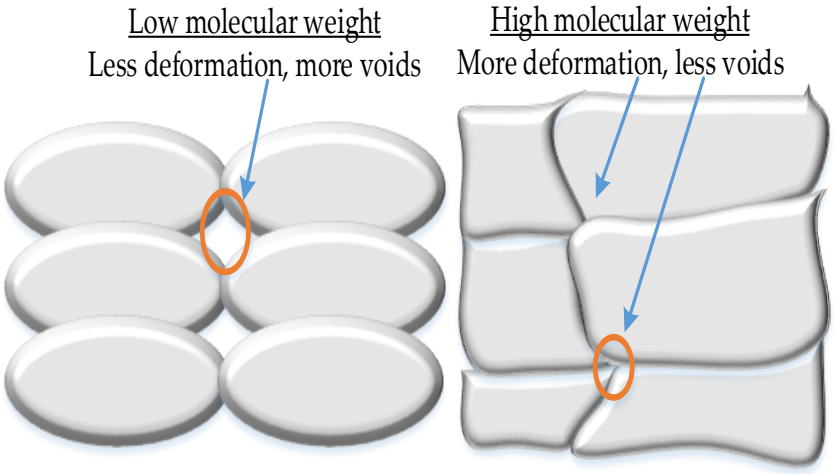


Figure 10. Illustration of effects of molecular weight on diffusion.

Acrylonitrile butadiene styrene (ABS) is the only ternary polymer in FFF. It is the most common elastomeric semi-crystalline polymer used for FFF that is considered one of the large-scale materials due to the introduction of entry level printers for domestic users. The tensile strength obtained from commercial ABS filaments ranges from 26 MPa to 38 MPa [41, 74, 144-148]. The highest strength (38 MPa) is reported for a commercial variant of ABS (ABSplus) for flat build orientation [149]. Multi-purpose injection molding grades of ABS (MG47 and MG94) are also used to extrude out filaments for FFF. A tensile strength of 34 MPa for high molecular weight MG47 at high feed rate (60 mm/s) has been achieved [41].

The effect of molecular weight is observable in SEM structure as illustrated in Figure 10 that shows high deformation for high molecular weight grade resulting in more fusion area among beads compared to less deformation for low molecular weight grade that causes less fusion area. Therefore, the research reveals the effectiveness of molecular weight for ABS [41]. Moreover, there is a recent research on acetone treatment of ABS in between layers during 3D printing that reports minor improvement in properties [76]. The above-mentioned literature also elaborates on the ability of ABS to generate desired results at an uncontrolled environment as presented in Table 3.

Polyetherether ketone (PEEK) has recently been reported as a potential research material [87, 146, 150]. However, it is the most difficult material to 3D print among all FFF materials [151]. The main reason for this is the highest melt temperature (>350 °C) among all FFF polymers that makes its processability extremely difficult. Another problem is the narrow optimal temperature range for successful printing (360–400 °C) [87, 150, 152]. FFF printing of PEEK has been performed on three kinds of custom-made physical setups: (1) syringe-based [150], (2) extrusion-based [153], and (3) filament-based [125]. Among these setups, screw-based extrusion achieves the highest tensile strength (≈100 MPa) [146], while the filament-based setups show the least strength (40 MPa) [151]. The syringe-based setup is conducive to only low molecular weights and it is reported to achieve incomplete printing [150]. Unlike other FFF materials, research on PEEK utilizes a common grade (Victrex 450G) with high molecular weight [83, 146, 153] that provides superior strength and elastic modulus with 45°/−45° raster orientation [146].

Table 3. Process factors for achieving high tensile strength of different single materials.

Material	Process Variables			Physical Setup	Environment	Tensile Strength (MPa)
	Variables	Set values of Variables	Significant Variable			
PLA [92]	Build orientation	Flat, on-edge, upright Layer	Flat, 50 mm/s, and 0.06 mm	Not specific designed	Uncontrolled	89.1
	Layer thickness	0.06 mm, 0.12 mm, 0.18 mm, 0.24 mm.				
	Feed rate	20 mm/s, 50 mm/s, 80 mm/s				
PLA [142]	Strain rate	2.5×10^{-4} S^{-1}, 1.25×10^{-4} S^{-1}	2.5×10^{-4} S^{-1}	Not specific designed	Uncontrolled	61.42
	Raster angle	0°, 45°, 90°	45°			
	Thermal comparison of material in different condition (for crystallinity)	As received filament, Extruded filament, Printed, Printed (annealed)	No significant difference in % crystallinity			
ABS [41]	Extrusion melt pump pressure	75 for MG47, 54 for MG94	Both grades	Not specific designed	Uncontrolled	34
	Two molecular weight grades	MG47 for high MW, MG94 for Low MW	MG47			
PEEK [146]	Infill percentage	20, 50, 100	Flat and 100% infill	Not specific designed	Uncontrolled	≈100
	Build orientation	Flat, vertical				
PEEK [150]	Two molecular weight grades	OPTIMA LT3 (low MW), VICTREX 450G (high MW)	VICTREX 450G 14%	Two kinds of setup Syringe based Filament based	Heated plate Lamp heated atmosphere	75.06
	Average Porosity %	14%, 31%				
	Printing speed	0 to 120 mm/min				
	Extrusion speed	0 to 120 mm/min				
	Nozzle diameter	621.052 µm, 512.03 µm, 407.96 µm				
PEEK [153]	Printing methods	Line printing, Plane printing	Plane printing	Pellet printer, Glass and steel plate		98
PEEK [83]	Build orientation	Flat, vertical,	Flat and 0°			82.5
	Raster angle	0°, 90°				
PP [36]	Infill percentage	20%, 60% and 100%	100% 0° 0.2	Custom extrusion head. Scrubbed glass bed with alcohol treatment [126]	Uncontrolled	36
	Orientation	45°, 0°, 90°, crossed 45° (±45°) and crossed 0°–90°				
	Layer thickness	0.20 and 0.35				
Nylon [98]	Build orientation	Flat, on-edge, supright (vertical)	T16 On-edge	Nozzle size T12, T16, T20	Uncontrolled	~55

Polypropylene (PP) is the only polyolefin in FFF materials in a short list of known FFF materials. It suffers excessive warpage and shrinkage (Figure 11) that produce dimensional instabilities making its printing a challenging job [36, 85, 154-156]. To overcome the printability problems associated with warpage and shrinkage as shown in Figure 11b, different techniques have been employed. For example, retrofitting PP sheet on a non-heated bed, managing the overlapping area between beads through calculating the shrinkage of each layer [85], addition of fibers [85, 156] and alcohol treated PP plate scrubbed with steel brush [36] are among the recently reported techniques. The commercial filament of PP is not available and, therefore, researchers use conventional polymer grades like extrusion molding grades. One of the rare works on PP used high feed rate, low printing (plotting) speed along with over-filled infill rasters on contour paths (Figure 11a) extruded through a custom designed extrusion head. The setup helped to achieve 36 MPa at 0° raster angle with constant layer thickness and 100% infill [11]. The literature doesn't provide any information regarding 3D printing of PP in controlled environments (thermal or vacuum) or in high precision commercial printers, which leaves a research gap to further explore.

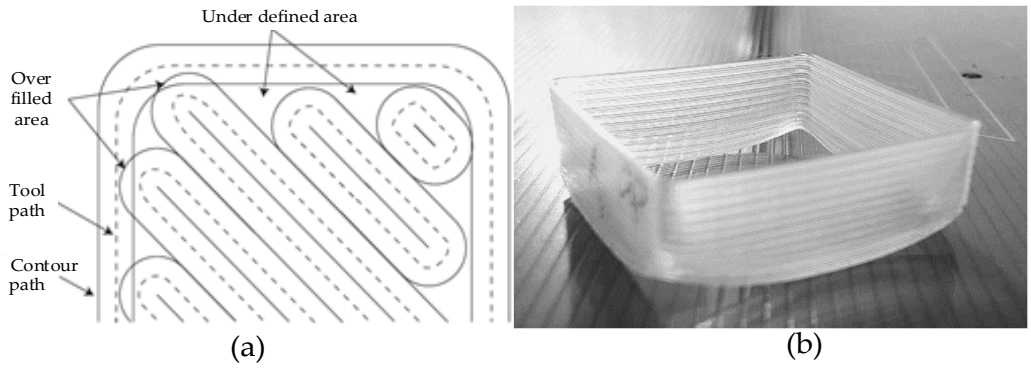


*Figure 11. Illustration of PP 3D printing: (**a**) over-filled infill with contour overlap, and (**b**) shrinkage in PP printed samples. Adapted from [36], with permission from © 2015 Elsevier.*

Polycarbonate (PC) is another FFF thermoplastic that has been reported to possess better mechanical properties compared to ABS. The major part of the research performed on PC is on the analysis of tensile properties [157], flexural properties [158], creep [159], and roughness [160] through modifications in process parameters like build orientation, layer thickness, raster angle, number of contours, air gap, etc. [157-161]. The literature predominantly utilizes similar commercial FFF setups (Fortus MC400 and MC360) that fabricate in a heated environment [157-160], except for one reference that reports both pre-

conditioning (ASTM D618) and in-process thermal treatment of PC (vender not provided) [162]. The tensile strength in the literature for PC ranges from as low as 18 MPa [162] to as high as 68 MPa [160]. The recent inclination of research combines the aforementioned process parameters with cyclic or fatigue analysis in heated and non-heated environments [158, 159]. It is worth exploring to analyze the effects on mechanical properties of neat (virgin) PC as it is still to be explored. The research will help to explore the real potential of neat polymer.

Nylon is the first semi crystalline polymer in polyamides that is available at commercial scale for FFF. The preference of this material is justified by its good flexibility, least water absorption (<1.5%), good resistance to chemicals, good mechanical properties (Figure 8) and high fatigue resistance.

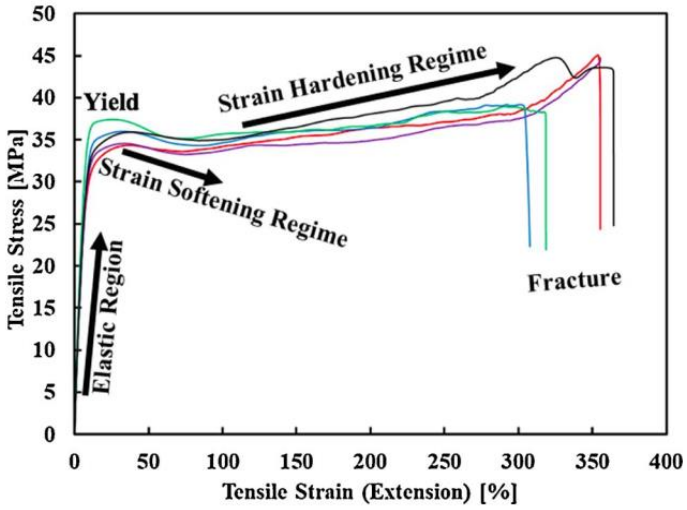


Figure 12. Large strain hardening of five FFF Nylon6 samples with 100% infill density. Adapted from [165], with permission from © 2018 Elsevier.

Various commercialized printer makers have utilized Nylon to make their mark in the global market like Markforged [163]. Nylon12 by Stratasys Inc. has experimented with different layer thicknesses, types of nozzles, and build orientations. The on-edge orientation provides the highest strength of ~55 MPa followed by flat orientation with a close difference in tensile strength [98]. Post-treatment of Nylon doesn't provide significant differences in tensile strength [85]. A recent research reports the addition of polyolefin elastomer grafted maleic anhydride (POE-g-MAH) to overcome the warpage [164]. During comparative analysis of stress–strain curves of FFF-based nylon, a wide range of strain hardening is found

in literature as shown in Figure 12 [165]. Therefore, one of the future prospects of motivating the researchers regarding 3D printing of nylon is the enhancement and utilization of large strain hardening in potential applications.

In conclusion regarding single FFF polymers, PEEK is the only polymer that has been reported to have all three kinds of modifications, i.e., parametric, physical setup, and heated environment. Non-commercial PEEK holds the highest tensile strength followed by commercial PLA as shown in Figure 7 and Table 3. Parametric modifications are preferred for commercial PLA and Nylon to extract the superior properties as shown in Table 3. However, Nylon also reports both parametric and physical setup-based modifications to derive better results. PP also shows successful printing with both parametric and physical setup-based modifications. Variants of commercial ABS in a heated environment provide better properties as compared to non-commercial grades with optimal process parameters.

As a whole, the commercial polymers are explored more in terms of elastic modulus as compared to FFF single polymers made from injection or extrusion grade polymers (Figure 7). Therefore, it indicates a need to research the elastic properties of FFF parts printed by polymer filaments made of injection or extrusion grade. Furthermore, the effect of moisture, thermal and soil degradation on chemical structures of biodegradable materials (PLA, PCL) has not been properly investigated. This highlights the need for thorough chemical analysis of biodegradable FFF materials through Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), etc.

2.3.2. Composites

The contribution of reinforced composite materials is the most significant among all FFF materials as it enables printing of functional parts with highest mechanical strength (Figure 13 and Tables 4–6). The fiber reinforcement of different forms (continuous or discontinuous) and sizes improves the mechanical [166-171], thermal, and conductive properties [172-174]. Apart from strength, the reinforcements are added to overcome the non-printability regarding high co-efficient of linear thermal expansion [36, 85]. The reinforced composites in FFF are made of either natural reinforcements (like fibers of palm, jute, hemp) or synthetic reinforcements (like carbon, glass, Kevlar, metal), as shown in Figure 6. The synthetic reinforcements are further classified into continuous and discontinuous reinforcements. Discontinuous synthetic reinforcements include fibers (short, micro, and nano), multiwalled

nanotubes (MWNT), and powders. This section describes the significant research associated with continuous and discontinuous reinforced FFF polymers.

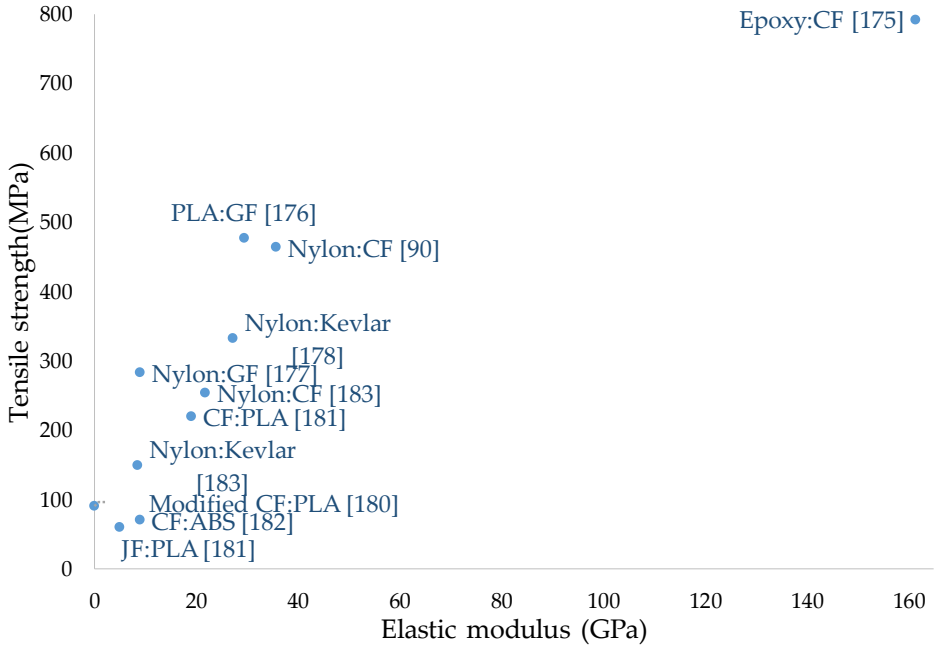


Figure 13. Tensile strength and elastic modulus of continuous fiber reinforced materials.

2.3.2.1. Continuous Fiber Reinforced FFF Materials

Continuous fiber reinforced polymers are directly fed into the FFF setup to achieve impregnation with polymer matrix. The accumulative strength of the composite is based on the strength and adhesion of both fiber and polymer matrix. To achieve the adhesion between fibers and polymer matrix, two kinds of physical setups are used in research. The pertinent setups are categorized with respect to the number of nozzles in this review, i.e., one nozzle for simultaneous impregnation (conventional FFF method) [175, 176], and two nozzles for separate fiber and polymer matrix feeding [90, 177-179] as shown in Figure 14.

One-nozzle physical setups include four kinds of approaches for fiber impregnation as reported in the literature: (1) chemically treating the fibers before impregnation in synchronized fiber and polymer filament feeding [180], (2) heating the fiber to fuse fiber surface with polymer matrix in synchronized fiber and polymer filament feeding [181], (3) heating the polymer to create a melt pool to pass fiber through it in a non-synchronized fiber and polymer filament feeding [175, 176], and (4) direct impregnation without any treatment or heating in synchronized fiber and polymer filament [28]. Each of these approaches achieves specific properties of tensile strength, flexural strength and ductility. Considering

the highest tensile strengths (792.8 MPa [175] and 479 MPa [176]), the prominent approach is the impregnation of carbon fibers and glass fibers in epoxy melt and PLA melt pool inside the nozzle during non-synchronized feeding, respectively [175, 176]. An additional three approaches, described below, further highlight different research gains in terms of understanding the nature of FFF composites.

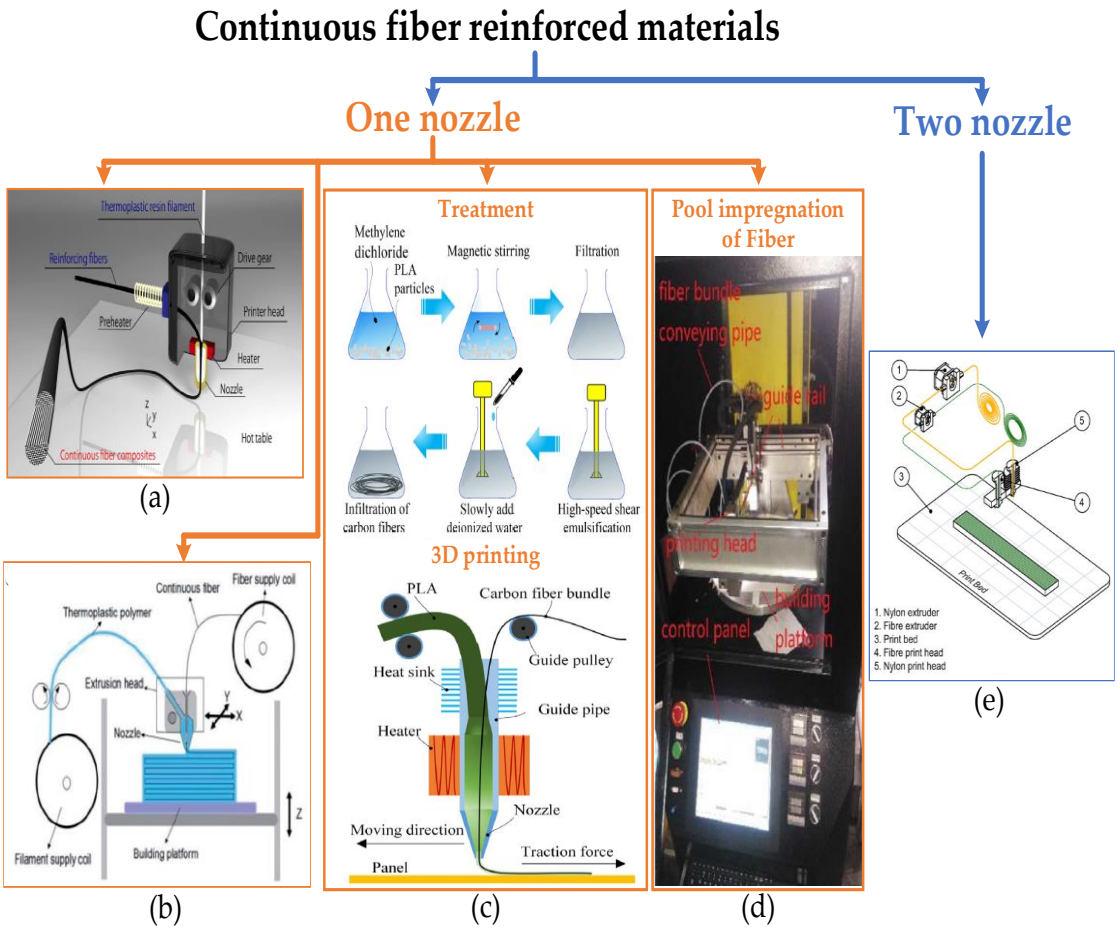


*Figure 14. One nozzle and two nozzle illustration: **(a)** feeding heated fiber [181]; **(b)** feeding non-treated fiber, adapted from [28], with permission from © 2016 Elsevier; **(c)** feeding treated fiber with methylene dichloride and PLA pellets, adapted from [180], with permission from © 2016 Elsevier; **(d)** passing fiber from pool of melt, adapted from [175], with permission from © 2018 Elsevier; and **(e)** separate feeding of filament and fiber from two separate nozzles, adapted from [179], with permission from © 2018 Elsevier.*

Table 4. Process factors for achieving high tensile strength for continuous fiber reinforced composites.

Materials	Process Variables			Physical Setup	Environment	Tensile strength (MPa)
	Variables	Set values of Variables	Significant Variable			
CF:ABS [182]	Different printers	Makerbot replicator, CubeX, Afinia and Solidoodle 3	All printers have significance Flat samples have maximum UTS	No	No	70.69
	Build orientation	Flat, Vertical				
Modified CF:PLA [180]	Pre-printing treatment of CF	Methylene dichloride solution with 8% PLA particles for CF.	Treatment	Customized	No	91
JF: PLA CF: PLA [181]	Pre-printing heating of continuous CF	210 ℃	Carbon fiber	No separate mechanism for pulling CF. Nichrome wire heater attached with printing head for heating CF.	No	220 (CF) 60 (JF)
	Fiber types	Carbon fiber (CF) and Jute fiber (JF)				
Epoxy: CF [175]	Epoxy pool impregnation of CF	Epoxy pool impregnation	Epoxy pool impregnation	Customized setup	No	792.8
	Printing schemes	Lamina, Honeycomb, Grid (not for UTS)				
Nylon: CF Nylon: Kevlar [183]	Fiber types	Carbon fiber, Kevlar fiber	Nylon: CF 0°	No (Mark One 3D printer)	No	254.8 (CF), 150.2 (Kevlar)
	Raster orientation	Orientations for Nylon: Kevlar (0°, ±45°), Nylon:CF (0°)				
Nylon:CF [175]	Fiber build strategy with discontinuity in fiber layup each path	Sandwiched Carbon fibers in middle of 10-layer specimen, i.e., 2 layers, and 6 layers	6 CF layer	No (MarkForged company printer)	No	464.4
PLA:GF [176]	Pool of PLA	Pool of PLA	Pool of PLA 49.3 0.3	Customized	No	479
	Fiber composition %	49.3,46.3,40.18,35.14,28.78,22.74				
	Extrusion width (mm)	0.22,0.25, 0.35, 0.4,0.5,0.6,0.8				
Nylon: GF Nylon: Kevlar [177]	Fiber composition %	25% and 50%	50% Isotropic 0°	Non-commercial two nozzle printing head	No	283.5
	Fill type	Isotropic and Concentric				
	Fill type category 1) Isotropic fill type 2) Concentric fill type	0°, 45°, and 90° 4 layers 8 layers, and 12 layers				

Table 5. Process factors for achieving high tensile strength for discontinuous synthetic reinforced materials.

Materials	Process Variables			Physical Setup	Environment	Tensile Strength (MPa)
	Variables	Set Values of Variables	Significant Variable			
PLA: TCP [184]	Specimen size	1:1, 1:2	1:2	No		27.5
	Printing temperature	215 °C, 225 °C, 235 °C	225 C			
PP:GF [36]	Infill degree %	20%, 60%, 100%	Infill 100%	Customized printer	No	39
	Raster orientation	45°, 0°, 90°, crossed 45° (±45°), 0°–90°	0°			
	Layer thickness	0.2mm, 0.35m	0.35mm			
ABS: TiO2, ABS: ZnO, ABS: $SrTiO_3$, ABS:$AL2O_3$ [145]	Build orientation	Flat, Vertical	Flat	No	No	32.9 (ABS:TiO_2) 20.7 (ZnO) 21.6 (ABS:$SrTiO_3$) 28.8 (ABS:$AL2O_3$)
	Type of fillers	TiO_2, No, $SrTiO_3$, $AL2O_3$	TiO_2			
CF:PPS [185]	Raster orientation	0° (longitudinal), 90° (transverse)	0°	No	No	93.22
ABS: OMMT [186]	Laboratory based OMMT (treated) content %	1%, 3%, 5%	5%	No	No	39.48
BioPE: TMP [187]	Laboratory prepared thermos-mechanical pulp fibers (TMP) %	0%, 10%, 20%, 30%	30%	No	No	38.72
ABS: ZnO CABS: ZnO [188]	Type of polymer matrix	ABS, CABS	ABS	Powder ZnO deposition by dispenser during printing	No	27.5 (ABS:ZnO) 12 (CABS:ZnO)
	Infill density	50%, 75%, 100%	100 %			
	Infill pattern	Line & rectilinear with 45° raster	Line			
PPGF: POE-g-MA [156]	Layer thickness	0.1mm and 0.4 mm	0.1 mm	Laboratory made PP tape for heating bed	No	34
	POE-G-MA contents %	10%, 20%, 30%	20%			
ABS: SCF: SAG [189]	SAG content %	0%, 1%, 3%, 5%, 7%	5%	No	No	73.3
ABS: SCF [86]	Type of reinforcement	Short carbon fibers (SCF), Carbon nanotubes (CNT)	SCF	No	No	39.05
	Raster angle	45°/-45°, 0° and 90°	0°			
PLA: CNF [190]	Nozzle geometry	Circle, and square	Square (less voids)	No	No	47
	CNF contents %	0.5%, 0.1%	0.5%			
Nylon12:CF [84]	CF contents%	0%, 2%, 4%, 6%, 8%, 10%	10%	No	No	93.8
	Raster angle	0°, 90°	0°			

Table 6. Process factors for achieving high tensile strength for discontinuous natural fiber reinforced materials.

Materials	Process Variables			Physical Setup	Environment	Tensile Strength
	Variables	Set Values of Variables	Significant Variable for Highest Strength			
ABS:JF [145]	Build orientation	Flat, Vertical	Flat	No	No	24.25 (ABS: JF)
	Type of fillers	Jute, TiO2, ZnO, $SrTiO_3$, $AL2O_3$	TiO_2			
TPU: Wood flour: MDI [191]	Wood flour contents %	10%, 20%, 30%, 40%	MDI	No	No	19
	Types of modifiers	EPDM-g-MAH, POE-g-MAH, chitosan (cs), polyethylene glycol (PEG), diphenyl methyl propane di-isocyanate (MDI)				
PHA-g-MAH:PF [39]	Treated palm fiber with Silane coupling agent.	Treated palm fibers (PF)	20% PHA-g-MAH	No	No	25
	PF composition	10%, 20%, 30%, 40%				
	Type of polymer matrix	Laboratory prepared PHA-g-MAH, PHA				
PLA: wood fill fine [10]	Sample width %	100%, 200%, 300%	100%	No	No	31
	Raster angle	0° and 90° (rectilinear infill)	0°			
ABS: Rice straw [192]	Number of contours	1, 2	2	No	No	28.89
	Rice straw content %	5%, 10%, 15%	15%			
PLA: Silk [193]	Types of fibers	Sheep and Silk wool(chemically treated)	Silk	No specific physical change. Just provided stay time between layers	No	24.58 (PLA: Silk) 23.63 (PLA: Sheep wool)
	Number of laminates	2, 3, 4	4			
	Infill density	20%, 60%, 100%	100%			
	Raster angle	0°/90°, 45°/135°, 30°/120°	0°/90°			
PP: Harakeke PP:Hemp [194]	Types of fibers	Harakeke, hemp	20 % Harakeke	LDPE & PP bed. warpage in glass	No	24 (PP: Harakeke) 16 (PP: Hemp)
	Fiber composition	10%, 20%, 30%				
PLA: Sugarcane bagasse [195]	Raster angle	0°/0°, 45°/-45°, 0°/90°, 90°/90°	45°/45° (only provided tensile strength at 45°/-45°) Sugar cane bagasse fibers	No	No	57
	Sugar cane bagasse fiber composition	3%, 6%, 9%, 12%, 15%				
	Raw sugarcane bagasse composition	3%, 6%, 9%, 12%, 15%				

Table 7. Process factors for achieving high tensile strength for blend materials.

Materials	Process Variables		Significant Variable	Physical Setup	Environment	Tensile Strength (MPa)
	Variables	**Set Values of Variables**				
PP: SEBS [196]	Composition of PP:SEBS	20:80, 40:60, 60:40	7.5 phr carbon black	PP print bed	No	18 (7.5 phr) 14 (40PP:60SEBS)
	Carbon black in 40PP:60SEBS	0-15 parts per hundred rubber (phr)				
	Injection molding	40PP:60SEBS				
PLA:PA11:Joncryl [197]	Composition of Joncryl (modified acrylic copolymer with epoxy functions)	0%, 1%, 2%, 3%	80:20:2 (PLA:PA11:Joncryl) Injection moulding	No	No	58.8
	Different processes	Injection moulding, FDM				
ABS:SEBS [145]	Build orientation	Flat, Vertical	Flat TiO_2 95:5 90:10:10	No	No	25.5 (ABS: SEBS) 23.07 (ABS: UHMWPE: SEBS)
	Type of fillers	SEBS, UHMWPE: SEBS, Jute, TiO_2, ZnO, $SrTiO_3$, $AL2O_3$				
	Composition	ABS: SEBS (95:5, 80:20) ABS: UHMWPE: SEBS (90:10:10, 75:25:10)				
TPS:ABS:SMA: MBS:TiO2:CB [198]	Types of polymers Polymers	Styrene maleic anhydride (SMA), methyl-methacrylate butadiene styrene (MBS), TiO_2, pigment CB	SMA 30ABS:70%:1SMA:0% TiO_2:0%CB	No	No	46.8
	Composition	SMA (1%), MBS (1%, 2%), TiO_2 (0%, 5%), CB (0%, 5%),				
ABS:SEBS-g-MAH [41]	Grades of ABS	MG47, MG940 (w.r.t molecular weight)	MG94 60 mm/s 75%:25%	No	No	25.09
	Feed rate	30mm/s and 60mm/s				
	Composition of ABS: SEBS-g-MAH	75:25, 50:50, 25:75 One additional for MG94 in 10:90				
PLA-g-MA: Chitosan [199]	Types of polymers	PLA, Laboratory prepared PLA-g-MA,	PLA-g-MA 20%	No	No	57
	Chitosan (CS) composition%	5%, 10%, 15%, 20%				
PLA-PBS [200]	PBS content %	20%, 40%, 60%, 80%	20%	No	No	55.6

For example, heated synthetic carbon fibers achieve high diffusion of fibers into PLA matrix that is complemented by high tow strength of carbon fibers to provide >220 MPa tensile strength. The research also reports natural jute fibers with PLA matrix that results in high ductility instead of tensile strength, as compared to carbon fibers' reinforced parts. Therefore, the brittle carbon fibers provide high strength and natural fibers exhibiting low brittleness attain higher ductility [181]. The non-treated carbon fibers with PLA matrix depicted the highest flexural strength of 335 MPa.

However, the tensile properties behave not been investigated for non-treated fibers through a single nozzle [28]. On the contrary, the treatment of continuous carbon fibers with methylene dichloride solution before printing through a single nozzle with PLA matrix provides tensile strength of 91 MPa and flexural strength of 156 MPa. Though the polymer matrix was reported to distribute unevenly around continuous fiber (Figure 15), the flattening of extrudate by nozzle through extrusion pressure and surface treatment are presented as the reasons to enhance interfacial strength shared between fiber and polymer matrix [180].

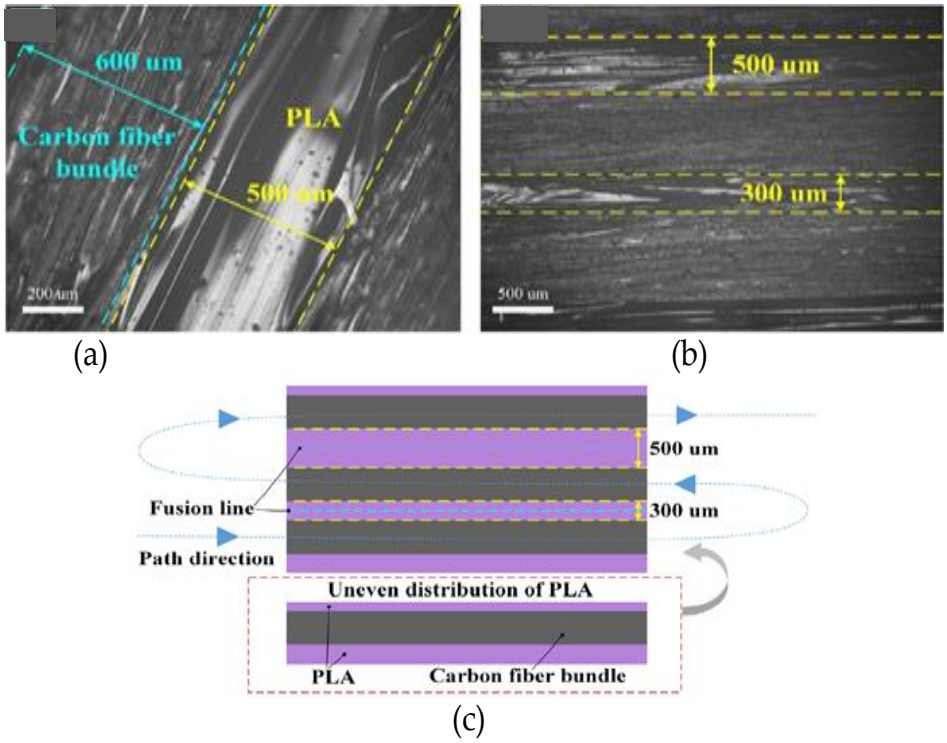


Figure 15. Surface morphology of 3D printed carbon fiber/PLA composite: (a) micrograph of carbon fiber bundle and PLA resin; (b) micrograph of PLA width between carbon fibers; and (c) schematic of the uneven distribution of PLA. Adapted from [180], with permission from © 2016 Elsevier.

The main emphasis of the research reporting two nozzles is on the build strategy (Figure 16) that is comprised of a few important variables: (1) number of fiber layers, (2) placement of fiber layers in composite, and (3) raster angle of fiber lay-up and polymer matrix. The continuous uninterrupted stacking of a high number of fiber layers along with linear (isotropic) fiber and polymer raster orientation result in high mechanical strength [90, 177, 178, 183].

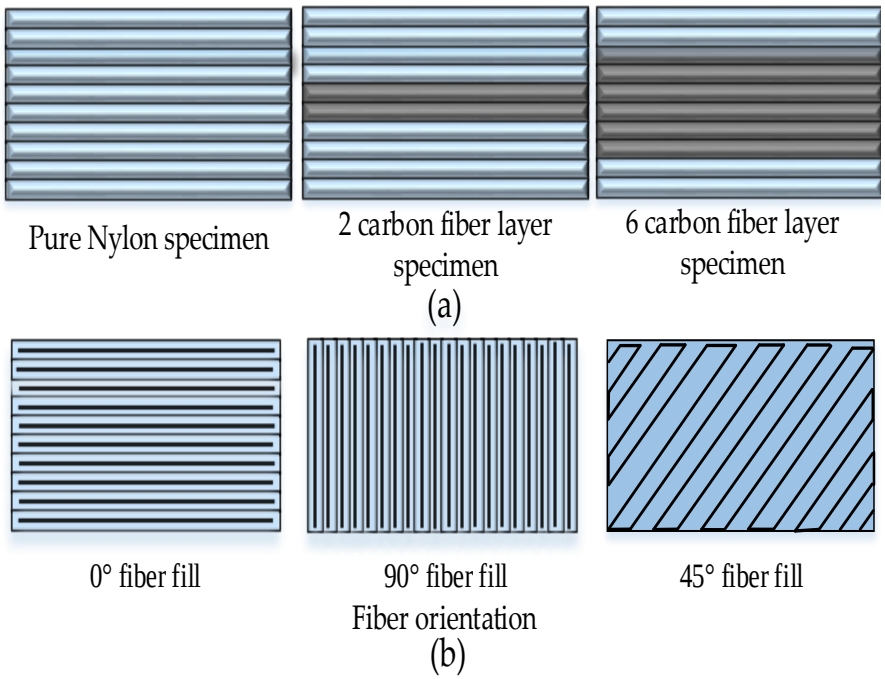


Figure 16. Illustration of two build strategies for FFF with two nozzles setups: (a) number and placement of carbon fibers in polymer [93]; and (b) illustration of fiber fill orientation.

2.3.2.2. Discontinuous Fiber Reinforced FFF Materials

The discontinuous reinforced composites are the most researched materials in reinforced FFF polymers as presented in Figure 17 and Tables 5,6. It is noticed in this review that the type of discontinuous fibers (synthetic or natural) also brings significant effects on the properties of fiber-reinforced composites as shown in Figure 17. Furthermore, the functional characteristics of discontinuous reinforced composites are dependent on polymer matrix, adhesion between fibers and polymer matrix [84, 86, 156, 188-190, 201-205] fiber length distribution (FDL), orientation of fibers in matrix [84, 185, 206-208], packing densities [206], etc. Recent literature elaborates the difficulties associated with discontinuous fibers in the material processing stage that cause breakage of relatively long fibers during shear mixing in extrusion compounding and then 3D printing [209-213]. In this regard, the preliminary research focus is to compensate

the uncontrollable breakage of long fibers through orienting the fibers in a dense FFF structure. The proper distribution (Figure 18a,b) and orientation (Figure 18c) attribute good tensile strength of about 70 MPa among discontinuous fibers reinforced composites [214].

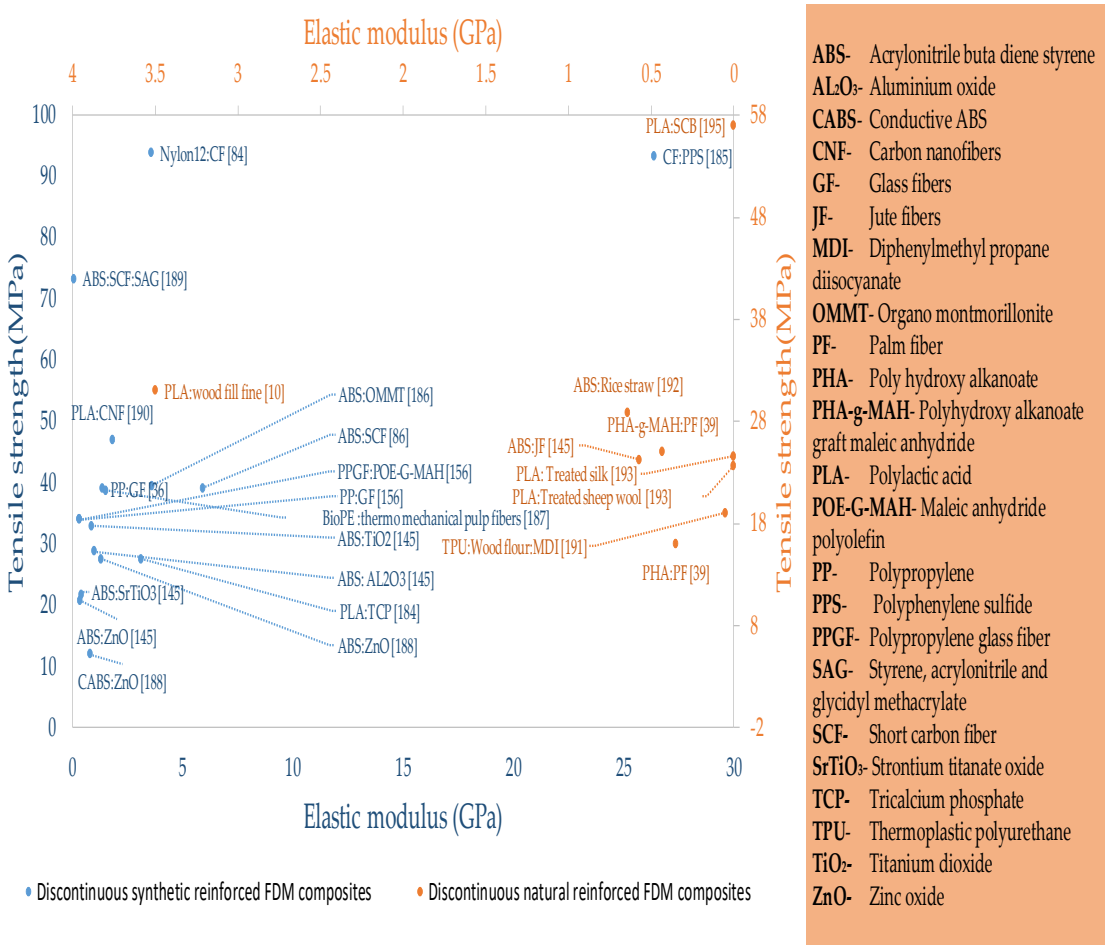


Figure 17. Tensile strength and elastic modulus of discontinuous fiber reinforced materials of fused filament fabrication.

The strategy of orienting the long fibers (12mm) with the help of high shear force during the FFF process results in the highest mechanical strength of 93.22 MPa for Big Area Additive Manufacturing (BAAM) that uses polypropylene sulphone (PPS) reinforced with carbon fibers [215]. The concentration of literature before 2018 is notable for the uniform dispersion to achieve homogenization of discontinuous entities (fibers, nanotubes, powder) in the polymer matrix. On the contrary, recent developments have focused on the introduction of compatibilization of fiber surfaces with polymer as shown in Figure 18. Two recent publications regarding discontinuous fiber reinforced FFF composites report different methods

of achieving compatibilization. One uses compatibilizer (styrene acrylonitrile glycidyl methacrylate, SAG) during ABS blending with short carbon fibers in a twin screw extruder (Figure 18d) [189], and the other treats ZnO powder with an ABS:acteone solution to form a surface layer of ABS for compatibilizing with ABS matrix [188].

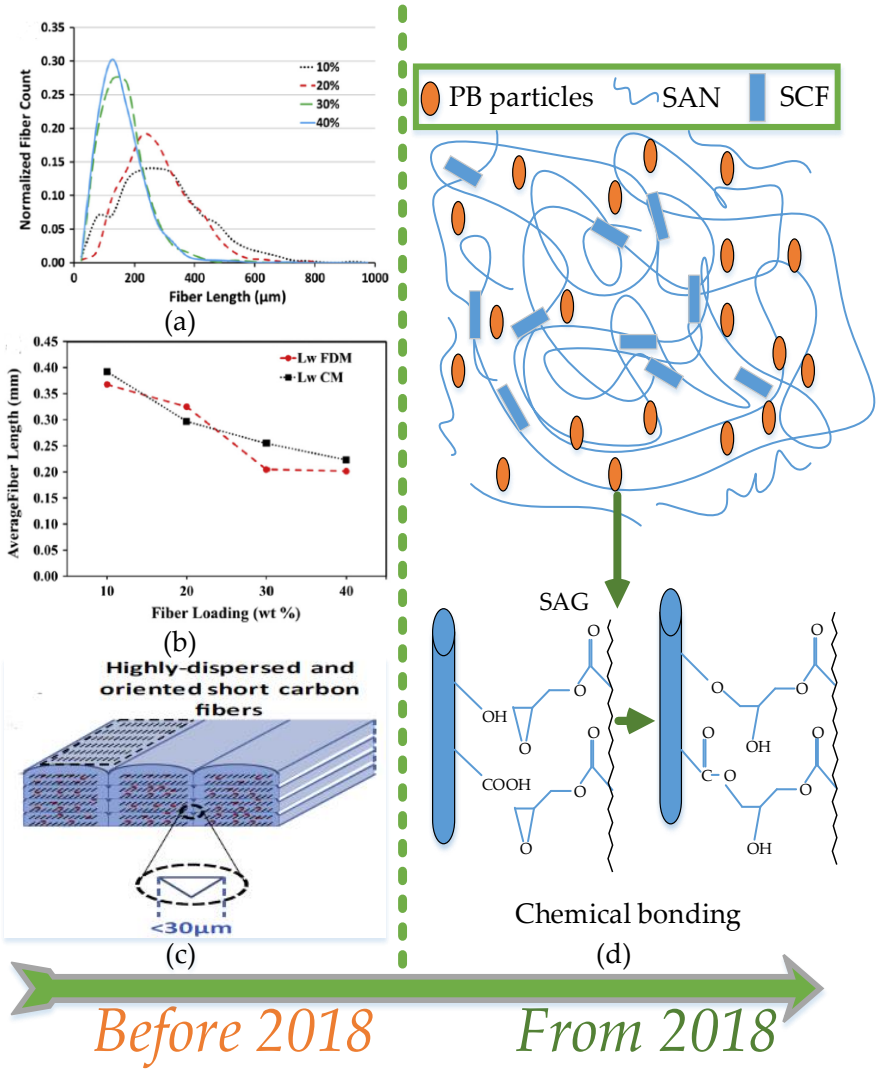


*Figure 18. Development in research of discontinuous fiber reinforced FFF polymers before and from 2018: (**a**) fiber length distributions in FFF printed specimen; (**b**) weight average fiber lengths of FFF samples, and (**c**) dispersion of fibers in specific orientation. Adapted from [214], with permission from © 2014, Elsevier. (**d**) Illustration of chemical reaction of styrene acrylonitrile glycidyl methacrylate (SAG) on surface of short carbon fibers, adapted from [189], with permission from © Taylor & Francis.*

Considerable efforts have been made to enhance the mechanical properties of natural fiber reinforced polymers (Table 6). However, in natural fiber reinforced polymers, the investigation

of optimal printing process parameters is not the prime consideration as observed for single FFF materials. In fact, parameters such as nozzle temperature, layer thickness, infill percentage, bed temperature, and feed rate are mostly adopted from appropriate references (Table 6). Instead of process parameters, the preference is found for fiber concentration to study swelling, apparent draw ratio of filament during the filament making process, post-printing deflection, hydrophobic and hydrophilic properties, biocompatibility and biodegradability testing. Furthermore, this review enlists various methodologies that are used to develop natural fiber-reinforced composites (Figure 6). For example: (1) an old conventional method of using commercial (patent) reinforced filament [10], (2) blending non-processed reinforcements with neat polymers [192, 216], (3) blending chemically processed reinforcements with neat polymers [193], (4) blending chemically processed fibers with laboratory prepared graft co-polymers [4], and (5) blending modified reinforcements with modifiers [191]. Each of these methodologies is discussed in further detail below.

Commercial wood-fill filament, made of recycled wood and binary polymer matrix of PLA and poly hydroxyalkanoate (PHA), is used to print the parts with a strength of 31 MPa. The high mechanical tensile strength is noted for samples printed at 0° orientation followed by compression with heating plates compared to simple 3D printed samples. The reason for enhancement in properties is the higher overlapping between beads at appropriate printing width that causes the reduction of porosities [10].

A recent novel research provides a new direction of in-laboratory designed graft polymer matrix and chemically processed natural fibers that show high compatibility during blending. The maleic anhydride grafting on polyhydroxyalkanoate (PHA) and treatment of natural palm fibers with silane coupling agent and acetone provides (Figure 19a) better mechanical properties for graft matrix. In this research, solid-state carbon-13 nuclear magnetic resonance (CNMR) was used for the first time for FFF materials to justify the presence of grafting and good bonding between treated palm fibers (TPF) and maleic anhydride grafted PHA [39].

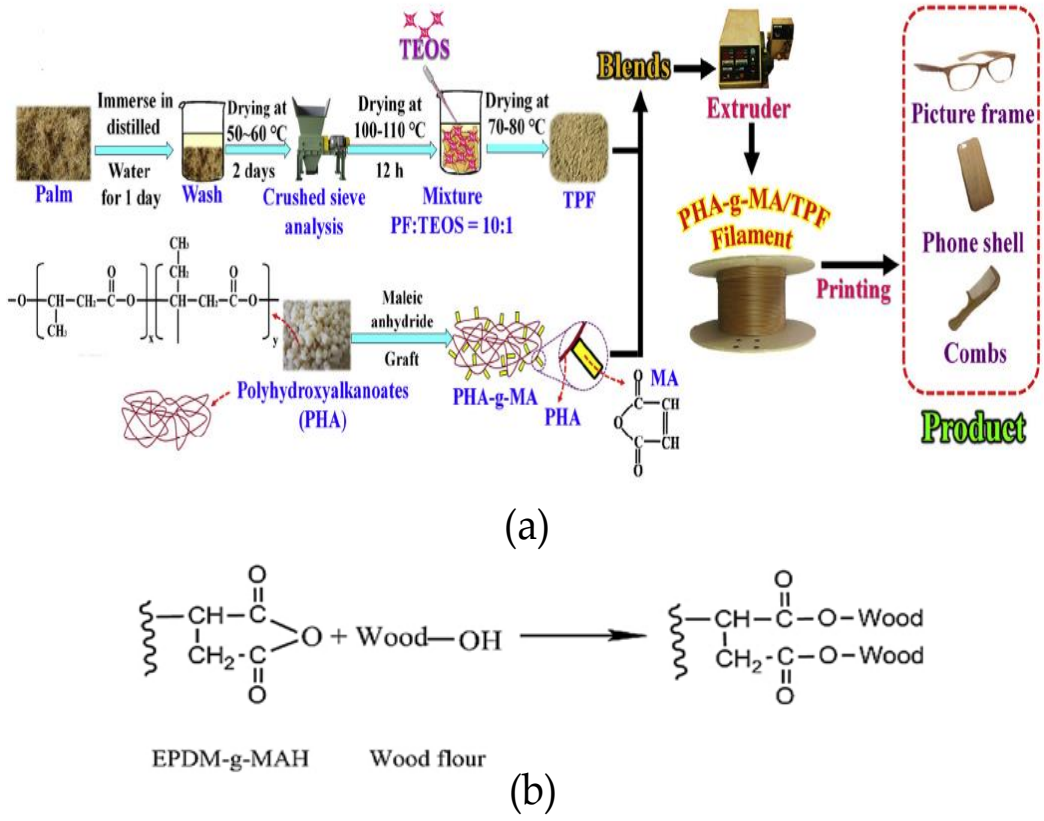


*Figure 19. Two methodologies to develop natural fiber reinforced FFF materials: (**a**) in-laboratory prepared graft polymer for chemical processed natural palm fibers, adapted from [39], with permission from © 2017 Elsevier; and (**b**) modification of fibers matrix (TPU/WF) with modifier (EPDM-g-MAH) adapted from [191], with permission from © 2018 Elsevier.*

Another study presents the effects of different modifiers (EPDM-g-MAH, MDI, POE-g-MAH) on wood flour with thermoplastic polyurethane (TPU) as shown in Figure 19b. Though the reported tensile strength (~16 MPa) is not appreciable, this research strengthens the concept of using appropriate functionalized graft polymers that have an affinity towards particular natural fibers [191].

A unique study that developed their own kind of natural fiber reinforced FFF composites reports a hand-layup of chemically processed fibers (silk and sheep wool) in neat PLA matrix. The hand-layup of fibers is performed during the programmed stay time between neat printed layers. The maximum tensile strength of 23.66 MPa is recorded for a silk fiber-reinforced FFF composite [193].

A recent significant development for discontinuous natural reinforced FFF composite is the utilization of the characteristic weakness of natural fibers, i.e., hydrophilicity. High moisture absorption ability of natural fibers is a major technical obstacle that obscures the FFF

parts to provide good resistance to moisture [217, 218]. In contrast, the high moisture absorption capability makes the natural hygromorphic fibers to act like self-shaped wood [219-221], when incorporated as reinforcements in polymer matrix, making them suitable for 4D printing [222-224]. This development has broadened the applicable area of natural reinforced FFF composites.

Overall, reinforced composite materials possess the highest potential in terms of strength. However, it is noted that the research foci vary due to change in the type of the reinforced composites. For example, research on discontinuous reinforced composites concentrates on the uniform dispersion [188] and surface compatibility [189] of the reinforcements, and research on the continuous reinforced composites concentrates on the surface impregnation with resin [175, 180, 181]. Generally, process variables, physical setup modifications, and chemical processing play significant role in dispersion, compatibilization, or surface impregnation. The literature is scarce on printing in heated environments. Therefore, printing in the heated environments along with the enhanced chemical processing can be a potential area of discovery for future research. The rationale behind this is based on the significant improvements in single materials due to printing in the controlled ambient environment [113]. Furthermore, the stability of composites made with natural fibers and biodegradable materials is yet to be explored in terms of stability against moisture, thermal and soil degradation.

2.3.3. Blend

Blending different polymers is an innovative concept, but very little research efforts have focused on this aspect of FFF (refer to Figure 20). Most FFF blends are listed in Table 7. The FFF blend materials are mostly made by either melt blending or reactive extrusion in a twin-screw extruder in the presence of additives like initiators, compatibilizers [41, 197, 199, 225], molecular chain extenders [226], and plasticizers [145]. The majority of research on FFF-based blend materials reports the use of patent (commercial) graft [7] or non-graft [145] compatibilizers from different companies. One of the reasons for moving on to blends is the vulnerability retained by FFF structures due to their anisotropy. Substantial, but still insufficient, efforts are made to overcome the anisotropy through optimal combinations of parameters like layer thickness, air gaps, infill percentages, feed rate and printing speeds and raster angles [227, 228], that cause large differences in tensile strength, particularly with Z-build orientation (vertical) [100, 227, 229-235].

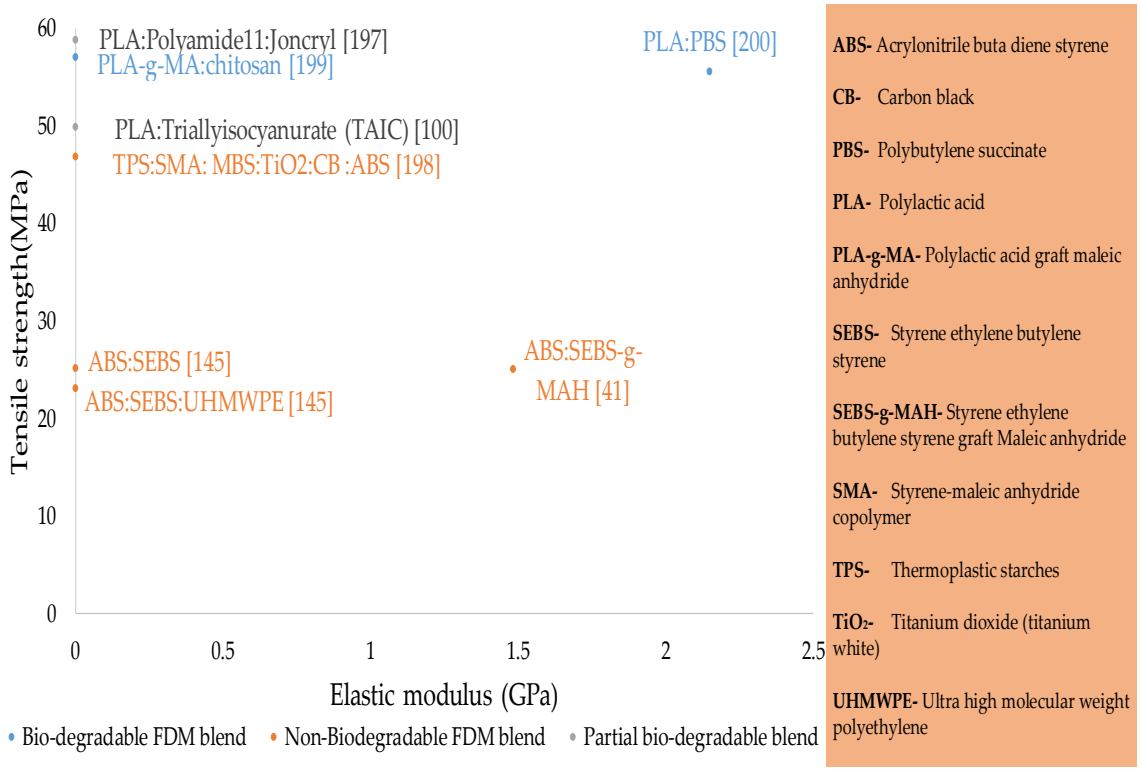


Figure 20. Tensile strength and elastic modulus of blend materials in fused filament fabrication.

The only reported strategy to overcome anisotropy is to develop new material systems by blending of printable materials with non-printable materials [145]. As mentioned earlier, a small amount of the research performed is associated with blends compared to single and composite materials. However, the significance of the limited research in blends overshadows their fewer numbers in terms of diversified functionalities such as enhancing inter/intra layer cross-linking, altering failure modes, improved biodegradable life, and an increase in ductility with reasonable strength.

In this review, the FFF blends are categorized into three classifications as shown in Figure 6: (1) partial biodegradable blends, (2) non-biodegradable blends, and (3) biodegradable blends.

A recent publication regarding partial biodegradable blends is of PLA with radiation sensitizer (triallyl isocyanurate, TAIC) in the presence of organic solvent (dichloromethane). The polymer system, after being exposed to gamma rays, provides 49.9 MPa for 0° raster orientation. The results of PLA blend are preferable to control ABS (UTS = 31.1 MPa) due to the improved adhesion achieved through post-printing cross-linking between intercalated layers. The cross linking also helps to reduce the anisotropy in the FFF structure [100]. In a

recent study [197], PLA has been blended with polyamide 11 in the presence of a novel compatibilizer known as Joncryl, which is a modified compatibilizer made of acrylic copolymer with epoxy functions. The results of this study showed the highest tensile strength (58.80 MPa) for 2% Joncryl among all FFF blends reported so far.

Significant work regarding non-biodegradable blends reports two novel polymer blends of ABS with: (1) styrene ethylene butylene styrene (SEBS) and (2) ultra-high molecular weight polyethylene and styrene ethylene butylene styrene (SEBS:UHMWPE) [145, 236]. Better mechanical strength (25.51 MPa) and ductility compared to pure ABS is obtained by binary polymer system (ABS:SEBS), even with poor interfacial adhesion that depicts the failure mode of a brittle nature in the corresponding research. However, the ternary polymer system (ABS:SEBS:UHMWPE) shows better layer bonding but with lower strength. The interfacial layer bonding is interpreted with complex viscosity measured by dynamic mechanical analysis (DMA) that reveals lower values for ternary blends than for control ABS. The low complex viscosity of ternary blends proves a high propensity to flow under shear that causes the extruded beads to spread on previous layers and hence reducing the anisotropy by filling the voids or air gaps [145]. The poor interfacial adhesion as reported in ABS:SEBS has been recently improved by the use of low molecular weight surface segregation additives (LMW-SuSAs) in a series of studies [237-239]. The most recent among those studies reports ABS with in-laboratory prepared SAN (styrene acrylonitrile), which results in better tensile strength (≈36 MPa) as compared to neat ABS [239].

Biodegradable blends are also rare, similar to the other two types. One such type of blend is the polylactic acid grafted maleic anhydride (PLA-g-MA) with chitosan (CS), the second richest natural polymer. The better compatibilization of CS with PLA-g-MA compared to pure PLA (Figure 21a and b) strengthens the importance of polymer blend systems for the future. The research derived UTS of ~55 MPa for PLA-g-MA with 20% CS by weight as compared to 25 MPa of PLA-CS as shown in Figure 21c [199]. Another recent research reports the bimodal blend of high molecular weight PLA with an in-laboratory prepared low molecular weight PLA. The low molecular weight PLA acts as surface segregation additives that diffuse on the surface during the FFF process due to the long molecular chain [237].

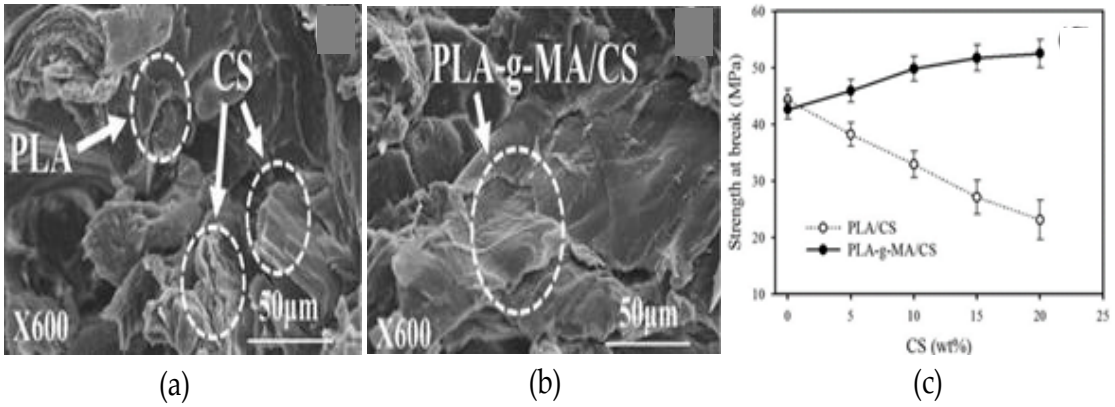


*Figure 21. Scanning electron microscopy (SEM) images showing the distribution and wetting of CS in (**a**) PLA/CS (10 wt%); (**b**) PLA-g-MA/CS (10 wt%) composites; and (**c**) effect of CS content on the tensile strength at failure for PLA/CS and PLA-g-MA/CS composites. Adapted from [199], with permission from © 2016 Elsevier.*

As a summary of the literature regarding FFF materials, it is observed that the research on development of new materials depends upon the type of applications. A common research solution reported in the literature is the modification of existing polymers to achieve desired properties instead of making new monomers. The preliminary goal in modified FFF materials is the ability to print. This material development strategy leads existing research to have more composition by weight percent of existing printable materials (ABS, PLA, PP, Nylon) with low composition of non-printable materials (UHMWPE, SEBS-g-MAH, CS, triallylisocyanurate). Thus, the newly developed polymer blends have inherited functional groups from existing printable materials. Furthermore, existing materials like PEEK, ABS, PP, and Nylon are hard to print as they shrink and do not stick to the printing bed due to curl distortion. This requires some additional measures to make printability possible, including, heated environment, glued printing bed (surface), or incorporation of fibers. On the contrary as a key observation, PLA is the only material that does not provide any problem regarding printability in any form (single, composite, blend).

The simple analysis of chemical structural formulas shows two kinds of observable signs: (1) number of carbons in a monomer, and (2) number and type of functional groups. As shown in Figure 22, PLA has the simplest monomer with three carbons and one carboxylic functional group, Nylon has a long monomer with 11 carbons and two functional groups, PEEK has a long monomer with three aromatic rings (18 carbons) along with the carbonyl group, ABS is a ternary polymer with multi-functional groups including an aromatic group, polypropylene has the simplest monomer but with one of the longest chain configurations. The discussion leads

to an understanding that polymers with a greater number of carbons, multi-functional groups, and complex groups (like aromatic) in a monomer are hard to print. However, polymers (like PLA) with a smaller number of carbon atoms in a monomer and one functional group are more suited to FFF printing. Therefore, there is a visible research gap for developing new, dedicated FFF polymers with short and single functional group-based monomers instead of blending printable with non-printable polymers.

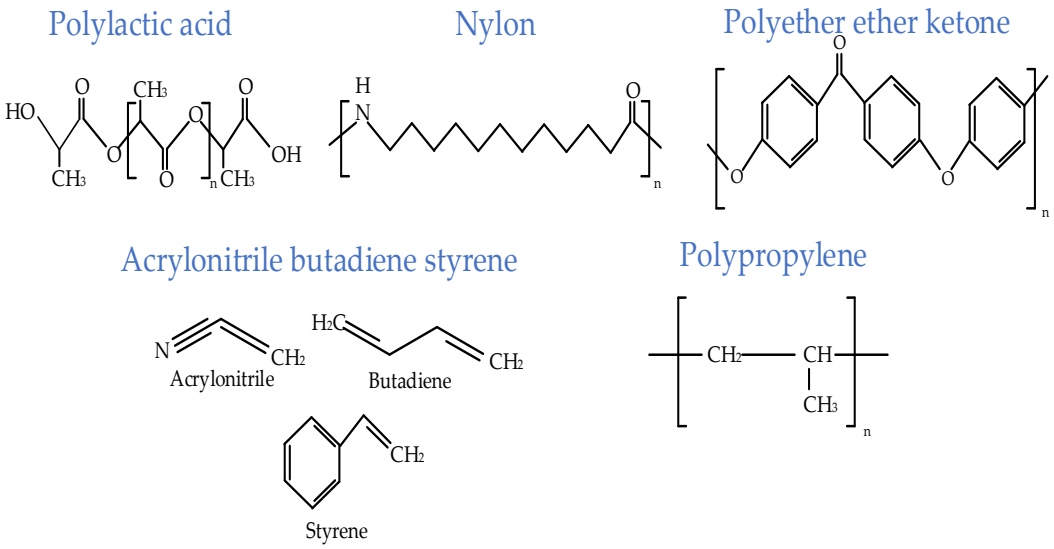


Figure 22. Chemical formulae of common FFF materials.

2.3.4. Summary

Additive manufacturing is well-known for layer-by-layer manufacturing of complex parts at high precision. FFF/FDM is one of the oldest and the most widely used AM technology. Various aspects of FFF structures have been investigated in the literature, the majority of which have the prime consideration to achieve optimal or high strength (tensile, compressive, flexural) by either developing new materials or optimizing process factors or through a combination of both. This review presented the three process factors (process parameters, physical setup modifications, ambient temperature) and types of materials developed with time that are simultaneously employed to achieve improvement in tensile strength.

A brief summary of the key findings in this review is as follows (Figure 23):

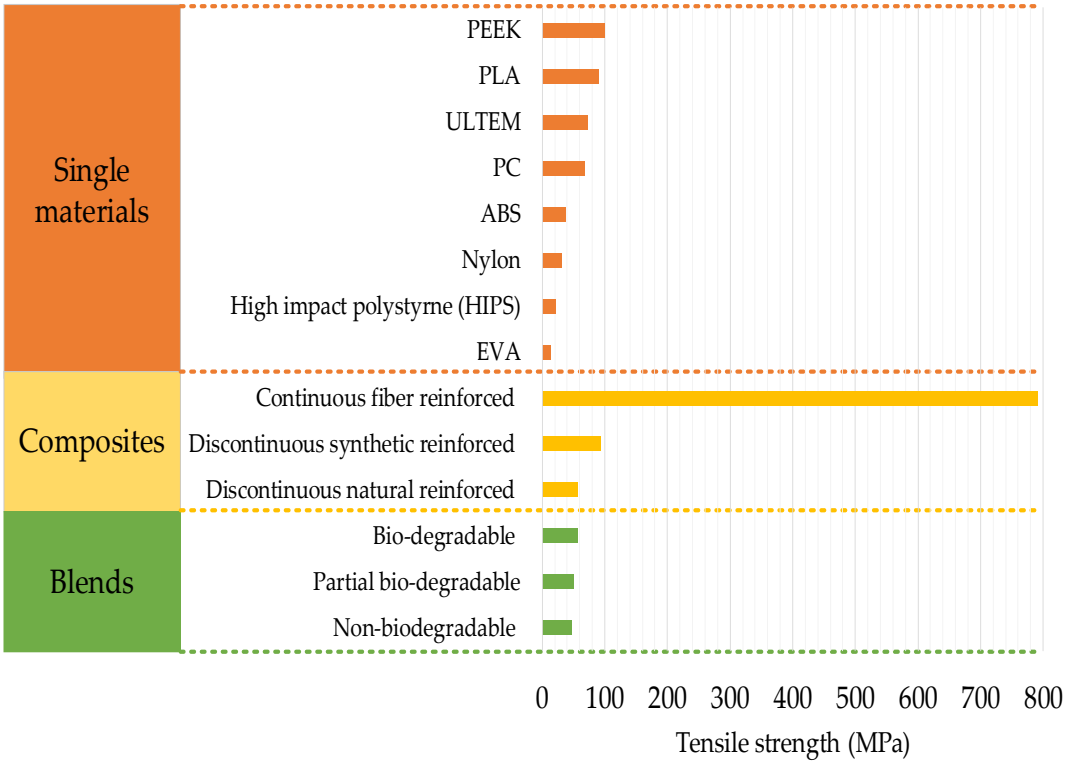


Figure 23. Strength range for different FFF materials.

- The basic three types of materials, i.e., single, composites and blends, are analyzed in terms of modifications in process parameters, physical setups and environmental conditions. Furthermore, the above-mentioned three basic types are classified into the sub-categories to explain the modifications in materials that present their true capability.
- Single materials are categorized into commercial and non-commercial. Commercial materials are researched more than non-commercial materials. However, non-commercial materials have shown more potential to reach high tensile strength. For example, injection molding grade PEEK has the highest strength of 110 MPa as compared to 89.1 MPa for commercial PLA. Most research on single materials has shown a lack of physical modification of the printing system or temperature control. The research mostly comprises process variables' optimization. The combination of physical setup modification and ambient temperature still has research potential for Nylon and ULTEM. Furthermore, biodegradable materials such as polycaprolactone (PCL), are not properly investigated for tensile properties as the literature generally reports the compression and flexural properties of PCL in FFF based medical applications.
- Composites are put into two main categories, continuous and discontinuous. Both of which are found in the form of natural and synthetic reinforcements. Discontinuous materials are

researched more than continuous. The review provides further segregation of continuous synthetic reinforced composites, and synthetic and natural discontinuous composites with respect to their physical modification and chemical processing. Continuous materials are prominent with the highest strength achieved till now among all FFF/FDM materials. Furthermore, composites are mostly investigated with optimization with process variables and physical setup modifications. Therefore, the effect of ambient temperature is still not fully explored.

- Blends are segregated into three types: biodegradable, non-biodegradable, and partial biodegradable. However, blends are the least researched type of materials in FFF. The highest strength of 58.5MPa has been shown by the partial biodegradable blend. Like composites, blends are not researched in an ambient environment with temperature control. Therefore, this provides a novel area of research to combine this with the other aspects of blends.
- The review highlights the importance of developing novel polymers with less carbon atoms and functional groups instead of blending the printable contemporary materials with the non-printable materials. Furthermore, the review highlights numerous novel research areas regarding three types of materials (single, composites, and blends) as given in Table 8.

Table 8. Novel areas of research for different types of FFF materials.

Material	**Novel Area/s to Explore**
PLA	Effects of moisture, thermal and soil degradation on chemical structure and tensile strength
ABS	-
Nylon	Large-strain behavior to be explored in structural applications
PP	Effects of printing in heated environment
PC	Effects of post-printing thermal treatment
PEEK	-
Composites	1. Printing in heated environment 2. Stability of biodegradable composites against moisture and soil degradation 3. Optimal composite properties considering process (printing) temperature as a variable.
Blends	1. Printing in heated environment 2. Stability of blends against post printing thermal degradation 3. Optimal blend properties considering process (printing) temperature as a variable.

2.4. Analysis of FDM to print milk vat insulation

2.4.1. Comparison by strength

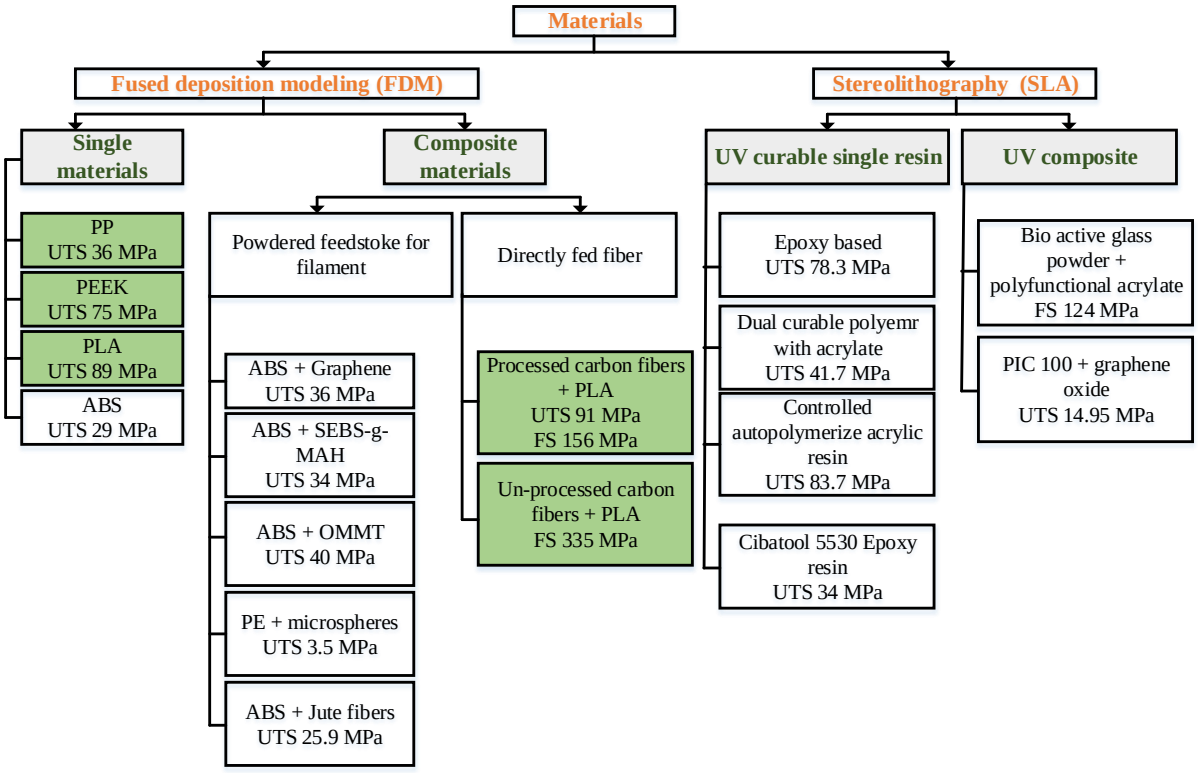


Figure 24. Overview of materials strength reported in literature review.

It is observed in the review and Figure 24 that the strength of FDM parts is high as compared to SLA. Meanwhile, there are other considerable benefits of FDM, which make it highly conducive for our project. Therefore, FDM is selected as the main additive manufacturing process to fabricate the milk vat insulation.

2.4.2. Dextrality

FDM is the simplest process among all AM processes. The dextrality is one of the requirements in this project for printing large milk vat insulation, which can be achieved in FDM by different robotic printing approaches. For example, the articulating robotic setup can be perceived for the large-scale FDM because articulating robotic setup is known for its

comparatively better degree of freedoms and dextrality [240] as compared to selective compliance assembly robotic arm (SCARA) [205].

2.4.3. Time and cost management

Despite the simplicity and dexterous space, the time and cost are the main limitation for FDM process at a large-scale like printing of milk vat insulation. In this regard, the factor of time for printing a milk vat insulation can be reduced in three ways as given below.

1. Increasing the nozzle size of the FDM extruder, i.e., 8 mm instead of 0.4 mm.
2. Using pellets as a raw material instead of filaments [205, 241, 242], which will save the manufacturing cost of making filament.
3. Improvising injection moulding (IM) thermoplastics or elastomeric based thermoplastics instead of using available expensive patented materials. This is further explained in chapter 3.

It can be confidently concluded based on the above three facts (i.e., strength, dextrality, time and cost management) that FDM is best suited for printing milk vat insulation.

2.5. Analysis for designing new FDM materials

The construction of a new FDM machine is not a part of this PhD. However, it would be a logical approach, if a simple FDM setup for large-scale polymer 3DP is conceptualized in the light of section 2.4. This will assist to predict few of the properties required in the desired FDM raw material. That is why, an articulating based 3D pellet extrusion machine is conceptualized in Figure 25 and all the subsequent research will be planned while considering this setup. This pellet 3D printer will have the nozzle diameter of 8-10 mm. As the nozzle is of large diameter, the material's flowability will increase from the nozzle. That is why, it will be installed with cooling mechanism surrounding long nozzle to control the high flowability.

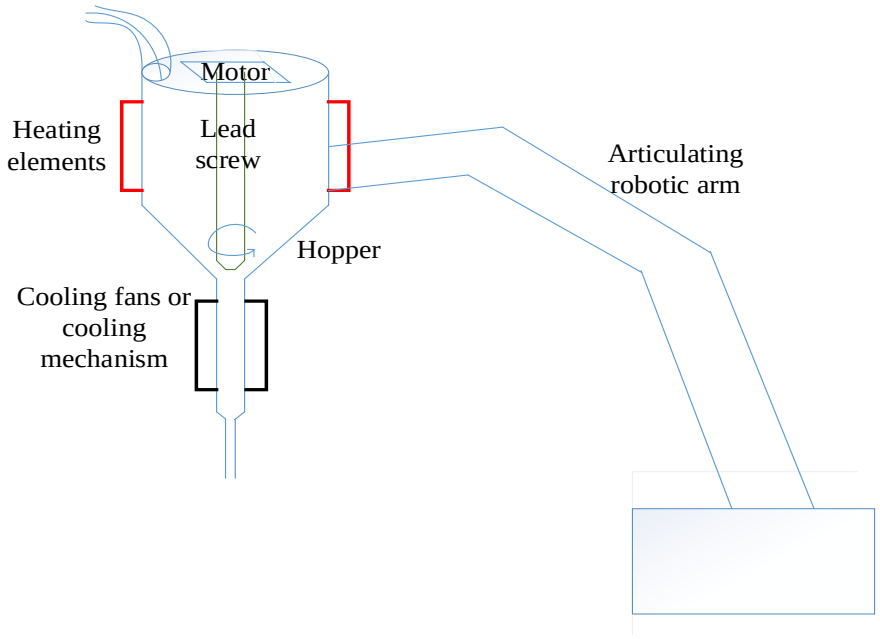


Figure 25. Conceptual 3D pellet extruder for largge scale products.

2.6. Cause and effect diagram

The current materials for FDM are designed for 3D printers with a nozzle of ≤0.6 mm and a smaller layer thickness. Meanwhile, the decision to go for IM materials need to consider that they are basically designed for IM setups. However, different material properties will be required for 3DP through a large diameter nozzle at large layer thickness. Therefore, it is needed to predict the required properties that will fulfill the processing and manufacturing essentials to 3D print from the conceptual large-scale pellet printer (Figure 8). In this regard, a "cause and effect" diagram is prepared to list a few main properties of materials that will be important for a big nozzle and large thickness extruded beads. The "cause and effect" diagram is shown in Figure 26.

The properties that are expected to vary for conceptualized pellet-based 3D printer are discussed below in the light of literature.

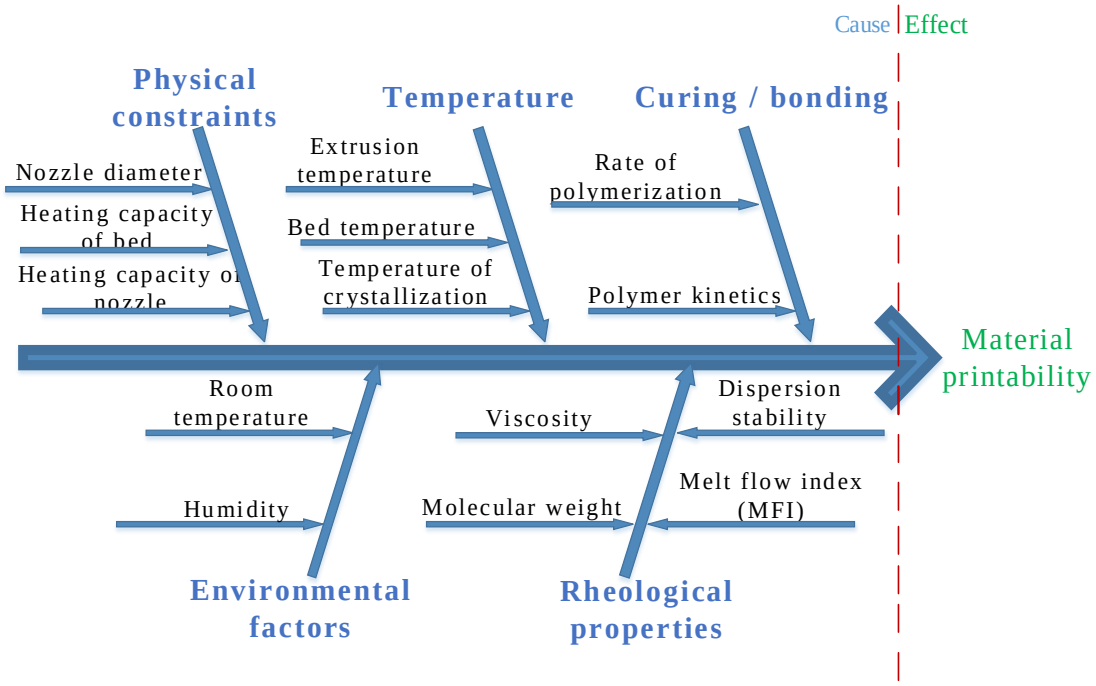


Figure 26. Cause and effect diagram for properties required in desired materials.

2.6.1. Temperature

The high temperature of crystallization will help to achieve better mechanical properties [243, 244]. The polymer is extruded out in melt form in injection moulding [243] and in semi-melt form in FDM [95, 115, 186]. Meanwhile, the material's cooling rate is rapid in FDM [245] that implies the crystallization starts early at as much high temperature as possible on cooling to allow good diffused joints among the extruded beads.

The reasonable high bed and in-process temperature can contribute by providing more time to filament to cool.

The extrusion temperature needs a careful consideration as too high extrusion temperature will lead to either degradation in worst scenario or uncontrollable melt flow to print.

2.6.2. Viscosity

The viscosity of injection moulding materials is low [246]. On the other hand, in FDM using 0.4 mm diameter nozzle the viscosity is required to be high [247]. However, in case of big nozzle of 8 mm, the viscosity should have to be higher than both the injection moulding and usual FDM to control the gravitational forces on the flow.

2.6.3. Molecular weight

High molecular weight provides high viscosity and good polymerization that also assists to overcome the polymer degradation due to the chain scission at high temperatures [82]. The extruded 3DP bead's thickness (5-8 mm) is aimed much larger by the conceptual FDM setup than the normal ones (0.1-0.4 mm). Therefore, more molecular weight is meant by more monomers that may cause better polymerization among thick beads.

2.6.4. Melt flow index

The MFI of injection moulding is high [246] as compared to one in usual FDM [247]. The reason is that the injection moulding requires high MFI to fill the complex small cavities [246] The MFI requires to be low for conceptual based FDM setup because the large diameter nozzle needs to have low flow rate of semi-melt material to overcome the gravitational effects.

2.7. Experimental work

Based on the literature, the experimentation for material development is performed in two parts as given below,

1. Thermal in-process treatment
2. Blends of polyolefins (Polyethylene and polypropylene).

The first part regarding thermal in-process treatment is published and the later one is in process of publication. These are provided in subsequent chapters.

Chapter 3. In-process thermal treatment of polylactic acid in fused deposition modeling

Chapter 3 includes the following article, “In-process thermal treatment of polylactic acid in fused deposition modeling” published in the journal of “Materials and Manufacturing Processes, Taylor & Francis”. According to the policy of Taylor & Francis, the article is republished with the permission from Taylor & Francis in this thesis.

The full text is included in the thesis without any modifications. However, there are formatting differences to keep the formatting same for the thesis. The formatting modifications involve page setup, font style, referencing style, reference citation style and bibliography style.

In-process thermal treatment of polylactic acid in fused deposition modeling

3.1. Abstract

Polylactic acid (PLA) is one of the most widely used open source fused filament fabrication materials due to its ease of extrusion, biodegradability, and mechanical strength. The mechanical strength of PLA largely depends on the proper growth of its semi-crystalline structure, which can be severely impaired by a low rate of crystallization, particularly in open source printers (e.g. UP02). This can be further aggravated by the non-uniform thermal distribution of heat that causes improper curing among the extruded beads of the printing material. As a result, PLA printed on open source printers does not achieve the best mechanical properties. This research, for the first time, proposes an additive-free solution implemented through a detailed set of experimentation to improve the curing rate through in-process temperature variations to cure the joints among the beads. The improvement in curing and crystallization is observed by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) respectively. The behaviour of the 3D printed PLA towards directional heat gradient through the shape of the beads and directional curing is also elaborated upon. Fourier transform infrared (FTIR) spectroscopy is used to confirm the improvements in the bead joints. This work is conducted in two phases of experiments. In the first phase, a full factorial ANOVA is used to investigate various process parameters and the important variables are used in the second phase to print test specimens in four different sets. Our results show significant improvement in the strength and ductility of the fabricated parts as compared to the parts printed on an unmodified printer.

Keywords

PLA; FDM; Thermal; Strength; ANOVA; SEM; DSC; FTIR.

3.2. Introduction

The revolution in additive manufacturing (AM) or three-dimensional printing (3DP) [248] was initiated in the late 1980's with the breakthrough invention of stereolithography and the

development of fused deposition modeling (FDM) in the early 1990's [11]. These technologies create 3D parts in a layer-by-layer process which was perceived to be successful in the research community in terms of geometric accuracy [11]. However, the use of these technologies remained limited to rapid prototyping [11] applications for a long time and the concept itself remained in oblivion due to its inability to find a way to penetrate into the regime of the mass production of the 90's [249]. Thereafter, rapid prototyping techniques were able to find a rationale of economies of scale achieved through mass customization [250] rather than mass production, along with their excellent ability to fabricate complexities in design with higher geometric accuracy [251]. This finally allowed the rapid prototyping technologies to be a part of main stream production setups in automotive and aerospace industries and SMEs [252].

Open source (OS) printers played a significant role in bringing 3DP to common users in the last decade or so, starting from the introduction of RepRap, which led to further developments and contributions through online uploads of assembly details of various OS printers [253-255]. Currently there are numerous OS printers that are supported by communities and contributors and the term has evolved into fused filament fabrication (FFF) rather than the equivalent commercial term FDM [249]. The increasing use of OS FFF is evident from the increased numbers from four to 4500 units from 2008 to 2011 [254]. Even the other OS printers derived from RepRap, like MakerBot, have registered sales of more than 13000 units since 2009 [95]. The price of OS printers has dropped drastically to as low as $1500.0 [95] and this has supported a rise in the uptake of these machines, which in turn has created a concept of distributed digital manufacturing at mass scale [254, 255]. Further, these printers make their mark in practical fields like the fabrication of toys, tools, household items and a few scientific instruments [95]. However, the OS printers are not free from problems and limitations in comparison with commercial-scale 3D printers [256], e.g., minimum accuracy of not more than 0.1 mm and limited capability of printing acrylonitrile butadiene styrene (ABS) [257-259], polylactic acid (PLA) and their modified variants only [95]. Another facet is the variations in the properties of the printed parts [95] as compared to the ones printed on the commercial printers like Stratasys [260] Fortus 250mc. The variations in the mechanical properties have been reported by numerous researchers [92].

PLA is one of the most preferred materials in the open source printers due to its mechanical strength, reasonably low melting temperature [261], medically safe [262], availability and cost. The literature on PLA printing reports investigation into many aspects like tensile, impact and flexural strength due to variations in the control parameters e.g. infill percentage, printing speed, bed temperature, build orientation, layer thickness (height), extruding temperature,

hatch spacing, etc [142]. The variation in tensile strength and modulus of elasticity of PLA due to printing on different OS printers, experimented with the same set of layer thickness and build orientation has been reported. Furthermore, different extruding and bed temperatures can lead to differences in tensile strength [82]. Another research on printing PLA by customized OS printer revealed the effect of the number of shell perimeters, orientation and layer thickness on tensile strength and strain. It was specifically noticed that an increase in the number of shells in the perimeter increases the strength [140]. The increasing infill percentage and flat (XY) build orientation was observed to produce good mechanical strength at fracture for PLA parts [88]. The literature also reported that the impact strength declined with an increase of layer height and bed temperature [82]. The change in the colour of the printed parts can also become another sign to analyze tensile strength and modulus of elasticity. The effect on colour is attributed to the extrusion temperature of the nozzle.

PLA is also highly credible for its biodegradability [261, 263, 264], renewability and low greenhouse gas emissions [265, 266]. It is made from dimers of D-Lactide acid or L-Lactide acid [266] produced through the fermentation of starch obtained from plants like wheat or corn [267]. The percentage of D-lactide (0.5 to 12%) in the dimer affects the rate of crystallization and degradation properties [267]. The best crystallization can be achieved from low D-lactide contents [266, 267]. Even with the lowest optimal contents of D-lactide, the PLA shows a very low rate of crystallization and low crystallinity temperature of 50 °C [268]. This lowers the growth of a semi-crystalline structure in the amorphous matrix. Therefore, various hardeners and plasticizers are added as nucleating agents to enhance the rate of crystallization [269]. The rate of crystallization can also be improved by in-process and post-process heat treatments [150]. While post process techniques have been reported to improve the properties of the printed parts in FDM [266, 270] in-process techniques have not been explored in OS printers for PLA.

In this research we report an additive-free manufacturing process to improve the rate of curing (crystallinity) at the joints among the beads through modifications in the OS FFF setup. We subject PLA during the printing process to a continuous heat transfer in three different directions. Our work is based on the premise that the joining of the intercalated layers depends on the shape of the beads, directional thermal effects, and diffusion among the beads. This research is conducted in two phases. In Phase 1, full factorial (with blocks) ANOVA is used to scrutinize the most influential control variables in the PLA printing process. The main variables considered are: 1) print speed, 2) bed temperature, 3) surface layers (boundary layers) and 4) location of printing on the bed of the OS printers. The variables found as insignificant in Phase

1 are kept as constants for the Phase 2 experiments. The experiments of Phase 2 involve: 1) layer thickness, 2) bed temperature and 3) ambient temperature as variables. They are then followed by the results of average tensile strength and elongation at break. The detailed SEM analysis is presented at the end to support the results achieved due to in-process thermal treatment. We also confirm the presence of strong bonds between beads through differential scanning colorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy.

3.3. Materials and Methods

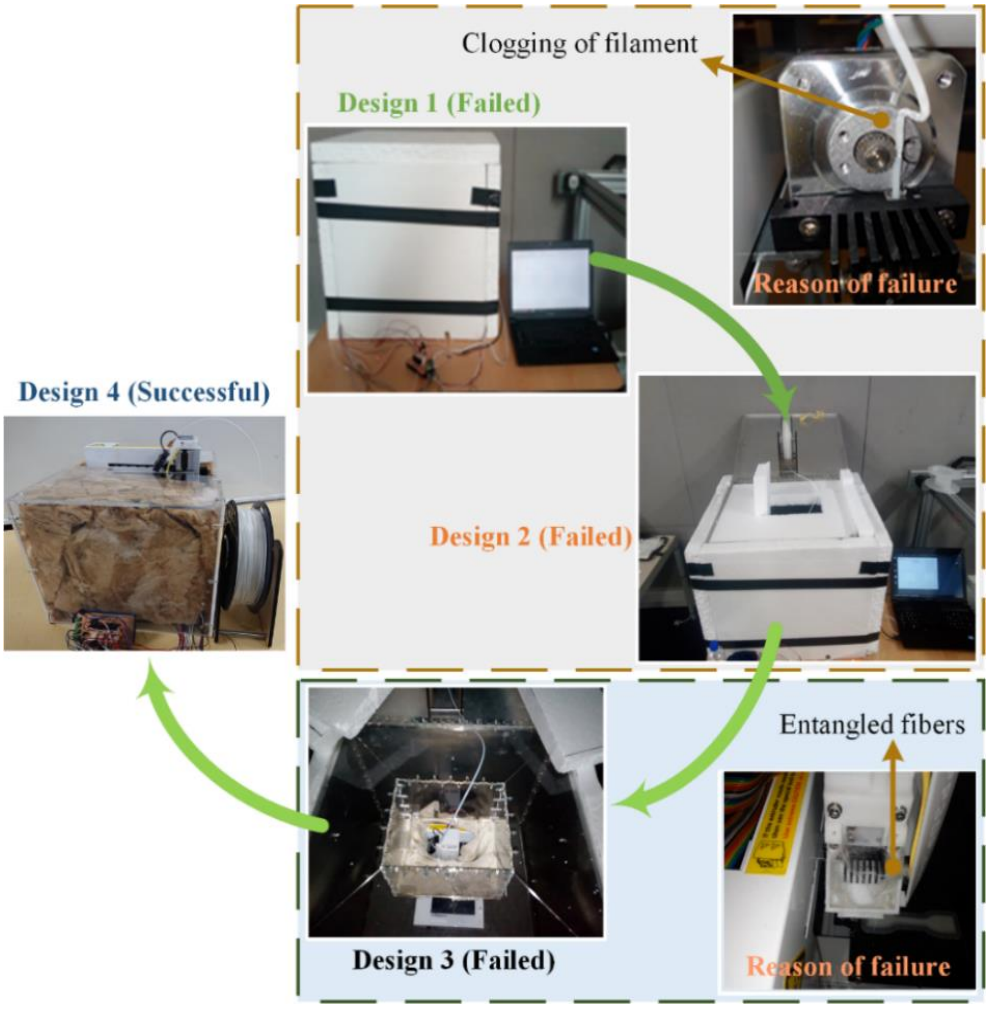


Figure 27. Various heating box designs for UP02 printer. Design 1 and 2 failed due to clogging of the filament and design 3 failed due to the entangled insulation

A new UP02 printer was procured for this work to minimize the possible variations in printing due to any inaccuracies associated with worn parts in old printers. Genuine white UP PLA filament of 1.75 mm diameter was used for the experimentations. The filament was preserved in air-tight plastic bags between the breaks to avoid humidity effects.

As the OS printers do not come with heated chambers, it is necessary to build a chamber or a box around the printer to control the ambient temperature. In our first design as shown in Figure 27, we used a closed aluminum box with a hinged lid to enclose the printer. Four inductive heating pads were installed on the inner side of the four walls of the box. For a uniform air temperature, a fan was also installed inside the box to circulate the heated air. Eight temperature monitoring sensors (LM317) were installed on all four sides in pairs and through a PID loop the temperature of the inside was controlled to the specified levels. However, this setup did not work well due to heating of the filament before entering the extruder head and causing clogging of the PLA inside the extruder head (Figure 27). Later, the lid of the box was partially opened in design 2 and the spool was also placed outside the box (Figure 27). However, this arrangement also failed to carry out proper printing of PLA dog-bones and caused the similar problem of clogging as was encountered in design 1. In the third attempt, an acrylic lid was designed that had vertical edges protruding downwards and mineral wool wrapping in the opening to prevent the hot air from circulating around the printing head. But this design also failed due to the entangling of the fibres of mineral wool in the fan as shown in Figure 27.

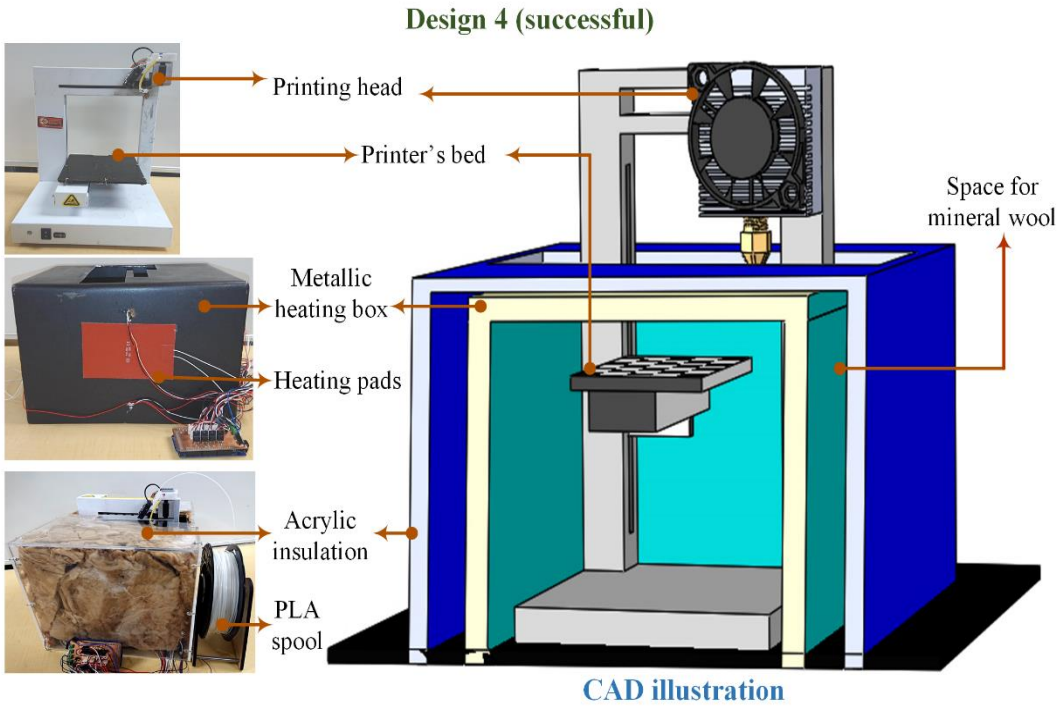


Figure 28. Layout of the successful heating box design (design 4) and the CAD illustration of the whole printing system.

Learning from the failed designs, design 4 as shown in Figures 28 was conceived in which the printer was placed inside a cast iron box leaving the print head outside. The box was covered with mineral wool and an outer acrylic box. In this design, as the print head stayed outside the heating chamber, the problem of pre-heating of the filament and later clogging inside the head was overcome. A PID loop similar to the one stated above was used for this chamber to control the temperature. A total of eight temperature sensors (LM317) were mounted on the inside of the four walls and read through a microcontroller (Arduino Mega 2560). The heating pads were also controlled from the Arduino board. A program developed in C-Sharp was used to set the temperature and monitor the progress of the closed loop heating system. This setup can maintain the desired temperature inside the box automatically with an accuracy of $\pm$2 °C. The temperature of the box was measured with a thermometer to quantify the measurement accuracy.

ATSM D638 type IV specimen is used to study the mechanical properties of the printed PLA. The CAD models of the specimens were drawn in SolidWorks 2017 and saved in STL format. We used UPStudio, control and monitoring software that comes with UP printers, for setting the parameters of the printer. The experiments were performed in two phases: Phase 1 involving identification of the process parameters through ANOVA on parts printed with an unmodified printer, and Phase 2 consisting of a detailed analysis of the parts based on the parameters found in Phase 1.

The following process control variables were analysed in Phase 1 using 2^3 full-factorial design of experiment (DoE) with blocks at 95% confidence level: print speed, bed temperature, surface layers (boundary layers) and printing at centre/side location with respect to the bed heating element. A full list of process parameters for Phase 1 of the experimentation is provided in Table 9. Each process variable was analysed at two levels. The printing location of the parts are considered as “blocks” as shown in Figure 29a. Five specimens were printed for each combination of parameters and their averages of tensile strength and elongation were used as input for 2^3 full-factorial analysis in MINITAB 17. As the optimal crystallinity has been reported for an extrusion temperature of 210 °C for PLA in the literature [271], we fixed the extrusion temperature to this value for all experiments. Similarly, natural white filament is chosen due to its highest crystallinity and good tensile and yield strength [271]. The layer thickness was also kept constant at 0.2 mm as the literature had reported reliable results [140], even optimal in some cases as well [95].

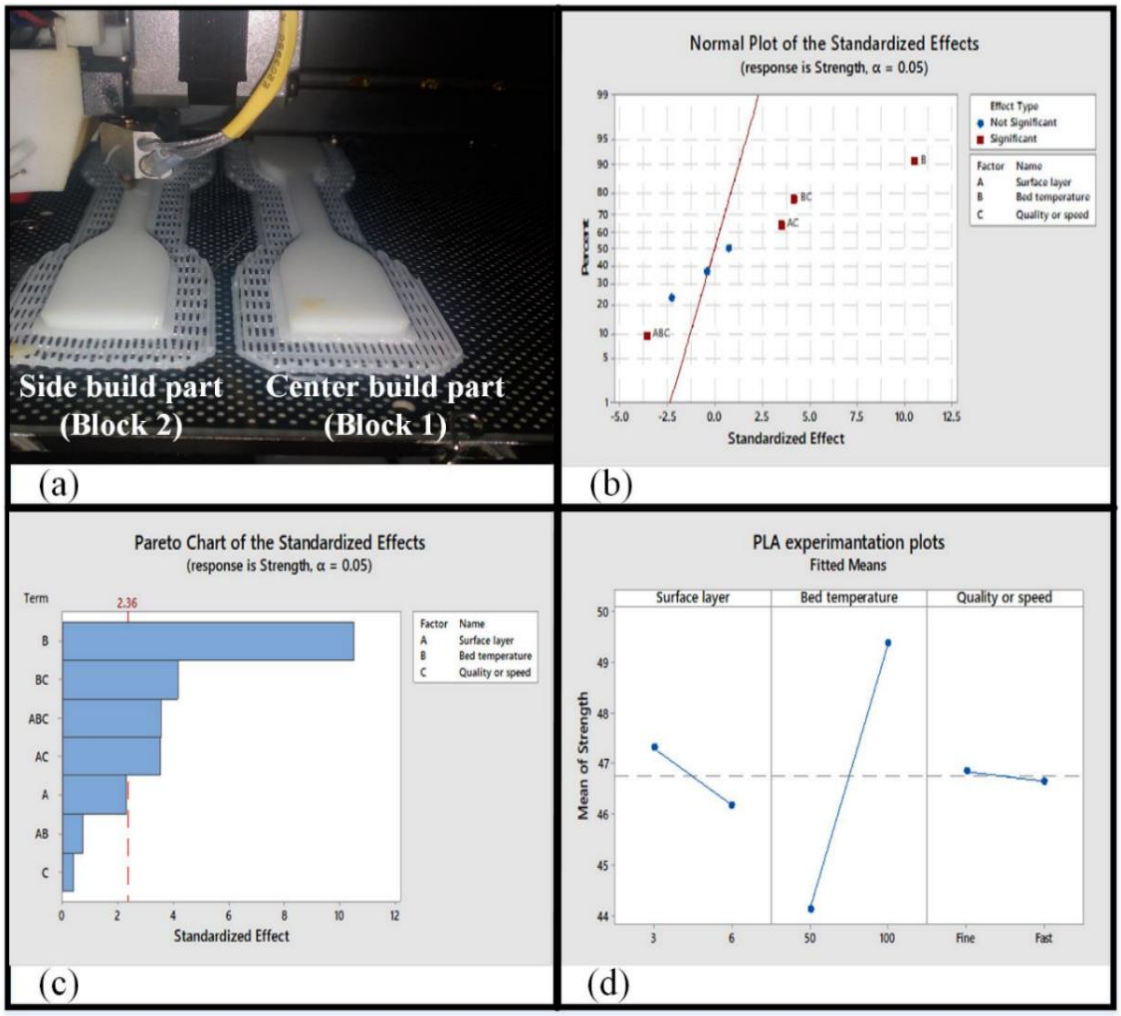


Figure 29. Identification of process parameters through ANOVA. (a) Blocks in ANOVA, (b) Normal plot, (c) Pareto chart, and (d) Main effect plot.

The ANOVA shows that the bed temperature is the significant "main effect" to affect the average tensile strength as shown in Figures 29b and 29c. Other parameters - print speed, surface layers and location of the printing part on the bed - are insignificant with the P-values of 0.056, 0.701 and 0.084 respectively. The results are shown in the normal plot, Pareto chart and main effect plots in Figures 29b, c, and d respectively. This provides a statistical reason to select the bed temperature as a variable and the remaining insignificant parameters as constants for further experimentation in Phase 2.

Table 9. Process parameters for Phase 1 experimentation.

	Parameter	Set value [with references]
Constants	Build orientation	Flat [142]
	Nozzle diameter	0.4 mm [92]
	Extruding temperature	210 °C [271]
	Layer thickness	0.2 mm [36]
	Layer orientation	45°/-45° [95]
Variables	Surface layer	3 layers
		6 layers
	Bed temperature	50 °C
		100 °C
	Quality or printing speed	Fine (slow)
		Fast
	Build location on bed	Center (right below the heating element)
		Left side from center

Phase 2 of experiments utilizes the build parameters identified in Phase 1. The modified design of the printer (as shown in Figure 28) is used in this phase. Initially, the bed and the ambient temperature were experimented with between 30 °C and 100 °C. However, some dimensional inaccuracies were found at a temperature of 100 °C and the parts were not sticking to the bed at a temperature of 30 °C. Therefore, to eliminate the effects of incomplete printing, an allowable temperature range of 40 °C to 80 °C was selected. The number of surface layers was kept at three following on Phase 1 results due to the insignificance in ANOVA. This phase consisted of four cases and a total of 180 samples. Table 10 contains the details of the parts. These samples were printed in approximately 114 hours in about a month.

Table 10. List of experiments for Phase 2. Case 1 corresponds to the same ambient and bed temperature. Case 2 refers to variated ambient temperature and constant 50 °C bed temperature. Case 3 refers to variated bed temperature and fixed room temperature. Strain rate of 0.2 mm/mm/min and 0.8 mm/mm/min are used for cases 1-3 and case 4, respectively.

Layer thickness (mm)	Case 1 (and 4*)		Case 2		Case 3	
	Ambient temperature (ºC)	Bed temperature (ºC)	Ambient temperature (ºC)	Bed temperature (ºC)	Ambient temperature (ºC)	Bed temperature (ºC)
0.2	40	40	40	50	Room temperature (22 ºC)	40
	50	50	50	50		50
	60	60	60	50		60
	70	70	70	50		70
	80	80	80	50		80
0.4	40	40	40	50		40
	50	50	50	50		50
	60	60	60	50		60
	70	70	70	50		70
	80	80	80	50		80

Instron 5967 with 30 kN load cell and a clip-on strain gauge extensometer (25 mm length) was used to test the tensile strength of the printed ASTM D638 type IV specimen. Each set of experiments was performed for five times to get the average of the overall readings of ultimate tensile strength (UTS, MPa) and elongation at break (mm). The rate of strain for tensile testing for cases 1 to 3 was 0.2 mm/mm/min and 0.8 mm/mm/min for case 4.

The fractured surface of the tensile test specimen was analysed on a Hitachi TM3030 Plus scanning electron microscope (SEM). Details pertaining to the different types of the effects on the joints of beads, shape of beads, voids and directional curing of beads are key aspects which are visually analysed in SEM analysis.

The DSC analysis was performed on TA DSC Q1000 and areas of particular sections are measured in ImageJ 1.52a. The analysis is performed at nitrogen purge flow of 50 mL/min with the heating rate of 10 °C/min. The range of temperature for analysis was -10 °C to 250 °C.

The FTIR spectrum was recorded using Attenuated Total Reflection (ATR) Single Reflection accessory of a Thermo Electron Nicolet 8700 FTIR spectrometer. The spectra were obtained in the range of 400-4000 cm^{-1} with resolution 4 cm^{-1} and averaged over 32 scans. Standard software (Omnic ESP, version 7.1) was used for data acquisition and analysis.

3.4. Results and discussions

The results for this case 1 (same bed and ambient temperature) are shown in Figure 30. The highest stress for this case, at a layer thickness of 0.2 mm, is observed to be 53.1 MPa at 40 °C. However, all of the rest of the measurements are above 46 MPa except for the lowest value at 60 °C. It is further noticeable that the printing at high ambient temperatures of 70 °C and 80 °C provides near 50 MPa for 0.2 mm and 41 MPa for 0.4 mm layer thickness. Nevertheless, the increase of layer thickness corresponds to low average tensile strength.

The average elongation at break for case 1 is found to be high for 0.2 mm layer thickness followed by 0.4 mm. The highest average elongation occurs at 60 °C, i.e., 2.51 mm. The standard deviation provides information about the range of variability at each temperature for average elongation. The highest upward positive standard deviation of 3 mm is recorded for 60 °C at 0.2 mm layer thickness. The results of 0.4 mm layer thickness are associated with large ranges of standard deviation, particularly at 40 °C and 50°C as observed for case 1 in Figure 30.

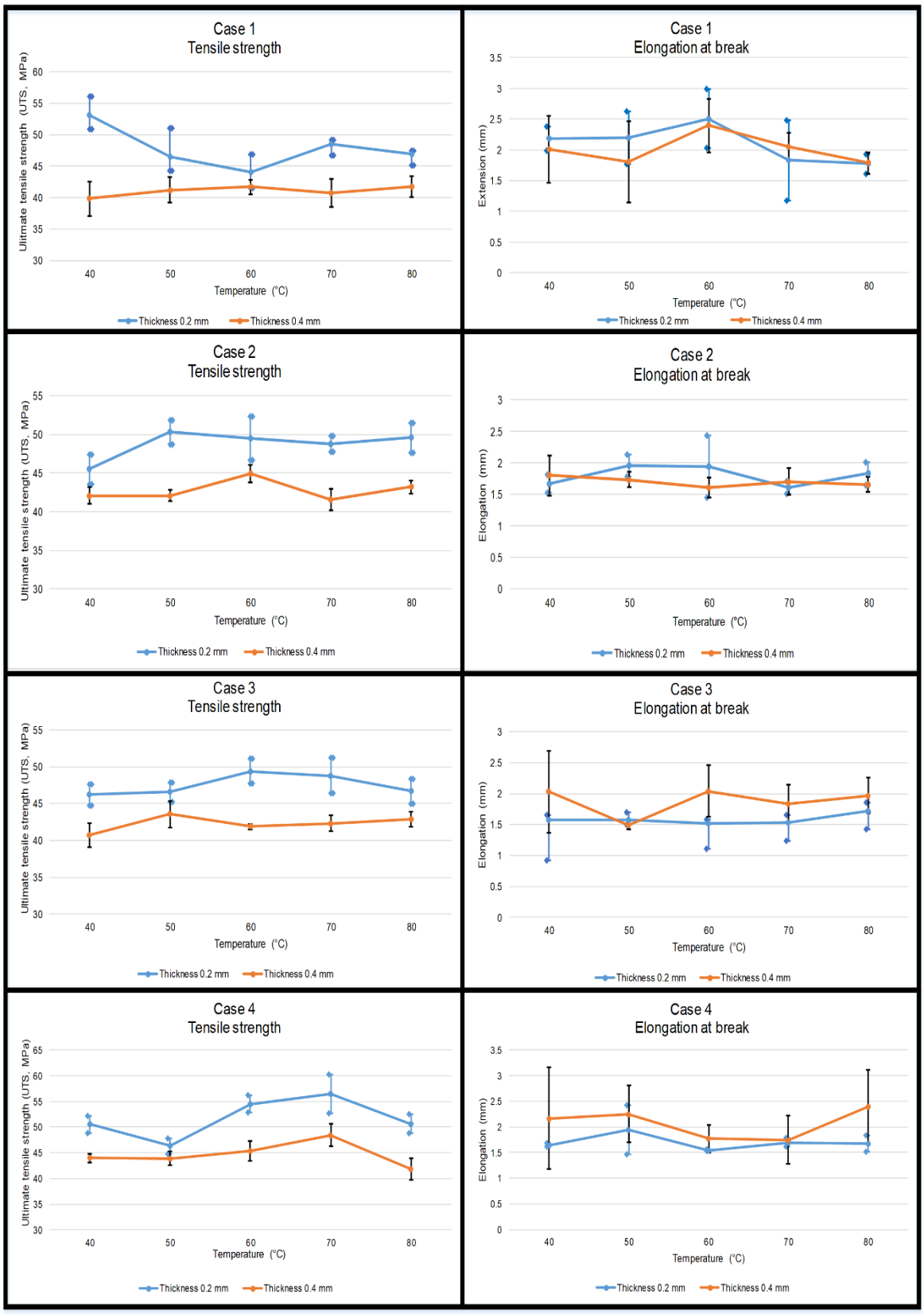


Figure 30. Average ultimate tensile strength (UTS, MPa) and average elongation at break for cases 1, 2, 3 and 4.

The PLA characteristics in case 1 for 0.2 mm layer thickness are inclined towards either strength or elongation. The tensile strength from 40 °C to 60 °C keeps on decreasing, while the elongation keeps on increasing. The opposite case is observed from 60 °C to 70 °C, where the strength is increased, and elongation is decreased. Hence only one property is achieved at the expense of the other up till 70 °C. The contradiction starts showing up from 70 °C onwards, showing decreasing strength with decreasing elongation. This contradictory behaviour is analysed later in the SEM analysis.

The results of tensile strength for case 2 are provided in Figure 30. At all temperatures except at 40 °C, consistent UTS of about 50 MPa is observed for 0.2 mm layer thickness. However, the increase in layer thickness to 0.4 mm causes the tensile strength to decrease as compared to 0.2 mm. The results at 0.4 mm are also consistent as all values of average ultimate tensile strength are near to 43.0 MPa. The range of standard deviation at all temperatures is small enough to predict less variability among the various samples tested at the same parameters (i.e., ambient temperature and layer thickness).

The average elongation at break for case 2 at 0.2 mm layer thickness as shown in Figure 30 is 1.96 mm and 1.94 mm at 50 °C and 60 °C, respectively. It is observed that the elongation at break is less for ambient temperatures of 70 °C and 80 °C for 0.2 mm layer thickness. The samples with layer thickness of 0.4 mm exhibit almost consistent elongation hovering around 1.65 mm.

In case 2, the nature of results for 0.4 mm layer thickness is similar to case 1, i.e., strength increases while elongation decreases and vice versa. However, the consistent tensile strength with a similar trend of elongation at 0.2 mm layer thickness is also observed.

Referring to case 3 in Figure 30, there is high tensile strength for layer thickness of 0.2 mm as compared to 0.4 mm. However, the consistency of UTS at different bed temperatures is not as uniform as observed in case 2. The highest tensile strength for 0.2 mm layer thickness specimens is 49.4 MPa at 60 °C followed by 48.8 MPa at 70 °C. The decrease in tensile strength up to 46.7 MPa is also noticed at high bed temperatures of 80 °C for 0.2 mm layer thickness.

The average elongation for the 0.2 mm layer thickness specimen in Figure 30 in case 3 seems to be uniform as it stays about 1.5 mm at all bed temperatures except at 80 °C. The average elongation plot shows large elongation for the 0.4 mm specimen as compared to 0.2 mm. The specimens printed with 0.4 mm layer thickness show non-uniform standard deviation as well.

The tensile testing of case 4 is performed at a high strain rate of 0.8 mm/mm/min. The highest average UTS of 56.4 MPa is achieved at 70 °C for 0.2 mm layer thickness (Figure 30).

However, an individual value of above 60 MPa is also prominent. This case depicts comparatively high average UTS as compared to cases 1-3 at 60 °C, 70 °C and 80 °C. The UTS achieved at 0.4 mm layer thickness is less than that at 0.2 mm, but the values achieved are still higher as compared to any one of the three cases at layer thickness of 0.4 mm that are described earlier.

The average elongation at break for case 4 at 0.2 mm is less than that of 0.4 mm layer thickness. In comparison with the other three cases, the results appear as the 2nd overall highest average elongation at 0.2 mm layer thickness. This proves that the thermally treated PLA structure behaves positively to increasing strain rates.

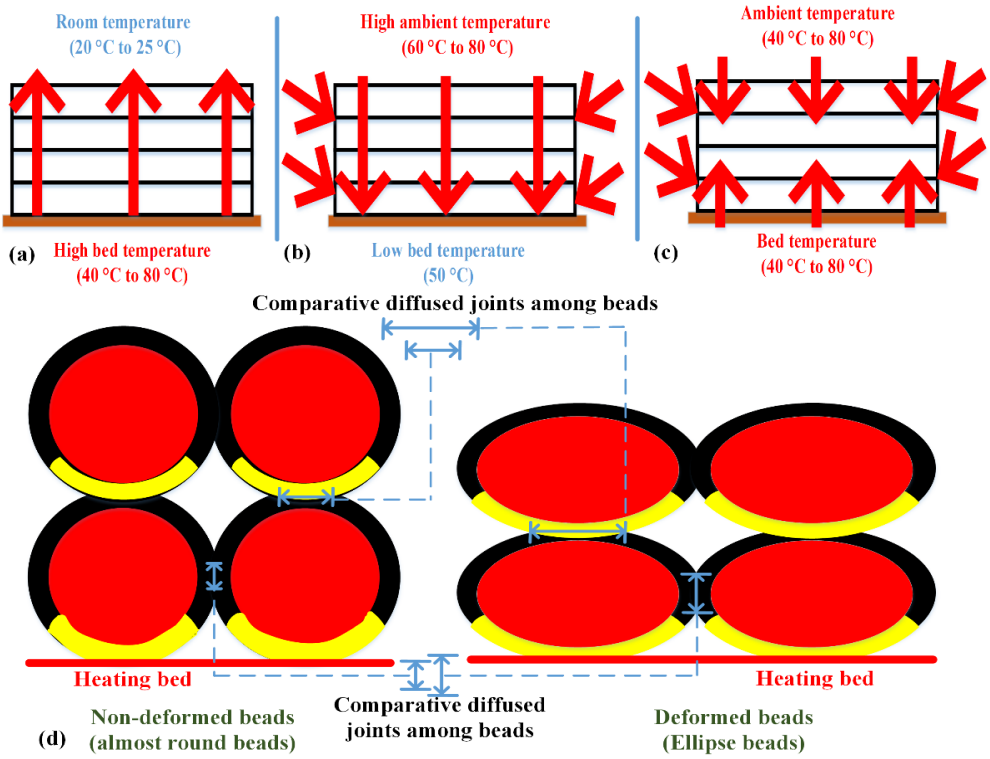


Figure 31. Illustration of types of directional heat transfer (a) high bed temperature, (b) high ambient temperature, (c) same ambient and bed temperature and (d) comparison of joining among beads.

Before moving on to discuss the results in the light of fractographic analysis, several of the observations are important to illustrate. Phase 2 includes a detailed set of experiments to analyse the thermal effects of same or different ambient and/or bed temperatures on the quality of the build parts. In this regard, three types of heat transfer are observed, as illustrated in Figure 31a-c. The direction of heat transfer is dependent on the highest temperature source (ambient or bed). This will lead to different thermal effects on the quality of the build parts. Moreover, the quality of printed parts is also dependent on the diffusion at the joints among the beads that

is dependent upon the shape of beads. Based on observation in the SEM analysis, two kinds of shapes of beads are formed, i.e. nearly round shape or elliptical shape. It is also observed that the joining area among elliptical beads is greater due to the greater overlapped surface area as illustrated in Figure 31d. Deformed beads have less voids as compared to well-maintained round beads. Therefore, the fractographic analysis includes information regarding three observations: 1) shape of beads and nature of overlapping, 2) voids and 3) directional heat transfer effect of high bed or ambient temperature on upper/lower sections of particular beads.

The SEM images in Figure 32 show that the shape of beads becomes better (round) for all cases (1, 2 and 3) as the temperature is raised from 40 °C to 70 °C. However, at 80 °C, the beads again begin to show minor deformation. The reason for minor deformation at 80 °C may be attributed to the high temperature that makes the PLA soft enough to start deforming. The effects of high temperature are evident as observed in the yellow ellipse at 80 °C for case 1 and in the red ellipse for case 2.

It is also observed in Figure 32 that the more deformed beads cause less voids as observed at lower temperatures (40 °C and 50 °C) for all three cases. However, the voids increase as the beads improve roundness in shape at higher temperatures (from 60 °C to 80 °C).

Case 1 in Figure 32 shows comparatively better bead shape as compared to cases 2 and 3 at high temperatures as marked in green ellipse at 60 °C and green rectangle at 70 °C for case 1.

The deformed beads (ellipse shaped) lead to a large overlapping of surfaces as observed at 40 °C and 50 °C for all three cases. The green and blue ellipses in Figure 32 are marked for case 2 and in red rectangle for case 3 to highlight the joining among beads at 40 °C. The large overlapping of beads as explained in Figure 31d causes good tensile strength of 53.1 MPa for case 1 at 40 °C as presented in results (Figure 30).

The directional thermal effects as illustrated in Figure 31a-c are evident from the level and placement of comparative localized curing among the beads. It is noticed in case 2 at 60 °C in Figure 32 indicated by yellow arrows, that the curing on the upper section of different beads is more as compared to the curing at the lower section of the same beads. This is the evidence of directional thermal processing through high ambient temperature. The effects of high ambient temperature are more visible at 80 °C for case 2, specifically in the upper layers, on the upper section of the beads as marked by red ellipse (Figure 32). On the other hand, the effects of higher bed temperature in case 3 are also more prominent in lower layers at 70 °C and 80 °C than can be noticed in the upper layers of the SEM images in Figure 32. Meanwhile, case 1 appears to be unique among all the thermal effects noted earlier because a similar nature of

curing is observed in the upper and lower sections of each bead, and particularly in the middle section of the SEM images in Figure 32. However, in each of upper and lower two to three consecutive layers of case 1, the build parts at 70 °C and 80 °C do show clear effects of direct exposure to high temperature as they seem to be melt joint in their upper and lower layers. Therefore, the directional effects of heat are vividly proven to cause specific changes in the mechanical properties.

The SEM images of 0.4 mm layer thickness for cases 1 and 3 are shown in Figure 33. It is observed that the beads in case 1 suffer an increase in softening as the temperature approaches 80 °C. The softening effect is confirmed by the grooves and long protruded beads after fracture. The protruded beads become similar looking at 80 °C for case 1. The elongated beads resemble the 0.2 mm layer thickness SEM images of Figure 32 at 80 °C, where the grooves and elongated beads after fracture were prominent.

On the contrary, case 3 also experiences a softening effect, but it is not as severe as in case 1 (Figures 32 and 33). This is evident from the SEM images at 80 °C, where the beads after fracture are less elongated as compared to those in case 1. The effect of higher bed temperature (upward heat transfer) is also evident as the beads in the lower layers in case 3 protrude more as compared to the upper layers. However, case 1 is found to have more longitudinal elongated beads in both upper and lower layers due to the similar bed and ambient temperature. This also explains the reason for less elongation in case 3 and relatively more elongation in case 1 as provided in Figure 30.

The shape of beads is hard to distinguish in cases 1 and 3 at different temperatures for 0.4 mm layer thickness in Figure 33. The beads are able to maintain their shape in case 1 at the extreme temperature of 80 °C. Even at the low temperature of 50 °C in case 1, the beads in the lower layers have a relatively well-maintained shape as compared to the middle layers. This is an opposite behaviour as compared to deformed beads for lower layer thickness (0.2 mm) at lower temperatures of 40 °C and 50 °C. In case 3, the bead shapes are the same at all temperatures. The voids are big in both cases 1 and 3 at all temperatures. This is also shown in the magnified images in Figure 33 and is a reason for less strength at 0.4 mm layer thickness as compared to 0.2 mm.

The directional thermal effects in terms of diffusion are hard to differentiate in Figure 33 for both cases. The reason is the insufficient time (~21 minutes) and large layer thickness (0.4 mm) that provides less time for heat to penetrate during the fabrication through layers. This leaves the parts unaffected by the non-uniform heat contents.

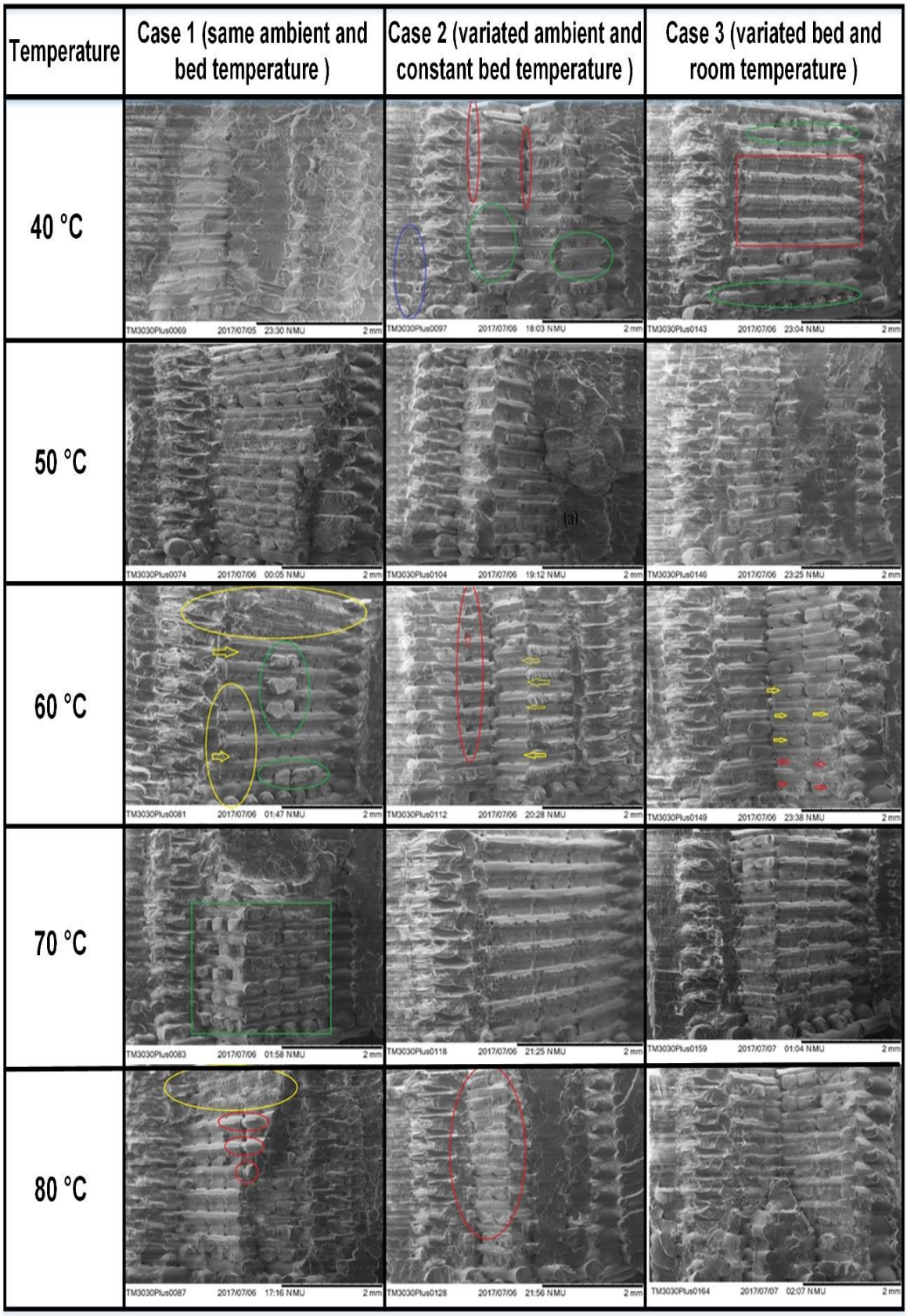


Figure 32. Comparison of 0.2 mm layer thickness fractured parts for cases 1, 2 and 3 in Phase 2 experimentation.

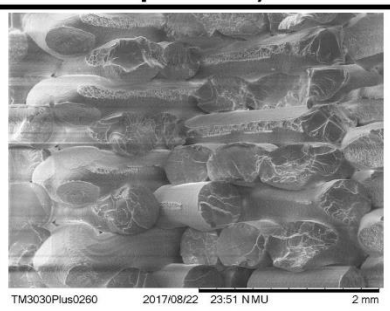
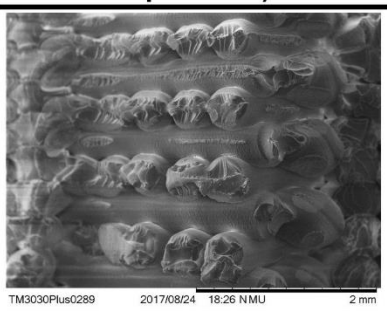
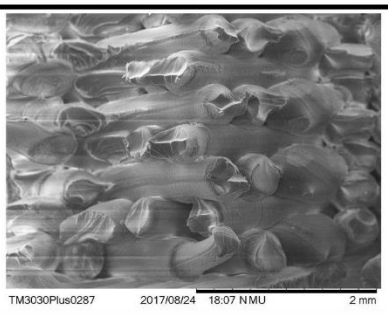
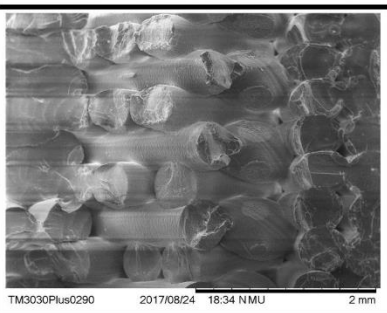
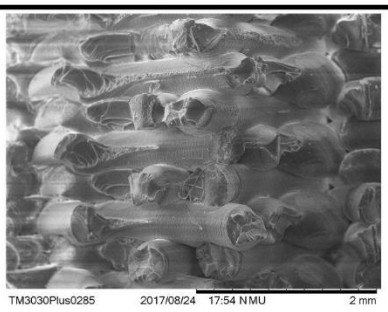
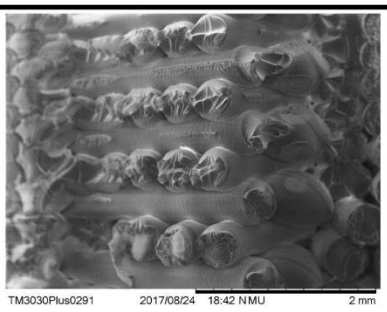
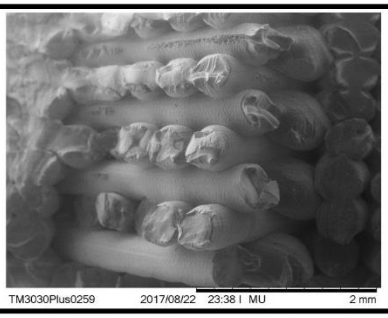
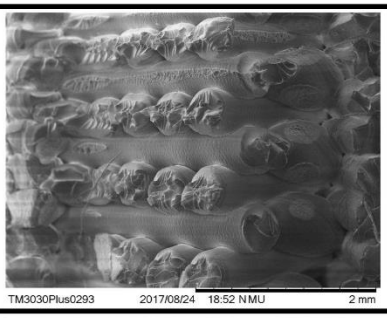
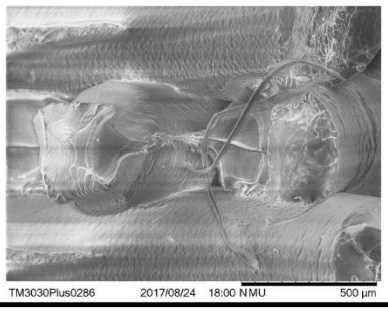
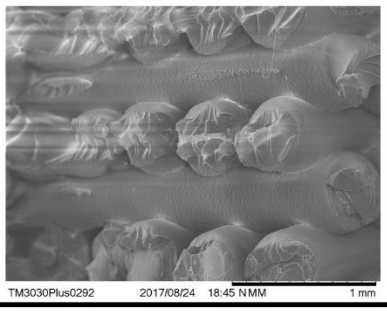
Temperature	Case 1 (Same bed and ambient temperature)	Case 3 (Variable bed and room temperature)
50 °C		
60 °C		
70 °C		
80 °C		
70 °C Magnified image		

Figure 33. Comparison of SEM images at 0.4 mm layer thickness for cases 1 and 3 in Phase 2 experimentation.

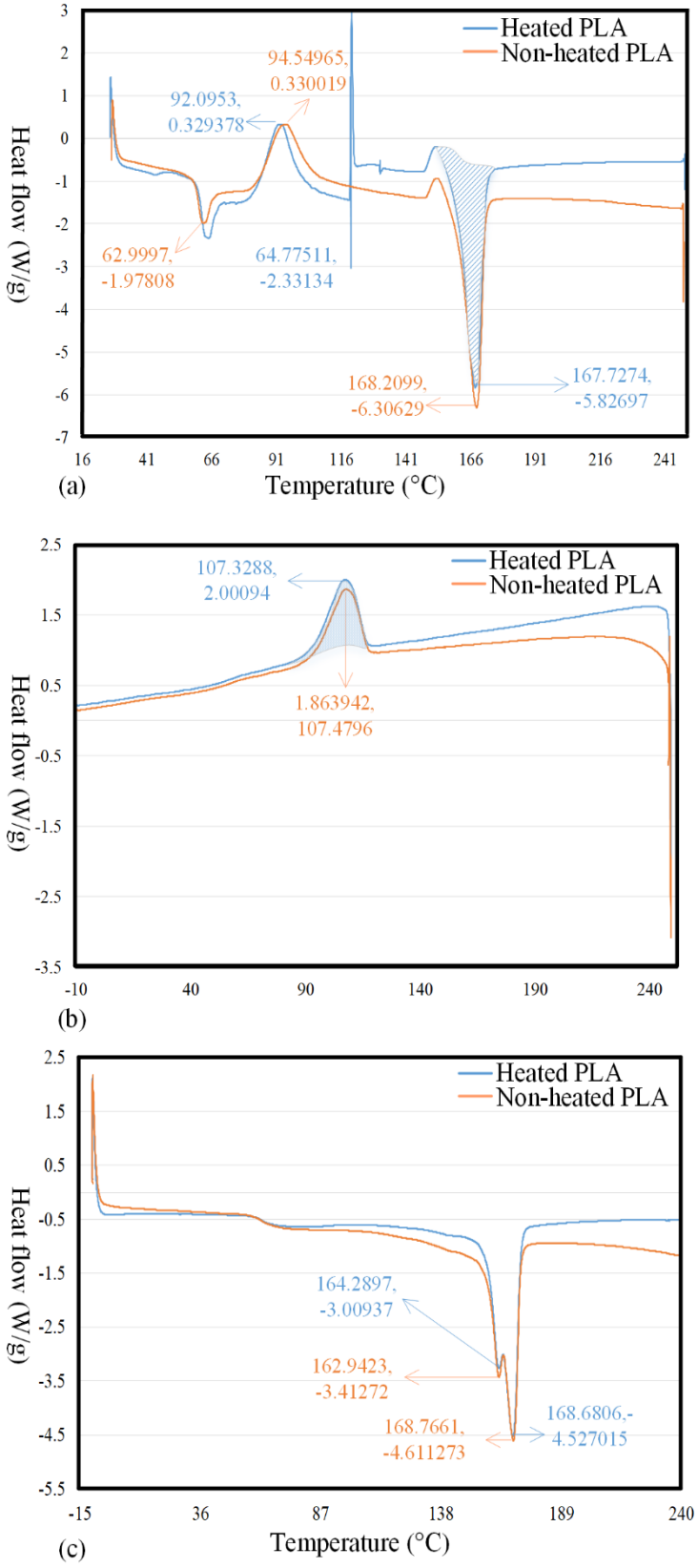


Figure 34. Differential scanning calorimetry (DSC) analysis of heated PLA at 80°C (case 1) and non-heated PLA at 50°C (case 3). (a) First heating run, (b) cooling run, (c) second heating run.

Differential scanning calorimetry analysis of first heating curve in Figure 34a shows a forward shift of glass transition temperature (T_g) for heated PLA compared to the non-heated PLA. The endothermic peak is like the one reported in the literature [142]. However, it appears at a higher temperature and heat flow for heated PLA. The forward shift is due to the in-process heat treatment providing sufficient mobility to the chains to orient in an arrangement that becomes resistant to further mobility at a temperature lower than 64.78 °C. The early on-set of crystallization in melting peak at a higher heat flow (0.1993725 W/g) and average ~10.8% (0.694 cm^2) more area of melting peak for heated PLA shows the presence of more crystallites. This is attributed to the high ambient and bed temperature that restricts the material from cooling rapidly as reported in the literature [142], which helps to align the chains in more regular crystalline clusters. More crystallinity allows the heated PLA to show good ductility and reasonable strength at an ambient and bed temperature of 80 °C as compared to non-heated PLA.

The DSC cooling run shown in Figure 34b of heated PLA is noticed at the higher heat flow. The cold crystallization occurs at higher heat flow (2.00094) with a ~10.2% (0.27 cm^2) larger area of the peak for heated PLA compared to non-heated. This associates comparatively more crystallization with heated PLA that also explains why the prints have better mechanical properties at 70 °C in the case 1 experimentation.

The DSC second heating run observed with two overlapping peaks is shown in Figure 34c. This shows the two types of crystallites with different orientations packed in one cluster [272]. It is also observed that the area under the heated PLA multi peak is more than non-heated. This again indicates more crystallization in the case of heated PLA, leading to better mechanical properties.

The DSC results show clearly that the crystallization is improved through thermal in-process treatment that helps to achieve good mechanical properties of tensile strength and ductility.

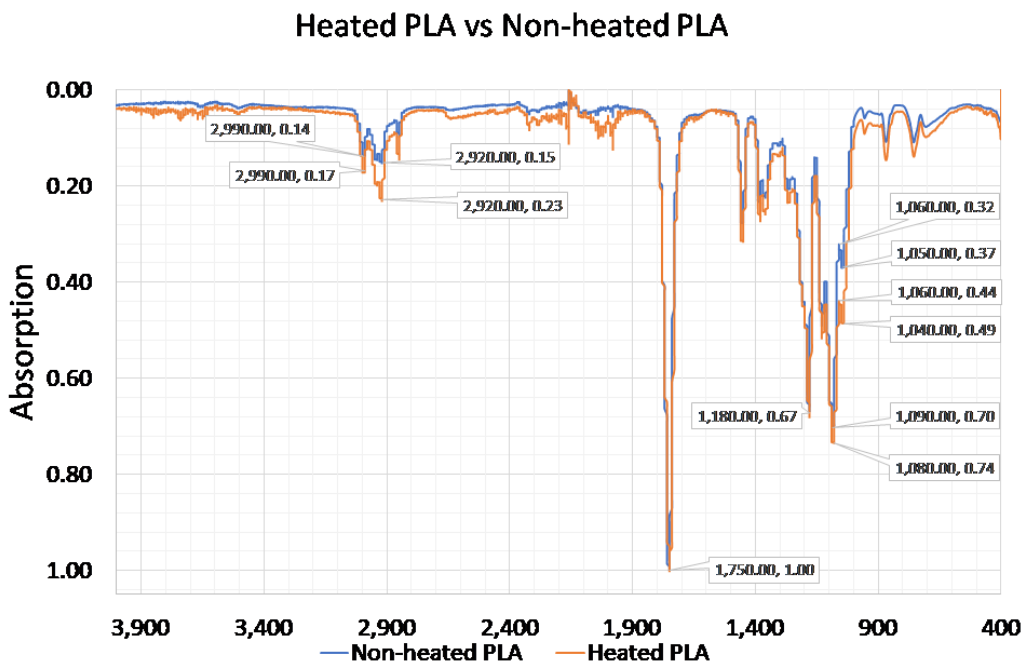


Figure 35. FTIR analysis of heated and non-heated PLA.

PLA is composed of either a ring opening reaction of lactide or a condensation reaction (esterification) of lactic acid that results in having C=O, C-O-C and C-H (saturated aliphatic hydrocarbons) groups in the main chain [273]. The FTIR graphs of heated and non-heated PLA in Figure 9 confirm the presence of all afore-mentioned groups. The results obtained are in accordance with the reported literature [272]. The significant difference appears between the absorption intensities of heated and non-heated PLA. The intensities regarding heated PLA are high for: saturated aliphatic C-H groups [274, 275] by 2990 cm^{-1} and 2920 cm^{-1}, C=O groups [272] by 1750 cm^{-1}, C-O-C groups [272] by 1180 cm^{-1} and O-C groups [275] by 1040 cm^{-1}. The vibrations in FTIR at high intensities for heated PLA show that the pertinent groups require more energy to vibrate that can be due to anyone of the following reasons: 1) increase of mass [275], 2) enhanced crosslinking [272] or 3) improved thermal stability. The former two reasons are not the valid reasons herein this research as the material is not chemically reacted or modified through addition of any additive. Therefore, the high thermal stability may be the appropriate reason for groups to have more absorption energy. The high thermal stability is also confirmed in the DSC curves, where the glass transition peak, cold crystallization peak and melt crystallization peak shift to higher temperatures.

3.5. Summary

A novel way of improving the mechanical properties of PLA printed on an open source printer has been presented. A feedback-controlled heating chamber was used to surround the print volume. Test specimens, as per the ASTM D638 Type IV, were printed under different conditions in and out of the heating chamber in two phases. Phase 1 was performed at room temperature and 0.2 mm layer thickness (constant). 2^3 full factorial ANOVA was used in Phase 1 to examine and select the significant parameters as variables and non-significant parameters as constants for Phase 2. Phase 2 was performed with three heating schemes (cases 1 to 3) and at variable layer thicknesses (0.2 mm and 0.4 mm). Tensile testing was performed for Phases 1 and 2 at a strain rate of 0.2 mm/mm/min. However, Phase 2 also included an extra case, case 4, that was conducted using the same heating scheme as that for case 1 but with an increased strain rate of 0.8 mm/mm/min.

A number of differences in the mechanical properties of parts printed with (Phase 2) and without (Phase 1) heated chamber were observed. In both phases, a range of behaviours was observed e.g. high strength and low elongation, low strength and high elongation, consistent strength and elongation, etc. The highest UTS of the parts printed inside the chamber was observed to be ≈60 MPa as compared to ≈46 MPa for the parts printed in the open environment. To explain the difference in the observed UTS, it was hypothesized that the average UTS and elongation were directly correlated with the beads' shape for thinner layers (i.e. 0.2 mm). SEM was used for fracture analysis and to ascertain the bead structure and directional thermal effects. It was observed that the average UTS and elongation (for 0.2 mm layer thickness) can be interpreted through SEM images and the effects of directional heat transfer are evident by the specific nature of curing and bead shapes. However, the less time and large layer thickness of 0.4 mm did not let the printed parts harness good effects in respect of tensile strength and elongation as in the case of 0.2 mm.

Differential scanning calorimetry (DSC) analysis was performed to further ascertain the effects of in-process heat treatment particularly for case 1 at high temperatures. DSC thermograms showed significant improvement in crystallization for in-process treated samples. Using FTIR, we also confirmed improvements in the thermal stability of the printed samples through high absorption intensities.

Chapter 4. Experimental approach 2: Blending

This chapter includes the reasons and challenges of using second approach of blending the printable materials with polyolefins in this PhD work.

Experimental approach 2: Blending

4.1. Blends with Polyolefins

Polylactic acid (PLA) is not able to withstand high temperatures above 70 °C as it starts softening as observed in previous experimentation. This makes PLA unsuited for milk vats insulation as they are required to be washed at 70 °C. Secondly, although the strength is improved by ~30% but it is not able to reach as high as required for milk vats. Additionally, the thermal stability at high temperature is still not up to up to the mark as PLA shows softening above 70 °C during in-process heat treatment. Therefore, despite the biodegradability obtained from PLA, it is needed to find other cost-efficient materials for this project.

In this regard, injection moulding (IM) thermoplastics are the most cost-effective option to opt. Polyolefins and their wide variety of grades (HDPE, LDPE, LLDPE, UHMWPE, PP) are renowned for its low cost, reasonable strength and flexible processing [276]. However, polyolefins like polyethylene is hard to 3D print in pure form as it swells. Secondly, the strength obtained by pure PE and PP is not as high as required for this project [277-281]. Literature shows that the HDPE, LDPE and PP based blends with other thermoplastics provide good mechanical properties with desired rheological modifications [277, 282-285]. Therefore, it is planned to go for blending HDPE and PP with other thermoplastics and elastomeric based thermoplastics.

4.2. Why Polyolefins (like PE) are not printable?

It is important to investigate the reason of inability to 3D print pure PE prior to start further experimentation. Pertaining to the analysis of non-printability of PE (or its grades), a comparison-based study is performed on few of the main chemical properties of PE. Which is given below,

4.2.1. Density and MFI

HDPE is non-printable, but PLA [271] and PP [36] are printable. It is hard to find a proper reason on basis of molecular weight or density as the both printable (PLA, PP) and non-printable (HDPE, LDPE) materials have a little difference between their densities, i.e., 0.91 of

PP and 0.956 for HDPE) as shown in Table 11. Neither the MFI provides distinguishable threshold values between printable and non-printable materials.

Table 11. MFI and density of different blends materials in conventional polymer processes (not 3D printing).

Material	Density	MFI	Domain & Ref
PLA	1.25 g/cm^3	12.5 g/10 min (190 °C/2.18 kg)	CPP [286]
Polystyrene (PS)	1.05 g/cm^3	7 g/10 min (200 °C/5 kg)	
Ground tyre rubber (GTR)	0.6 to 0.7 g/cm^3		CPP [287]
EDPM (ethylene–propylene–diene terpolymer) rubber	0.86 g/cm^3	0.5 g/10 min (230 °C, 2.16 kg)	
EPR	0.86 g/cm^3	26 g/10 min (230 °C, 2.16 kg)	
Polypropylene homo-polymer	0.91 g/cm^3	35 g/10 min (230 °C, 2.16 kg)	
Recycled polyethylene (RCPE)			[276]
Ground tyre rubber (GTR)			
Styrene–butadiene–styrene three block copolymer			CPP [277]
HDPE 6006-L	0.956 g/cm^3		
LDPE 302R (density)	0.924 g/cm^3		
EPDM (ethylene–propylene–diene terpolymer)			
PLA	1.25 g/cm^3 (21.5 °C)	12.5 g/10 min (190 °C/2.18 Kg)	CPP [282]
PLA Ingeo (experimented with carbon fiber)	Specific gravity 1.24	7-9 g/10min	FDM [180]
Acrylonitrile butadiene styrene (ABS) polymer	1.04 g/cm^3	23 g/10 min (220 °C/10 kg).	FDM [99]
Graphene nanoplatelets	2.2 g/cm^3		
PP		3 g/10 min	FDM [36]
PP + glass fibers POLIFOR L6 GF/30 NATURALE, from SOFTER, PP reinforced with 30% GF		2.5 g/10 min	

4.2.2. Polar and non-polar

HDPE, LDPE and PP are non-polar thermoplastics. However, it is possible to conveniently print PP [36] as compared to non-printable HDPE or LDPE. This shows that polarity is also not an absolute reason for any material to be assured for its printability.

4.2.3. Specific heat capacity

The specific heat capacity of PE is the lowest among most of the commonly used thermoplastics. E.g., PLA, PET, Nylon, ABS, PP etc. [29]. The specific heat capacity of PE is 10.1 J/mol K. This means that polyethylene requires just 10.1 J/mol K of heat energy to raise its temperature by 1 K as compared with 77.8 J/mol K of PET, 30.7 J/mol K of PS, 17.3 J/mol K of PP, 145 J/mol K of nylon66 and 33.5 J/mol K of PMMA [29]. Hence, PE will also cool down comparatively rapidly as compared to the other polymers. FDM is a layer by layer process [47] in which the diffusion among the extruded beads are dependent on temperature of each bead at the time of joining [245]. It is reported that ABS extruded out at a temperature of 270 °C takes just 16 seconds to drop down to 70 °C due to the heat losses through convection and radiation [245]. Therefore, it is understandable that PE filament cools down more rapidly due to lowest specific heat capacity that leads to severe warpage and shrinkage of filaments during 3DP.

4.3. Research novelty in experimental approach 2

Specific heat capacity is revealed out to be a reason of non-printability of PE based on the above theoretical investigation. Therefore, it is expected that productive materials can be designed if the PE is melt blended with such polymers which are printable or have high specific heat capacities. From research perspective, it is observed in literature review that numerous blends of different thermoplastics with PE [276-285, 287-292] are yet not experimented in FDM. This provides a novel research gap to explore different blends of thermoplastics that have following objectives to achieve as per in accordance to the PhD objectives that are,

1. 3D Printability
2. Low cost
3. Strength
4. Thermal insulation (high R values)
5. Resistant to aging

The research work mentioned in subsequent chapters will cover three blends in separate chapters that are developed, experimented and investigated to analyze the potential of achieving objectives.

Chapter 5. Polylactic Acid and High-density Polyethylene Blend: Characterisation and Application in Additive Manufacturing

Chapter 5 includes the following article, “Polylactic Acid and High-density Polyethylene Blend: Characterisation and Application in Additive Manufacturing” submitted for publication to “Journal of Applied Polymer Science” of Wiley Online Library.

The full text is included in the thesis without any modifications. However, there are formatting differences to keep the formatting same for the thesis. The formatting modifications involve page setup, font style, referencing style, reference citation style and bibliography style.

Polylactic Acid and High-density Polyethylene Blend: Characterisation and Application in Additive Manufacturing

5.1. Abstract

This research reports a novel Polylactic acid (PLA) blend with high density polyethylene (HDPE) and polyethylene graft maleic anhydride (PE-g-MAH) to mitigate the PLA degradation issues associated with high temperatures, soil and water exposure. The blend was prepared with a melt blending process and directly printed with a custom-built pellet printer to maintain the 'as prepared' properties. Thermal stability was analysed in terms of mechanical strength at different bed temperatures and post-printing aging for 10 days. Soil burial degradation and water absorption were investigated in terms of mechanical strength and effects on mass at three intervals (15 days, 30 days, 45 days). The proposed blend revealed high stability to all three degradation mechanisms due to the chemical grafting along with physical interlocking. Finally, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) were used to confirm the enhancement in molecular interactions, melt crystallization, onset temperatures and phase distribution respectively.

5.2. Introduction

PLA is the most prominent biodegradable material not only in the conventional polymer industry [293] but also in additive manufacturing (AM) [294-296]. It is a polyester-based thermoplastic that is recommended due to its superior properties like printability, biodegradability, low cost and hydrophobicity [199, 294]. But, besides its beneficial attributes PLA has serious issues like: brittleness, poor thermal resistance, low glass transition temperature [297, 298] and poor stability to enzymatic chain cleavage due to the poor resistance to biodegradation [113, 199, 293].

Table 12. Materials for different applications designed for compression or flexural properties.

Domain	Applications	Materials	Classification of material
Medical	Human Tissues, Human organs	Diisocyanate/Methylene diphenyl diisocyanate (MDI) [122], Polyols-polyether/PCL, Chain extender/ Butanediol (BDO) [123].Poly caprolactone (PCL) [115], Poly(Ethylene Glycol) Terephthalate Poly(Butylene Terephthalate)(PEGT/PBT) [116], Chitosan/hydroxyapatite [117], Corn starch/dextran/gelatin [119], Polylactic acid/Poly caprolactone [115], Chitosan/Hydroxyapatite (HA) [120], Chitosan/PLA/Keratine [121].	Blend
Aerospace	Ceramic and metal filled parts	Zirconia/Wax [124], PP/Tricalcium phosphate (TCP) , Polylactic acid/Hydroxyapatite (HA)/ceramic particles [125], Iron/nylon, Copper/ABS , Nylon 6/Al-Al_2O_3 [126, 127], PC-ABS/Graphene	Reinforced composites
Electrical	Conducting products	ABS/Steel, PLA/Graphene/MWCNT [128], Polyurethane/ MWCNT [129]	
Electronics	Sensors	ABS, Wax blend, Nylon [132]	

One of the cost effective methods of overcoming the problems associated with neat PLA (and other polymers) is melt blending [299]. In this regard, there have been numerous research efforts as shown in Table 12. However, they are mostly intended for compression or flexure-based applications. For example, Woodfield et al. [116] developed a scaffold for articular cartilage with polyethylene glycol terephthalate/polybutylene butylene terephthalate (PEGT/PBT), Wang et al. [300] printed polycaprolactone (PCL) scaffold with a pore size of 250 µm, Ang et al. [120] introduced the chitosan/hydroxyapatite (CS/HA) scaffold, Grone et al. [301] used the anatomic model-based implants made by FDM in patients suffering from posterior fossa defect and large cranial defect, and Tanase et al. [121] uses PLA, keratine and chitosan composite to show the feasibility for osteoblast attachment. However, the PLA blend materials designed for tensile applications are scarce and, additionally, they are not yet capable of meeting the commercial standards due to insufficient degradation life [2], high cost, insufficient strength [145, 199, 302], and poor thermal and moisture resistance [199]. The range of ultimate tensile strength for PLA blends reported in the literature falls below 59 MPa with low thermal resistance [100, 145, 199, 302, 303]. However, there is no information on stability against thermal aging and soil degradation of the reported PLA blends [100, 197, 199, 200]. As a result, there is a potential research gap to explore more blend systems of PLA for

AM/FDM that can withstand high temperatures with enhanced stability against soil and moisture degradation.

High density polyethylene (HDPE) is one of the widely used commercial polymers that is renowned for its linear polymeric structure, low cost and good hydrophobicity [304]. However, it has not yet been reported in FDM-based literature. Furthermore, the high composition (>20%) of non-biodegradable constituent (polyamide11) for achieving optimal properties is one of the main environmental concerns regarding eco-friendly blends with PLA. The high molecular weight of HDPE [304] can be used to achieve better toughening and moisture resistance with low composition. Moreover, the long linear chains of HDPE can act as an entangled structure that is highly suitable for either grafting in the presence of a compatibilizer or physical interlocking. Better graft or interlocked molecular structures are reported to achieve better resistance to degradation. Therefore, there is a potential research gap to explore the partial biodegradable blend systems of PLA with HDPE for FDM that can withstand moisture and high temperatures with enhanced biodegradable life.

In this research, we present a partial biodegradable blend of PLA with HDPE in the presence of polyethylene graft maleic anhydride (PE-g-MAH) as a compatibilizer. PE-g-MAH is selected as the compatibilizer because it has been reported in [305] as an optimal compatibilizer. The novel blend includes the lowest composition of non-biodegradable material to achieve better properties as compared to blending systems reported in the literature [304]. This research reports another novel approach to print the new PLA blend system by pellet extrusion 3D printer (developed by our group [73]) that uses pellets instead of filament as a raw material. The pellets provide a functional benefit over filament like avoiding the filament cost [153] and thermal modifications in original polymer properties that occur during the filament-making process. Therefore, the parts printed by pellet printer are expected to be as near as possible to the true characteristics of the raw material [73]. The effects of thermal aging, soil degradability and water absorption on mechanical properties of the proposed blend are thoroughly investigated. The results include tensile testing, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric (TGA) and scanning electron microscopy (SEM).

5.3. Materials and methods

5.3.1. Materials

Polylactic acid (grade 2002D) was supplied by Scion, a New Zealand Crown Research Institute. HDPE (DOWLEX IP-10) with a high melt flow index of 10g/10min and 0.96 g/cm^3 density was procured from TCL Hunt, New Zealand. PE-g-MAH (A8525) having 50:50 composition (by weight percent) was procured from Shenzhen Jindaquan Technology Co. Ltd, China.

5.3.2. Blending

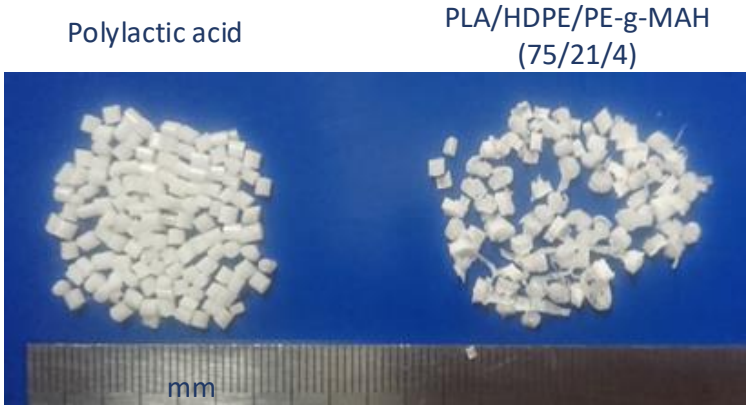


Figure 36. Shape of pellets.

PLA, HDPE and PE-g-MAH were dried in an oven for 6 hours at 50 °C. All three polymers were mixed in specific compositions (Table 13) in a mixer for 5 minutes before extrusion. The polymer compounding was performed in a single screw extruder at Scion. The temperature settings for ten sections of the extruder from feeder to nozzle were: 175 °C, 175 °C, 180 °C, 180 °C, 180 °C, 180 °C, 180 °C, 170 °C, and 150 °C. The screw speed of extruder was kept at 100 rpm with die pressure of 65-85 bar. The pelletizer unit was set at 13 mm/min to cut approx. 1.3 mm pellets.

Due to the intended application of the proposed eco-friendly blend for FDM 3D printing, the printability of the composition was considered as the main factor while finding the correct final composition. Therefore, we printed each blend before moving on to the next composition. In this regard, the literature was used for selection of the compositions. Owing to the reported optimal properties of polyethylene blends with >20% by weight of polyethylene [306-308], the

first composition was prepared with 21% HDPE. The compatibilizer, PE-g-MAH, was selected as 4% by weight due to the optimal properties reported in the literature [309, 310]. This composition depicted problems during single screw extrusion like large die swelling and non-uniformly shredded pellets as shown in Figure 36. It is noteworthy that the large die swelling in extrusion shows unsuitability of the material for printing with an extrusion-based process (video1, supplementary material). Therefore, this composition was rejected, and further compositions were tried by reducing the percentage of HPDE and PE-g-MAH. The composition shown as Blend 2 in Table 13 was found to be the best in terms of printability and contents of HDPE in line with the overall objective of the proposed material to be eco-friendly. The compatibilizer for Blend 2 was selected as 0.5% based on the properties reported in [311].

Table 13. Compositions prepared for ternary blend systems.

Blend	PLA	HDPE	PE-g-MAH
1	75	21	4
2	92	7.5	0.5

5.3.3. 3D printing

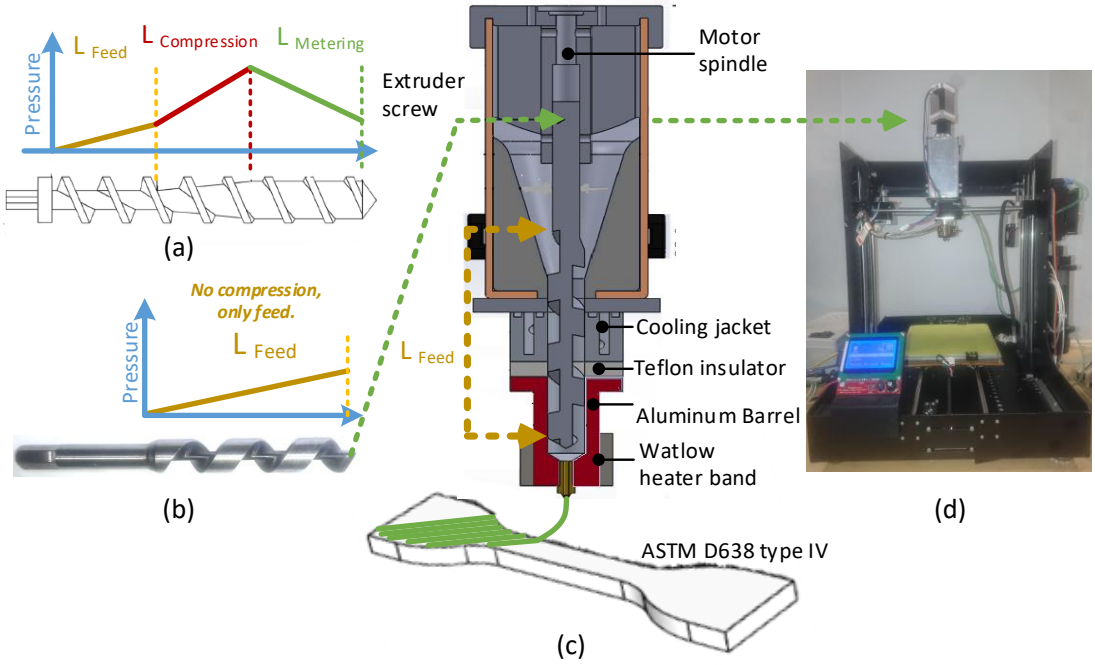


Figure 37. Pellet 3D printer: a) sections of conventional extrusion screw, b) section of a drill, c) illustration of different parts of the pellet extruder, and d) the pellet extrusion printer [73].

As mentioned earlier, 3D printing of the blend compositions while keeping the properties of developed blend compositions intact is the preliminary goal of this research. Therefore, we modified our previously reported pellet 3D printer as shown in Figure 37 for this work [73]. This pellet printer has a unique extruder design for feeding the pellets that extrude the beads without affecting the thermal history that could be the result in the case of filament-based printers during the filament-making process. Unlike conventional screws, the printer's extruder used in this research had only a feeding section (Figure 38b) that does not compress the pellets. Furthermore, the liquid cooling system in the extruder (Figure 37c) [73] helps to avoid the thermal deterioration of the pellets that could be caused with the uncontrolled temperature of extrusion. Therefore, the absence of compression and the filament-making process and the presence of a proper cooling system avoids the expected thermal modifications in the prepared blends and, hence, serves the purpose of keeping the as-prepared properties of the pertinent blend composition.

The pellet printer uses open source Slic3r software to operate [73]. Slic3er software helps to achieve printing at a high multiplier (material quantity) [73] that aims to fill the voids as much as possible as compared to commercial printers like the Stratasys mc series [249]. All the samples (ASTM type IV dog-bones and films) were printed with the same parameters. The parameters for printing were: 0.2 mm layer thickness [249], 45°/-45° build orientation [95], one surface/surface layer, 15 mm/min speed, 1.5 mm nozzle diameter [73] and 15 multiplier. The printing was performed with Composition 2 (Table 13) as the Composition 1 pellets resulted in no printing due to extremely slow extrusion even at high extrusion pressure by the extruder (video1, supplementary material). Additionally, the uncontrollable swelling in Composition 1 was about three times the printer's nozzle diameter; this was not appropriate to achieve dimensional accuracy in printed parts.

5.3.4. Tensile testing

Tensile testing was performed on Instron 5967 on ASTM D638 Type IV dog-bones. The load cell capacity of Instron 5967 is 30 KN and a 25 mm clip-on gauge extensometer was used to record the values of extension. The testing was performed at a strain rate of 0.1 mm/mm/min. A minimum of three samples were tested for each variable and averaged for calculating average ultimate tensile strength and strain.

5.3.5. Thermal stability

PLA has poor thermal stability due to its low glass transition temperature (i.e., 50-55 °C) and percent crystallization. As a result, it cannot achieve good mechanical properties [294, 306, 312]. As this research aims to achieve a printable and enhanced PLA blend system that will have improved thermal stability, the set of experiments was specifically designed to analyze the effects of thermal aging (pre-printing processing) and operating (in-printing processing) temperatures on stability in terms of tensile strength. The research about thermal treatment reports 65-100 °C pre- or post-heat treatment for 10 minutes to 1 hour to achieve optimal properties [243, 270, 313]. Beyond this range, the literature reports a decrease of strength and weakening of intermolecular structure [314]. Therefore, in pre-printing thermal analysis, the PLA and PLA blend raw materials were aged for 10 days in furnace (no vacuum) at 75$\pm$5 °C to analyze the signs of thermal aging (degradation). For operating (in-printing) analysis, the samples were printed with a range of temperatures, i.e., 161 °C, 167 °C, 173 °C and 179 °C.

5.3.6. Soil degradation

The biodegradation was assessed by measuring the degradation of material in real soil following the techniques proposed by [39, 315].The samples were buried near one of the car parks of Massey University, New Zealand (Figure 38). The geographic coordinates of the burial location are: longitude -36° 43’ 33’’ latitude 174° 41’ 41’’. Since the existing literature only reports mass loss due to degradation of films [315] and does not provide any information about the effects on strength, we also printed dog-bone samples to analyze the effects of biodegradation on the strength.

The films were printed with the following dimensions: 40 mm × 20 mm × 0.5 mm [39]. For the dog-bone samples we retained the size (ASTM D638 Type IV) used for the non-aged and aged samples in order to have uniformity for comparative analysis.

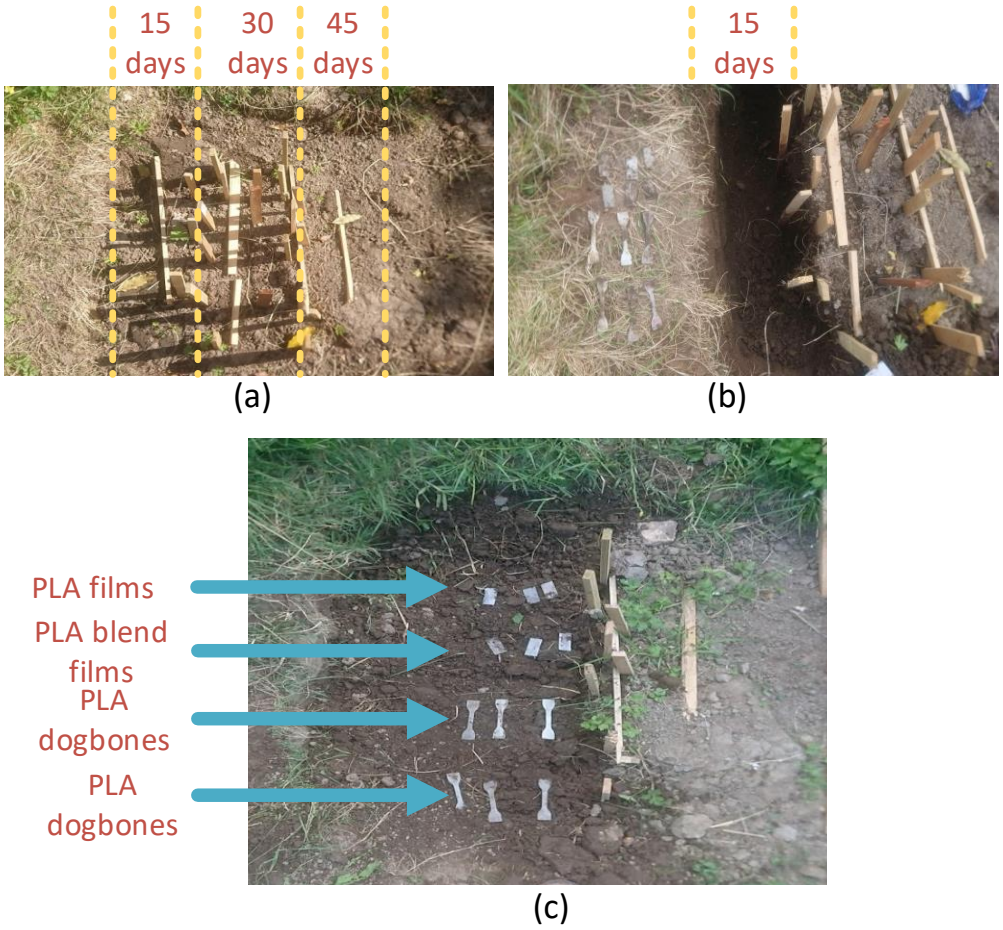


Figure 38. Sample burial location for soil degradation analysis: a) samples burial positions for three intervals, b) samples excavated after 15 days, and c) samples excavated after 30 days.

The mass of films was measured using a Sortorius Entris laboratory balance before burial with an accuracy of 1 mg. After each of three burial intervals (15, 30, 45 days), the samples were taken from the soil, washed with water, dried in a furnace for one day at 50 °C and again weighed. The dog-bones were also tensile tested with the same parameters as used for aged PLA, non-aged PLA and PLA blend on Instron 5967. The simple relationship used to measure the weight retention in the films [315] is as follows:

$$m_R = \frac{m_1}{m_0} \times 100\% \quad \text{..... (1)}$$

In equation 1, m_R is the film weight retention in grams, $m_1$is the mass of degradable sample in grams, and m_o is the mass of the as-prepared sample in grams.

5.3.7. Water absorption

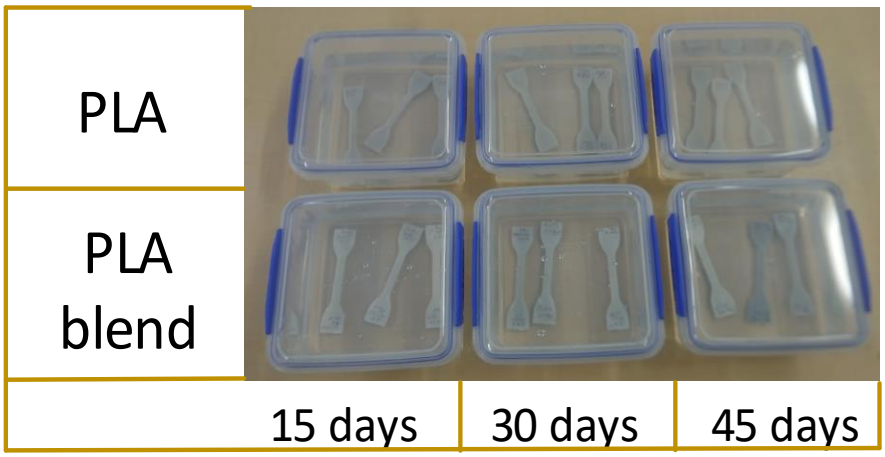


Figure 39. Samples immersed in plastic containers for water absorption testing.

One of the well-known tests for water absorption is the percentage mass gain due to water absorbed in the samples designed specifically for voidless or uniform membranes that have characteristics of resisting water seepage [39]. The amorphous FDM structure consists of voids which act as permeable channels for water absorption that later cause structural erosion. The resultant erosion due to trapped moisture in voids, is a constant source of degradation that considerably decreases the strength [316, 317]. Therefore, the water absorption % mass gain analysis is performed on ASTM D638 Type IV dog-bones instead of membranes to obtain the effects on ultimate tensile strength and elongation at break.

The procedure for conducting moisture absorption measurements started with weighing the samples with an accuracy of 1 mg on a Sortorius Entris laboratory balance before immersion in water to obtain m_0. The immersed samples (Figure 39) were taken out after specified intervals (15, 30 and 45 days), dried in an oven, then cooled in a desiccator. The cooling was then followed by immediate weighing of the samples on the balance to obtain m_1. The dog-bones were also tensile tested with the same parameters as used for aged PLA, non-aged PLA and PLA blend on Instron 5967. The following relationship is used to calculate the percentage increase in mass due to water absorption ($\%m_G$) [39].

$$\%m_G = \frac{m_1 - m_0}{m_0} \times 100\% \quad \text{..... (2)}$$

In equation 2, m_G is the mass gain in percent, m_1 is the mass of wet sample in grams, and m_o is the mass of the dried sample in grams.

5.3.8. Fourier transform infrared spectroscopy (FTIR)

The effect of thermal processing on molecular bonding was analyzed with Fourier transform infrared spectroscopy (FTIR). Thermo electron Nicolet 8700 FTIR spectrometer was used for FTIR analysis. An attenuated total reflection single reflection accessory was used to record the spectrum in the range of 400-4000 cm^{-1}. A 32 scan averaged resolution of 4 cm^{-1} was used and data was recorded using OMNIC E.S.P software version 7.1. All the FTIR spectrums were normalized and corrected with respect to the baseline.

5.3.9. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed to analyse the effects of thermal processing on glass transition temperature and melt crystallization. It is also planned to further analyse the nature of chemical interaction (grafting of interlocking) found in FTIR. TA Instruments DSC Q1000 was operated at a nitrogen purge flow rate of 50 mL/min with 10 °C/min rate of heating. The range of analysis was set from 25 °C to 550 °C.

5.3.10. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on NETZSCH STA 449 F1 Jupiter to analyse the onset of thermal degradation and chemical interaction (grafting or interlocking). The rate of temperature increase was 10 °C/min with the nitrogen purging at a flow rate of 50 mL/min. The range of analysis was set the same as DSC (25 °C to 550 °C).

5.3.11. Scanning electron microscope (SEM)

The fractured surfaces of tensile specimens were analysed by a scanning electron microscope (Hitachi TM3030 Plus). The SEM analysis was performed for aged and non-aged PLA and PLA blend systems.

5.4. Results

5.4.1. Thermal stability

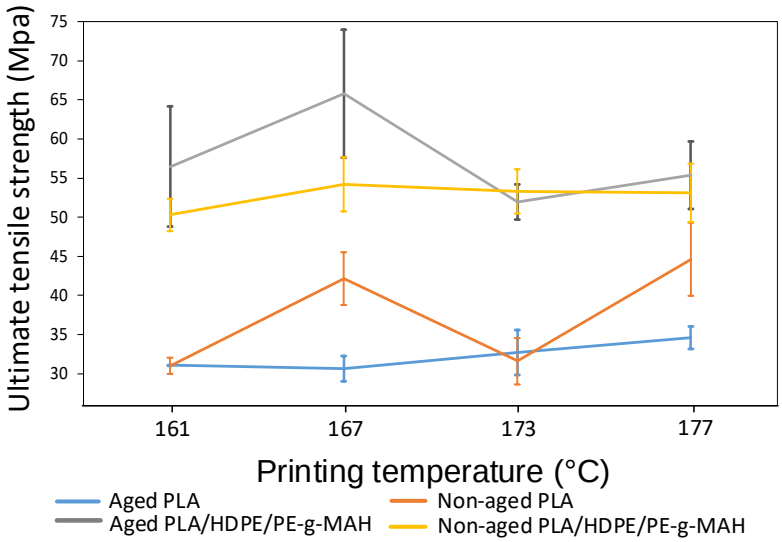


Figure 40. Tensile strength of aged and non-aged materials: PLA and PLA/HDPE/PE-g-MAH.

The results of average ultimate tensile strength (UTS) in Figure 40 affirm the thermal stability of PLA/HDPE/PE-g-MAH against each of its competitors. The aged PLA was not able to withstand thermal aging, showing poor thermal stability, specifically at 167 °C and 179 °C as revealed by 30.6 MPa and 34.6 MPa respectively. Instead of degrading, thermal aging enhanced the tensile strength significantly for PLA/HDPE/PE-g-MAH. The highest average tensile strength of 65.8 MPa for PLA blend was achieved at 167 °C followed by 56 MPa at 161 °C. The standard deviation further highlights the enhanced thermal stability at 167 °C by the highest mark of 74 MPa. The average UTS of 65 MPa achieved for aged PLA blend system is the highest among the scarce literature reported on blends of FDM [39].

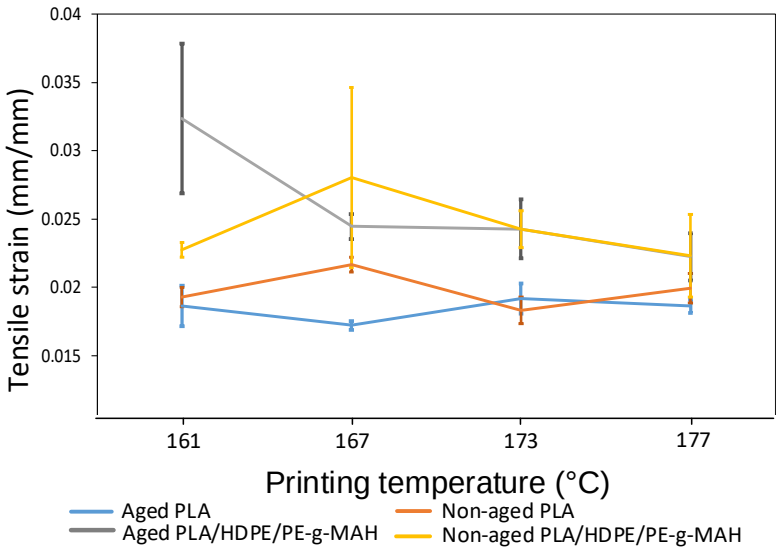


Figure 41. Tensile strain of aged and non-aged materials: PLA and PLA/HDPE/PE-g-MAH.

Average tensile strain in Figure 41 also confirms the superiority of PLA/HDPE/PE-g-MAH. The low average tensile strain of aged PLA at most of the printing temperatures (161 °C, 167 °C and 179 °C) as compared to the non-aged PLA and the blends (aged and non-aged) shows higher instability against higher temperatures. The aged blend with the highest average tensile strain of 0.0323 mm/mm at 161 °C as compared to 0.0227 mm/mm of non-aged blend shows remarkable enhancement resulting from thermal aging. This also indicates that the blends have better ductility as compared to pure PLA.

Figure 42 shows the elastic modulus for different temperature settings. A significant increase in the elastic modulus for aged blends as compared to aged and non-aged PLA can be seen. It is clear that the neat PLA is not able to withstand aging. However, the blend shows significant resistance to aging and obtains high elastic modulus with the highest mark of 2.7 GPa achieved at 167 °C.

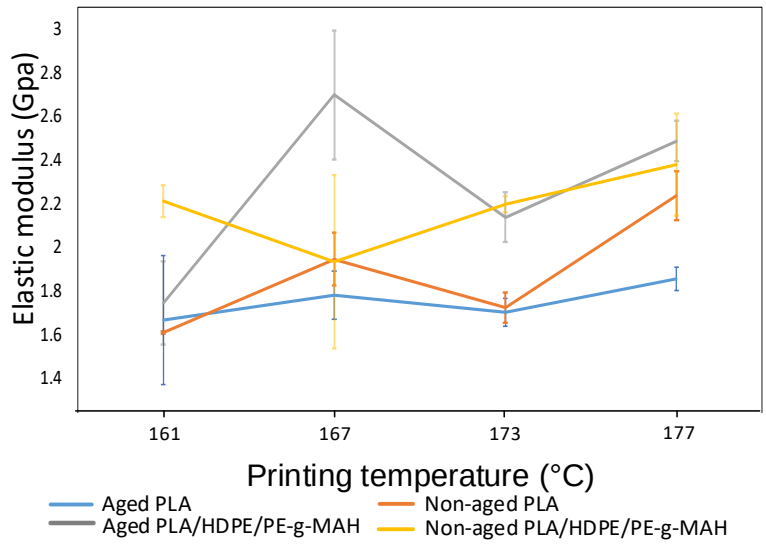


Figure 42. Elastic modulus of aged and non-aged materials: PLA and PLA/HDPE/PE-g-MAH.

5.4.2. Soil degradation

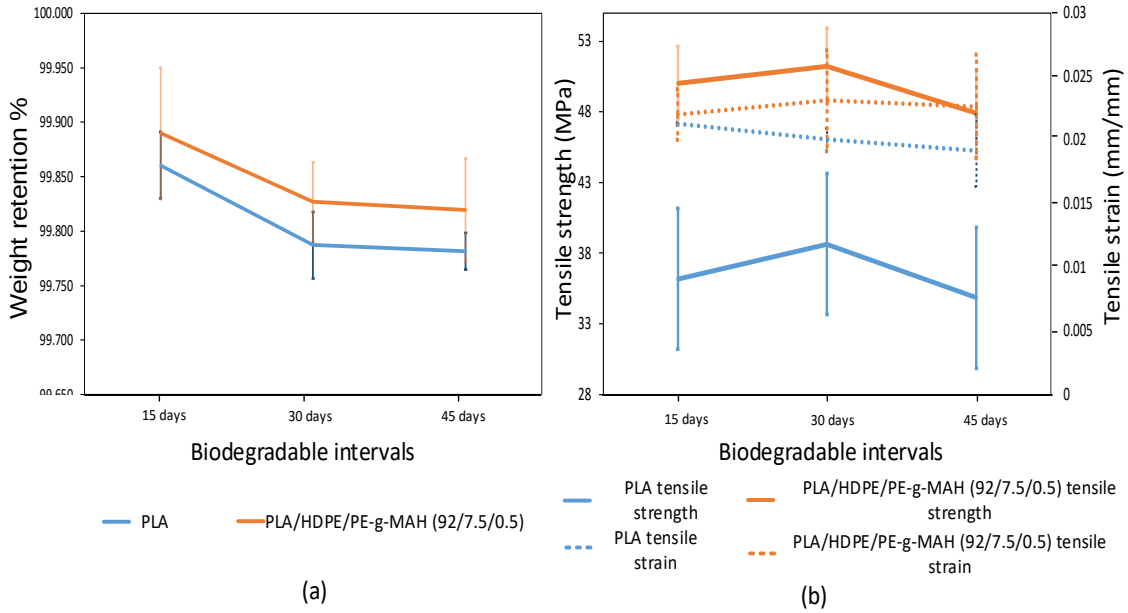


Figure 43. Soil biodegradable tensile properties and mass loss percent: a) Mass loss percent, and b) Tensile strength and strain.

The effects of soil degradation on weight retention (m_R) and tensile properties are shown in Figure 43a and b respectively. The graph in Figure 43a shows clearly the high degradation of PLA as compared to PLA/HDPE/PE-g-MAH. The weight retention after 15 days on PLA films (99.86 %) is less as compared to the blend system (99.82%) that further falls to 99.79 %

for PLA after 30 days. However, the soil degradation from 30 days to 45 days in neat PLA shows a minor decrease to 99.78 %. As compared to PLA, the blend retains high m_R 99.82 % after 30 days that shows thereafter a negligible decline to 99.81% after 45 days. The weight retention of blend followed the visible pattern of PLA but with a far higher retention rate showing less mass loss. The blending helps to control the rapid biodegradability of pure PLA without affecting the original behavior of degradability by a mark.

The high degraded strength of PLA/HDPE/PE-g-MAH showed high stability as compared to PLA in Figure 43b. The achieved values of blend after 15- and 30-days' degradation are higher than PLA at all three intervals. Moreover, the blends show consistent endurance per mass loss (Figures 43a and b) to degradation as the tensile strength sustained at about or above 50 MPa. The 50 MPa is the achieved strength for non-degraded PLA printed on a pellet printer [73]. Therefore, the comparable degradable strength to reported non-degradable strength [73] validates the stability of blend developed in this research. The tensile strain in Figure 43b also shows the dominance of blends over neat PLA. The consistency maintained in strain loss by blend as compared to continuous decrease in neat PLA again supports the presence of intermolecular interaction (chemical grafting or physical interlocking) that will be analyzed in discussion.

5.4.3. Water absorption

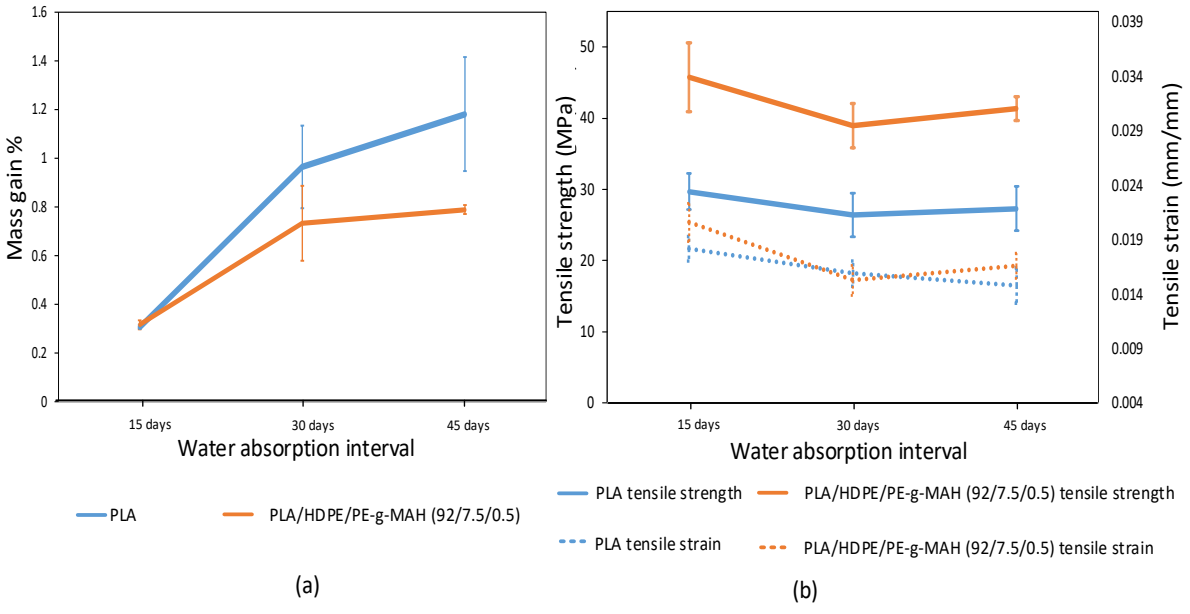


Figure 44. Water absorption effects on (a) percentage mass gain, and (b) tensile strength and strain.

The effects of water absorption are reported in Figure 44. The mass gain in Figure 44a shows comparatively less increase in mass of PLA/HDPE/PE-g-MAH from 15 to 30 days that later shows a decrease in water uptake after 45 days as compared to PLA. The difference shown by PLA blend as compared to PLA shows the inherited hydrophobic characteristic persisted and improved in the blend.

The effect of water absorption on tensile strength and strain is shown in Figure 44b. The water absorption has shown catastrophic effects on PLA as the strength and strain drop down below 30 MPa and 0.014 mm/mm respectively. The achieved values are the lowest as compared to one achieved in thermal and soil degradation. The lowest values also prove water absorption to be the most vulnerable method of degradation for PLA as compared to thermal and soil degradation.

From the results presented above, the improved mechanical properties provide evidence of changes in the molecular structure of novel FDM polymer. From the results presented above, the novel FDM blend outperforms the existing materials (neat or blend) in mechanical properties [318]. However, these are observed at a bulk level in mechanical testing and a more rigorous chemical analysis is needed to understand the changes in the properties of the blend that result in the improved mechanical strength. In this regard, the notions that the modifications in melt blending can cause chemical grafting in the case of miscible blends [305], and physical interlocking in the case of immiscible blends [319], are taken as the basis for further analysis. To observe interlocking or grafting we used the following well-known techniques from polymer chemistry: Fourier transform infrared spectroscopy (FTIR) for modifications in chemical bonds, differential scanning calorimetry (DSC) for modifications in crystallization and pertinent temperature for uniform or distinct phases, Thermogravimetric analysis (TGA) for uniform or distinct phases, and scanning electron microscopy (SEM) for confirming topographical modifications.

5.5. Discussion

5.5.1. Analysis of intermolecular interactions

FTIR has been used to analyse the effects of blending on the intermolecular interaction like chemical bonds and functional groups. It is also used to study the effects of thermal and soil degradation on the chemical interactions to analyse the stability.

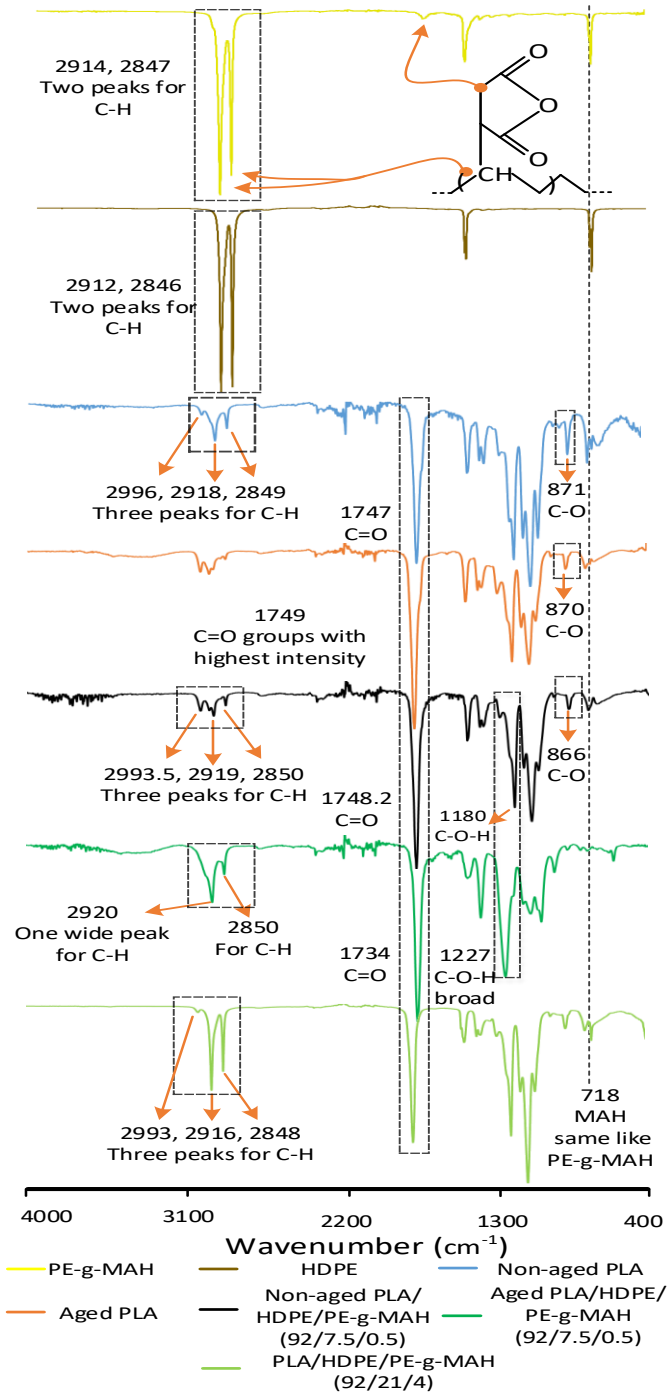


Figure 45. FTIR analysis of chemical interactions.

Table 14. Assignment of transmittance peaks in FTIR. "WN" stands for wave number (cm^{-1}) and "IN" stands for "intensity".

Neat PLA		Aged PLA		HDPE		PE-g-MAH		PLA/HDPE		Non-aged PLA/HDPE/PE-g-MAH		Aged PLA/HDPE/PE-g-MAH		Chemical group
WN	**IN**	**WN**	**IN**	**WN**	**IN**	**WN**	**IN**	**WN**	**IN**	**WN**	**IN**	**WN**	**IN**	
2995 2918 2849	0.16 0.29 0.23	2993 2944 (Broadening of peak) 2849	0.18 0.19 0.11	2912 2846	0.69 0.66	2914 2847	0.4 0.4	2994 2919 2850	0.152 0.262 0.182	2993 2919 2850	0.166 0.192 0.139	2921 (Two peaks into one wide peak) 2850	0.219 0.368	C-H stretching vibrations
1748	0.89	1749	1					1750	1	1749	1	1734	1	C=O vibrations
1185	0.88	1181	0.65					1182	0.65	1180	0.677	1227 (Synergizing effect)	0.762	C-O-H vibrations
1085	1	1083	0.66					1084	0.67	1082	0.750	1021	0.471	C-O-C vibrations
				1462	0.19									CH_2 bending vibrations
				718	0.24									CH_2 rocking (bending vibrations)
						1463	0.1							CH_2 and CH_3 bending vibrations
						1715	0.02							C=O vibrations of MAH
871	0.36	869	0.16					870	0.14	866	0.157	868	0.089	C-O vibrations [306]
729 755	0.33 0.4	729 755	0.13 0.16							754 (Two into one peak)	0.164	756	0.09	CH bending vibrations

FTIR graphs obtained for PLA, PE-g-MAH and HDPE are in accordance with the literature as shown in Table 14 and Figure 45. For example, the presence of PLA is confirmed by the transmittance peaks of C=O, C-O-C and C-H groups [320, 321] by 1748 cm^{-1}, 1085 cm^{-1} and 2995-849 cm^{-1} respectively. The HDPE graph is also validated [322] through the C-H groups by 2913-2847 cm^{-1} and CH_2 groups by 1462 cm^{-1}. PE-g-MAH is confirmed through C-H stretching vibration peaks of polyethylene [321] at 2915 cm^{-1} and 2848 cm^{-1}, and C=O peak of MAH [321] by 1705 cm^{-1} and 718 cm^{-1} . The absence of alkene (double bond) group at about 3090 cm^{-1} [321] shows the grafting of PE on the shared electrons of double bond as shown by the formula in Figure 45.

The melt blending of PLA and HDPE in the presence of PE-g-MAH shows visible differences in the FTIR spectrum (Table 14 and Figure 45) as compared to neat PLA, and this confirms grafting. The differences are in the form of a shift in peaks and increase or decrease in the intensities. For example, the shift of transmittance peak associated with C-O [306] at 871 cm^{-1} in neat PLA shifts to lower wavenumber to 866 cm^{-1} in non-aged compatibilized blend. Furthermore, the differences in intensities are also providing evidence of grafting or chemical

crosslinking [272]. The relative intensity of the C-O-C group is highest for non-aged PLA that decreases to second place in the non-aged PLA/HDPE/PE-g-MAH (Figure 45 and Table 14). Similar decrease in C-O-C groups is observed in aged PLA (Table 14). Based on the observed thermal degradation of the C-O-C group in aged PLA (Figure 45), the reason for a decrease in the C-O-C group in aged blend can be the melt blending process that degrades the C-O groups by thermal shearing [323].

The thermal stability of the blend as compared to the neat PLA is also evident in Figure 45 and Table 14. The decrease in intensities of C-O-C groups in aged PLA (0.66) is much higher than the blend (0.75). It is noted the C-O-C groups are in abundance in non-aged PLA at 1085 cm^{-1} that decrease significantly in aged PLA as shown by the peak at 1082 cm^{-1}. Meanwhile, the difference of intensities of C-O-C groups is comparatively less for non-aged and aged blends that proves the superior thermal stability achieved through grafting in the blend. The grafting also describes the superior tensile strength and ductility of the printed dogbones of the blend as compared to the aged and non-aged PLA (Figures 40 and 41). Furthermore, the broadening of the C-O-H peak in aged blend [184] at 1227 cm^{-1} as compared to the narrow peak in non-aged blend at 1180 cm^{-1} shows better synergy among blend constituents due to thermal aging [324-326]. This synergy leads to an improved diffusion among printed beads that results in higher tensile strength for aged blends than non-aged blends as shown in Figure 40.

The reasons behind distortion of extruded pellets and non-printability of the blend (75/21/4) are also investigated in FTIR analysis. For most of the spectra of 75/21/4 blend, the spatial locations are replicating the exact types of peaks as in non-aged PLA except one at 719 cm^{-1}. The peak at 719 cm^{-1} is associated with PE-g-MAH as shown in the individual spectrum in Figure 45. It shows a high concentration of PE-g-MAH in the blend as a non-reacted polymer. The inability of MAH to graft has already been reported by L. Zhang et al [327] to decrease after a specific increase in its concentration. On the contrary, the absence of a corresponding MAH peak in blend (92/7.5/0.5) shows complete utilization of 0.5% compatibilizer as observed in the form of improved grafting. Furthermore, the wide peak at 2921 cm^{-1} for aged blend (92/7.5/0.5) as compared to the two narrow peaks of 75/21/4 blend not only shows enhancement in alkane contents proving more grafting [304] of HDPE in an 0.5%-based blend but also reveals the poor grafting [328] of HDPE in the 4%-based blend. Therefore, the composition of MAH leads to non-compatibilized blending that causes distorted pellets and non-printability.

The analysis of biodegradable films and dogbones reveals the significant degradation of C-O-C groups in both PLA and aged/no-aged blend as shown in Figure 46. The blend shows a decrease in intensity of C-O-C groups to 0.66 (Figure 46) as compared to the 0.75 of non-degraded PLA/HDPE/PE-g-MAH (Figure 45). The C-H bonds in blend dogbones show synergistic effects through broadening into one wide peak at 2920 cm^{-1}. The degradation of C-O-C bonds in PLA films and dogbones significantly drops down to 0.67 from highest relative intensity (i.e. 1.0) in non-degraded PLA (Figure 45). This shows that the soil degradation brings in chain scission of C-O-C groups in PLA, which is also supported by the literature [329]. The blend also suffers minor degradation, but the grafting slows down the comparative C-O-C degradation. This degradation represents the decrease in mass and tensile strength of PLA and the compatibilized blend.

Apart from information regarding grafting, this analysis provides inadequate information about the sufficiency or insufficiency of PE-g-MAH to graft all HDPE contents (7.5%) with PLA. This necessitates the need for complementing FTIR with DSC and TGA analysis.

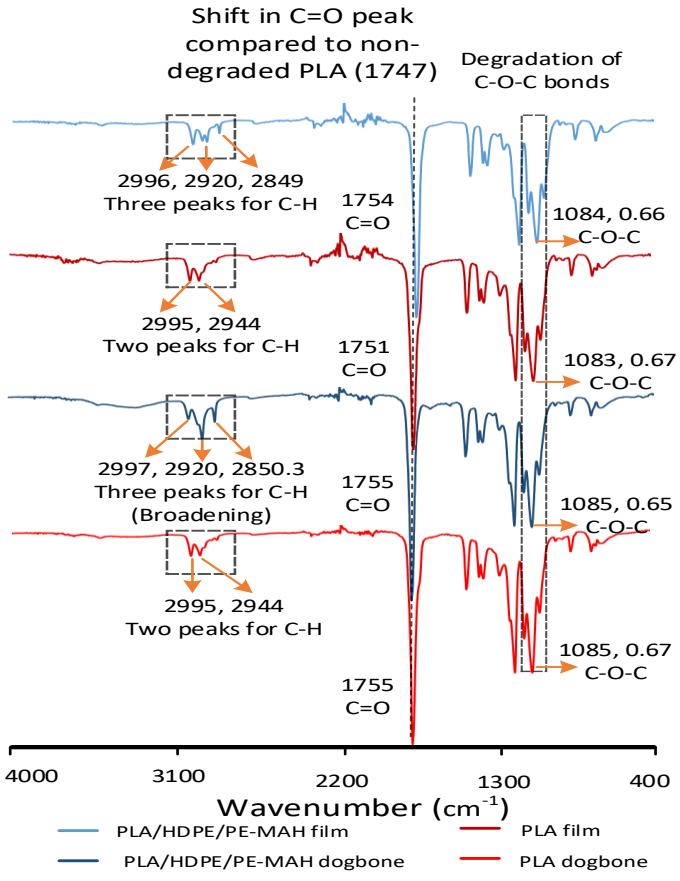


Figure 46. FTIR analysis of soil biodegraded samples.

5.5.2. Analysis of grafting and interlocking

Differential scanning calorimetry (DSC) has been used to further investigate the nature of chemical interaction (grafting or interlocking) between PLA and HDPE in the presence of PE-g-MAH as from the FTIR analysis interlocking could not be confirmed. It is further used to find a logical rationale for the increase of tensile strength and ductility of the aged blend.

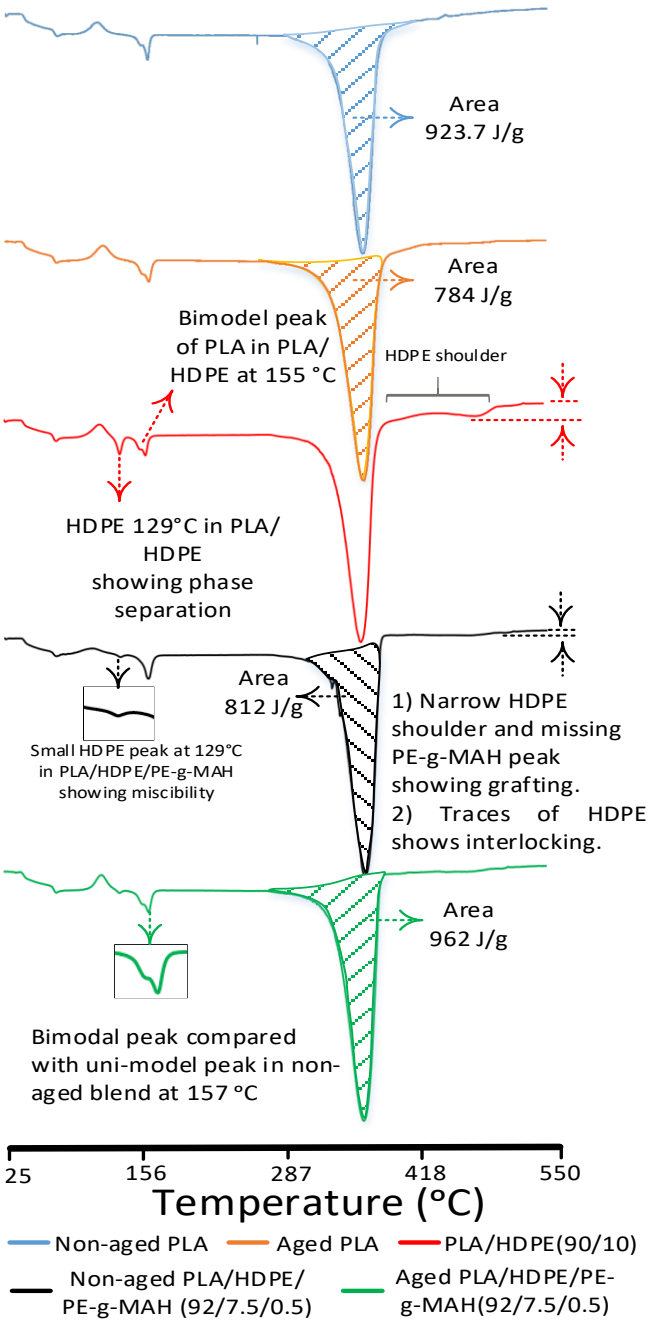


Figure 47. DSC analysis for intermolecular interactions (grafting and interlocking) and thermal degradation of PLA and the blend.

The analysis of compatibilized and non-compatibilized blend is provided in Figure 47. The immiscibility of PLA/HDPE blend is observed in the form of: 1) distinct endothermic bimodal melt crystallization peaks for HDPE and PLA [328] (at 129 ºC and 155 ºC) , 2) distinct cold crystallization peak of PLA [330] at 109.8 ºC, and 3) bimodal peaks for PLA and HDPE with a wide shoulder on the right above 368 ºC. The compatibilized non-aged PLA/HDPE/PE-g-MAH shows the progression in the miscibility of HDPE in the PLA matrix through: 1) transformation of distinct HDPE exothermic peak into a small dip at 129 ºC, and 2) the narrow shoulder associated with HDPE on the right side above 811.7 ºC (Figure 47), and 3) the decrease in T_g (58.2 ºC) and T_c (101.5 ºC) as compared to PLA/HDPE that is in accordance with the reported literature [304] showing improvement in miscibility. Meanwhile, the meagre signs of non-reacted HDPE in the partial graft matrix show interlocking. The interlocking resists proper reorientation in the melt state [312] that is observed by a decrease of area under the melt crystallization peak of compatibilized non-aged blend (24.96 J/g) as compared to non-aged PLA (27.13 J/g). Therefore, the incomplete but enhanced grafting confirms interlocking that forms a strong entangled intermolecular structure.

The effects of thermal aging on neat PLA are analysed in Figure 47. Apart from a minor increase in cold crystallization (Tc) and melt crystallization (T_m) temperature (Table 15), owing to the re-arrangement in molecular structure due to the heating [270, 313] during aging of neat PLA, the melt crystallization decreases significantly (Area=24.90 j/g). The reason for the decrease in melt crystallization is the degradation of C-O groups as confirmed by FTIR analysis in Figure 45. This supports the chain scission in aged PLA and also explains the poor thermal stability of neat PLA that is observed in the form of lowest tensile strength (30.6 MPa) among all experimentations.

The effects of thermal aging of PLA/HDPE/PE-g-MAH are shown in Figure 47. This analysis reveals re-arrangement in endothermic (cold crystallization) and bimodal exothermic (melt crystallization) peaks associated with PLA in aged blend at 110.7 °C and 157.7 °C respectively. The re-arrangement of HDPE and PLA monomers helps to gain high melt crystallinity as shown in Table 15(28.43 j/g) [325, 326]. The heat provided in aging not only results in a higher re-arrangement of the monomeric chains of the remaining (non-grafted) PLA and HDPE but also helps to enhance the grafting of traces of HDPE with PLA. The enhanced grafting along with the re-arrangement results in the highest melt crystallization as well as an increase in Tm (Table *15* 15) for aged blend as compared to neat PLA, PLA/HDPE and non-aged PLA/HDPE/PE-g-MAH. The thermal stability of the aged blend can also be noted by its

largest area of endothermic degradation peak (961.8 J/g) that shows the high resistance of grafted and entangled intermolecular interactions to degrade. The increase in melt crystallization area and degradation area depict the highest tensile strength (67 MPa) and strain (0.0323 mm/mm) of 3D printed aged blend as compared to non-aged blend and neat PLA.

Table 15. DSC analysis of different materials.

	Aged PLA	**Non-aged PLA**	**Aged PLA/PE-g-MAH/HDPE**	**Non-aged PLA/PE-g-MAH/HDPE**	**PLA/HDPE**
Glass transition temperature, T_g (°C)	59.4	59.8	58.9	58.2	58.8
Cold crystallization temperature, T_c (°C)	111.9	105.7	110.7	101.5	109.8
Melt crystallization temperature, Tm (°C)	157.2	155.9	157.7	156.7	129 and 155
Degradation temperature, T_d (°C)	369.2	367.9	369.8	370.1	368.3
Area T_c peak (J/g)	29.43	30.18	34.91	19.45	21.19,
Area Tm peak (J/g)	24.90	27.13	28.43	24.96	30 (combined)
Area Td peak (J/g)	785	924	961.8	811.7	741.7

5.5.3. Validation of effects of grafting and interlocking

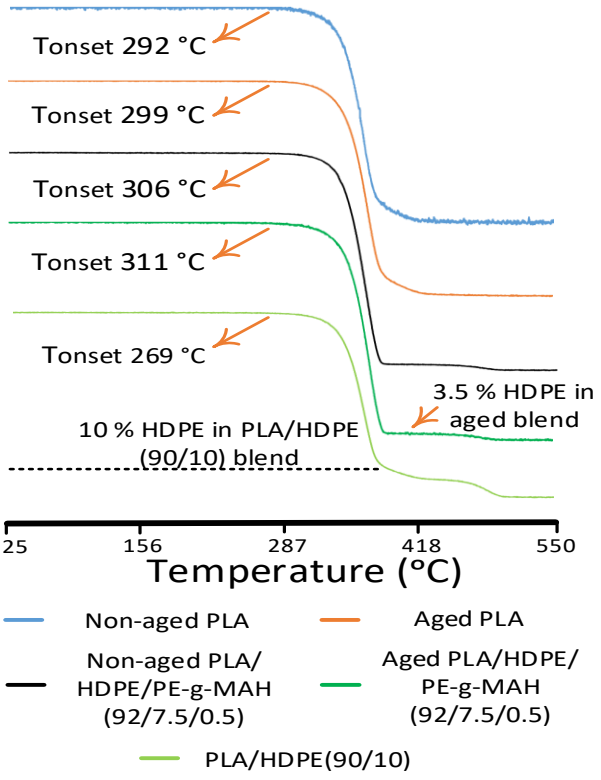


Figure 48. TGA analysis for grafting and interlocking.

The TGA analysis to validate the FTIR and DSC results regarding partial grafting and interlocking is shown in Figure 48. The inertness of PLA [331, 332] and HDPE [304] blend is depicted in Figure 13 through two distinct dips. The onset of mass loss appears at exactly 10% percent (the second dip) associated with HDPE composition in the PLA/HDPE blend. This validates the immiscibility of PLA/HDPE as also observed in the FTIR and DSC analysis. On the contrary, the non-aged PLA/HDPE/PE-g-MAH blend shows a better chemical bonding for 7.5% HDPE. The mass loss only appears (the first dip at 3.5%) when the compatibilizer is used up. It is noteworthy that, if the compatibilizer (PE-g-MAH) percentage is increased, the remaining HDPE will also be grafted. Overall TGA analysis elaborates on the fact that the high mechanical strength and ductility are caused by a combination of grafting along with interlocked traces of HDPE for aged and non-aged blends.

Table 16. TGA analysis for different materials.

Materials	**Onset temperature**	**End temperature**
Aged PLA (°C)	299	492
Non-aged PLA (°C)	292	438
PE-g-MAH (°C)	391	493
PLA/HDPE (°C)	269	529
PLA/PE-g-MAH (°C)	256	523
HDPE/PE-g-MAH (°C)	421	519
Aged PLA/HDPE/PE-g-MAH (°C)	311	498
Non- aged PLA/HDPE/PE-g-MAH (°C)	306	497

Figure 48 and Table 16 show the results of TGA analysis from another perspective, the thermal stability. It can be seen that the onset temperature of aged PLA/HDPE/PE-g-MAH is higher than the non-aged blend, which means the aged blend has achieved better interlocking and grafting. A similar trend was seen in the DSC analysis where the melt crystallization area also increased to show reoriented intermolecular interactions. From this it can be inferred that the blend showed better mechanical properties.

5.5.4. Scanning electron microscopy (SEM)

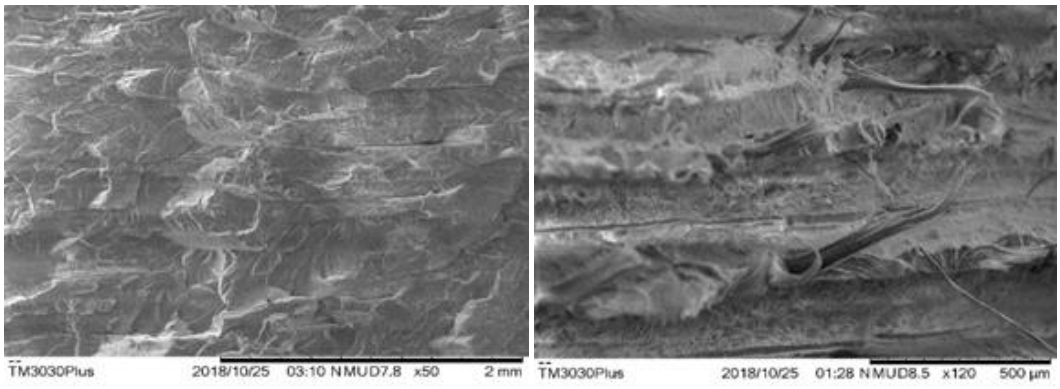


Figure 49. SEM analysis of (a) non-aged PLA at 179 °C, and b) non-aged PLA: HDPE: PE-g-MAH at 179 °C.

To further analyze the observed grafting and interlocking mechanism, supported by the FTIR, DSC and TGA analysis, scanning electron microscopy (SEM) has been used. It is observed in the SEM fractographs (Figure 49a) that the non-aged PLA has a layered appearance in contrast to the fibrous fracture of other material compositions (Figure 49 and Figure 50). The nature of fibers formed in PLA and PLA blend samples relates to the ultimate tensile strength and strain. It can be seen that the fibers in aged PLA are short and appear weak as they break due to the propagation of the crack (Figure 50b). On the other hand, PLA blends exhibit long fibers either entangled or being pulled outwards. This entangled network of fibers in Figure 50d shows the stiffness against high loads (≈74 MPa). Therefore, we can infer that the stiff and entangled networked fibers supported the grafting of HDPE with PLA through PE-g-MAH.

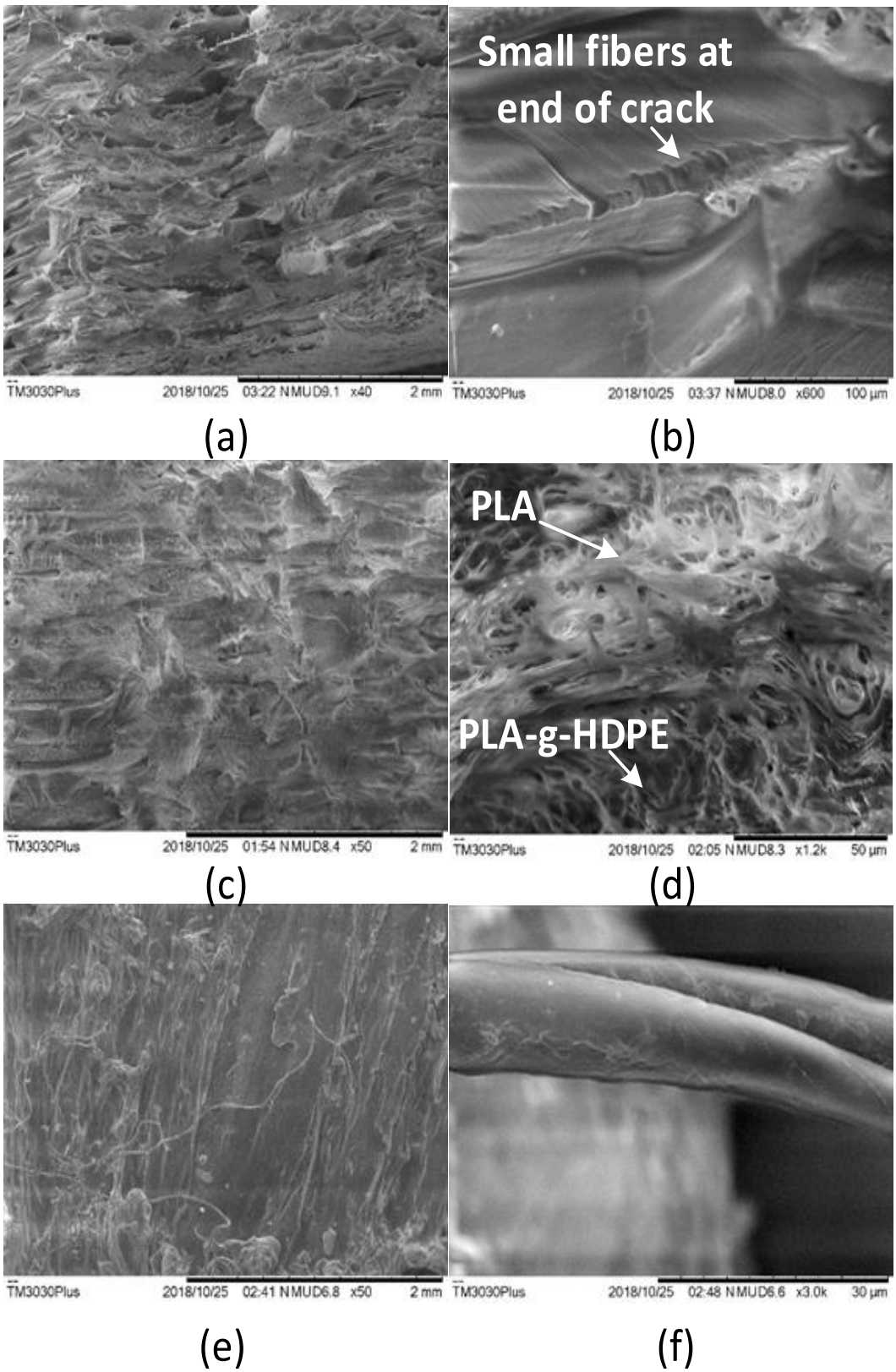


Figure 50. SEM analysis of aged materials (a) PLA at 161 °C, (b) 600x PLA at 161 °C, (c) PLA/HDPE/PE-g-MAH at 167 °C, (d) 2000x PLA/HDPE/PE-g-MAH at 167 °C, (e) PLA/HDPE/PE-g-MAH at 179 °C, (f) 3000x PLA/HDPE/PE-g-MAH at 179 °C.

5.6. Summary

PLA is melt blended with HDPE in the presence of PE-g-MAH for fused deposition modeling. A pellet 3D printer is used to print the proposed blend. Printing with pellets avoids the chemical modifications in the structure of neat and new polymer blends due to thermal history generated during the usual filament-making process. The mechanical properties (UTS and strain) are measured for the ASTM D638 samples for analysis of the effects of thermal aging, biodegradation in soil, and water absorption.

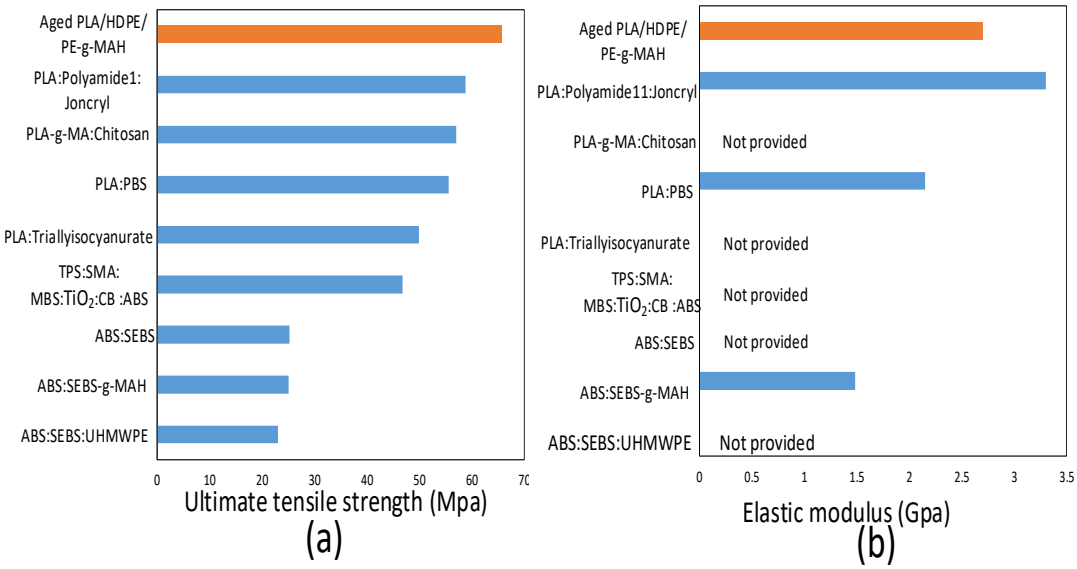


Figure 51. Comparison of novel printing blend with the literature.

Thermal aging on raw materials (neat and blend) is performed for 10 days at 75 $\pm$ 5 °C. The blend shows high thermal stability as compared to neat PLA that is observed through high tensile strength of 67.8 MPa at 167 °C and tensile strain of 0.0323 mm/mm at 161 °C. The achieved tensile strength is the highest and the tensile strain is the second highest among FDM blend materials proposed/developed to date (Figure 51). The soil degradation analysis for the blend system not only shows low percentage mass loss (i.e., 99.81%) but also depicts high tensile strength and strain as compared to neat PLA (i.e., about 50 MPa and 0.02263 mm/mm respectively). The blend system shows more resistance to moisture degradation in the water absorption test by achieving high strength of 30 MPa as compared to approx. 15 MPa of PLA.

FTIR, DSC, TGA and SEM analyses show grafting of HDPE with PLA in the presence of PE-g-MAH and traces of HDPE left as a physically interlocked constituent. The combination of grafting and interlocking causes a high tensile strength and strain against each type of degradation mechanisms as compared to neat PLA. FTIR analysis reveals the C-O groups to be the most susceptible linkage that is being depleted due to shearing in melt blending, thermal aging, soil degradation, and water absorption. The grafting and interlocking show high resistance to further depletion of C-O groups as compared to neat PLA, thus providing superior strength and strain.

The future work on this aspect will be based upon investigation of the effects on the mechanical properties of the optimal composition of PE-g-MAH and HDPE. This will lead to a noteworthy comparison of a 100% miscible blend with a combined grafted and interlocked blend.

Chapter 6. Thermally stable acrylonitrile butadiene styrene blend with high density polyethylene for fused filament fabrication

Chapter 6 includes the following article, “Thermally stable acrylonitrile butadiene styrene blend with high density polyethylene for fused filament fabrication” published in journal of “Materials and Manufacturing Processes, Taylor & Francis”. According to the policy of Taylor & Francis, the article is republished with the permission from Taylor & Francis in this thesis.

The full text is included in the thesis without any modifications. However, there are formatting differences to keep the formatting same for the thesis. The formatting modifications involve page setup, font style, referencing style, reference citation style and bibliography style.

Thermally stable acrylonitrile butadiene styrene blend with high density polyethylene for fused filament fabrication

6.1. Abstract

Acrylonitrile butadiene styrene (ABS) is a well-known material used in fused filament fabrication (FFF) for industrial and research applications. However, it has poor thermal stability due to the thermo-oxidative degradation of butadiene monomers. This makes ABS unsuitable for high temperature structural applications. This research reports a novel FFF blend of ABS with high density polyethylene (HDPE) in the presence of polyethylene graft maleic anhydride (PE-g-MAH) to improve the thermal stability. A 3^3 full factorial ANOVA analysis is used to analyze the tensile, flexural and compressive strength of the blend. The novel FFF blend reveals one of the highest mechanical properties in its class in FFF. The thermal stability is significantly enhanced due to the chemical grafting. The results are discussed with the help of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy.

6.2. Introduction

Acrylonitrile butadiene styrene (ABS) is a well-known elastomeric thermoplastic in fused filament fabrication (FFF) due to its wide range of applications [296]. The large-scale manufacturing in big area additive manufacturing (BAAM) [333] performed with ABS and carbon fibers has particularly increased the research value of ABS. Abedini et al. [334] presents the salient characteristics like tensile strength, ductility, hydrophobicity, etc. as a reason for its wide use. Arostegui et al. [335] finds that these characteristics are due to its basic polymeric structure that is composed of poly butadiene (PB) and styrene acrylonitrile (SAN). SAN forms an amorphous continuous phase that is grafted as branches on a rubbery dispersed phase of PB. Furthermore, the composition, molecular weight and the nature of interaction in each of the co-polymers (PB and SAN) determine the final characteristics. For example, PB controls the toughness and SAN controls the heat resistance, chemical resistance and surface hardness. Tiganis et al. [336] reports that despite the ability of SAN co-polymer to resist heat, thermal degradation has been noted due to the hydrogen abstraction of PB. Furthermore, Tiganis et al.

[336] and Ramli et al. [337] find the chemical and mechanical characteristics of ABS to decline with time due to different weathering conditions above 40 °C. Such types of thermal degradation can potentially affect the reliability of ABS in various additive manufacturing (AM) applications.

Zhong et al. [338] report the increase in thermal stability of ABS by melt-blending with high temperature thermoplastics. One of the most successful commercial blend systems is ABS/polycarbonate (PC) [339]. ABS/PC is also one of the few blends of ABS prepared specifically for FFF. For example, ABS/UHMWPE/SEBS, ABS:SEBS [145, 236], ABS/SEBS-g-MAH [41], ABS/PMMA [340], ABS/SMA [341]. The high temperature polymer (PC) not only increases the thermal stability but also the mechanical properties (tensile, compression and flexure) of the blend system [342]. However, the improvement in thermal stability is limited to the on-set of thermal degradation with the inclusion of suitable thermal agents or stabilizers [343]. The blend shows poor thermal resistance to annealing. Chaudhry et el. [343] also finds significant effects on the morphology of annealed ABS/PC that shows a decrease in thermal stability. This highlights a need for a blend of ABS for FFF that will have better mechanical properties and thermally stability.

High density polyethylene (HDPE) is one of the main polymers among the polyolefin family. Recently, a successful 3D printing of HDPE [344] using a styrene ethylene butylene styrene (SEBS) plate as an adhesive to stick the printed layers to the printing bed. However, the low mechanical strength [344] and high thermal degradation of HDPE [345] are the main reasons to explore blend-based alternatives that can provide high strength with good thermal stability. HDPE has been reported to have significant thermal stability during blending with various polymers. Shahrajabian et al. [346] reports improved thermal characteristics for high density polyethylene/recycled polyethylene terephthalate/maleic anhydride polyethylene (HDPE/rPET/MAPE). Similarly, Lu et al. [347] note down the increase in thermal stability in DCS thermograms with an increase of HDPE contents in PLA. Camacho et al. [348] observes the improvement in resistance to thermo-oxidative degradation in a polypropylene/high density polyethylene (PP/HDPE) blend. Mir et al. [349] reports the improved mechanical and thermal properties with HDPE and chitosan. However, these proposed blends have not been analyzed against aging. Furthermore, the mechanical strength does not meet the commercial requirement.

The aim of this research is to develop a blend of ABS with HDPE in the presence of a polyethylene graft maleic anhydride (PE-g-MAH) for FFF that can provide high mechanical properties even after thermal aging. 3^3 full factorial design of experiments (DoE) is used to analyze the effects of three variables (bed temperature, printing temperature and aging temperature) on tensile properties. The significant combination of variables from full factorial design are used to print samples for compressive and flexure analysis. The results show significant thermal resistance of a novel FFF blend through enhanced mechanical properties. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) are used to analyze the reasons for improved thermal and mechanical properties.

6.3. Materials and methods

6.3.1. Materials

ABS with a melt flow index of 13 g/10 min was purchased from TCL Hunt, New Zealand. The commercial grade of ABS was Polylac PA-747. High density polyethylene (HDPE) was also purchased (DOWLEX IP-10) with a melt flow index of 10g/10min and 0.96 g/cm^3 from TCL Hunt. PE-g-MAH (A8525) was procured from Shenzhen Jindaquan Technology Co. Ltd., China.

6.3.2. Blending

All three polymers (ABS, HDPE, PE-g-MAH) were dried at 50 °C for 6 hours in an oven. The polymers were mixed for 5 minutes in a mixer. The melt blending was performed in a single screw extruder. A single screw extruder was preferred over a twin screw extruder to avoid any thermo-mechanical degradation due to high pressure and temperature as reported by [350]. The pelletizer was set at a pellet size of 1.3 mm and 20 meter/minute. The processing parameters are given in Table 17.

Table 17. Parameters for single screw melt blending.

Variable	Value
Feeder to nozzle temperature	175 °C, 175 °C, 180 °C, 180 °C, 180 °C, 180 °C, 180 °C, 180 °C, 170 °C and 150 °C.
Feed rate	20 rpm
Screw speed	200 rpm
Torque	46%
Die pressure	52 bar
Number of strands	2

The printability of blend compositions is the main objective in this research. The printability can be affected by the compositions of each constituent in a blend. Zhang et al. [327] reports that the excessive composition of PE-g-MAH can cause rheological defects due to excessive non-grafted MAH. The defects in rheology can potentially make printing difficult. Similarly, excessive HDPE can potentially cause high shrinkage during printing [344] and also observed in our experiments (video1, supplementary material). Therefore, 4% PE-g-MAH was selected due to the optimal results [309] and a maximum of 48% HDPE is selected for the first blend (Table 18). All blend compositions were prepared based on the results of printing. Composition 4 was decreased to 0.5% of PE-g-MAH [311] that provides the best results in form of good printing with no warpage. Therefore, no more than 4 compositions were prepared as shown in Table 18.

Table 18. Compositions prepared for the blend, printing bed type and effects on printability.

Composition	ABS	HDPE	PE-g-MAH	Printing bed	Printability
1	48	48	4	Perf board and adhesion tape	No
2	75	21	4	Perf board and adhesion tape	No
3	85	11	4	Perf board and adhesion tape	Yes, but excessive warpage caused separation of intercalated layers
4	92	7.5	0.5	Adhesion tape	Yes

6.3.3. 3D printing

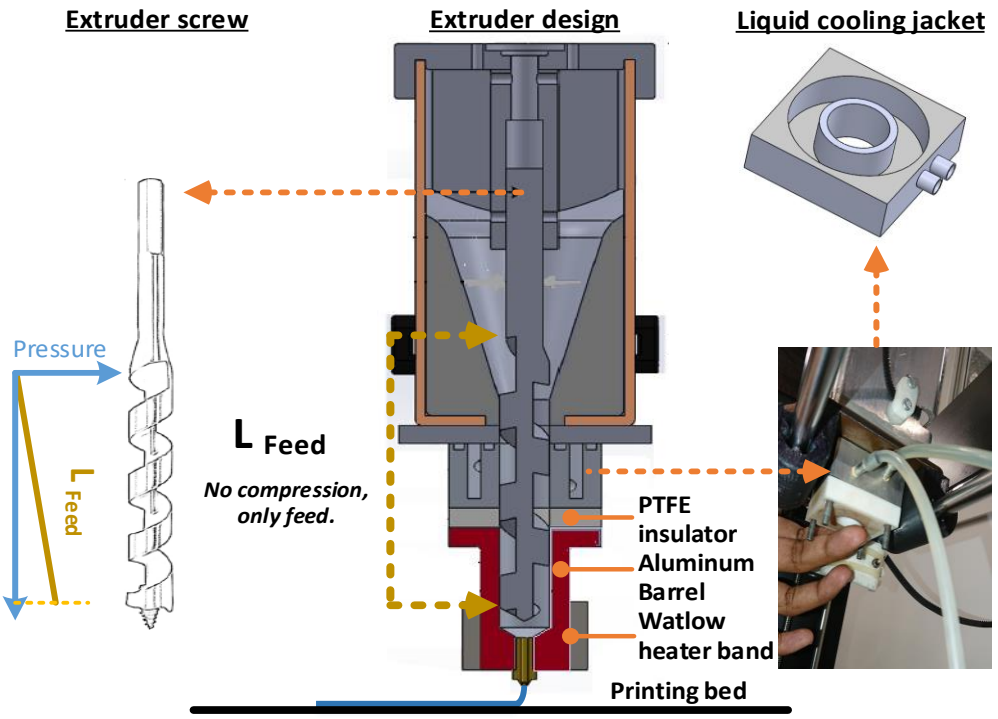


Figure 52. Pellet 3D printer: a) sections of conventional extrusion screw, b) section of drill, and c) illustration of different parts of pellet extruder [73].

The blend is printed on our previously reported pellet 3D printer [73] with some modifications for this work as shown in Figure 52. The extruder design was refined, and a liquid cooling system was added to stop the heat flowing through the extruder (Figure 52). The extruder screw was used with only one feeding zone as compared to a regular screw with multiple zones. The absence of a compression zone helps to achieve extrusion without thermal shearing. Whyman et al. [73] reports that thermal shearing can potentially change the original characteristics of the raw material and may cause thermal degradation. Furthermore, the improved cooling system avoids an uncontrolled rise in the temperatures inside the heating barrel that helps to maintain the uniform extrusion temperature. Therefore, the improved extruder design along with the cooling system ensures the properties of printed samples are as near as possible to the developed compositions.

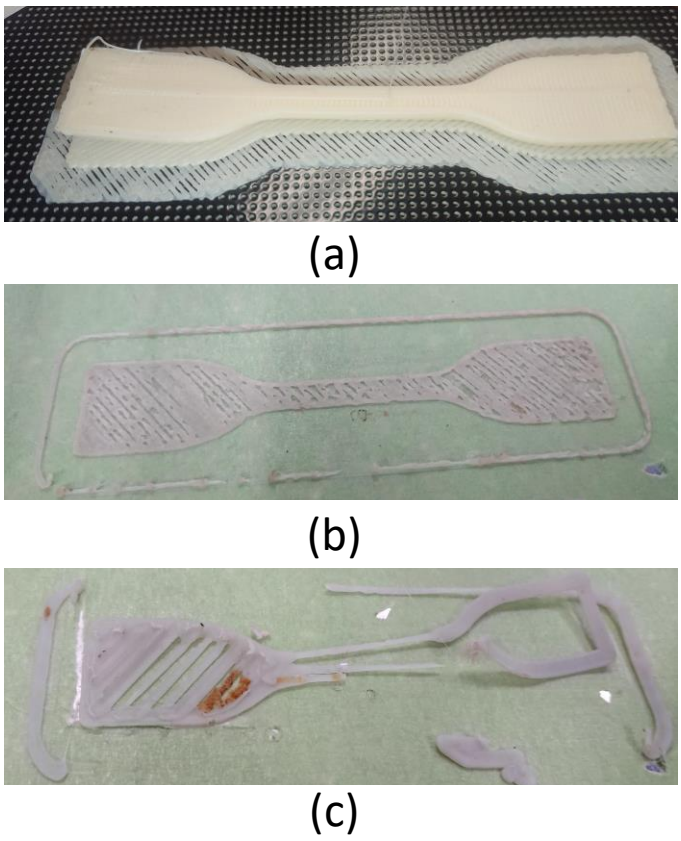


Figure 53. Printing conditions for (a) perforated printing bed (composition 3), (b) below 180 °C for composition 4, and (c) above 210 °C for composition 4.

The pellet printing is performed using an open source Slic3er software to set the printing parameters. The parameters for printing are given in Table 19.

Table 19. Parameters for screw extrusion 3d printing.

Parameters	**Values**
Feed rate	5 mm/min
Printing speed	5 mm/min
Layer thickness	0.2 mm
Raster width	0.2 mm
Raster angle	45°/-45°
Infill density	100%
Multiplier	15
Number of contours	1
Nozzle diameter	0.4 mm

The tensile, compression and flexure samples are printed according to the ASTMD 638 type IV [351], ISO 604 [352], and ISO 178 [353] respectively. The dimensions are shown in

Figure 54. The first two compositions (Table 18) were not printed due to the large die swelling during extrusion. The swelling was approximately 3 times of extrusion diameter which is unsuitable for printing if good dimensional accuracy is desired. Furthermore, the extrusion was too slow to meet the lowest printing speed of 1 mm/min. The composition 3 (Table 18) was printable but the excessive warpage during printing resulted in incomplete prints of the tensile samples. Different kinds of printing beds for composition 3 were also used to assist the printing process as shown in Table 18. The perforated board shows the separation of layers due to poor adhesion between layers and excessive warpage (Figure 53). The composition 4 (Table 18) was printed successfully using adhesive tape on the printing bed with good dimensional accuracy. Therefore, the subsequent experimentations are performed with composition 4 on the printing bed with adhesive tape.

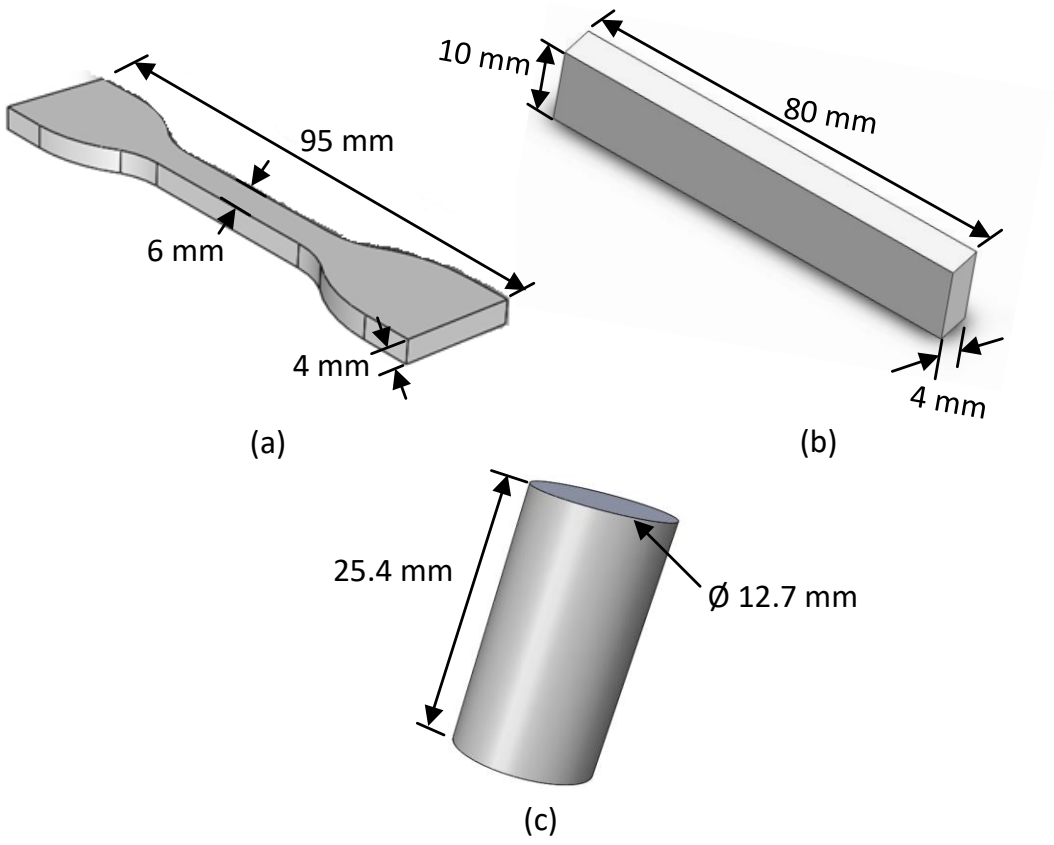


Figure 54. Standards for printing samples (a) ASTM D638 type IV (tensile), (b) ISO 178 (flexural), and (c) ISO 604 (compression).

6.3.4. Design of experiment

3^3 full factorial randomized ANOVA analysis in Minitab2019 is used to design the experiments for tensile testing. The ANOVA analysis was performed at a confidence level of 95%. As the objective of this research is to investigate the thermal stability of the blend, printing temperature, bed temperature and thermal aging are selected as variables. Three levels of printing temperature are set at 185 °C, 195 °C and 205 °C. The blend shows poor extrusion below 180 °C and degradation in the form of burn marks above 210 °C as shown in Figure 53. Three levels of bed temperature are set at 25 °C, 50 °C and 75 °C. A bed temperature below 25 °C is not possible in an uncontrolled environment and 75 °C is the highest bed temperature for ABS. The three aging periods are selected based on literature [345].

Full factorial analysis is used for tensile testing. The significant experimental combinations based upon tensile testing are used to analyse the compressive and flexure properties.

6.3.5. Mechanical testing

Mechanical testing was performed on Instron 5967 with a load cell capacity of 30 KN. A clip-on strain gauge extensometer (25 mm) was used to record the values of extension. The testing was performed at an extension rate of 5 mm/min as per the ASTM standards. The three-point flexure testing was performed using the ISO 178 standard at a crosshead speed of 2 mm/min. The span between the loading anvils was 64 mm. The compressive testing was performed using the ISO 604 standard at 2 mm/min. A minimum of three samples were tested for each set of parameters, as suggested by Minitab DoE. As the compressive testing required accurate vertical alignment of the cylinders to measure the compressive loads without any buckling, special attention was given to the printing of the vertical samples (cylinder). The samples that showed buckling during compression testing due to the minor eccentricity in vertical alignment were discarded as shown in Figure 55.

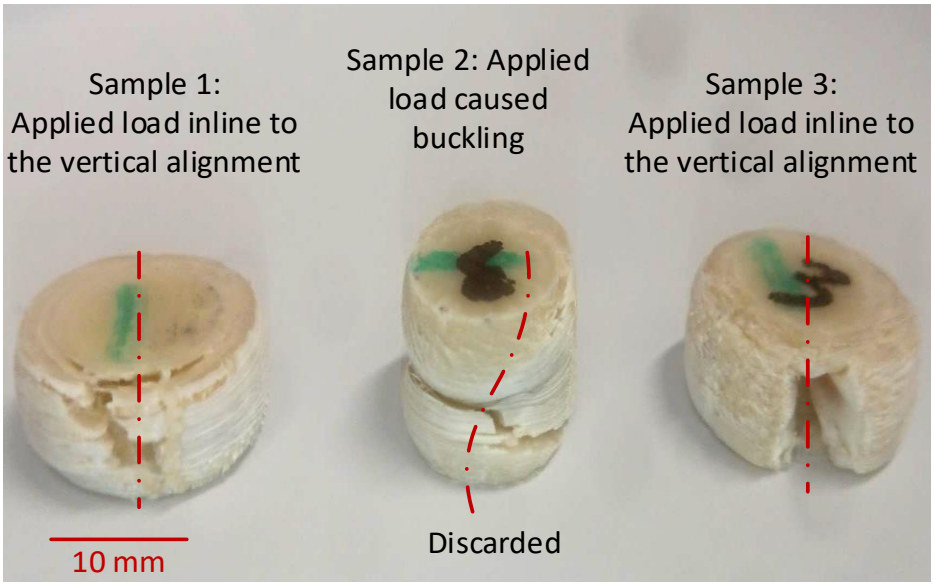


Figure 55. Compression testing of combination 27 and criteria for discarding samples based on buckling.

6.3.6. Fourier transform infrared spectroscopy (FTIR)

The effects of aging interval, bed temperature and printing temperature on intermolecular interactions is analysed with Fourier transform infrared spectroscopy (FTIR). Thermo electron Nicolet 8700 spectrometer is used to perform the FTIR analysis. The range of spectrum is 400-4000 cm^{-1} and attenuated total reflection single reflection accessory is used to record the spectrum. A total of 32 scans are averaged at a resolution of 4 cm^{-1}. OMNIC E.S.P software version 7.1 is used to record the FTIR data. Baseline normalization and correction is also performed to maintain uniformity among the FTIR results.

6.3.7. Differential scanning calorimetry (DSC)

The nature of intermolecular interactions (grafting or interlocking) obtained from FTIR is analysed with differential scanning calorimetry. The analysis uses the cold crystallization and melt crystallization data to analyse the thermal stability to high print temperatures and aging. DSC Q1000 from TA Instruments is used at a nitrogen purge flow rate of 50 mL/min. The rate of heating for DSC analysis is 10 °C/min for a range of 25 °C to 550 °C.

6.3.8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is performed on NETZSCH STA 449 F1 Jupiter to analyse the onset of thermal degradation and chemical interaction (grafting or interlocking). The rate of temperature increase is 10 °C/min with the nitrogen purging at a flow rate of 50 mL/min. The range of analysis is set the same as for DSC (25 °C to 550 °C).

6.3.9. Scanning electron microscope (SEM)

The tensile tested specimens are analysed by a scanning electron microscope (Hitachi TM3030 Plus). It is used to analyse the effects of high temperature and aging on the novel blend. The analysis is also used to detect any phase separation.

6.4. Results

6.4.1. Tensile testing

The randomized design of experiment (DoE) with the average tensile strength is shown in Table 20. The ANOVA analysis reveals the bed temperature and printing temperature as the significant factors in the Pareto Chart (Figure 56a). The P-values for bed temperature and printing temperature were 0.001 and 0.005 respectively. This provides statistical evidence of the thermal stability of the blend against aging for long intervals.

The Main Effects Plot in Figure 56b shows that tensile strength increases with an increase in bed and printing temperature. The thermal aging shows an increase in tensile strength for 3 days followed by a minor decrease in tensile strength for 6 days. It is considerable that the aging is not a significant variable as shown in the Pareto Chart and P-values. Therefore, the minor decrease in tensile strength is statistically not considerable.

Table 20. 3^3 full factorial ANOVA design of experiment with average tensile strength and strain.

Combination or standard order	Run Order	Bed temperature	Nozzle temperature	Aging interval	Tensile strength	Tensile strain
16	1	50	205	0	24.456	0.024
13	2	50	195	0	23.395	0.0252
22	3	75	195	0	30.895	0.0221
2	4	25	185	3	23.851	0.019
7	5	25	205	0	28.084	0.0193
11	6	50	185	3	27.378	0.0213
12	7	50	185	6	28	0.0185
5	8	25	195	3	26.346	0.0181
3	9	25	185	6	23.526	0.02
26	10	75	205	3	34.847	0.023
14	11	50	195	3	28.731	0.025
8	12	25	205	3	28.726	0.0192
25	13	75	205	0	30.592	0.0236
6	14	25	195	6	27.893	0.0131
21	15	75	185	6	28.459	0.0224
17	16	50	205	3	28.777	0.0202
1	17	25	185	0	24.724	0.0204
23	18	75	195	3	30.176	0.0232
15	19	50	195	6	28.603	0.023
27	20	75	205	6	30.0554	0.0232
10	21	50	185	0	25.533	0.0201
24	22	75	195	6	29.198	0.0236
19	23	75	185	0	27.714	0.0222
18	24	50	205	6	29.629	0.022
20	25	75	185	3	26.5711	0.0231
4	26	25	195	0	25.04	0.0202
9	27	25	205	6	27.4954	0.017

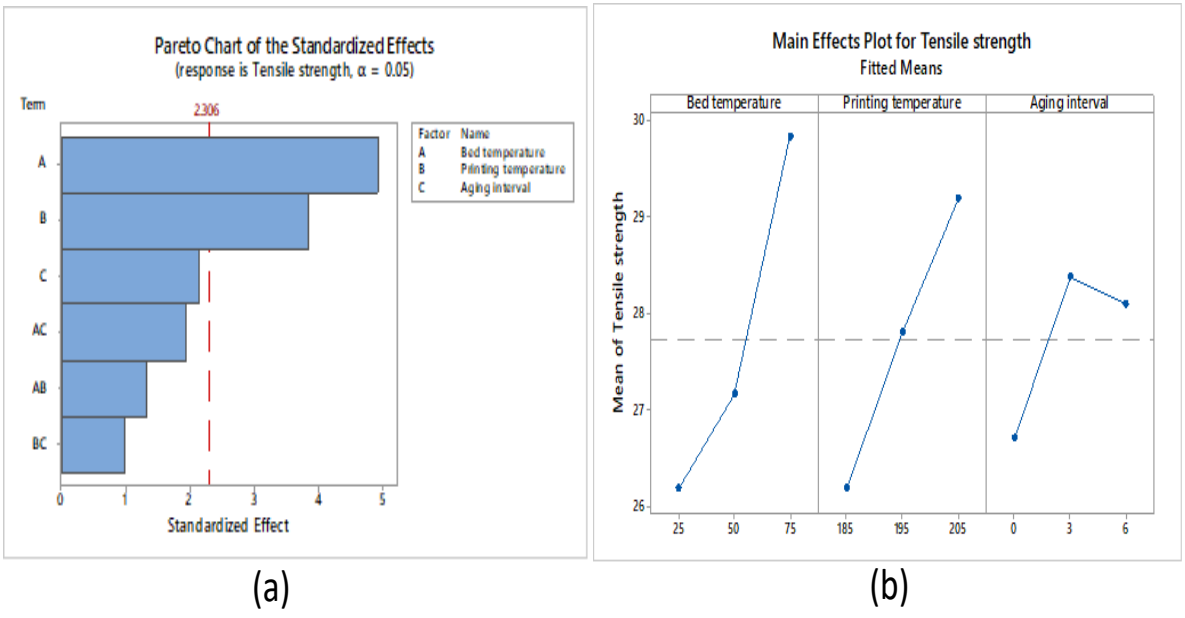


Figure 56. Minitab ANOVA analysis (a) Pareto Chart, and (b) Main Effects Plot.

The surface plots in Figure 57 explain the effects of binary interactions on the tensile strength. It is noted in Figure 57a that highest tensile strength is obtained at highest bed and printing temperature. This provides information about the stability of the blend against high melt temperatures. On the other hand, the aging provides maximum strength at 3 days in interaction with printing and bed temperature (Figures 57b and c). The results showed that the blend is resistive to thermal aging as it shows significant enhancement with the increase of aging instead of decreasing.

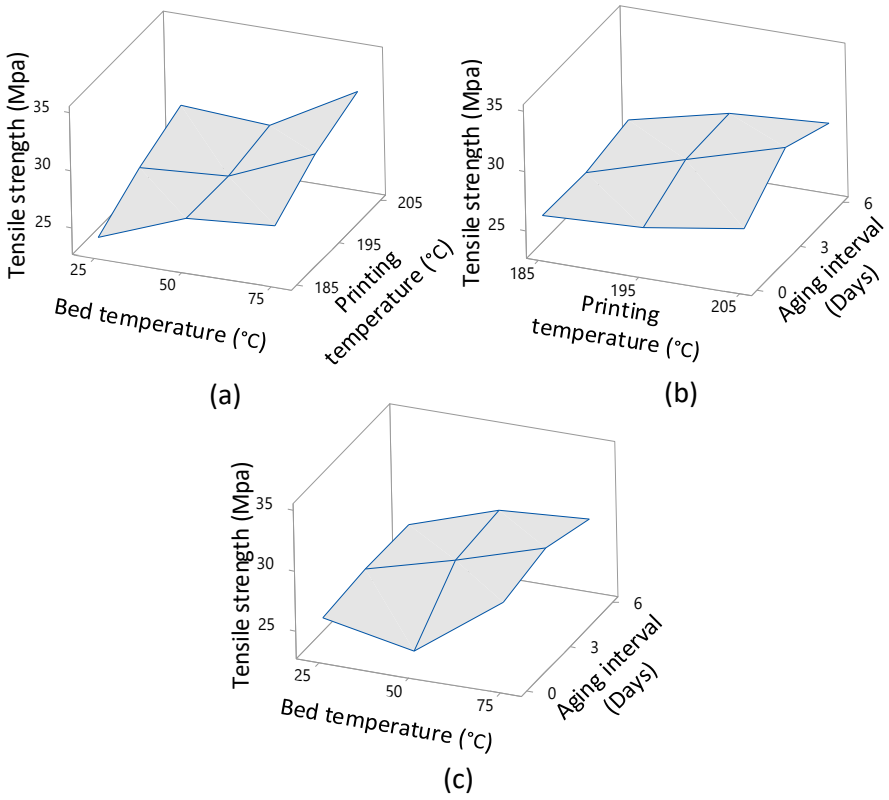


Figure 57. Surface plots for ANOVA 3^3 full factorial analysis with respect to tensile strength.

6.4.2. Flexural and compressive testing

The ultimate flexural and compressive strength of the samples printed for combination 25, 26 and 27 is shown in Figure 58. It is noted that the flexure strength increased with the increase of aging interval. The flexure strength of aged blend is the highest as compared to various well-known commercial filaments like Stratasys ABSPlus-P430 [251], Mark two [354], etc..

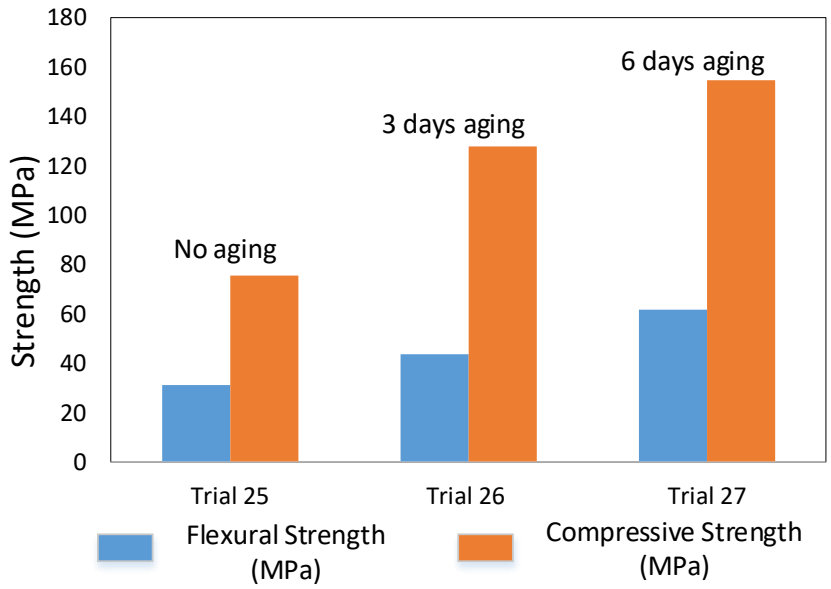


Figure 58. Compressive and flexural strength of ABS/HDPE/PE-g-MAH (92/7.5/0.5).

The compressive strength of the blend significantly increased with an increase in aging interval. As compared with literature [354-359], the ultimate compressive strength of 162 MPa achieved for 6 days aged samples is the one of the highest in FFF to date, to the best of our knowledge. The high compressive strength irrespective of increase in aging is evidence of the thermal stability of the novel FFF blend.

6.5. Discussion

6.5.1. Effect of melt-blending and aging

FTIR analysis is used for analyzing the effects of melt-blending and thermal aging on molecular interactions in single polymers and the blend (Figure 59). HDPE is confirmed by the stretching vibrations of C-H aliphatic hydrocarbons [322] as noted at 2913 cm^{-1} and 2846 cm^{-1}. PE-g-MAH is identified by corresponding peaks: two peaks for C-H stretching vibrations of grafted HDPE by 2914 cm^{-1} and 2847 cm^{-1}, and one peak of MAH at 1705 cm^{-1}. The absence of un-saturated hydrocarbon double bond (C=C) above 3000 cm^{-1} shows that the grafting of HDPE in PE-g-MAH is formed on the missing pair of electrons as reported by [321]. ABS is validated with four peaks [321]: nitrile (-C≡N) at 2237 cm^{-1}, butadiene double bond in C=C stretching vibrations at 1637 cm^{-1} and the aromatic ring stretching vibrations of styrene by 1494

cm^{-1}. Additionally, the deformation of hydrogen attached with carbons (alkene carbons) is found at 966 cm^{-1} and 913 cm^{-1}. 966 cm^{-1} presents the hydrogen attached with 1,4 butadiene and 913 cm^{-1} presents the 1,2 butadiene.

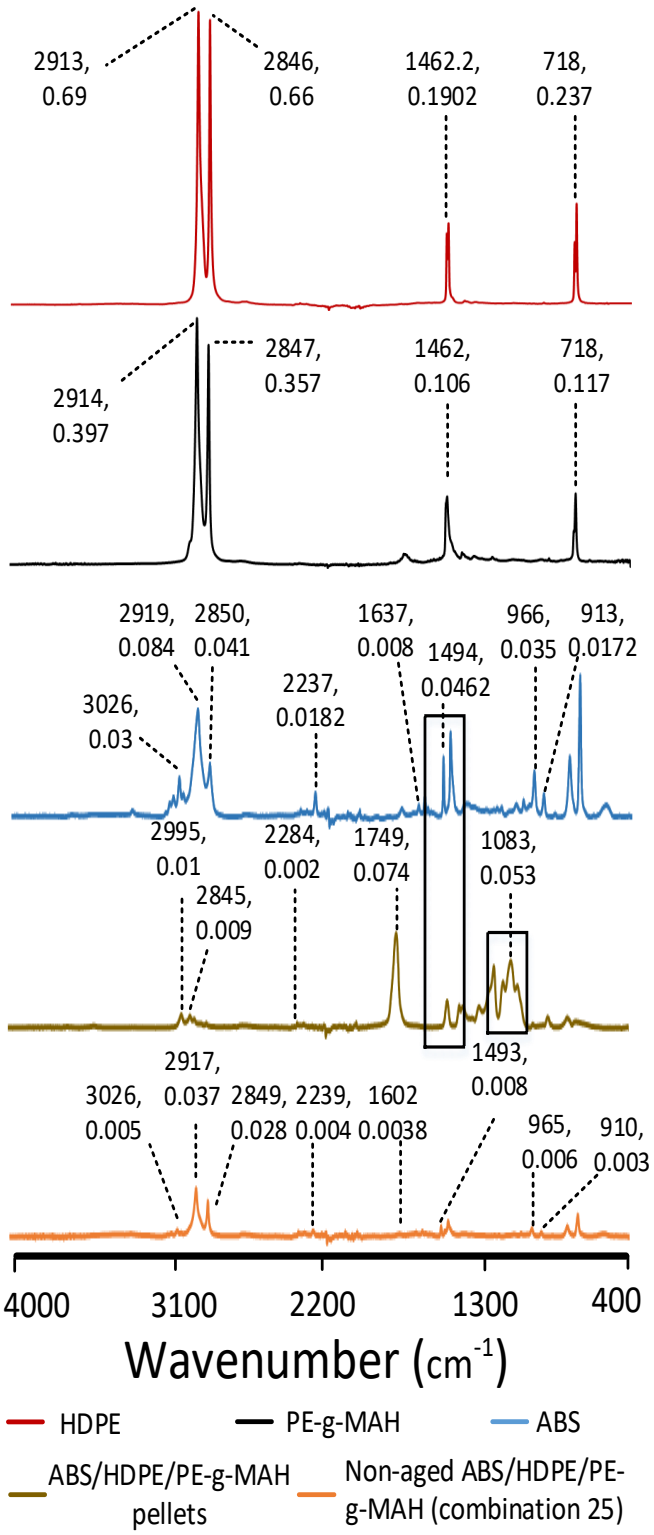


Figure 59. FTIR for analysis for chemical reactions due to blending and 3D printing.

Analysis in Figure 59 shows that ABS/HDPE/PE-g-MAH pellets made by single screw extrusion display modifications in bonding as compared to neat HDPE, PE-g-MAH and ABS. For example, the ABS/HDPE/PE-g-MAH pellets do not have the stretching vibrations of unsaturated hydrocarbons as found in ABS at 3026 cm^{-1} and the styrene peak at 1494 cm^{-1}. The peaks associated with hydrogen vibration of 1,4 butadiene and 1,2 butadiene found in ABS are merged into a big peak at 1083 cm^{-1} in the blend pellets.

However, when the pellets are printed (combination 25), the infrared spectrum comes quite close to the neat ABS but with noticeable differences (Figure 59). The differences in the printed blend sample as compared to the neat ABS are in the form of shifts and variations in the intensities. For example, a major shift is noted for butadiene units [321] from 1637 cm^{-1} in neat ABS to 1602 cm^{-1} in the printed blend. Furthermore, various minor shifts in the blend as compared to neat ABS are also noted. For example, C-H shift from 2919 cm^{-1} to 2917 cm^{-1} and 2850 cm^{-1} to 2849 cm^{-1}, -C≡N from 2237 cm^{-1} to 2239 cm^{-1}, styrene from 1494 cm^{-1} to 1493 cm^{-1}, hydrogen attached to alkene carbons from 966 cm^{-1} to 965 cm^{-1} and from 913 cm^{-1} to 910 cm^{-1}. This shows visible chemical interactions happening due to the blending that describes the improved mechanical properties of the printed blend as compared to ABS. Moreover, pellet printing with a non-compressive zone in a screw helps to recover the chemical reactions that are important to show blending.

The effects of thermal aging are also analyzed in FTIR graphs in Figure 60. The aged blend (combination 27) shows the absence of stretching vibrations of butadiene units as found at 1637 cm^{-1} in neat ABS. This may occur due to the chemical grafting on the double bond of butadiene. Furthermore, the significant decrease in intensities of all groups (unsaturated hydrocarbons, acrylonitrile and styrene) shows either the depletion or restriction of their movement. This shows that the long aging intervals, and high bed and printing temperatures resulted in significant intermolecular interactions that resulted in improved mechanical properties.

Apart from chemical interactions, FTIR analysis is not providing any information regarding the exact nature of intermolecular interactions (grafting or physical interlocking). Therefore, this requires DSC and TGA.

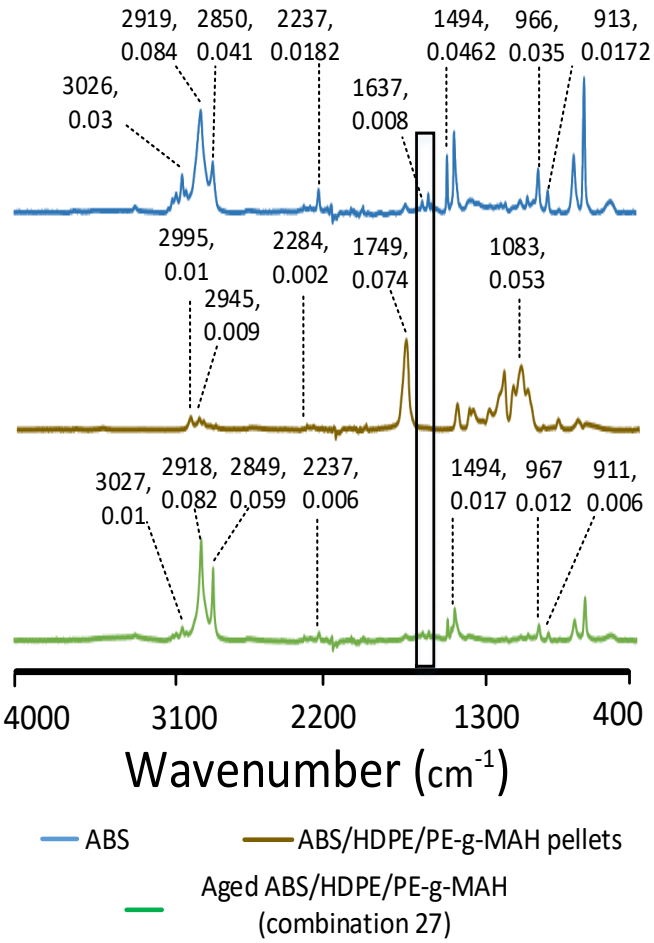


Figure 60. FTIR analysis for effects on intermolecular interactions due to the thermal aging.

6.5.2. Analysis of chemical grafting

Differential scanning calorimetry is used to analyze the nature of intermolecular interaction (grafting or interlocking) and thermal stability of the novel blend as compared to the neat polymers. As shown in Figure 61 and Table 21, HDPE has a melt crystallization at 133 °C and ABS has a glass transition peak at 108 °C which is in accordance with Sohel et al. [360] and Cao et at. [361]. The blend pellets show the superimposition of glass transition with the melt crystallization peak of HDPE (at 133 °C). The melt crystallization for pellets occurs at 129.2 °C. The drop-in melt crystallization (Table 21) shows the presence of intermolecular interaction according to the [361]. Furthermore, the absence of separate peaks of ABS and HDPE in blend (combination 25) is also an indication of chemical grafting. However, the bimodal peak in combination 25 (Figure 61) has been reported in the literature to be one sign of partial immiscibility or partial grafting as found by Vadori et al. [362]. This can be resulted from incomplete reactions during single screw extrusion as reported by Fu et al. [363] and Gale

et al. [364]. Therefore, analysis of the printed blend is also taken into consideration to analyze the grafting in the blend.

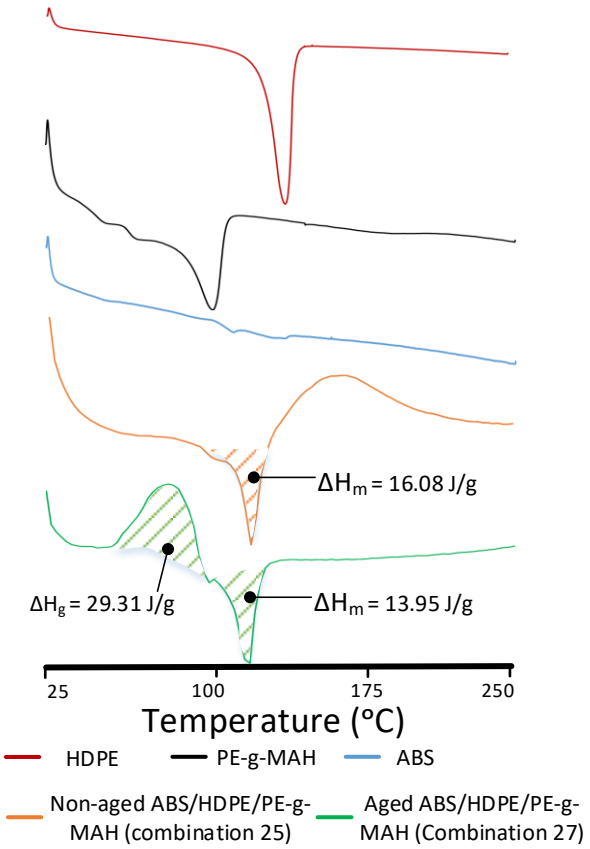


Figure 61. DSC analysis for effects of blending and thermal aging.

The aged blend printed at the highest bed and printing temperature (combination 27) shows a visible difference when compared to the non-printed blend pellets and neat ABS (Figure 61). The bimodal peak of non-aged blend (combination 25) is converted into a single modal transition in aged blend (combination 27) after 3D printing followed by aging. This shows that both the main constituents (ABS and HDPE) have now chemically interacted and incomplete blending is the main reason for the bimodal peak in pellets. Furthermore, the cold crystallization peak at 89.7 °C is observed in aged blend but was not detected in pellets (Figure 61 and Table 21). This presents the heterogeneous crystallization of grafted constituents as presented by Vadori et al. [362]. It is also noted in Table 21 that the enthalpy of glass crystallization (29.31 J/g) is more than the melt crystallization (13.95 J/g) for aged blend. This shows the high printing parameters and the aging accelerates the nucleation activity resulting

in an increase in heterogeneous orientation of the intermolecular polymeric chains. Furthermore, the melt crystallization temperature at 129.3 °C (Table 21) is the same as for the non-aged printed samples. This shows that the novel FFF blend is thermally stable due to the high printing temperatures and 6 days aging.

Table 21. DSC analysis of ABS, HDPE, non-aged (combination 25) and aged (combination 27) blend.

Polymers	**T_g (°C)**	**T_m (°C)**	**ΔH_g (J/g)**	**ΔH_m (J/g)**
HDPE	-	133.24	-	116.6
ABS	108	-	-	-
ABS/HDPE/PE-g-MAH (Non-aged)	Not detected	129.2	Not detected	16.08
ABS/HDPE/PE-g-MAH (aged)	89.7	129.3	29.31	13.95

6.5.3. Validation of thermal stability

Thermogravimetric analysis is shown in Figure 62 and Table 22. It is noted that the degradation in blend occurs in a single step showing formation of compatibilized blend according to the literature [365]. The onset of degradation for neat ABS is 378 °C and it produced 4.5% residues at 550 °C. The onset of degradation for ABS is in accordance with the Hong et al. [366]. Suzuki et al. [367] report the onset of degradation due to the oxidation of alkene bonds or hydrogen abstraction associated with butadiene monomers.

As a comparison, the onset of degradation for non-aged blends was significantly enhanced to 404 °C (Table 22). Elnaggar et al. [368] associates the enhancement in onset with thermal stability of butadiene groups due to the compatibilized blending of HDPE. However, the FTIR analysis shows an opposite perspective with the decrease of butadiene intensity at 1604 cm^{-1} of non-aged blend (combination 25) in Figure 59. This decrease is due to the grafting of PE-g-MAH on free electrons of butadiene groups after the thermal degradation of alkene bond or hydrogen abstraction. The grafting of HDPE with ABS through PE-g-MAH obstructs the movement (vibrations) of butadiene that causes the decrease in FTIR vibration intensities of corresponding peaks. Similar decrease in FTIR intensities is reported by Staurt et al. [325] due to the obstruction of movement.

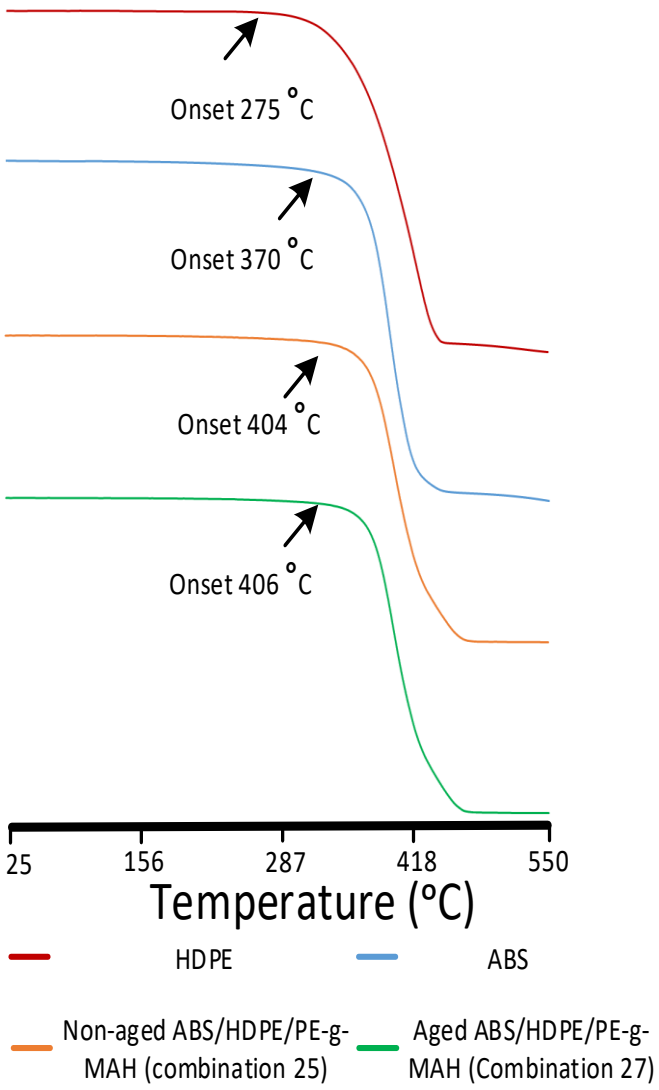


Figure 62. TGA analysis for effects of blending and thermal aging.

The analysis of aged blend shows a further increase in the onset temperature than non-aged blend (Figure 62 and Table 22). This explains the enhanced chemical interactions (grafting) of HDPE with ABS in the presence of a compatibilizer according to Elnaggar et al. [368]. The increase in onset temperature of aged blend is also depicted by DSC analysis in the form of a prominent cold crystallization peak. This shows that the aging helps to increase the nucleation for crystal growth. The enhanced intermolecular interactions due to the grafting of HDPE with ABS in the presence of PE-g-MAH is the main reason for an increase in mechanical properties (tensile, compressive and flexure) as well.

Table 22. TGA analysis of ABS, HDPE, non-aged (combination 25) and aged (combination 27) blend.

Polymers	Onset temperature
HDPE	275
ABS	378
ABS/HDPE/PE-g-MAH (Non-aged)	404
ABS/HDPE/PE-g-MAH (aged)	405.8

6.5.4. Scanning electron microscopy (SEM)

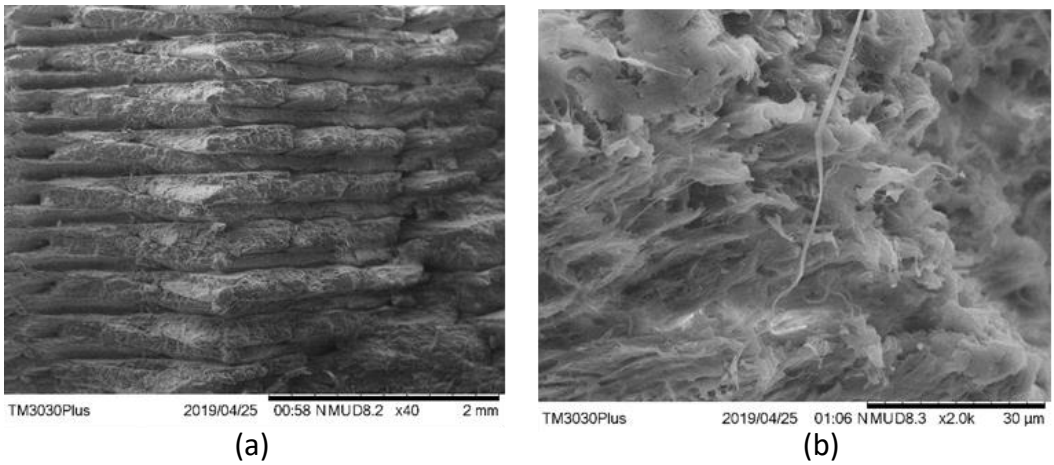


Figure 63. SEM analysis for: (a) combination 4 (bed temperature 25 °C, printing temperature 195 C and no aging), and (b) magnified image at 2000x zoom for combination 4.

The SEM micrographs of tensile testing are given in Figure 63. The micrographs in Figures 63a and b depict the stiffness in the blend. However, the magnified image in Figure 63 further helps to clarify the original nature of the fracture. The micrograph in Figure 63 displays elongated flakes that show the ductile behavior of the samples. Similar kinds of sheared flakes are linked with ductility by Balakrishnan et al. [369] for ABS/PC blend. The visible ductility is due to HDPE. It is also noted there is no sign of phase separation between ABS and HDPE. This confirms the results of chemical grafting between ABS and HDPE due to the compatibilizer (PE-g-MAH).

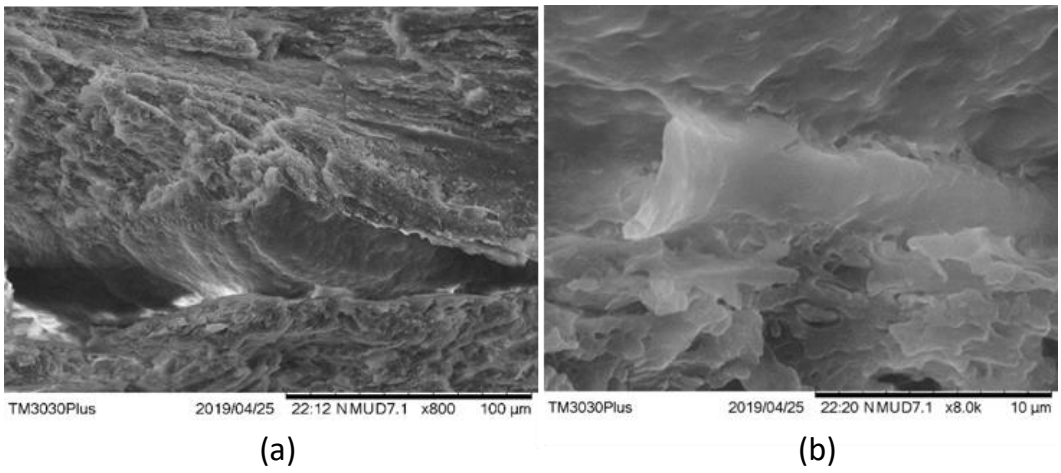


Figure 64. SEM analysis for thermal effects of aging: (a) combination 27 (bed temperature 75 C, printing temperature 205 C and 6 days aging), and magnified image at 8000x zoom of a particular section of combination 27.

The analysis of the thermal effects on adhesion between the beads of polymers is provided in Figure 64. The magnified image in Figure 64b shows the fusion between two beads. The quality of the fused area is clearly seen to be improved due to aging instead of degradation. The stiff extension in the fused area is a sign of high resistance to the applied forces. The improved inter-layer diffusion due to aging is one of the reasons for the high strength of the tensile specimens at 6 days aging.

6.6. Summary

In this research the thermal stability of ABS is improved by proposing a blend with HDPE in the presence of PE-g-MAH. 3^3 full factorial design of experiments is used for analysis of thermal resistance of the blend against printing temperature, bed temperature and thermal aging. The thermal resistance is evaluated in terms of tensile strength. The best three combinations of tensile strength are used for conducting the flexure and compressive testing. The printing blends are analyzed through FTIR to detect chemical interactions and effects of thermal aging. DSC is used to assess the resistance of the proposed blend to thermal aging through glass transition and melt crystallization. TGA is also used to evaluate the thermal stability of ABS blend through onset temperatures of degradation. Finally, SEM is used to observe the morphological effects of the compatibilized blend and to analyze the diffusion between deposited layers. The research has the following outcomes:

1. The blend has one of the highest mechanical properties among the existing FFF blend materials. The tensile strength is the second highest, flexural strength and compressive strength is the highest among existing literature on blends for FFF.

2. The aging has significantly increased the mechanical strength (tensile, flexure and compressive) instead of degradation. This shows the thermal stability at high temperatures.

3. Thermal aging has improved the cold crystallization as observed in DSC. This heterogeneous crystallization has improved the diffusion among beads during 3D printing that leads to improved properties.

4. The increase in on-set temperature to 406 ^{o}C of the blend after six days aging as compared to 378 ^{o}C of ABS in TGA analysis further elaborates upon the thermal stability of the blend.

Chapter 7. Acrylonitrile butadiene styrene and polypropylene blend with enhanced thermal and mechanical properties for fused filament fabrication

Chapter 7 includes the following article, “Acrylonitrile butadiene styrene and polypropylene blend with enhanced thermal and mechanical properties for fused filament fabrication”, published in the MDPI journal of “Materials”. This article is open access and has been republished in this thesis under the Creative Commons Attribution License.

The full text is included in the thesis without any modifications. However, there are formatting differences to keep the formatting same for the thesis. The formatting modifications involve page setup, font style, referencing style, reference citation style and bibliography style.

Acrylonitrile butadiene styrene and polypropylene blend with enhanced thermal and mechanical properties for fused filament fabrication

7.1. Abstract

Acrylonitrile butadiene styrene (ABS) is the oldest fused filament fabrication (FFF) material that shows low stability to thermal aging due to hydrogen abstraction of butadiene monomer. A novel blend of ABS, polypropylene and polyethylene (PP) graft maleic anhydride (PE-g-MAH) is presented for FFF. ANOVA analysis is used to analyze the effects of three variables (bed temperature, printing temperature and aging interval) on tensile properties of the specimens made on a custom-built pellet printer. The compression and flexure properties are also investigated for the highest thermal combinations. The blend shows high thermal stability with enhanced strength despite of six days' aging, high bed and printing temperatures. Fourier transform infrared spectroscopy (FTIR) provides significant chemical interactions. Differential scanning calorimetry (DSC) confirms the thermal stability with enhanced enthalpy of glass transition and melting. Thermogravimetric analysis (TGA) also reveals high temperatures for onset and 50% mass degradation. Signs of chemical grafting and physical interlocking in scanning electron microscopy (SEM) also explain the thermo-mechanical stability of the blend.

7.2. Introduction

Acrylonitrile butadiene styrene (ABS) is the most common terpolymer in conventional polymer processes and fused filament fabrication (FFF) [296, 370]. It is composed of styrene acrylonitrile (SAN) grafted with polybutadiene (PB) that provides diverse properties (tensile strength, ductility, hydrophobicity) to suit a wide range of applications in conventional polymer processes [335]. Meanwhile, it is one of the oldest FFF materials that has been used to 3D print a wide range of additive manufacturing (AM) applications. For example, prototypes, airfoils, clamps, etc. The recent application of ABS with carbon fibers in big area additive manufacturing (BAAM) has re-defined its importance at large-scale manufacturing [333, 341]. The large-scale applications demand enhanced stability that can withstand high applied loads at high temperatures. Though ABS has good mechanical, chemical and thermal properties at room temperature [371], the hydrogen abstraction from PB at high temperatures results in the

decline of thermal stability [336, 372]. The hydrogen abstraction has reported a significant impact on the mechanical and thermal properties due to the different weathering conditions above 40 °C [336, 337, 345]. Therefore, a need arises to explore a solution for a thermally stable ABS for large-scale and high temperature FFF applications.

Different methods have been adopted to increase the thermal stability of ABS [373, 374]. For example, blending [373, 374], addition of flame retardants[338], stabilizers [373], etc. The most recommended method in terms of gaining both thermal and mechanical stability is blending with high temperature polymers [338, 339, 374]. In this regard, polycarbonate (PC) is the most successful polymer that reports the best-in-class blend properties with ABS [339] as compared to the contemporary ones in FFF. For example, ABS/UHMWPE/SEBS, ABS:SEBS [145, 236], ABS:SEBS-g-MAH [41], ABS/PMMA [340] and ABS/SMA [341]. The addition of PC in ABS has been reported with improvements in both thermal and mechanical properties (tensile, compression and flexure) [338, 342]. However, thermal improvement is interpreted as an improvement in the onset of the degradation temperature of the non-aged blend obtained in thermogravimetric analysis (TGA) [343]. The researchers have found detrimental effects of annealing on the morphology of an ABS/PC blend that resulted in a decrease of thermal stability [343]. Therefore, it reveals a need to explore a blend of ABS that can withstand thermal aging at high temperatures with good mechanical properties (tensile, compression and flexure).

Polypropylene (PP) is one of the eminent polyolefins with good chemical and mechanical properties [375]. It has been found with warpage and swelling in FFF process. This is overcome by blending with different printable polymers or fillers (fibers). For example, Peng. X. et al [376] reports enhanced mechanical strength with the addition of polyamide (PA6) and POE-g-MAH. Ramis. X. et al [375] reports the enhanced thermal stability in a TGA analysis of PP/starch. Mourad. A.H.I. et al [377] finds good resistance to thermal aging and un-affected tensile strength in a PP/PE blend. Carneiro. O. S. et al. [36] and Sodeifian .G. et al. [156] report improved mechanical strength with the addition of glass fibers in PP. It is noted that the proposed blends with or without fillers provided either good mechanical strength or resistance to aging. Furthermore, the mechanical characterization of the blends is mostly limited to either tensile or flexural strength. The improved overall mechanical stability (tensile, compressive and flexural) at higher temperatures (thermal aging) for long numbers of days is still not reported in FFF literature for PP blends.

This research proposes a novel FFF blend of ABS with PP compatibilized with polyethylene graft maleic anhydride (PE-g-MAH) that can withstand thermal aging for days with good mechanical properties (tensile, compressive and flexure). A statistical design of experiments (DoE) constituted of 3^3 full factorial is designed to analyze the tensile properties and thermal stability against three variables (bed temperature, printing temperature and aging interval). The compression and flexural experimentations are performed at three such combinations from the ANOVA analysis that have the highest levels of thermal variables. The results display significantly enhanced mechanical properties even after thermal aging. The blend is further investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) to ascertain the reasons for the improved thermo-mechanical properties.

7.3. Materials and methods:

7.3.1. Materials

Polylac PA-747 ABS pellets with high melt flow index of 13 g/10 min were purchased from TCL Hunt, New Zealand. DOWLEX IP-10 PP with a melt flow index of 10 g/10 min was also purchased from TCL Hunt. The A8525 PE-g-MAH (compatibilizer) with a composition of 50:50 by weight percent was purchased from Shenzhen Jindaquan Technology Co. Ltd., China.

7.3.2. Blending

ABS, PP and PE-g-MAH were dried at 50 °C in an oven for six hours. The drying is followed by mixing all three polymers in specific compositions in a mixer for five minutes. The compositions were blended in a single screw extruder. Which was specifically selected for blending in order to avoid any probable degradation due to shearing pressure at high temperatures [350]. The pellets are produced in a size of approximately 1.3mm with the pelletizer unit operating at 20 meter/minute. Further processing parameters are provided in Table 23.

Table 23. Parameters for single screw melt blending.

Variable	Value
Feeder to nozzle temperature	175 °C, 175 °C, 180 °C, 180 °C, 180 °C, 180 °C, 180 °C, 180 °C, 170 °C and 150 °C.
Feed rate	21 rpm
Screw speed	200 rpm
Torque	45%
Die pressure	51 bar

Successful 3D printing is one of the main objectives in this research. The compositions of each of the three polymers in the blend can potentially affect the printability. For example, Zhang et al. [327] reports defects in rheological properties due to an excess of maleic anhydride (MAH). Rheological defects can lead to serious problems in the printing. On the other hand, the high composition of PP is reported to cause large die swelling during extrusion [378] and warpage during printing [36, 379]. Therefore, the first blend is prepared with 48:48 by weight percentage of ABS/PP (Table 24) with 4% of PE-g-MAH [309, 310], whose printing failed. For the second and third compositions (Table 24), the composition of PP was decreased while keeping the compatibilizer the same at 4%. However, failed printing for the second, and partial printing with high warpage for the third composition, led to the preparation of a fourth composition. The fourth composition, prepared with 0.5% of PE-g-MAH [311], provides the best printing. Therefore, no further composition needs to be prepared.

Table 24. Compositions prepared for the blend, printing bed type and effects on printability.

Composition	ABS	HDPE	PE-g-MAH	Printing bed	Printability
1	48	48	4	Perf board and adhesion tape	No
2	75	21	4	Perf board and adhesion tape	No
3	85	11	4	Perf board and adhesion tape	Yes, but excessive warpage caused separation of intercalated layers
4	92	7.5	0.5	Adhesion tape	Yes

7.3.3. 3D printing

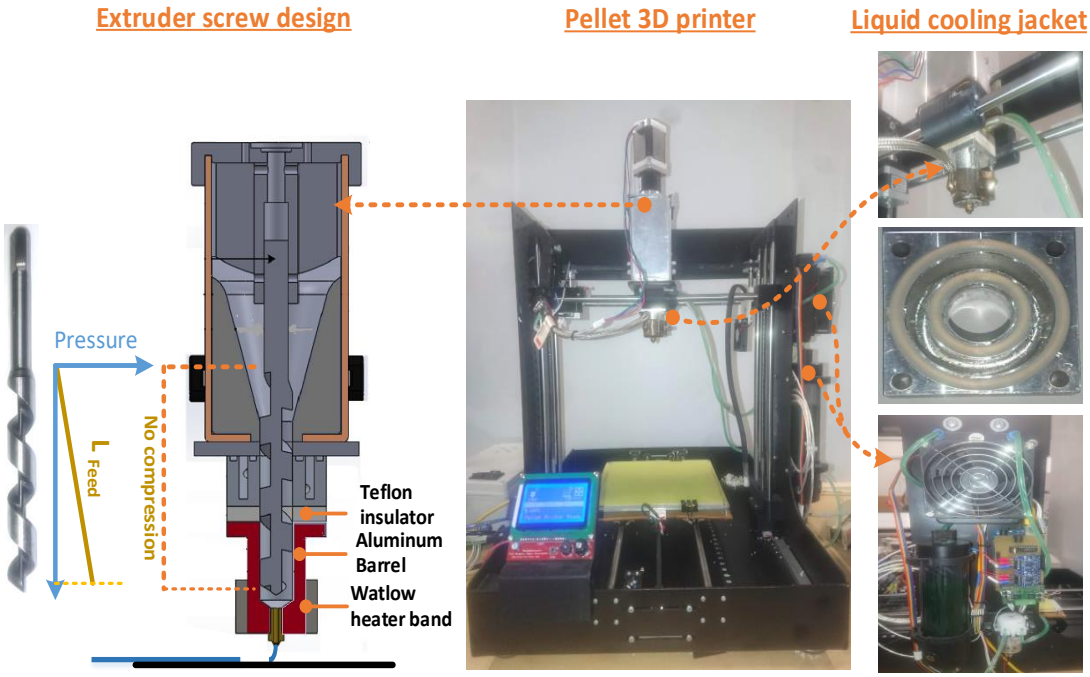


Figure 65. Illustration of different parts of pellet 3d printer [73] and the modifications in extruder screw and cooling system.

3D printing is performed on our in-house-built pellet 3D printer (Figure 65) that has been previously reported [73]. The modifications are particularly made in the cooling system, insulation and extruder screw to avoid variations in the material properties during printing. The liquid cooling system has been improved with an enlarged liquid channel in the liquid cooling jacket. The "Teflon insulation" plate is included as a thermal barrier. Both the liquid cooling system and the Teflon plate has improved the resistance to the heat transfer through the extruder. The better resistance has helped to enable printing at high temperatures above 200 °C. Furthermore, the extruder screw design is refined (Figure 65) with the exclusion of the compression and metering zones unlike regular screw extruders. The screw extruder's feeding zone avoids any thermal compression of the melt. This helps to overcome variations or degradation in the material properties due to any thermal shearing [73, 380]. The three main modifications (cooling system, Teflon insulation and screw extruder) are expected to achieve printing with characteristics as near as possible to the original blend.

Table 25. Parameters for screw extrusion 3D printing.

Parameters	Values
Feed rate	5 mm/min
Printing speed	5 mm/min
Layer thickness	0.2 mm
Raster width	0.2 mm
Raster angle	45°/-45°
Infill density	100%
Multiplier	15
Number of contours	1
Nozzle diameter	0.4 mm

An open source software named “Slic3er” is used to control the printing parameters (Table 25) and “Pronterface” is used to operate the printer.

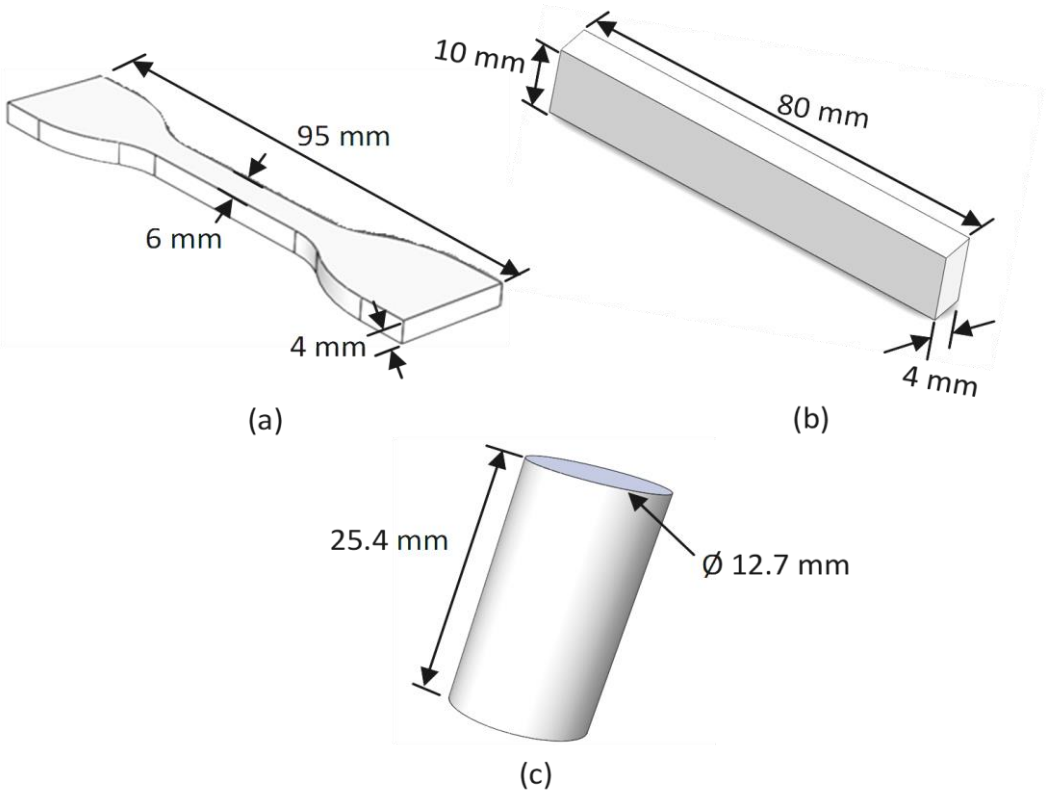


Figure 66. Standards for sample testing: (a) ASTM D638 for tensile testing, (b) ISO 604 for compression testing, and (c) ISO 178 for flexure testing.

ASTM D638 type IV [351] is used as the tensile testing standard, ISO 604 [351] for compression, and ISO 178 [353] for the flexural testing standard (Figure 66). The first two

compositions show large die swelling during extrusion printing. Furthermore, the extrusion rate during printing was too slow to even meet the lowest printing speed of 1 mm/min. The third composition was partially printed. The excessive warpage causes incomplete printing (Figures 67c and d). Different types of surfaces (perforated, flex) are also used to improve the adhesion of composition 3 specimens with the printing bed. However, the sample results in high delamination and incomplete printing due to the excessive warpage (Figure 67c). The fourth composition is printed on an adhesion tape printing bed. It shows minimum to no warpage. Therefore, the remaining experimentation of this research is conducted with composition 4.

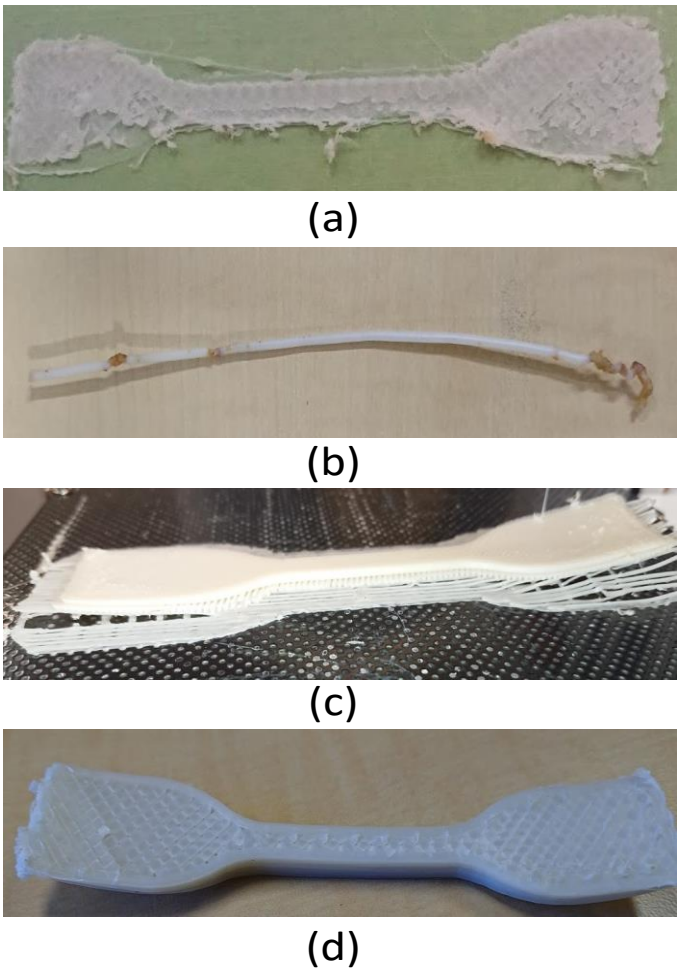


Figure 67. Failed printing for: (a) printing at 175 °C, (b) thermal degradation in extruded filament above 210 °C, (c) printing composition 3 with perforated board, and (d) deflection after printing in composition 3.

A randomized general 3^3 full factorial ANOVA analysis in Minitab2019 is performed for tensile testing at a confidence level of 95%. Three variables are selected to analyse the thermal

stability on tensile strength. Each variable has three levels, i.e., bed temperature is set at 25 °C, 50 °C and 75 °C, printing temperature at 185 °C, 195 °C and 205 °C and aging interval at 0 day, 3 days and 6 days. Noted is an incomplete printing below 178 °C as the temperature is too low to melt the material. Further, the printing above 210 °C results in burnt marks in the extrudate. Similarly, the minimum temperature of the bed is set at 25 °C with reference to the room temperature, and the highest of 75 °C in this research is based upon the literature. The aging intervals are also selected according to the literature [345]. Three samples are printed for each of 27 combinations and an average of tensile strength and strain is used in the analysis. However, the analysis is performed with respect to tensile strength, not tensile strain.

Based on the objective of evaluation of thermal stability of novel FFF material and significance of bed and printing temperature, the combinations with highest bed and printing temperature are used to print and analyse the compressive and flexure properties.

7.3.4. Mechanical testing

Instron 5967 with a 30 KN load cell is used to perform the mechanical testing (tensile, compression and flexure). The tensile testing on ASTM D638 type IV dogbones is performed at an extension rate of 5 mm/min and with a 25 mm clip-on gauge extensometer for measurement of tensile extension. The flexure testing of ISO 178 rectangular bars is performed on a three-point flexure setup at a rate of 2 mm/min. The horizontal span between the two loading anvils is set at 64 mm as per ISO 178. The compressive testing of ISO 604 cylindrical samples is performed at 2 mm/min. The variations in the flexural samples of combination 27 are particularly monitored and the samples with too high dimensional instability are discarded. Similarly, the vertical alignment of layers during printing leads to a proper compression. The vertically mis-aligned samples display buckling and therefore were discarded as well.

7.3.5. Fourier transform infrared spectroscopy (FTIR)

FTIR is used for analysis of effects of the blending, 3D printing and thermal aging on a Thermo electron Nicolet 8700 spectrometer with a spectrum range of 400-4000 cm^{-1}. OMNIC E.S.P 7.1 is used to collect the data from an attenuated total reflection accessory that provides

an average spectrum of total of a 32 scans at a resolution of 4 cm^{-1}. All FTIR spectrums are corrected and normalized with respect to a baseline.

7.3.6. Differential scanning calorimetry (DSC)

The effects of three variables (bed temperature, printing temperature and aging interval) on the glass crystallization, melt crystallization and degradation are measured with DSC Q1000 from TA Instruments. The instrument is operated at heating rate of 10 °C/min in nitrogen gas purged at a flow rate of 50mL/min. The range of temperature for DSC analysis is 25 °C to 550 °C.

7.3.7. Thermogravimetric analysis (TGA)

The effects of experimental variables on the onset temperature and 50% degradation is analysed on STA 449 F1 Jupiter by NETZSCH. The thermal analysis is conducted at a rate of 10 °C/min in nitrogen gas purged at 50 mL/min. The analysis is performed in a range of 25 °C to 550 °C.

7.3.8. Scanning electron microscope (SEM)

The visual phase separations between ABS and PP at the fractured surfaces were analysed by an SEM (Hitachi TM3030 Plus). It is also used to analyse the effects of aging interval, bed temperature and printing temperature. The images are used to describe the tensile properties in ANOVA analysis.

7.4. Results

7.4.1. Tensile testing

The 3^3 full factorial design of experiment with tensile strength and strain is given in Table 26. ANOVA analysis of the data in Figure 68 shows the bed temperature and printing temperature as the significant variables in a Pareto Chart. The interval plots are further elaborating the individual effects of each variable on the tensile strength. It is noted that the printing temperature results in the decline of strength with a rise from 195 °C to 205 °C. This

also explains the burnt marks above 210 °C. However, the decline is not significant. Therefore, it cannot be considered as a degradation of thermal stability at 205 °C.

Table 26. 3^3 full factorial design of experiments with tensile strength (MPa) and strain (mm/mm).

Std Order	Run Order	Bed temperature	Nozzle Temperature	Post printing aging	Tensile strength	Tensile strain
18	1	50	205	6	28.7	0.022
4	2	25	195	0	25.4	0.02
1	3	25	185	0	28.2	0.020
7	4	25	205	0	24.9	0.019
14	5	50	195	3	31.1	0.025
16	6	50	205	0	28.7	0.024
27	7	75	205	6	31.6	0.023
15	8	50	195	6	29.8	0.023
2	9	25	185	3	28.9	0.019
9	10	25	205	6	23.3	0.017
10	11	50	185	0	22.9	0.020
24	12	75	195	6	31.2	0.023
5	13	25	195	3	24.9	0.018
20	14	75	185	3	29.7	0.023
25	15	75	205	0	30.3	0.025
3	16	25	185	6	29.1	0.02
21	17	75	185	6	19.6	0.022
11	18	50	185	3	27.5	0.021
17	19	50	205	3	31	0.020
13	20	50	195	0	30.1	0.025
12	21	50	185	6	25	0.018
23	22	75	195	3	30.8	0.023
6	23	25	195	6	26.2	0.013
19	24	75	185	0	28.2	0.022
26	25	75	205	3	28.8	0.023
22	26	75	195	0	30.3	0.022
8	27	25	205	3	26.4	0.019

The surface plots and contour plots show the significance of high printing and bed temperature (Figure 5a). The three binary plots (surface and contour) show a decline of tensile strength at lowest bed temperature (25 °C) and printing temperature (185 °C). The decrease is the result of low diffusion between the beads due to either of low bed or printing temperature [381]. It is also noted that at the highest aging interval (6 days), the strength decreases for lowest printing and bed temperature and increases for the highest corresponding variables

(Figures 5b and c). The increase in tensile properties after six days of aging depicts the non-significance of the aging interval and hence the thermal stability is statistically proved based on the non-replicative DoE in this research.

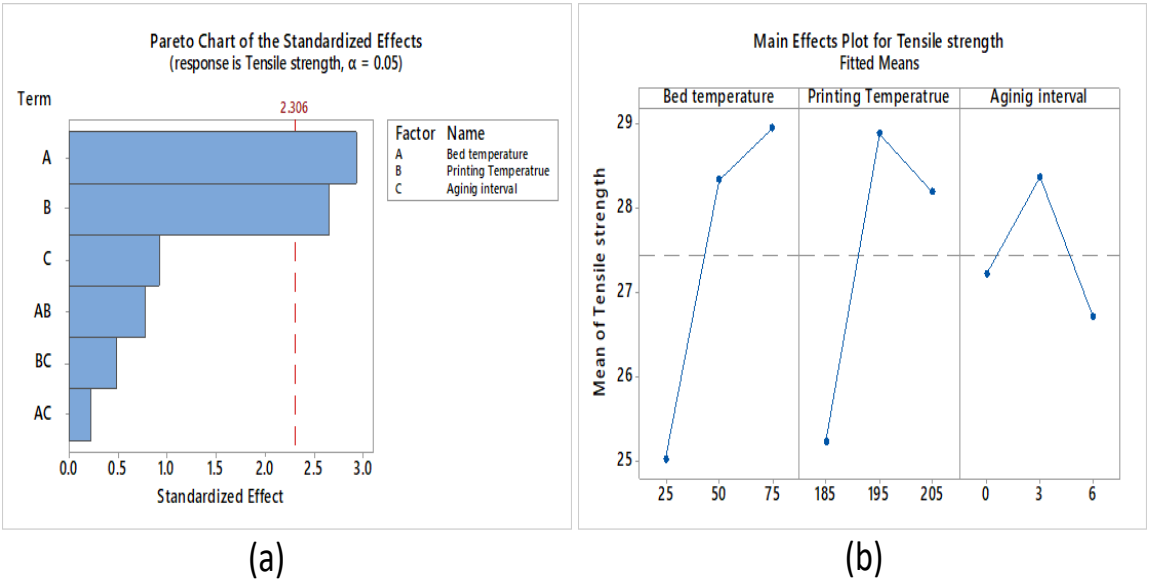


Figure 68. ANOVA analysis: (a) Pareto Chart, and (b) Main Effect plot.

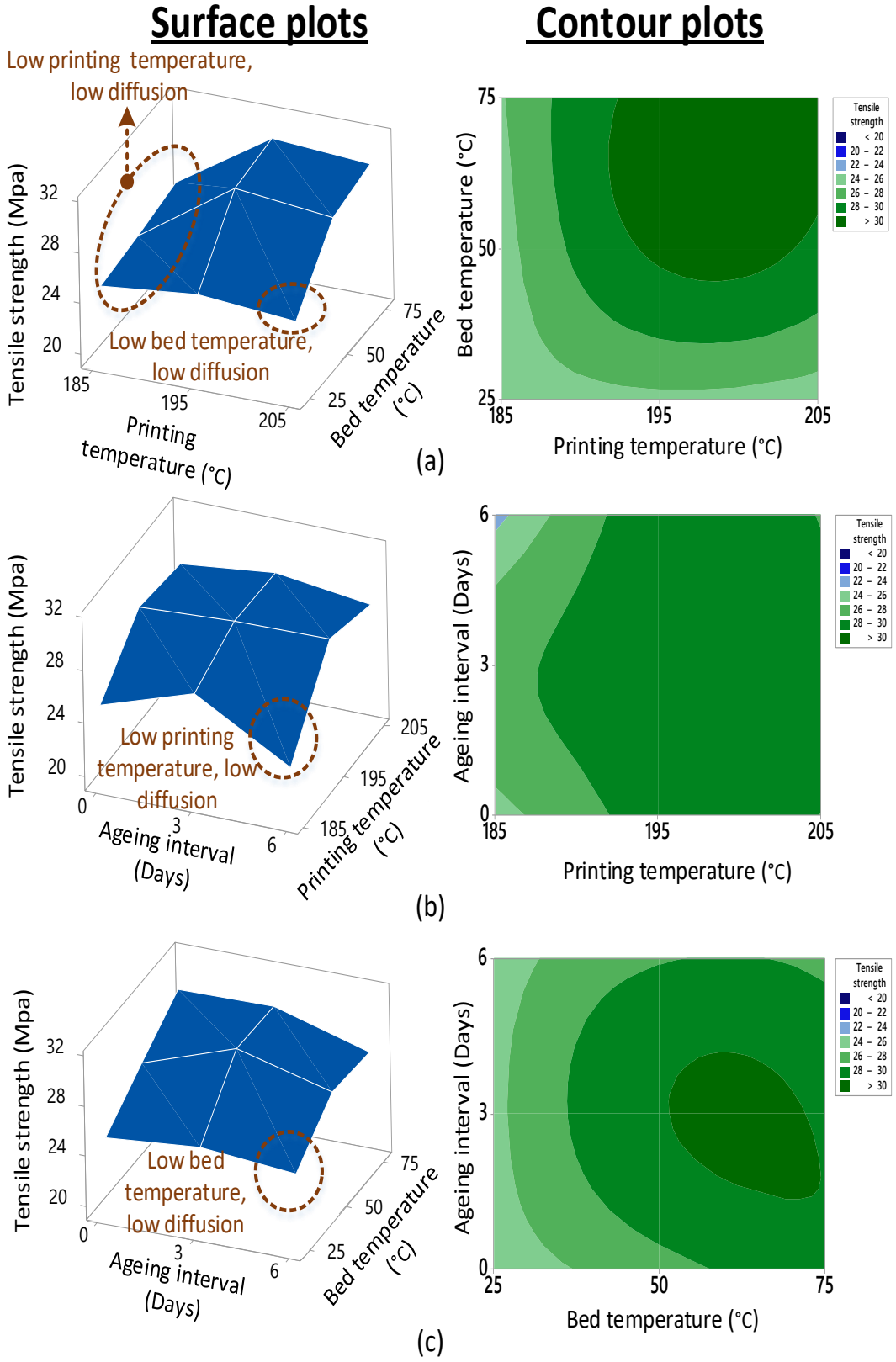


Figure 69. Surface and contour plots for:(a) printing vs bed temperature, (b) aging interval vs printing temperature, and (c) aging interval vs bed temperature.

The analysis of stress-strain graphs in Figure 6 shows far higher stiffness for the blend as compared to neat ABS at combination 27 (bed at 75 °C, printing at 205 °C, aging 6 days). This shows the improvement in one of the important mechanical characteristics(stiffness) of the novel FFF blend.

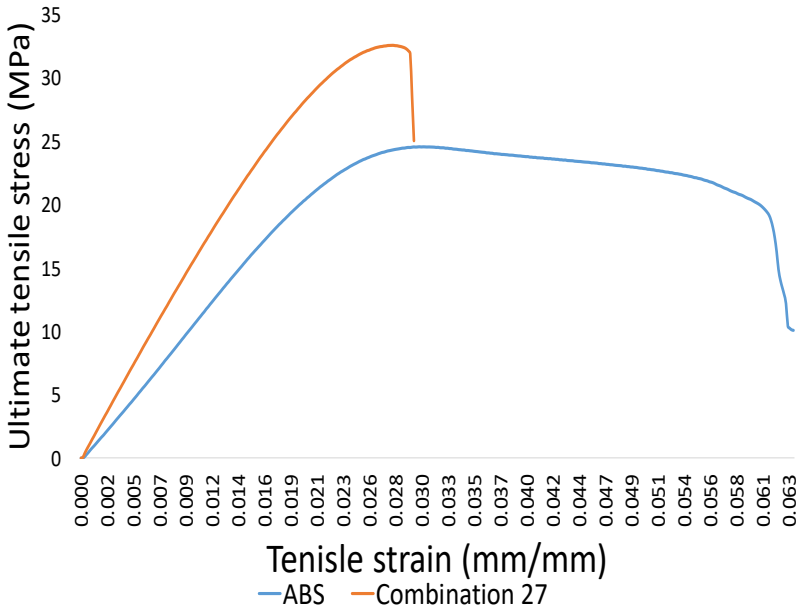


Figure 70. Stress-strain graphs for ABS and blend (combination 27).

7.4.2. Compressive and flexural testing

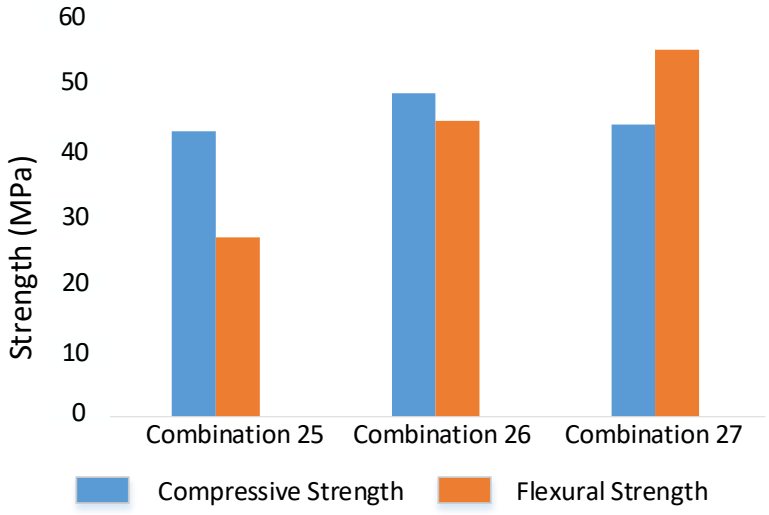


Figure 71. Compression and flexure strength of three combinations at highest bed and printing temperatures.

Similar resistance to thermal aging like tensile strength is observed for compression and flexure properties (Figure 71). The flexure properties increase to as high as 54.9 MPa with an increase of aging interval. This may be due to the improvement in diffusion between printed layers during aging instead of degradation. The compression strength shows significant enhancement from 0 to 3 days of aging, when the compression properties increase to 48.4 MPa. However, it drops down to 43.7 MPa after six days of aging. But this decrease in compression values for six days seems not significant considering the number of days as the drop is of just 4.7 MPa.

7.5. Discussion

7.5.1. Effects of blending, printing and thermal aging

The effects of blending, printing and thermal aging on the intermolecular interactions as compared to neat ABS are shown in Figure 72 and Table 27. PP is noted with the asymmetric and symmetric stretching vibrations of CH_2 and CH_3 in the range of 2800-3000 cm^{-1} along with numerous other peaks provided in Table 27. A similar spectrum for PP is confirmed by Morent et al. [382]. PE-g-MAH is confirmed by the two C-H stretching peaks at 2914 cm^{-1} and 2847 cm^{-1} along with the MAH peak at 1715 cm^{-1} [321]. ABS is identified by -C≡N at 2237 cm^{-1}, C=C stretching vibrations at 1637 $cm^{-1}$and styrene aromatic ring stretching vibrations at 1494 cm^{-1}. The deformation of hydrogen attached with 1,2 butadiene at 913 cm^{-1} and 1,4 butadiene at 966 cm^{-1} [383] is also noted in ABS.

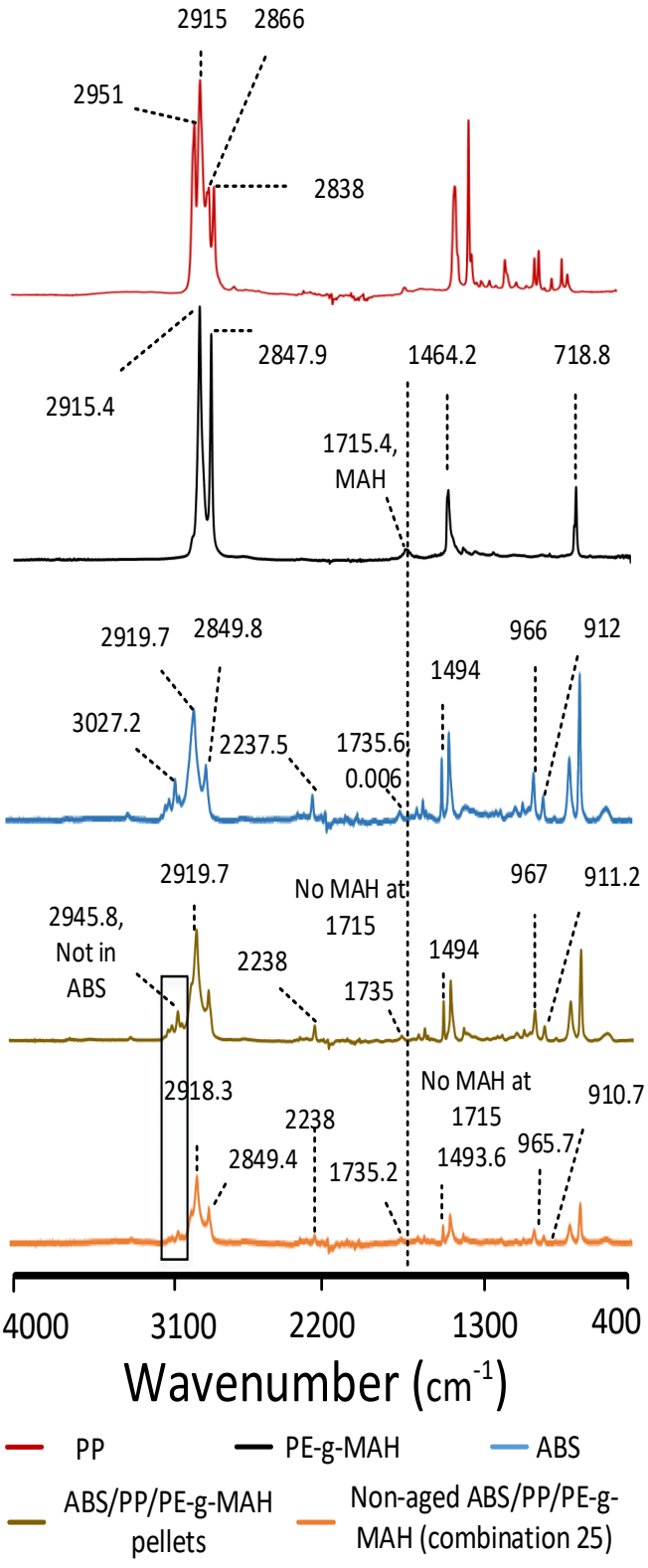


Figure 72. FTIR analysis of neat polymers, blend pellets and non-aged blend.

The single screw extrusion of the polymers presents notable differences in the blend pellets as compared to the neat ABS (Figure 72). The presence of the CH_3 group from PP [382] in the blend pellets is noted by a step merged into a wide peak at 2945.8 cm^{-1} that is absent in neat ABS. The merging of associated group (CH_3) of PP into ABS blend shows the synergy [326] between the saturated hydrocarbons of three polymers. The absence of MAH peak at 1715 cm^{-1} of PE-g-MAH in blend pellets is also a sign of the chemical interactions [321] between three polymers. Furthermore, it is analyzed in Table 27 that apart from butadiene groups at 1637 cm^{-1}, all remaining groups show high intensity as compared to the neat ABS with no to minimum shift. This can be interpreted from three aspects: 1) the increase in intensities for most of the groups have achieved high synergy [326] among each other to show chemical interactions, 2) the decrease of butadiene intensity shows restricted movement that can be caused due to the chemical reactions at butadiene monomers [336], and 3) the minimum to no shift in wavenumber presents the safe blending without degrading any groups in neat ABS [336].

The printed blend (combination 25) presents similar peaks as found in the blend pellets but with a significant decrease in the intensities of most of the chemical groups (Figure 72). The low intensities present the restriction in the movement of different monomers and hence it proves the chemical interactions [336, 384]. This also provides a chemical reasoning for better strength of the printed parts as compared to ABS. On the other hand, the shifts in the wavenumbers of the non-aged printed blend groups are not significant even after 3D printing. The minor (negligible) shifts in the intensities present the unaffected quality [326] of printed material due to modifications in the pellet printer, like improved cooling system and insulation.

The analysis of thermal aging on the printed specimen (combination 27) as compared to ABS is shown in Figure 73 and Table 27. Apart from minor shifts of CH_2 stretching [382] from 2919.7 cm^{-1} to 2918 cm^{-1} and butadiene hydrogen [336] from 912 cm^{-1} to 910.7 cm^{-1}, all remaining groups are detected at the similar wavenumbers. Moreover, most of the chemical groups show a decrease in corresponding vibrational intensities. For example, the hydrogen attached with alkene carbons [336, 384] at 994.6 cm^{-1} and the alkanes groups [336] at 1375 cm^{-1}. This describes the effects of chemical interactions between the three polymers that impede the free movement of the groups [336]. Therefore, the aging interval enhances the chemical reactions to achieve better strength as compared to the non-aged blend.

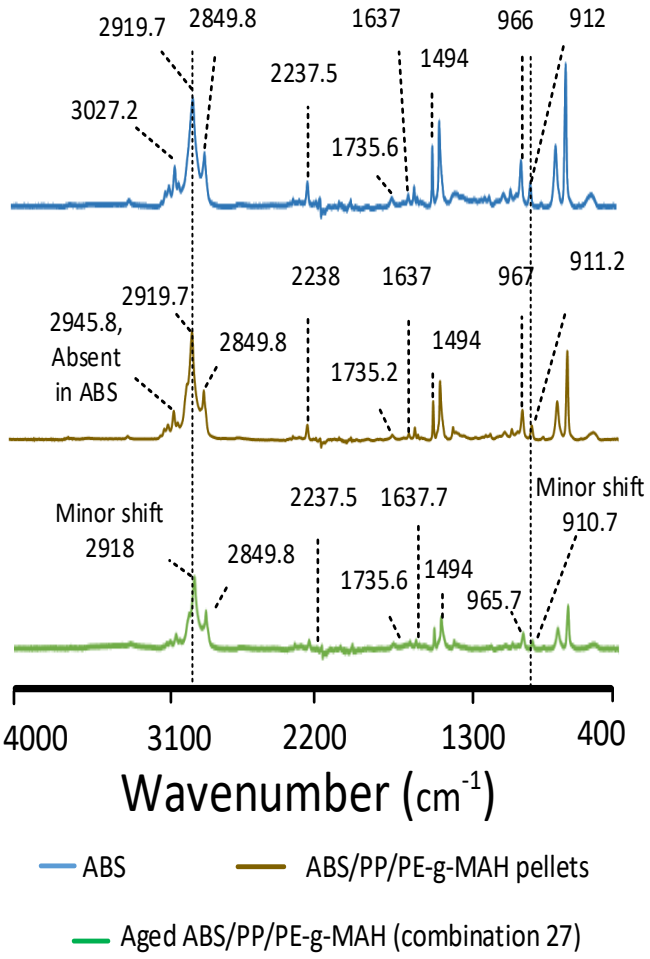


Figure 73. FTIR analysis for effects of thermal aging.

Table 27. FTIR analysis, WN stands for wavenumber (cm^{-1}).

ABS		PP		PE-g-MAH		ABS/PP/PE-g-MAH pellets		ABS/PP/PE-g-MAH combination 25		ABS/PP/PE-g-MAH combination 27		Comments
WN	Intensity	WN	Intensity	WN	Intensity	WN	Intensity	WN	Intensity	WN	Intensity	
		2950.6	0.177			2945.8	0.078	2949.6	0.024			CH_3 stretching [382]
2919.7	0.084	2915.8	0.219	2915.4	0.404	2919.7	0.152	2918.3	0.050	2918	0.0567	CH_2 stretching [382]
2849.8	0.041	2866.2	0.114	2847.9	0.360	2849.8	0.068	2849.4	0.025	2849.8	0.0293	
		2838.3	0.114									CH_3 stretching [382]
2237.5	0.018					2238	0.019	2238	0.0052	2237.5	0.0059	C≡N bond [383]
1636.8	0.008					1637	0.007	1637.7	0.0039	1637.7	0.005	Butadiene stretching [383]
1602.5	0.0147					1603	0.016	1602	0.0042	1602.1	0.006	
				1715.4	0.02							MAH group [321]
1735.6	0.006					1735.2	0.005	1735	0.0029	1735.6	0.0035	
1494	0.046					1494	0.053	1493.6	0.0122	1494.1	0.0155	Styrene ring
1453	0.066	1456.98	0.114	1464.2	0.113	1453	0.0816	1452	0.0205	1452.6	0.0248	
		1375	0.181			1377	0.0166	1375	0.006	1375	0.0059	Alkane CH_2 & CH_3 deformation, C-H asymmetric [382, 385]
						994	0.0106			994.6	0.0024	Out of plane bending (=C-H & $=CH_2$)
966	0.035					967	0.0409	965.7	0.009	965.7	0.0115	H attached to 1,4 butadiene [383]
912	0.017					911.2	0.0189	910.7	0.0043	910.7	0.0053	H attached to 1,2 butadiene [383]

7.5.2. Effects of printing variables on crystallization

Differential scanning calorimetry is used to obtain information about the true nature of chemical reactions in a non-compatibilized blend (ABS/PP) and pellets and printed blend (non-aged). It is also used to investigate the reason for a decrease of strength after six days of aging in blend.

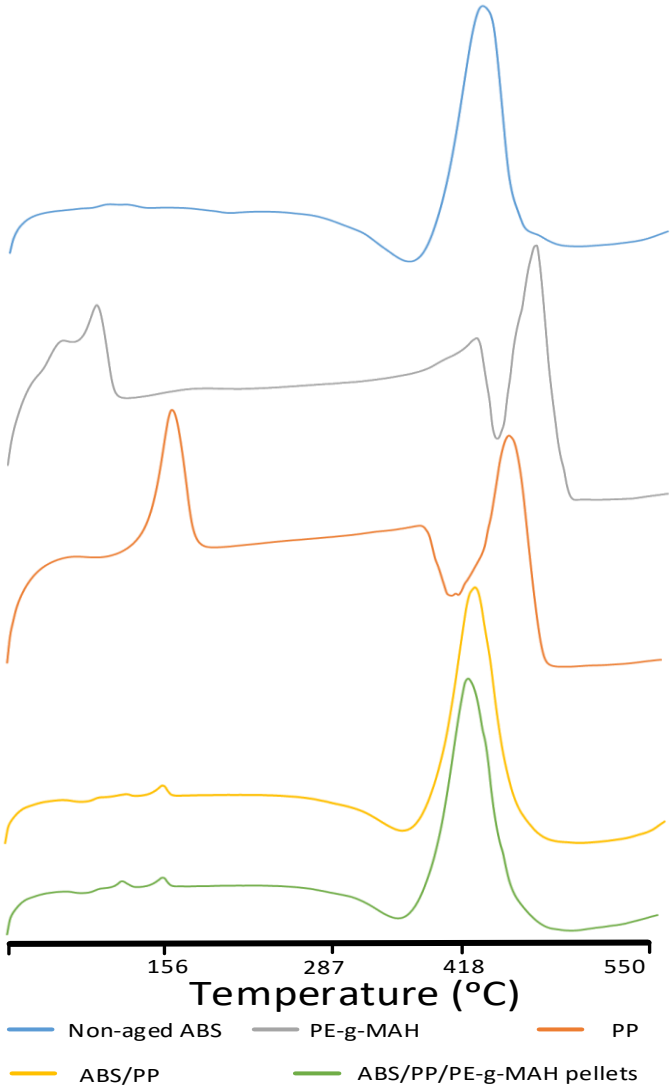


Figure 74. DSC analysis of effects of melt blending.

ABS/PP shows a decrease in glass transition temperature ($T_{g(ABS)}$) associated with ABS and melt crystallization temperature ($T_{m(PP)}$) associated with PP as compared to neat ABS (Table 28 and Figure 74). On the contrary, the increase in H_g (2.464 j/g) and H_d (488.8 j/g) in

compatibilized blend pellets presents enhanced blending [386] due to PE-g-MAH. The increase in glass crystallization shows a rearrangement of intermolecular bonds at an earlier temperature [386] than neat ABS and the high degradation energy in H_d presents improved resistance to thermal degradation.

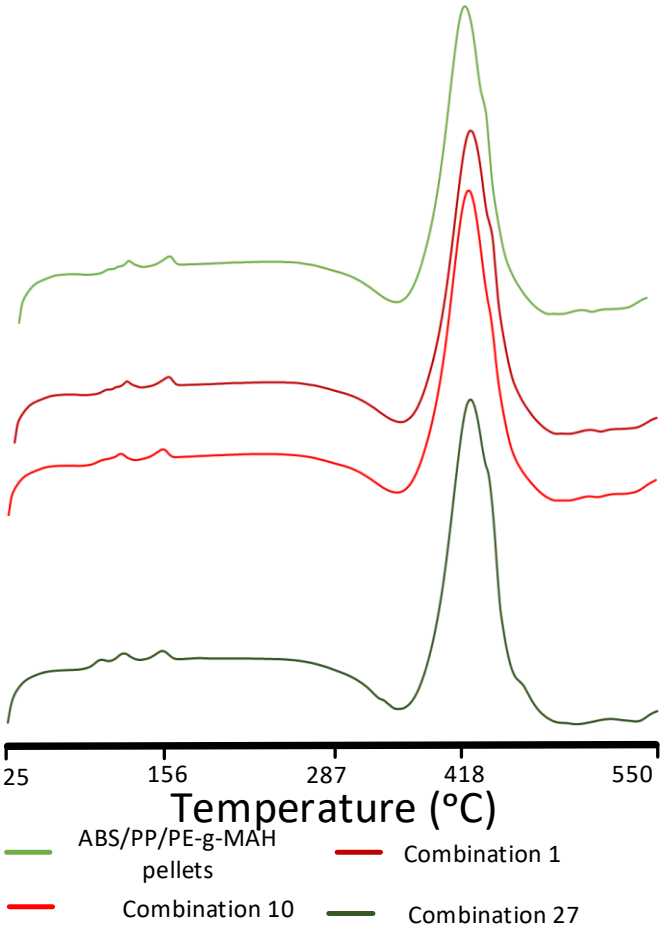


Figure 75. DSC analysis of effects of thermal variables.

The effect of bed temperature, printing temperature, and aging interval on thermal stability of ABS/PP/PE-g-MAH is displayed with respect to non-printed pellets in Figure 75 and Table 28. The increase of either of bed temperature, printing temperature and aging interval has resulted in a decrease in $T_{M(ABS)}$ and $T_{M(PP)}$ as compared to the non-printed pellets up till three days of aging, after which it showed a minor increase of 0.6 °C for six days of aging. The decrease may be due to the high viscosity and nucleation abilities of ABS that helps to achieve oriented crystalline polymeric chains at low temperature [360]. Moreover, the minor

(negligible) increase in $T_{M(ABS)}$ after six days' aging (combination 27) shows the high thermal stability of the material. The high thermal stability also displayed with significantly enhanced H_d (>500 j/g) is also notable as compared to non-printed pellets (488.8 j/g) and neat PLA (445.8 J/g).

The absence of glass transition at 100 °C and visible appearance of a new melt crystallization transition at 109.3 °C in aged blend (combination 27) are the significant chemical modifications due to aging. The $T_{M(ABS)}$ at 109.3 °C is associated with ABS in the blend that occurs at 111 °C in neat ABS. However, the six days' aging results a significant decrease in T_d and enthalpy of degradation (500 j/g) as compared to three days' aging. The appearance of a new melt crystallization peak, the decrease of corresponding enthalpies and temperature of degradation as compared to 0-3 days' aged combinations point towards the degradation of intermolecular bonds. Furthermore, the decrease in T_d and H_d provides a chemical interpretation for a decrease of tensile strength for six days' aged samples (combination 27) as compared to 0-3 days aged samples. This degradation in Combination 27 describes the decrease in mechanical strength noted in surface plots (Figure 69).

Table 28. DSC analysis.

	T_g	**T_m**	**T_d**	**H_g**	**H_m**	**H_d**
ABS	100.2	111.8 131	430.4	--	3.0 (Combined peak)	445.8
PP		170.6	458		82.5	148
PE-g-MAH		108.6	475.8		27.22	164.5
ABS/PP	94.1	132.7 (ABS) 163.4(PP)	427.5	2.251	1.09(ABS) 4.6 (PP)	489.5
ABS/PP/PE-g-MAH pellets	93.5	128.7(ABS) 163.6(PP)	424.8	2.464	3.61(ABS) 2.72 (PP)	488.8
ABS/PP/MAH combination 1	91.6	127.7(ABS) 163.7(PP)	425.9	2.53	1.69(ABS) 4.075(PP)	525.6
ABS/PP/MAH combination 10	93.8	127.4(ABS) 163.5(PP)	426.1	2.502	2.93(ABS) 4.39(PP)	529.4
ABS/PP/MAH combination 27	---	109.3(ABS) 129.3(ABS) 163.9(PP)	427.1		1.37(ABS) 2.86(ABS) 4.03(PP)	500

7.5.3. Analysis of mass degradation and resistance to thermal aging

TGA analysis is shown in Figure 76 and Table 29. The onset of neat ABS and PP are in accordance with the literature [366]. The low onset temperature of degradation of ABS is a result due to the hydrogen abstraction from butadiene monomers [367]. The non-compatibilized ABS/PP shows an increase in onset temperature to 398.8 °C. The increase in onset of ABS is due to the addition of PP that provides sites for partial nucleation [387]. However, the addition of PE-g-MAH as a compatibilizer in ABS/PP pellets significantly raised the onset of degradation to 407.7 °C. This significant rise in onset shows the enhanced thermal stability of the blend system [368]. The increase in onset also justifies the high Tg and T_D values of DSC for compatibilized pellets.

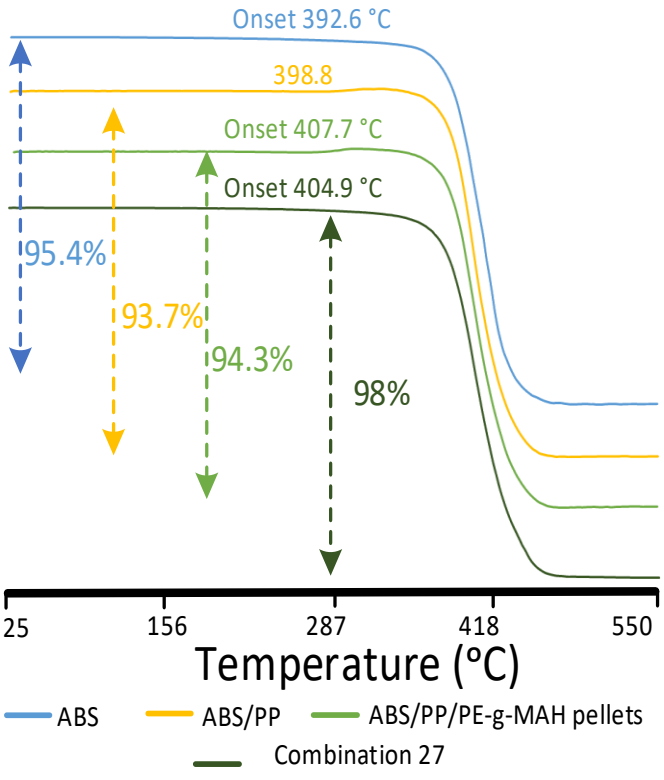


Figure 76. TGA analysis for effects of blending and thermal aging.

The effects of printing parameters are also analyzed in Table 29. It is noted that an increase in bed temperature (combinations 1, 10 and19) results in a decrease in onset temperature as compared to pellets. This shows that the printing parameters effect the chemical behaviors of

the blend that is also noted in the FTIR analysis in the form of a decrease in vibrational intensities of the printed blend as compared to neat ABS. However, the differences in onsets among different printing combinations are not significant as observed in Table 29. This shows a consistent thermal behavior of the blend towards stability regardless of high temperatures and aging intervals.

The six days' aging at highest printing and bed temperature (combination 27) presents an increase in onset temperature (403.9 °C). Furthermore, the 50% mass degradation occurs at the highest temperature (433.3 °C) among all combinations that ends up with just 0.2% more degradation in mass (97.9%) at 590 °C. The high temperatures for onset [368] and 50% degradation at highest temperature show the high thermal stability of the blend material as compared to neat ABS. The meagre 0.2% increase in thermal degradation at 590 C is basically the main reason for a decrease of T_d and enthalpy of degradation (ΔH_d) in DSC for Combination 27. This negligible 0.2% degradation is detected as a non-significant factor in ANOVA analysis. Therefore, this proves that the blend shows high thermal stability to high temperatures and aging intervals.

Table 29. TGA analysis.

Polymers	**Onset temperature**	**Degradation**	
		Temperature at 50% mass degradation (°C)	**Mass degradation at 590 (%)**
PP	409.1	457.8	100
ABS	392.6	436.1	95.4
ABS/PP	398.8	433.3	93.2
ABS/HDPE/PE-g-MAH pellets	407.7	433.7	94.3
ABS/HDPE/PE-g-MAH combination 1	403.8	432	98.18
ABS/HDPE/PE-g-MAH combination 10	403.5	431.6	97.7
ABS/HDPE/PE-g-MAH combination 19	402.7	429.3	97.7
ABS/HDPE/PE-g-MAH combination 27	403.9	433.3	97.9

7.5.4. Validation of physical interlocking or chemical grafting

The SEM analysis is used to analyze the phase separation for confirming blending. It is also used to analyze the visual effects of six days' aging on fractured surfaces.

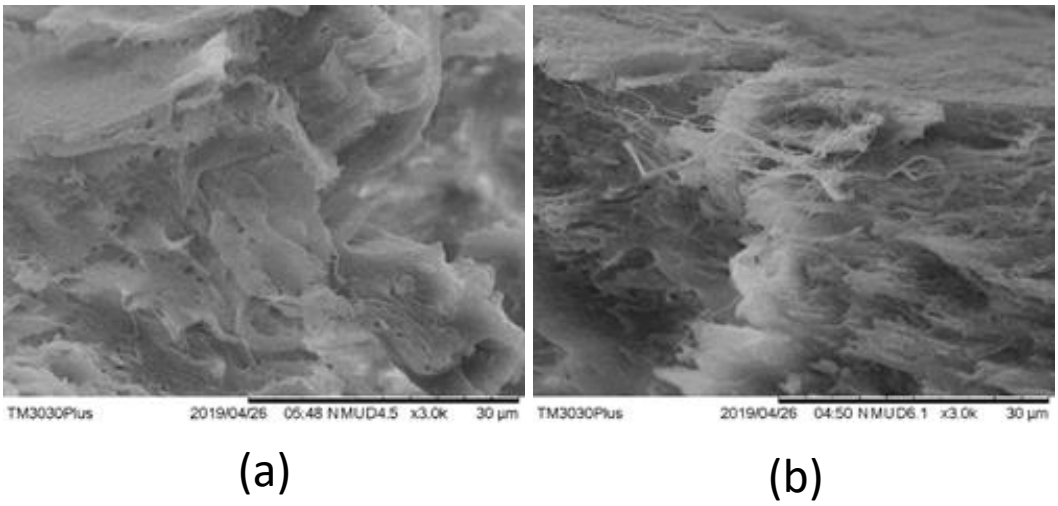


Figure 77. SEM images for: (a) Combination 4, and (b) Combination 21.

Most of the SEM images show no phase separation as observed in Figure 77a. Which shows the chemical grafting of PP on ABS through PE-g-MAH. However, there is one rare case (combination 21, sample 2) in which minor signs of phase separation are observed. Figure 77b shows PP in the form of fibers interlocked in an ABS matrix. These elongated fibers are produced out of the ABS matrix as a result of high tensile loading during breakage. The entangled fibers of PP confirm the good tensile strain (0.0224 mm/mm) for combination 21. The individual clusters of PP in the ABS matrix were also detected in FTIR analysis (Figure 72) as a distinct "step" at 2945.8 cm^{-1} that is merged into the wide peak of ABS saturated hydrocarbon. Therefore, the chemically grafted PP in ABS through a compatibilizer along with localized physical interlocking is the main reason deduced for the high thermo-mechanical properties of the novel FFF blend system.

The effects of six days' aging and highest printing temperature (205 °C) on the blend (Combination 18) are observed in the form of the large pulled-out fibers after fracture (Figure 78). The enhanced ductility shown by the pulled-out fibers is also confirmed by the high strain (0.023 mm/mm) as provided in ANOVA Table 26. This shows the ability of the novel blend to maintain at least either or both the strength and the ductility at severe thermal conditions.

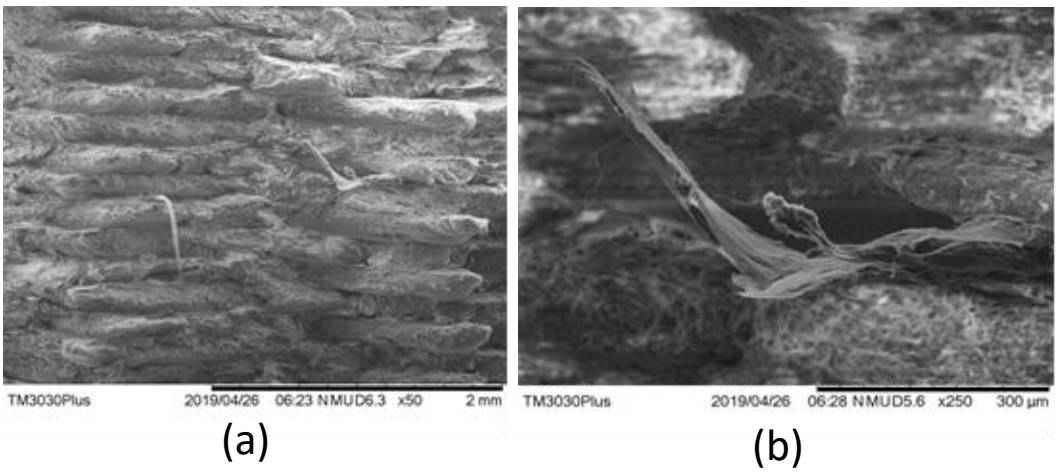


Figure 78. SEM images for: (a) Combination 18, and (b) magnified image for Combination 18.

7.6. Summary

ABS is the one of the known commercial polymers for FFF. Despite its commercial benefits, it has poor thermal stability to aging at high temperatures. The degradation leads to the hydrogen abstraction from the butadiene monomer of the terpolymer that results in degraded mechanical properties. This requires ABS to have strong thermo-mechanical stability, particularly in current scenarios, where the FFF is moving towards large-scale manufacturing. This research presents a novel blend of ABS with PP in the presence of a compatibilizer (PE-g-MAH) that can withstand high temperatures and long days of thermal aging. A 3^3 general full factorial experimentation is designed with three variables of bed temperature, printing temperature and aging interval to analyze tensile properties. Each of the variables has three levels that are set to the minimum and maximum possible limits in the given resources. The highest bed and printing temperature-based Combinations (25,26 and 27) are selected to print samples for compression and flexure testing. The specimens of tensile, compression and flexure are printed with a custom-designed pellet printer that is specifically modified with improved cooling system, thermal insulation barrier and refined extrusion screw with no compression zone. The modifications help to achieve the printing properties similar to an as-made blend without any chemical deterioration. Following are the main highlights of the blend materials,

1. The ANOVA analysis statistically proved the aging to be a non-significant factor.
2. The blend provides improved tensile strength (31.6MPa) at the highest bed and printing temperature with six days of aging (Combination 27) instead of degradation.

3. The blend material has high stiffness as compared to neat ABS.

4. The compression and flexural properties also show a significant increase with an increase of the aging interval instead of degrading.

5. The blend shows one of the highest mechanical properties among the current FFF blends in the literature.

6. The enhanced thermo-mechanical properties are the result of chemical grafting along with the localized physically interlocking observed in SEM.

Chapter 8. Conclusions and future research

This chapter includes the overall conclusions and recommendations for future research.

Conclusions and future research

8.1. Conclusion of PhD

This research has generated five journal papers, out of which 2 are published and 3 are in process of review. Furthermore, the research also generated 2 peer reviewed conference papers and 4 posters. The main objective of this research work is to develop low cost 3D printing polymer materials for insulation of milk vats that will have good mechanical properties with reliable life against aging. In this regard, two experimental approaches are adopted. The first approach registers the in-process heat treatment of PLA. This includes the printing of PLA on a low-cost open source 3D printer enclosed in a custom build heating chamber. The experimentation ends up with 30% increase in tensile strength. However, the softness induced at high temperatures (>70 °C) during printing is not required as the cleaning operation of milk vats is performed with 70 °C hot water. Therefore, the second experimental approach of blending the printable materials (ABS and PLA) with HDPE and PP is adopted. Three new FDM blend materials are developed that are analyzed against different aging criterions. For example, the partial bio-degradable blend of PLA/HDPE/PE-g-MAH is analyzed for resistance against 10 days thermal aging at 75 + 5 °C, 45 days water immersion and 45 days soil degradation. The two non-biodegradable blends of ABS/HDPE/PE-g-MAH and ABS/PP/PE-g-MAH are analyzed against 6 days thermal aging at >70 °C. The highlights for each of three blend materials are as follow,

1) Each of three materials will cost less than 15 NZD per Kg.

2) PLA/HDPE/PE-g-MAH shows excellent resistance against three types of aging (thermal, moisture and soil degradation) with good mechanical properties. The material achieves the highest strength of 67.8 MPa among existing FDM literature even after 10 days of thermal aging. The mass loss % is reduced to 99.81% after 45 days of soil degradation test while retaining good mechanical strength of about 50 MPa. The novel material delivers double strength (30 MPa) as compared to the neat PLA (15MPa) after 45 days of water absorption. The FTIR, DSC, TGA and SEM show strong intermolecular interactions (grafting) along with physical interlocking that is the main reason for superior properties of the novel blend material.

3) ABS/HDPE/PE-g-MAH presents high mechanical properties (tensile, compressive and flexural) even after 6 days of thermal aging at >70 °C and high printing temperature (205 °C).

The material shows the thermal aging as an insignificant factor in ANOVA analysis. Furthermore, the material's strength increases with an increase in other thermal parameters (bed temperature and printing temperature). The blend provides one of the highest mechanical properties (tensile, compressive and flexural) as compared to the existing ABS blends in literature. The FTIR, DSC and TGA analysis confirms the chemical grafting along with some sign physical interlocking as a reason for the superior properties at high thermal conditions.

4) ABS/PP/PE-g-MAH provides good thermal resistance to 3 days thermal aging at >70 °C along with good mechanical properties (31.6MPa). However, the material shows a slight decrease in tensile properties against full 6 days aging. The decrease was recognized as insignificant in ANOVA analysis. The material shows good high tensile stiffness along with good compressive and flexural properties. The SEM analysis shows the chemical grafting along with localized physical interlocking as the main reason for improved properties against severe thermal conditions.

8.2. Future direction

This research has aimed the following future directions based on two experimental techniques (in-process heat treatment and blending) used to enhance the properties of different materials.

1) The in-process heat treatment of Nylon to explore the effects on strain hardening is one of the potential research gaps.

2) The effects of in-process heat treatment are still to explore for each of the three blends. The motivation arises from the significant enhancement of tensile strength (30%) of neat PLA. It will be noteworthy to observe the effects of high ambient temperature on the quality of diffused beads of the each of the three blends (PLA/HDPE, ABS/HDPE and ABS/PP).

3) Different compositions of PE-g-MAH and HDPE in PLA/HDPE/PE-g-MAH blend is still to explore as one of the future experiments. This experimentation has a scope to explore the optimal compositions of additives with PLA to further optimize the mechanical properties along with a good resistance to thermal, moisture and soil degradation.

4) The superior properties of three novel blend materials has provided a low-cost alternative for producing new blend materials with polyolefins. The blend of PLA with PP compatibilized with a suitable compatibilizer is one of the next potential materials to explore in future. The compositions are already prepared, and the blend is in the phase of 3D printing.

5) Based on the significant effects of polyolefins on ABS and PLA, polyethylene terephthalate (PET) with HDPE and PP is one of the next considerable blends for FDM.

6) PE-g-MAH is the only compatibilizer used to make all three blends in this research. The future research includes the analysis of the effects on 3D printing of different types of compatibilizers and the range of their compositions. This also includes the in-laboratory grafting of novel co-polymers for making different blend materials.

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Appendix 1

Appendix 1 includes the following two peer reviewed conference papers in IEEE.

1) Large scale 3D printing: Feasibility of novel extrusion based process and requisite materials

2) Evaluation of the effects of controlled ultrasonic acetone vaporization on Fused Deposition Modelling 3D Printed Acrylonitrile Butadiene Styrene

Large scale 3D printing: feasibility of novel extrusion based process and requisite materials

Muhammad Harris, Johan Potgieter, Khalid Arif
School of Engineering and Advanced Technology
Massey University
Auckland 0632, New Zealand
m.harris@massey.ac.nz

Richard Archer
Massey Institute of Food Science and Technology
Massey University
Palmerston North 4442, New Zealand

Abstract— The predominance of conventional polymer processes (CPP) is undoubtedly formidable regarding monetary benefits gained in lieu of mass production in the global market. In this research, profitable commercial status of CPP is critically questioned in case of a specific large-scale application in low quantities, considering the following three factors: cost, time, and complexity. This research paper reports the subjective analysis-based exclusion of conventional processes (injection moulding) that brings the ball in the court of additive manufacturing (AM) technologies which are superior to injection moulding in low volume production. However, the AM techniques are limited to print only small-scale products in low quantity. This paper proposes a novel application of large scale products in low quantities by extruding polymer pellets from conceptual extrusion based deposition modeling setup. The requirement of a suitable material for conceptual extrusion setup entails the analysis of various factors to verify the feasibility of current fused deposition modeling materials for the conceptual large extrusion based deposition modeling setup. Therefore, this research contributes through providing a feasibility report for the CPP, AM techniques and their materials to print large-scale products.

Keywords— Large scale 3D printing, fused deposition modeling, injection moulding FDM materials, additive manufacturing

I. Introduction

The feasibility of 3D printing materials to make large products is associated with various points and queries to ponder upon. It is inevitable to analyze 3D printing materials in the light of particular techniques, e.g., stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS) etc. These techniques need to be first examined in certain aspects in a strict comparison with conventional plastic manufacturing techniques [3]. Few of the common ones are injection moulding (IM) [5], extrusion moulding (EM) [7], rotational moulding (RM) [9] etc. Injection moulding is the strongest and oldest contender to challenge the global market place of 3D printing techniques and therefore the materials as well [7, 9, 10]. Indeed, it is analyzed in this research paper as an initial proposal that the future stability of 3D printing techniques in global market pertaining to its existence and growth are dependent on the strengths of CPP; that are indeed the weaknesses. The large-scale application in low quantity basically entails the apparent strengths of conventional polymeric processes to be transformed into weaknesses.

Three indispensable factors: 1) Cost, 2) Time and 3) Complexity, are thoroughly investigated in the light of literature considering the scope of injection moulding for a large-scale product in small quantities. The adopted approach and summary of analysis is provided in Fig. 1.

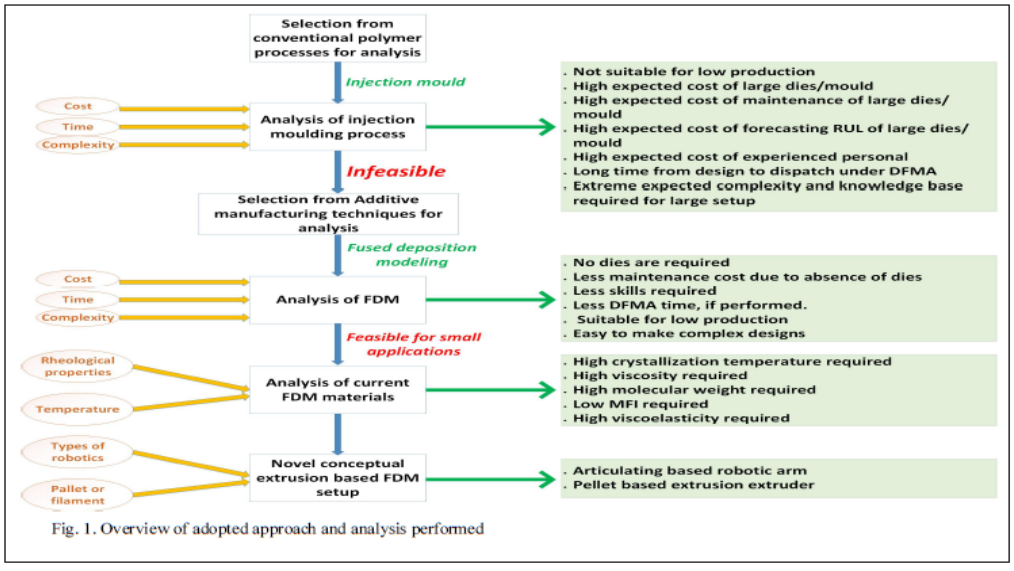

Fig. 1. Overview of adopted approach and analysis performed

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2018 25th International Conference on Mechatronics and Machine Vision in Practice (M2VIP)

Evaluation of the effects of controlled ultrasonic acetone vaporisation on Fused Deposition Modelling 3D Printed Acrylonitrile Butadiene Styrene

Juan Schutte
School of Engineering and advanced technology
Massey University
Auckland, New Zealand
J.Schutte@massey.ac.nz

Pamitha Wijisundira
School of Engineering and advanced technology
Massey University
Auckland, New Zealand

Muhammad Harris
School of Engineering and advanced technology
Massey University
Auckland, New Zealand
M.Harris@massey.ac.nz

Johan Potgieter
School of Engineering and advanced technology
Massey University
Auckland, New Zealand
J.Potgieter@massey.ac.nz

***Abstract*—The application of vapour exposure systems upon 3D printed objects as a means for surface modification is a thoroughly established technique. This study investigated the utilization of a generated controlled vapour chamber device to further derive the relationship between surface modification exposure to that of part structural properties, namely interlayer bonding. This controlled utilization of vapour is intended to identify potential for future sequential 3D printing methodologies. The study mirrored previous work as such an UPBox Fused deposition modelling printer was required to produce thirty acrylonitrile butadiene styrene ASTM D638 Type IV dog-bone samples. Each of these was subjected to controlled vapour exposure relative to defined sample sets, namely groups of 5 representing exposure intervals at 0%, 20%, 25%, 50%, and 100% printing completion. Analysis for these was conducted via Instron 5967 tensile testing and a Hitachi TM3030Plus Scanning electron microscopy. These samples depicted a directly proportional increase in ultimate tensile strength and layer fusion with increased vapour exposure. These values contradicted the previous uncontrolled study.**

Keywords— Additive Manufacturing, 3D Printing, Surface modification, Coating

I. INTRODUCTION

Fused Deposition Modelling (FDM) 3D Printing (3DP) has achieved widespread popularity due to its simplicity and affordability. Typically these systems are comprised of a 3-axis gantry system upon one of which is fastened an extruder system, namely a heated nozzle through which polymer filament is directed/fed[1-3]. One of the major drawbacks of this technology is its relative tendency towards poor surface finish quality (namely the striated appearance caused by the layers)[4, 5] . A popular and common method amongst both industry and hobbyist markets is the utilisation of acetone exposure on Acrylonitrile Butadiene Styrene (ABS) FDM 3D printed parts[6, 7]. The apparent nature of this technique is that it chemically initialises a reactivity within ABS which promotes the merging of the distinctive extruded pathways and layering common in this form of additive manufacturing (AM)[3, 8, 9]. As such this seemingly has an effect upon the bonding/bonded features of the material/part. One of the fundamental weaknesses of 3D printing (3DP) or AM parts is delamination, namely the separation/splitting of generated parts/objects along a layer commonly due to forces applied. It is generally accepted that these failures are derived from weak interlayer bonding (ILB) [7, 10], namely the strength of the merged/linked material with prior and subsequent layering. Typically the application of acetone either as uncontrolled rubbing or simplistic vapour bath systems which do not actively monitor how much of the exposure occurs. Given these techniques have the apparent ability to merge ABS polymer layers, there is interest to investigate the possibility and potential benefits for the controlled application of these agents at defined stages of the printing process.

One technique to accomplish this would be to submerge printed parts into acetone solution (immersion treatment)[6], however, this will not guarantee a uniform exposure due to run-off and acetones low rate of evaporation. A more precise implementation could take the form of an inkjet sequential 3D printing process however this will result in a high degree of complexity[11]. Thus this research was inclined to investigate the potential utilisation and control of vapour bath systems. Namely, this research aims to identify a plausible methodology for the controlled application of initialiser (e.g. Acetone) or adhesive elements to promote ILB within a 3DP process.

Vapour is unique in that it can comprise of submicron and nanoparticulate which can be manipulated as a gas. Controlled vapour production has occurred through many physical and chemical techniques [12]. Often these require relatively high temperatures, pressures and complexities uncommon in typical FDM 3DP systems [9]. As such this study was driven to utilise simplistic vapour generation technology capable of operation at lower temperatures and pressures.

A technology particularly **suited** for this type of work is ultrasonic atomisation/vaporisation. This functions through the application of high frequency signals to a piezoelectric transducer (generally a stretched film which contracts when exposed to an electric signal) yielding high-frequency mechanical actuation[13-15]. The coating of the surface of these devices in liquid yields a high degree of surface agitation. This stems from the generation of waves which at a critical frequency collide, resulting in the dispulsion of liquid particulate in the form of vapour. The rate of vapour generation and size of vapour particulates have been associated with modification of the delivered signal frequency [13]. This manner of control will allow for device output variability.

This study will leverage off previously identified evaporant orientated Acetone-ABS studies[6, 7, 16]. Through the utilisation of a derived device for controlled vapour addition, the following will be investigated:

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Appendix 2

Appendix 2 includes following three posters presented in different conferences in New Zealand.

1) Effects of moisture degradation on poly lactic acid in fused deposition modeling

2) Cost effective approach for fused deposition modeling

3) Visual predictive approach for strength and ductility in open source 3D printer.

Visual predictive approach for strength and ductility in open source 3D printers

Muhammad Harris[1], Dr. Johan Potgieter[1], Dr. Khalid Arif[1]

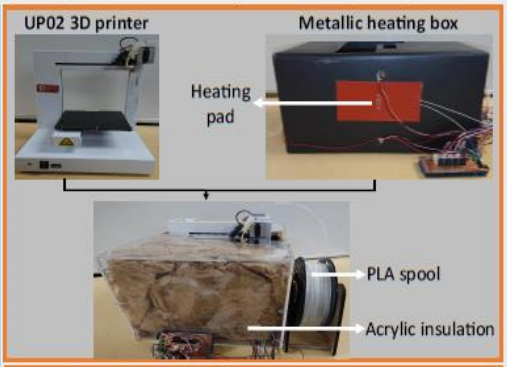
[1]School of Engineering and Advanced Technology (SEAT), Masse University, Auckland (0632).

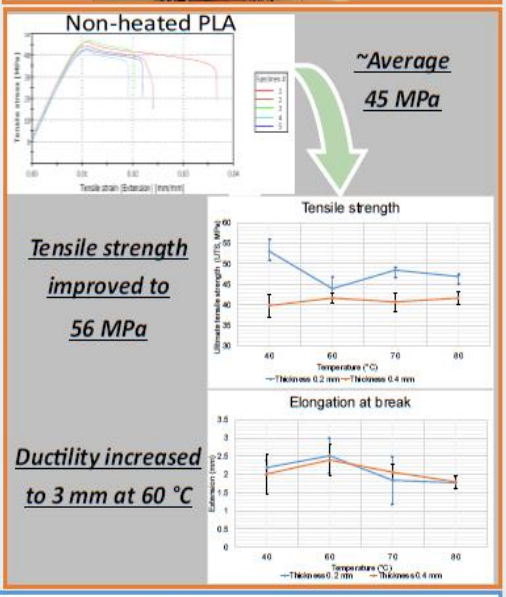
- 3D printing dominance now-a-days
- Open source 3D printers
- Disadvantage of cost-cutting measures compared to commercial printers in small open source 3D printers
  1. Less accuracy
  2. Materials unable to reach capable strength and ductility

- *Mechanism* governing strength and ductility
  1. Area of fusion between layers or beads
  2. Nature of fusion between layers or beads
- Fusion occurs at maximum four sides around the beads

- *Method* to achieve the lost properties of PLA
  1. ASTM D638-02 Type IV dog-bones
  2. Thermal in-process heat treatment
  3. Heated ambient atmosphere

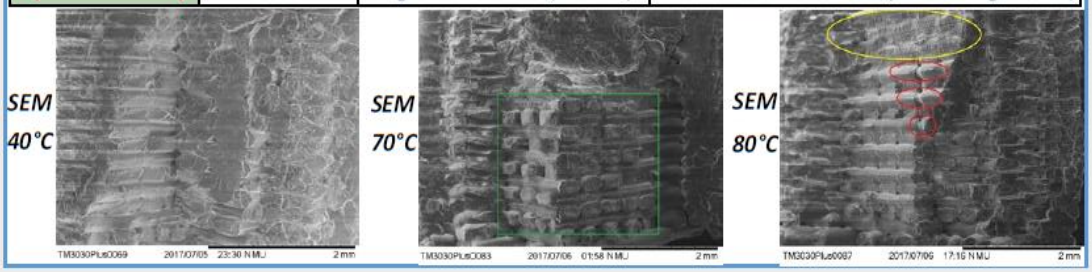
Experiment	*Bed temperature (°C)*	*Ambient Temperature (°C)*
1	40	40
2	60	60
3	70	70
4	80	80





- *Predictive* approach is analysed through Scanning electron microscopy (SEM).

Analysed factors	*Experiment 1*	*Experiment 3*	*Experiment 4*
Beads shape	Deformed	Almost ellipse or oval	Well maintained shape as 70 °C
Voids	Least	Large voids	Larger and highest in number
Extended beads	No	No, but protruded beads	Yes, extended grooves (Red ellipse)
Expected strength	Highest	Lesser than 40 °C	Lesser than 70 °C
Expected ductility	Least	Higher than 40 °C(2.5mm)	Should be same or less (due to large voids)



Cost-effective approach for fused deposition modelling

Muhammad Harris[1], Johan Potgieter[1], Khalid Arif[1], Richard Archer[2], Sudip Ray[3], Karnika De Silva[4].
[1]School of Engineering and Advanced Technology (SEAT), Massey University, Auckland (0632).
[2]Institute of Food Science and Technology, Massey University, Palmerstone North (4442).
[3]Chemical Sciences, University of Auckland (1142).
[4]Chemical and Materials Engineering, University of Auckland (1142).

Key conclusion

- Injection moulding grade polylactic acid (PLA) can replace commercial 3D printing PLA filaments used in fused deposition modelling (FDM).
- Thermal treatment enhanced the tensile strength of commercial 3D printing PLA by 10% as compared to non-treated one. Therefore, heat treatment can be used for enhancing the properties of injection moulding grade PLA that will be a potential alternate to commercial 3D printing PLA filament.
- PLA is known for its good bio-degradability and strength. This research will help to bring down the high cost to make it an attractive option for domestic user.

Introduction

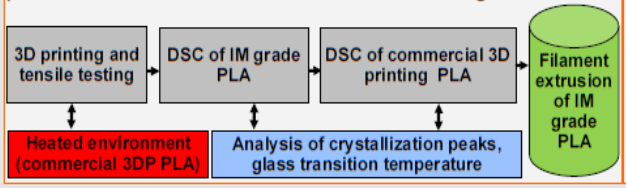
- FDM has applications for bio-degradable materials.
- High cost and low strength are obstacles for commercial 3D printing grade PLA . E.g., NZD 90 per 1 kg.
- Injection moulding grade PLA is a novel alternate due to low cost, i.e., NZD 10 per 1 kg. But injection moulding grade lacks high strength.
- In this research, the cause of low strength of injection moulding grade PLA is investigated, i.e., low crystallization.
- Based on the experimentations performed on commercial 3D printed grade PLA. The low crystallization of injection moulding grade PLA can be enhanced through heat treatment.

Objectives

- To decrease the cost of Bio-degradable PLA in FDM.
- To enhance the properties of injection moulding grade PLA to replace commercial 3D printing PLA.

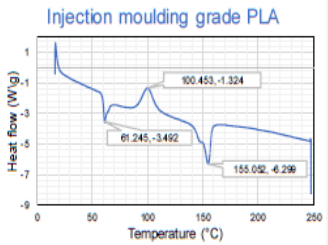
Methodology

The methodology includes tensile testing performed on ASTM D638 dog-bones printed with 3DP filament in heated and non- heated environment. Differential scanning calorimetry (DSC) analysis of IM grade and commercial 3D printing grade PLA were performed. Based on the results, it is proposed to make cost-effective filament from IM grade PLA.



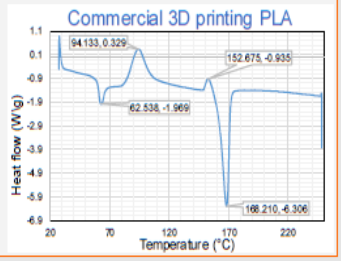
Differential scanning calorimetry analysis

Injection moulding grade PLA



- Low glass transition temperature. i.e., 61.245 °C
- Less are of crystallization peaks
- Low crystallization and % crystallinity at 155.052 °C

Commercial 3D printing PLA

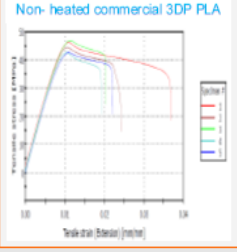


- High glass transition temperature. i.e., 62.538 °C
- High crystallization and % crystallinity at 168.210 °C

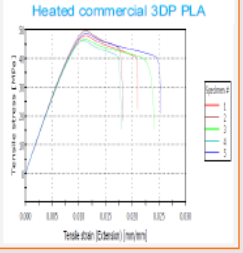
Improved strength of commercial PLA

- Heat treatment improved strength by 10%.
- Strength is corelated with increase in % crystallinity.
- Therefore it is proposed on basis of improvement to use heat treatment for compensating and enhancing the crystallization and % crystallinity of injection moulding grade PLA.

Non- heated commercial 3DP PLA



Heated commercial 3DP PLA



Effects of moisture degradation on poly lactic acid in fused deposition modeling

Muhammad Harris[1], Johan Potgieter[1], Khalid Arif[1], Richard Archer[2], Sudip Ray[3], Karnika De Silva[4]

[1]School of Engineering and Advanced Technology (SEAT), Massey University, Auckland.

[2]Massey Institute of Food Science and Technology, Massey University, Palmerston North.

[3]Chemical Sciences, University of Auckland, Auckland.

[4]Chemical and Materials Engineering , University of Auckland, Auckland.

Abstract

Fused deposition modeling (FDM) is the most common Additive manufacturing technique (AM) due to an affordable access to the open source 3D printers with a range of known polymers, i.e., Acrylonitrile butadiene styrene (ABS), Poly lactic acid (PLA), Nylon and Polycarbonate. FDM structures have inherited porosities at the point of contact between two beads that make the structure weak. These porosities are also vulnerable to adsorb moisture that can lead to moisture degradation of internal structure. This research reports the effects of moisture degradation on PLA ASTM D638 Type IV dog-bones manufactured by FDM and injection moulding. The dog-bones are immersed in water for 15 days to allow the water to adsorb into the porosities. The research includes the tensile testing of dog-bones to analyze the effects on tensile strength and strain. It also reports the Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) to correlate and explain the effects on tensile strength with moisture degradation of chemical groups in PLA. The research is aimed to assist the research community to understand the stability of FDM structures against an important environment factor, i.e., moisture.

Samples Manufacturing

- Pellet printing of samples at 45°/ -45°, 0.2 mm layer thickness, 167 °C printing temperature, 50 °C bed temperature and 100% infill density (Figure 1).
- Three samples are manufactured for each of FDM and injection moulding.
- ASTM D638 type IV dogbones (Figure 2)

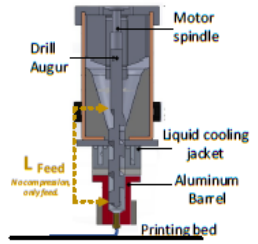


Figure 1: Pellet printer extruder.

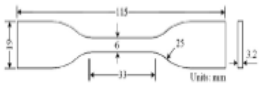


Figure 2: ASTM D638 type IV

- Samples immersed in water containers for 15 days (Figure 3).

Figure 3: Dogbones immersed in water.

Tensile testing

- Performed on Instron 5967 machine.
- Clip on gauge extensometer of 25 mm was used.

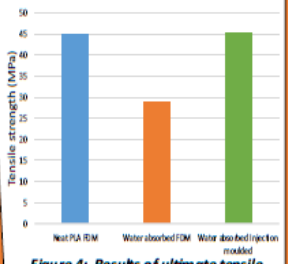


Figure 4: Results of ultimate tensile strength (UTS).

- Tensile strength of water absorbed FDM sample decreases significantly to 29 MPa (Figure 4)

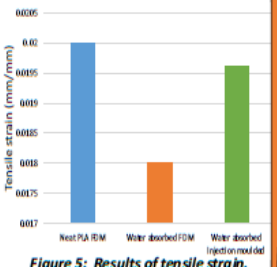


Figure 5: Results of tensile strain.

- Tensile strain of water absorbed FDM sample also decreases significantly to 0.018 mm/mm (Figure 5).

Fourier transform infrared spectroscopy (FTIR)

- Thermo electron Nicolet 8700 FTIR spectrometer
- Range of 400-4000 cm^{-1}

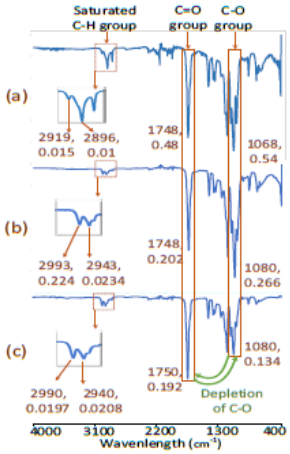


Figure 6: FTIR analysis: a) Neat PLA FDM, b) Injection moulding PLA (water absorbed), c) Water absorbed FDM PLA.

- C-O groups degrade significantly in FDM water absorbed sample (Figure 6).
- Depletion of C-O means chain scission.

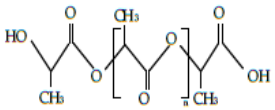


Figure 7: Chemical formula for PLA.

Scanning electron microscopy (SEM)

- Thermo electron Nicolet 8700 FTIR spectrometer
- range of 400-4000 cm^{-1}
- Resolution of 4 cm^{-1}.

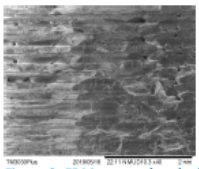


Figure 8: FDM water absorbed samples images.

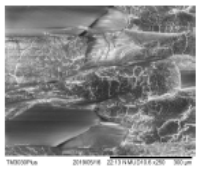


Figure 9: FDM water absorbed samples magnified images.

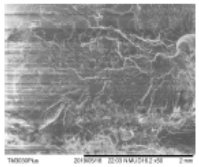


Figure 10: Injection mould water absorbed samples magnified images.

- Voids in FDM samples are main reasons for degradation (Figures 8 and 9)
- Unaffected samples of Injection moulding (Figure 10).

Conclusions

- Water absorption do effects the hydrophobic biodegradable PLA in terms of:

1) Tensile properties, and

2) Chemical interactions

- The water absorption cause chain scission.

Future recommendations

- Further research is required to ascertain the effects of water absorption on PLA and other biodegradable FDM polymers like Polybutylene succinate (PBS) and Polyhydroxy alkanoate (PHA).
- Detailed design of experiment is required for evaluating the percentage strength over a long periods of time. For example, 6 months or 1 year.

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The Appendix 3 includes the seven DRC 16 forms.

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