PREPARATION AND CHARACTERIZATION OF PURE PLA FILAMENT AND PBAT-REINFORCED PLA FILAMENT FOR FDM 3D PRINTING

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All praise to Allah Almighty for endowing me the blessing of achieving my goal. I am forever grateful to Him for blessing me with good health throughout the journey and giving me the strength and guidance to overcome the challenges I faced along the way. I pray that, May Allah Pak continues to shower His bountiful blessings and guidance upon me throughout my life.

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I have faith that the knowledge and skills I have acquired during this research will be utilized for the betterment of the society and its people.

DEDICATION

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Abstract

This study focuses on preparing pure polylactic acid (PLA) and polybutylene adipate –co-terephthalate (PBAT)-reinforced PLA filaments. PLA and PBAT are biodegradable aliphatic polyesters and have recently received considerable attentions. Due to its brittle nature, PLA has limited application in various fields. To overcome this challenge, numerous efforts have been made to incorporate various additives to enhance its performance. In this work, pure PLA filament and PBAT-reinforced PLA filament with diameter 1.75 ± 0.02 mm were prepared in the lab. Their thermal and mechanical properties were analyzed and compared with the commercial PLA filament bought from the market. Following the previous research works and suggestions of incorporating no more than 10 wt.% PBAT, we have mixed 8 wt.% PBAT into the PLA mixture. We then proceeded to extrude pure PLA and PBAT-reinforced PLA filaments at a temperature range of 170 ^{o}C to 180 ^{o}C, utilizing single screw extruder. Next, we printed tensile and flexural specimens using an FDM 3D printer, in accordance with Taguchi L9 OA. Due to PBAT's high ductility, 92-8 wt.% PLA-PBAT filament demonstrated a significant increase in elongation at break, reaching up to 12%. Likewise, the PLA-PBAT filament displayed tensile and flexural strengths of up to 48.34 MPa and 107.295 MPa respectively. These values are comparable to the tensile and flexural strengths of pure PLA, which is a great indication that the addition of 8 wt.% PBAT did not cause any unacceptable reduction in the tensile and flexural strengths. Additionally, it was found through DSC analysis that PLA-PBAT filament exhibited a higher degree of crystallinity (X_c) of up to 38.7%, which is significantly higher than that of pure extruded PLA. Furthermore, the TGA curve indicated that thermal stability of PLA-PBAT filament was improved by adding 8 wt.% PBAT. Moreover, digital microscopy results revealed that PLA-PBAT filament had a ductile fracture after necking, whereas pure PLA had a brittle fracture. Lastly, statistical analysis showed that both material type and layer thickness had significant impact on the results. The addition of this new PLA-PBAT filament provides an additional alternative to the current FDM filaments, and it will aid in reducing the constraints of the materials when it comes to additive manufacturing (AM) progress.

Keywords: PLA filament extrusion, additive manufacturing, fused deposition modelling, PBAT reinforced PLA filament, tensile and flexural properties, signal to noise ratio, ANOVA.

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Chapter 1 Introduction Manufacturing Processes

The word manufacturing has been derived from Latin word, manus means hand and factus means making. The English word “Manufacturing” is several centuries old and it means “made by hand”. The history of manufacturing is divided into two portions i.e first is the human’ s discovery and inventions of materials and processes to make things and second is the development of system of productions. Industrial revolution (1760 -1830 A.D) had huge role in transforming the way of manufacturing or production, because, it helped a lot in producing new tools and machines that are considered critical for modern manufacturing. It also redefined and marked the change from an economy based on handicrafts and agriculture to one based on manufacturing and industry. The change started in England, where a series of steam machines were invented and those steam machines replaced wind, water and animal power. These transition gave significant benefits to British industry as compared to other countries, and England tried to restrict export of new technology to other countries. Despite all efforts to restrict the export, the technology still reached to United States and other European countries.

Some of the inventions of industrial revolution i.e., Watt’s steam engine, spinning jenny, machine tool, power loom, and the factory system, contributed significantly to the development of manufacturing sector. The twentieth century was a time of more technological advancement than all the other centuries combined. Automation and manufacturing experienced most of those developments [1].

Manufacturing processes and techniques have changed over time according to the requirements and availability of resources. Manufacturing techniques have been divided into three broad categories i.e. subtractive, additive and, formative as shown in Figure 1. In formative manufacturing, the final geometry is obtained either by deforming a bulk of a material in the solid state (called bulk deformation processes i.e., forging, extrusion, rolling, etc.) or by pouring the molten material into the mold (called casting processes such as lost wax casting, sand lost foam). Similarly, the subtractive category involves the gradual removal of the material from large work piece till the required shape is obtained. Some examples of subtractive manufacturing are drilling, lathe turning, drilling, sawing, etc. On the other hand, additive manufacturing (AM) methods

create parts by adding material layer-by-layer until required shape is completed. Formative and/or subtractive methods are traditional manufacturing techniques and have limitations to produce complex shapes, while AM is a more advanced and suitable technique to manufacture customized parts.

In addition to above three basic manufacturing types, there is one more type of manufacturing processes, known as hybrid manufacturing process. Hybrid manufacturing process combines two or more different manufacturing processes in order to get maximum benefits from their specific potential. This process is usually done by using two separate pieces of equipment, but all in one machine, for example one that combines 3D printing with CNC Milling and they are available commercially. Combining AM with CNC machining into a hybrid additive and subtractive manufacturing is seemed to be logical set-up for multi-tasking technology. However, there some critical challenges to such hybrid set-up like technical challenges and cultural/adoption challenges. Another major issue is to train staff regarding the proper operation of hybrid manufacturing systems. Despite all these challenges hybrid manufacturing system has grown significantly since last 10 years [2, 3].

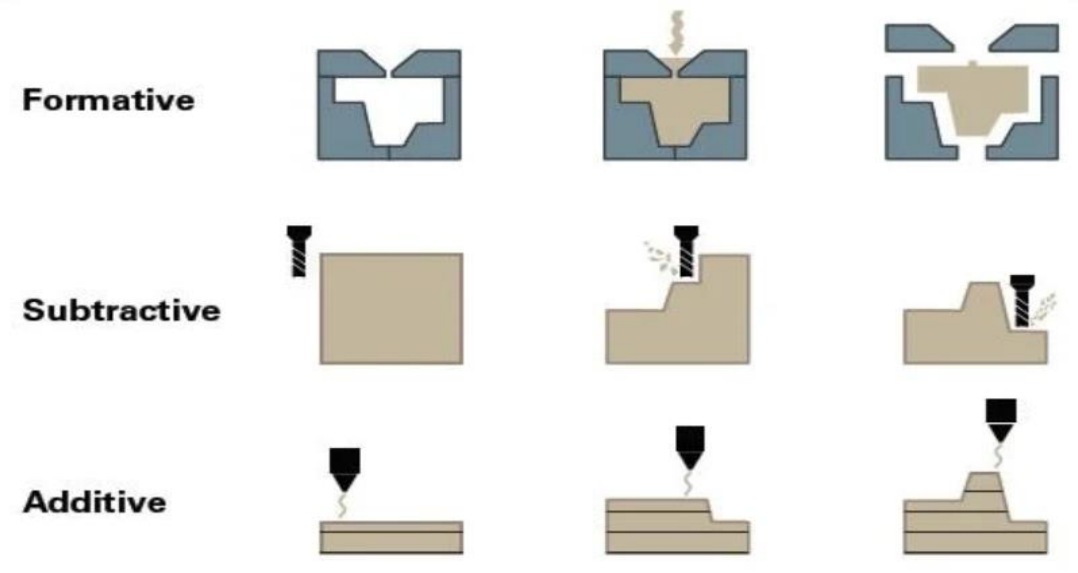

Figure 1. Three main categories of manufacturing processes (ref: AZO Materials)

Since Manufacturing has direct relation with the environment, because, a huge emission is emitted from manufacturing processes. To minimize the environmental damages caused by the industries, it is necessary to develop and encourage manufacturing process i.e. green

manufacturing, carbon free manufacturing etc. Green manufacturing is also called sustainable manufacturing or eco-friendly manufacturing. It is achieved by greening or cleaning operations, supply chain, applications and life cycle management. Such green manufacturing processes should have least carbon foot print or carbon emission and must use least amount of natural resources. The end products should be naturally biodegradable or recyclable. Clean and green manufacturing can be viewed as an opportunity to expand market share in local and global level. An in-depth knowledge of green manufacturing processes will help manufacturer to realize, that unlike other competitive manufacturing factors i.e., time, cost etc., being green manufacturer will have positive impacts on all manufacturing and development factors like, flexibility, cost, quality, time, and expanding the number of customers [4, 5].

AM is constantly growing techniques, but still have some limitations that need to be addressed in order to get full benefits of the technology. But as compared to the growth rate of other two traditional approaches, AM is growing fast and have got reasonable attention recently. The trend of competition based on sustainable design using superior materials e.g., superalloys, metals, composites with desired properties, has gone down, and now customers are looking more for customized products. One of the reasons behind this shift in customer's behavior could rise of Additive Manufacturing (AM) technology [6]

1.1 Additive Manufacturing (AM)

According to the definition given ASTM F42 Technical Committee AM as the "technique of joining materials to create objects from three-dimensional 3D-model, usually layer-by-layer unlike subtractive and formative manufacturing technologies" [7]. AM is a technique of joining materials to create components layer-by-layer. A virtual model is created and then the model data is transformed to two dimensional (2D) cross sections and the created file is called stereolithography or Standard Tessellation Language (STL). Slicing software is used to slice CAD model and generate geometric-code (G-code) and this G-code contains instructions that will then be used to

by the 3D printer to print product layer-by-layer. These sliced triangles or STL file contains information about each single layer that is to be printed. Although, there are different types of AM files, but, STL is being considered a standard file for AM technology. These cross-sections are then forwarded or transferred to AM machine so that it can printed layer-by-layer to prepare physical part. 3D printing is a subclass of AM. AM is a broad topic and describes the whole process from the very initial stage to the final stage including finishing etc., while 3D printing only describes that specific printing process [8, 9].

The commercial use of AM appeared in 1987 for the first time with stereolithography (SLA) from 3D Systems, a process where lase is used to solidify ultraviolet (UV) light-sensitive liquid polymer. 3D system and Ciba-Geigy, started working in collaboration to develop SLA material and commercialized the first generation acrylate resin. Originally, AM methods were used for concept visualization and validation. However, the advancement of the technique has led to the development of end-use products and tools. The other three AM technologies were commercialized in 1991, were solid ground curing (SGC) from Cubital®, fused deposition modelling (FDM) from Stratasys®, laminated object manufacturing (LOM) from Helisys®. FDM extrudes thermoplastic materials in filament form and will be discussed later in detail, SDG used a UV-sensitive liquid polymer, solidifying one full layer in a single pass. LOM used electronically guided laser to cut and bond sheet material. Helisys® and Cubital® have gone out of business since many years [10, 11].

For many industrial applications, the mechanical properties of the samples printed by AM are considerably low. AM has ameliorated over the past years, but, is still quite young, and many developments are yet to come. Researchers are working on the limitations, that have hindered AM in large-scale production. Efforts are underway to enhance mechanical properties through orientation analysis, material studies, machine designs, and parameters optimizations. Innovations in AM processes are increasing substantially. If current barriers to AM are resolved, then it offers great potential to assist in the development manufacturing field. In the current technological era, industry 4.0 is steering the consolidation of advanced information technologies and intelligent production systems. As a result, AM is considered a crucial element in this movement [12]. Figure 2 shows different types of AM technology [6] [13]. In this study, Fused Deposition Modelling (FDM) has been used to print polylactic acid (PLA) samples to perform mechanical testing.

Manufacturing light weight product has got great importance today. Although, every organization strives for that, but, automotive and aerospace industries are specially focusing on it. AM technology has got the ability to manufacture products, that have customized infill density or infill according to the required applications. If any part or component does not to be completely dense, then its infill density can be reduced, and thus overall weight can be reduced by customizing their individual infill densities as per their applications. Similarly, the trend of customization has prevailed other features like use of super alloys, metals etc. and AM is an ideal approach to make customized products as compared to subtractive and formative manufacturing processes. Architects usually create architectural models by hand and sometimes it becomes very difficult especially, when complex models are to be prepared. Similarly, AM technologies are widely used in medical field by upgrading medical practices, with highly efficient tools, creating rapid prototypes and models of the damaged bones. AM methods allow to scan and create or print a physical design of the defective bones AM being specifically ideal for organ or bone printing, because every person has unique organ or bone shape with specific dimensions. Such type of products are highly customized products and AM has specially been designed for printing customized low volume products instead of bulk. Similarly, AM is being used in cell printing, tissue engineering and medical equipment manufacturing. Furthermore [9, 14].

Currently, AM is at the beginning stage and its applications to produce or manufacture functional parts or final products needs further research and development. There are some limitations with AM technology and due to these limitations, AM cannot compete with other manufacturing processes i.e. subtractive and formative processes. Although, almost all type of materials can be used in 3D printing. For example, many types of plastic and polymers are extensively being used by some types of AM. Similarly, metals like aluminum, brass, gold, platinum, sterling, silver etc can also be used as 3D printing material. Ceramic models are made from alumina silica ceramic powder. Moreover, other materials like wood, organic tissues, nylon food and concrete are also used in some AM technologies. Almost all types of materials are used in AM up to some extent, but there still needs a huge research works to improve material's availability for 3D printing technology [15].

A comprehensive and systematic investigation of the static, dynamic and high temperature properties of AM materials is needed to perform. By doing so, it will be helpful to establish basic

knowledge, relationship between microstructure of the materials. Although, design of the product can be closely observed at optimal parameters, because real optimization of the product or component is possible for AM process, but, still there are tremendous challenges to include some manufacturing constraints into the real optimization process. Since multiple material printing are widely in use. Other manufacturing processes are far ahead in handling multiple materials, but, AM processes that are capable to handle mixed materials are limited and dependent on the processes. AM technologies, that are based on extrusion and jetting can use several nozzles to jet the molten polymer material and hence suit to a multiple material printing, but powder bed and liquid bed technologies such as selective laser melting (SLS), selective laser sintering (SLS) and stereolithography (SLA), are less suitable for multi-material printing [16, 17].

The innovative nature of AM is truly remarkable as it provides new opportunities and endless possibilities for companies seeking to improve their manufacturing efficiency. Some of key benefits of AM compared to traditional manufacturing are, innovation, quality, transformation, impact, cost and speed. In addition, AM has many sustainability benefits. This innovative process, generates less waste during production, due to the additive nature of the process. Similarly, it allows for the creation of optimized geometries and light weight components, which can minimize both material usage during manufacturing and energy utilization during use. This also leads to less transportation requirements in supply chain and can reduce inventory waste as components can be prepared or printed according to the demand. In a nutshell, AM is believed to be a crucial manufacturing technology in the sustainability of the society. Moreover, AM can be used to manufacture consolidated parts, creating thin walls and other complex objects or products that are too much difficult or cannot be manufactured by other traditional manufacturing process [18-20].

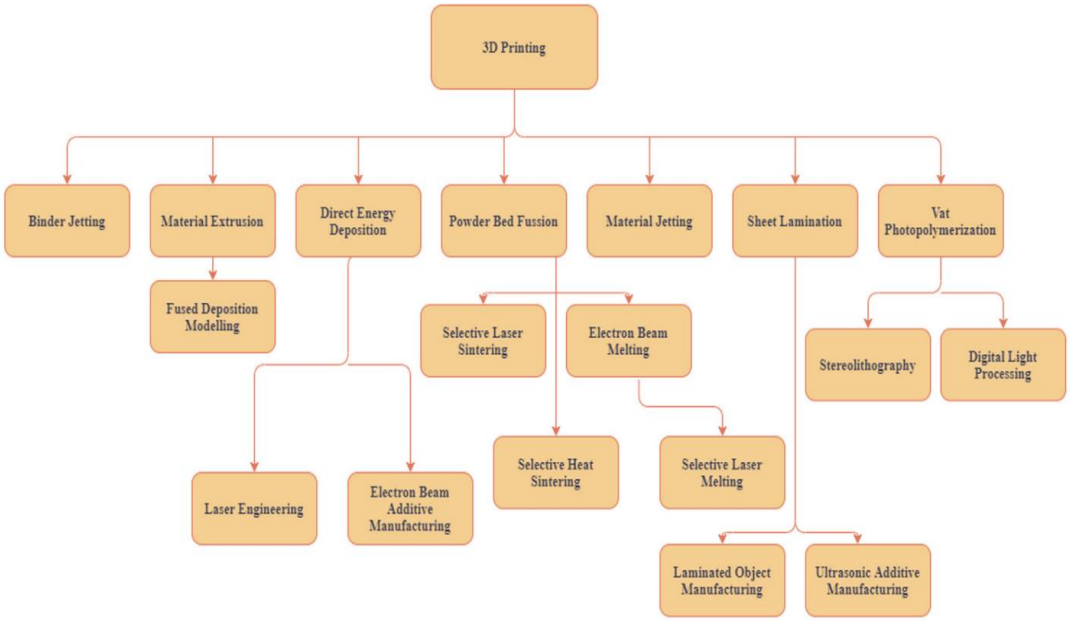

Figure 2. Types of 3D printing

1.1.1 Fused Deposition Modelling (FDM)

Fused Deposition Modelling is a layer-by-layer 3D printing technology and has been founded or introduced by Stratasys for fabricating complex geometric parts. It integrates three important components of a system: software, hardware and materials. This integration of three key components begins with the understanding of the basic requirements of the machine and ends up an operating procedure to select the parameters for optimal model output and efficiency. FDM is a popular AM technology due to its cost efficiency, fast production, ease of access, capability to produce complex components and broad material adoption. In FDM process, a thin thread of thermoplastic polymer is heated to its melting range, and then the heated filament is printed on a printing platform, also known as bed of FDM 3D printer, following a pre-defined pattern. This phenomenon of printing is continued until first layer is completed and then the platform is slightly displaced and printing of the second layer is started and the process is continued till the completion of the required component. Once the sample printing is completed, it is removed from the build platform and required post processing is carried out before using the product in real time situation. Before the deposition of a new layer, it must be ensured that the previous layer is well-solidified so that the surface can be considered stable for the next layer addition. FDM method can be used

to produce very complex shape in a single process with offering complete freedom of creation. Figure 3 shows the schematic of the FDM. [11, 21-23].

Like other processes, FDM process has got some crucial parameters, which can cause great impact on the properties of the printed part. In order to enhance the market share of FDM printed components, all the printed parts must meet some requirements. It would be better to optimize the parameters first and then printing process should be carried out on those optimal parameters. Some of the key printing parameters are air gap, extrusion temperature, build orientation, infill density, infill pattern, print speed, raster width, raster orientation, layer thickness.

- Air gap: It is space between two neighboring rasters on a deposited layer is known as the air gap.
- Nozzle temperature: It is the highest temperature, which is used to melt the filament and extrude the molten material through its nozzle. A layer is formed using that molten filament and then another layer is added to it. Range of nozzle temperature varies depending on the type of material being used. For example, for PLA nozzle temperature is normally being maintained from 200 ^{o}C to 230 ^{o}C.
- Extrusion temperature: The temperature at which the filament is heated and extruded in melt form through the nozzle of the printer to build the part.
- Build orientation: It is the way of orienting the part in a build platform or printing bed with respect to X-, Y-, and Z-axis. Build orientation may also be represented in term of angle with respect to base. In this work, we have printed sample at 0^{o} w.r.t the base. It can also be described as a horizontal direction.
- Infill density: The outer layer or wall of the printing object is always solid. While infill the inner portion and is an invisible part covered by the outer layer. Infill can be of different shape, size and pattern. Infill density is the percentage of the inner portion, that is to be filled with filament material. This percentage will have direct impact on the mass and strength of the FDM printed part. The range of infill is from 0% to 100%. A product with 100% infill will be completely dense component with highest possible strength and mass.
- Print Speed: The distance travelled by the extruder along the X-Y plane while extruding and adding the layer on one another. It is measured in mm/sec and total printing time

depends on printing speed. Normally, 45 mm/sec to 55mm/sec printing speed is used for PLA material and we have used 50 mm/sec to print our samples.

- Raster width: It is the width of the deposited layer of the pattern through nozzle. Its direction is same as that of raster orientation.
- Raster orientation: This is the direction in which filament is deposited with respect to x-axis on the printing bed of FDM 3D printing machine.
- Layer thickness: The height of the deposited layer along z-axis, that is normally considered as a vertical axis of the FDM printer. Generally, it depends on the diameter of the nozzle and usually less than that. Layer thickness can be varied using slicing software. Lower layer thickness value will have good surface finish as compared to higher thickness value, but, it will take less time to print the product if layer thickness has high value along with reduced number of infill layer.

A variety of thermoplastic materials can be used in FDM as a filament. The commonly used filament materials are polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), polycarbonates (PCs), polyether ether ketone (PEEK), polyetherimide (PEI), and nylon. In addition to the above commonly used materials, some other materials that are not being used frequently, are high-impact polystyrene (HIPS), polyphenylsulfone (PPSF), thermoplastic polyurethane (TPU), polyethylene terephthalate glycol-modified (PETG), ceramic and bio-composite filaments, and other composite material filaments. Majority of them are either still in the developmental phase or are not easily available in the market. It is also possible to use composite materials by mixing one of these materials with other type of materials, especially mixing with materials that are in powder form, and create filaments from this mixture. Work is also in progress in many organizations to develop new ceramic and metallic material for rapid fabrication of real time functional products or components with higher mechanical and thermal properties by FDM technology. However, sometimes development and testing of new materials become very difficult due to closed system. Filament for the system is supplied in cartages that cannot be refilled with other materials. To address the issue Manufacturing Department of the AGH University of Science and Technology has purchased a production of 3D printers, that feed materials from trays reel. This type of system allows to use materials of different types. This has

inspired 3D printing community and most of the later works have followed their foot step. [24-26].

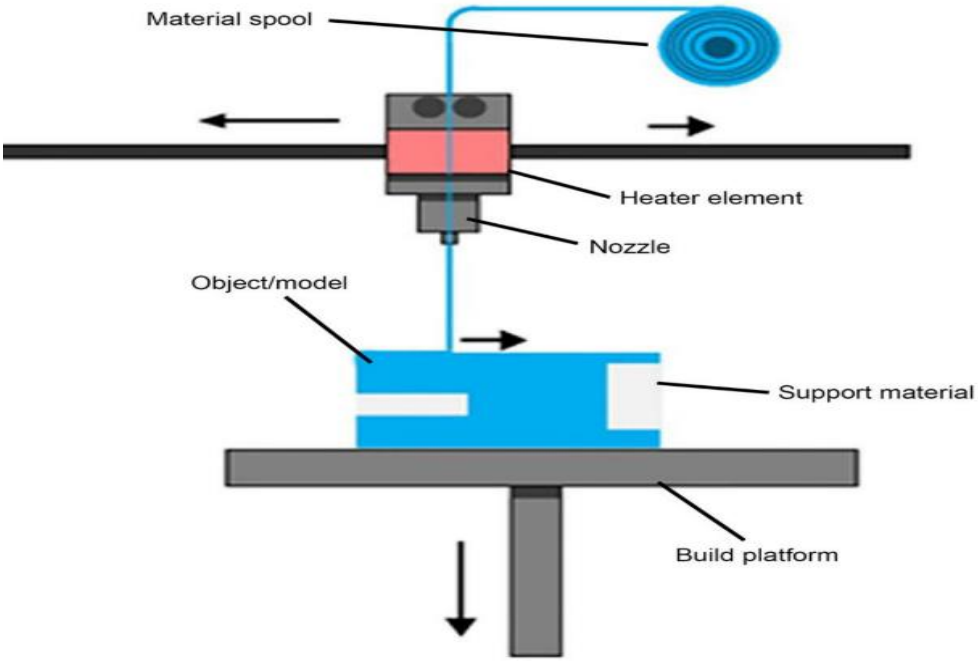

Figure 3. Schematic of FDM (Ref: AM Research Group, Loughborough University)

Among other AM processes, FDM became popular due to low cost and flexibility to use different materials. Over the years, FDM has been used for making products from a wide range of materials and the invention of new materials have enabled production of FDM-fabricated functional parts. It produces high-quality parts from materials that are durable with sound mechanical properties. You will find FDM machine in industrial scale as well as lab scale. Both of them offers high dimensional accuracy. If FDM is compared with other AM processes in industrial scale, then FDM is more economical and cost efficient than other AM processes and because of this AM is being used widely in both industrial and lab scale when compared with other AM technologies. Furthermore, the ability of FDM to print high melting materials is continuously improving [27].

There are some disadvantages of FDM technology as well. The main disadvantage of FDM is its low resolution. Also, FDM thick layer height results in poor surface finish with high degree roughness along with weak capability to incorporate small details. Since FDM printers place filament layer by layer in one direction and thus resulting component will be anisotropic and prone to breaking and the case becomes very critical if the layers' overlap. FDM parts will easily break

when compressing forces acted parallel to their layer. Although, light weight components are being considered for various applications, but, on the other hand lighter weight causes reduction in strength and this is very serious problem when such product or component is supposed to perform required functions under continuous stress or high pressure. If such components are not monitored regularly, then sudden failure can cause huge and irreparable damages. If you have to print complex structure, then you need supports to assist in proper printing of the sample. Such supports need extra materials, extra printing time and post processing operations [28].

Chapter 2 Literature review

Since PLA is biodegradable thermoplastic polymer, therefore significant work has been done on its preparation and applications. PLA is not being used wide application because of its high brittleness. A lot of efforts have been made to address this issue and enhance its capability to be used in real time applications. Various additives have been added to PLA in order to achieve this objective. Some of them have been mentioned below.

PBAT is a material that has become very popular for toughening PLA in the world of biodegradable polymer modification. When PLA is modified with PBAT, it has been observed that it becomes much more flexible and easier to process. PBAT is actually a biodegradable aliphatic-aromatic co-polyester that comes from fossil resources. It has a high elongation at break, as well as good hydrophilicity and water resistance. The ratio of the different types of structural units that make up PBAT can be easily adjusted to tailor its properties. These structural units are the rigid butylene terephthalate (BT) segments and the flexible butylene adipate (BA) segments [29]. Plasticizers have been added to PLA to lower its brittleness. BY adding plasticizer, the effects have been studied regarding the enhancement and an improvement in the elongation at break, obtained due to adding PBAT. It has been seen that by mixing triphenyl phosphate as a plasticizer has increased the spherulitic growth rate of PLA with increasing the equilibrium melting temperature due to plasticization of the chains. Also, addition of acetyl tributyl citrate (ATBC) has caused reduction in glass transition temperature T_g with improving the mechanical properties of PLA-PBAT blend [29].

Since both PLA and PBAT are biodegradable and are therefore, ideal components to be mixed together. Apart from PBAT, other materials can also be added to PLA according to the required application of resultant reinforced PLA. In this work [30] PBAT has been added to PLA at different ratios i.e. 10%, 20% and 30% by weight. Mechanical testing results show that, PBAT has shown significant effect on the properties of PLA. Although, the impact strength has increased for every ratio, but 30% by weight, has increased the impact strength from initial value of approximately 30 J/m to more than 700 J/m. This increase in the impact strength has occurred at the cost of up to 15 MPa reduction in tensile strength. Another work [31], where a blend of PLA/PHBV/ PBAT has been prepared. The blend is then used to make testing specimen by injection molding process and

3D printing process. Samples printed using FDM 3D printer exhibited superior elongation at break and 3 times more tensile strength, as compared to the sample made by injection molding process. Furthermore, cold crystallization temperature T_{cc} of PLA is increased and the reason behind this increase has been stated that PHBV and PLA disrupt the ordering of the blend by chain diffusion and folding into the crystalline lattice. Also, elongation at break is increased, and it is concluded that elongation at break of PLA could reach up to 65% when the content of PHBV is 25%.

Virgin PLA and PLA-PBAT filaments were prepared and then again crushed into pellets. The pellets were then used in micro compounder to prepare specimen. PLA60/PBAT30 or PLA-PBAT filament with 30 wt.% PBAT enhanced impact strength from 2.36 kJ/m^2 to 5.30 kJ/m^2 and elongation at break up to 13.91%, which is thrice as high as virgin PLA. Similarly, glass transition temperature T_g and melting temperature T_m for pure PLA are 66.98 ^{o}C and 150.97 ^{o}C, while T_g and T_m valued for PLA70/PBAT30 are 66.13 ^{o}C and 149.98 ^{o}C. In this paper [32], glass fibers and microcellular cellulose have been added to PLA. The composition of microcellular cellulose and glass fibers are 4 % and 8% by weight. After extruding filaments, their properties have been evaluated by performing various mechanical tests. Addition of microcellular cellulose improved the bending capacity, toughness and elasticity with lowering the brittleness of PLA. Similarly, due to addition of 8wt% microcellular cellulose, hardness of PLA is significantly increased, which caused cutting or breaking it off more difficult. While adding 4wt% glass fiber to PLA, increased the hardness and brittleness and its toughness is decreased. And by adding 8 wt.%, and by comparing with the wire with 4% glass fibers, it was found that brittleness and hardness have greatly improved, while curling and bending appeared blunter.

Continuous fiber reinforced thermoplastic composites (CFRTPCs), were fabricated in [33] using FDM 3D printer, but by modifying its setup. 15% by weight short carbon fiber and 20% by weight copper were mixed with PLA, and, tensile and flexural specimen were then measured. It was found that tensile strength increased dramatically up to 105 MPa as compared to baseline value equal to 37MPa. Similarly, huge improvement was seen in flexural strength and it was increased up to 128 MPa, much higher than baseline value of 78 MPa. Effect of carbon fibers by reinforcing them with PLA was also observed by a group of researchers [13], and observed huge improvement in the tensile and flexural strength of PLA. They obtained tensile strength upto 112 MPa and flexural strength up to 116 MPa and these obtained values were almost three times higher than tensile and flexural strength of pure PLA printed specimen. However, the methodology of reinforcing was

same as mentioned above i.e. passing carbon fibers through another nozzle of dual nozzle FDM printer in parallel to PLA.

To fully understand how the chain extender affects the interfacial properties of PLA-PBAT blend, it's essential to analyze the evolution of their rheological, morphological, and mechanical properties. Many studies have focused on quantifying the interfacial tension of the incompatible polymer blends using the rheological method (RM) by analyzing droplet deformation. Experimental studies show that in the case of Newtonian droplets in a viscoelastic matrix, an increase in the elasticity of the fluid matrix leads to a higher deformation of the droplets in shear [34]. Using polymeric toughеners with has appeared to be an efficient and cost-effective method of increasing its toughness. However, the toughening process of a PLA blend is influenced by various factors i.e. volume fraction, size, substructure and inherent properties of the dispersed phase, as well as the inter facial adhesion. Moreover, it has also been observed that, while there is a considerable increase in the impact strength, there is also a significant decrease (30 % to 50 %), in the stiffness of strength of PLA materials and this is an impermissible. Therefore, this is a main challenge to enhance toughness without much reduction in the tensile strength. Additionally, the role of tacticity and crystallization, such as crystalline structure and degree of crystallinity of the PLA matrix in PLA toughening are not yet well understood and deserve more attention [35].

Blends of PLA-PBAT with and without addition to Perkadox were prepared using twin-screw extruder. The addition of Perkadox in the blends led to a reduction in particle sizes of PBAT phases compared to those without Perkadox. This was observed across all blend ratios and can be accredited to the improved interfacial adherence between PLA and PBAT phases. MFI values of all blend ratios were reduced by adding more Perkadox due to cross linking reaction. Although, the tensile strength and Young's modulus remain unchanged, while elongation at break appeared reducing with adding more Perkadox. The tensile strength of PLA-PBAT (80-20 wt.%) remain unchanged, while the impact strength of PLA-PBAT (70-30 wt. %) was increased by 110% when 0.5 phr Perkadox was added [36].

The researchers developed a new method to create nanocomposite, that are free from toxicity using biodegradable PLA-PBAT blends and expanded organoclay. SEM images revealed that a better nanodispersion and compatibility was observed between PLA and PBAT, when 2.5 wt.% of antimicrobial (ROC) was added, particularly in the case of 7525 ROC or 2575 ROC samples. Similarly, TEM result proved the existence of intercalated structures in 2575 ROC and 7525 ROC

samples, where both exfoliated and intercalated structures existed in the polymer matrix when the amount or ratio of PLA was 75% (7525 SOC and 7525 ROC samples), which indicates the penetration ability of PLA short chains between clay layers leading to clay exfoliation and formation of nanocomposites. Similarly, DSC result showed that degree of crystallinity of PLA was significantly affected, when the content of PBAT is increased. PLA-PBAT nanocomposites based on rosin acid, revealed significant antimicrobial activity in opposite to Gram-negative and Gram-Positive bacteria and also fungi, as compared to pure PLA or other types of nanocomposites. Also, significant increase in the tensile and viscoelastic properties was noticed for bio nanocomposites, when SOC or ROC was used as a toxicity-free nanofillers as compared to pristine polymer [37].

Based on the previous works, the effect of additives on the mechanical properties was discussed above. We have mentioned very few above, and apart from that a lot of other carried out to identify the effect of additives on the mechanical and thermal properties of PLA. Furthermore, mixing such additives with PLA are also effecting thermal properties and crystallization ability of PLA. It has been observed in [38], that crystallization temperature is increased as compared to virgin PLA and this has happened because PBAT blend with PLA has influenced the crystallization behavior of PLA and the same effect of PBAT on the crystallization temperature of PLA has been depicted in [30]. Similarly, in the same paper [38], it has been discussed on the basis of TGA curve, that both 30% and 40% PBAT as an additive, has reduced the thermal degradation temperature i.e T_{onset} and 5% weight degradation temperature ($T_{5\%}$), $T_{10\%}$ and $T_{50\%}$ of PLA when compared with virgin temperature. In addition, DSC results show that enthalpy value (ΔH) reduced from 6.9 J/g to 1.4 J/g by adding PBAT and this reduction is attributed to the addition of PBAT. Further, no peak was observed during cooling stage, that indicated slow crystallization kinetics behavior of PLA. Value of the peaks were remained unchanged during second heating. Also, it can be seen that addition of PBAT into PLA matrix did not influence the thermal stability and heat resistance of PLA, because PBAT demonstrated higher thermal stability than PLA.

The degree of crystallization for pure PLA filament was calculated in [39] by using the area under the cure and the calculated value was 30.9%, but the degree of crystallinity increased to 34.5% by adding cellulose nanocrystals (CNC). This increase in X_c is because, presence of CNC accelerates the crystallization of PLA. By increasing the amount of thermal degradation temperature also increased, indicating that thermal stability of PLA is increased by adding CNC while it did not

alter T_g and T_m of PLA but it can be seen as a nucleating agent for PLA (at 5% CNC loading. Lastly, the researchers in this work [40], have shown that the starting point of decomposition T_{onset} of PBAT started later than in PLA, which is 30 ^oC higher than PLA. In this paper, it has also been stated that TGA measurements are not representative to real decomposition during processing and cannot give any information about the real mechanism governing the phenomenon under processing conditions (temperature, residence time and shear rate). The paper has compared the degree of crystallinity of pristine PLA or PLA pellets and PLA extruded at 180 ^oC and 190 ^oC. And has found that degree of crystallinity X_c of PLA has significantly improved by extruding it. The obtained X_c values for PLA pellet is 1.7%, while it is 35% for PLA extruded at 180 ^oC and 39% for PLA extruded at 190 ^oC. It has also been identified that addition of glycidyl methacrylate (GMA) to PLA/PBAT matrix has enhanced tensile modulus from 820 MPa for PLA/PBAT to 1095 MPa for PLA/PBAT/GMA composite. Similarly, elongation at break has increased from 50% PLA/PBAT blend to 135% PLA/PBAT/GMA blend.

Isothermal crystallization kinetics and morphology of biodegradable PLA/PBAT blends were studied with POM, DSC and WAXD in detail. The isothermal crystallization kinetics of both neat and blended PLA were thoroughly examined using DSC, and were subsequently analyzed through the application of the Avrami equation. Despite the addition of amorphous PBAT and changes in crystallization temperature, the Avrami exponent remained nearly identical. This suggests that the addition of PBAT did not significantly impact the crystallization mechanism of PLA, when subjected to a temperature of 128 ^oC. On the other hand, it was observed that the crystallization rate showed an upward trend as the PBAT content increased, except in the case of the PLA blend containing 60 wt.% PBAT. The overall increase in crystallization rate can be attributed to two factors: changes in the melting temperature T_m^o and a reduction in the glass transition temperature T_g. Neat PLA did not distinctly show cold crystallization peak, while PLA blend displayed cold crystallization peaks at the range of 100 to 104.5 ^oC. This proves that, addition of PBAT increases crystallization temperature, with narrowing down the peak's width, which indicates the enhanced crystalline tendency of PLA. With utilizing hot stage POM, the growth and morphology of spherulites were evaluated within a temperature range of 123-142 ^oC. The spherulitic structure of PLA was considerably affected by the temperature of crystallization and introduction of PBAT. It was observed that blending did not alter the crystal structure of PLA and the structure remained unchanged, as determined by WAXD measurement [41].

Polymer deposition on textiles can be influenced by several factors, including the combination of polymer and textile, adhesion, material compatibility, adhesion and technology used for deposition. It's important to consider these aspects in order to achieve optimal results in material and polymer science. It has also been proved that different 3D printing parameters have considerable effect on the adhesion of polymers to fabrics. The analysis of most suitable model indicated that, adhesion force of Nylon on PA66 fabrics is significantly impacted by both printing speed and the extruder temperature. Specifically, it was observed that temperature has linear effect while printing speed has a quadratic effect on the properties of Nylon and PA66. Platform temperature would not have significant effect on the adhesion force, if the temperature is lower than glass transition temperature of applied fabric. This has been explained by the diffusion theory, which explains the adhesion of polymers to each other, by the diffusion of chain like molecules, which results to the formation of a strong bond between adhesive and adherent. In addition, increased extruder temperatures can lead to decreased strength between 3D printed layers, indicating that using high extruder temperatures may result in heightened fragility and vulnerability [42].

In order to check the biodegradation rate, pure PLA, pure PBAT and PLA-PBAT were buried under the soil for four months and their degradation rate was measured through various tests and analysis. According to results obtained by infrared spectrum, the residual PLA, PBAT and PLA/PBAT blend samples showed same characteristic peaks after degradation as they did before. However, from the elementary analysis, it was found that the carbon atom content in the molecular structure of the PLA, PBAT and PLA/PBAT blend had decreased, while the content of oxygen atom had increased. This shows that the samples had experienced degradation. The TG and DSC curves show that PBAT's melting temperature decreased slightly after degradation, while melting temperature of PLA increased after degradation. Additionally, the melting temperature and melt point changes of various components in PLA/PBAT blend before and after degradation mirrored the changing process of the individual polymers. Upon analyzing both the elemental analysis and TG curve, it became evident that the degradation rates of PLA, PBAT, and PLA/PBAT blend were different from the degradation rate of the individual polymer. Similarly, by looking at the scanning electron micrographs of PLA and PBAT samples before and after degradation, it is clear that there are different or varying degradation mechanisms for each material [43].

Printing parameters can have significant effect on the properties of the printed specimen. These effects were examined and analyzed in [44]. It was found that the specimen with a 45^{o} raster orientation proved to be the strongest printed specimen as compared to others. Meanwhile, the fatigue testing revealed that the specimens with 90^{o} orientation, were the least resistant to the fatigue loadings. It was also found that the fatigue lives of 0^{o} and 45^{o} specimens were quite similar. However, it must be mentioned that the 45^{o} specimens exhibited the highest fatigue endurance limit. Similar results were obtained by testing the filaments. This is supposed to be helpful to determine, whether failed printed specimen can again be recycled to extrude new filament, which will then be used for printing purpose again. In addition, it was also identified by conducting microscopic evaluation of the specimens, and it was found that gaps were left between the layers and this evaluation helped in determining those gap sizes in the specimen. The average gap thickness was 181.47 µm, and during high stress fatigue tests, it was also noticed that outer shell of the specimen was completely separated from the main part of the specimen and had no contribution in the stiffness of the specimen. In another study, on determining the effect of FDM printing parameters on the properties of PLA [45], it was found that nozzle temperature had significant effect on the tensile properties of PLA. Same trend was observed for the infill density, where increasing the infill density had caused increased to tensile properties. While printing speed has acted as an insignificant factor. The selected optimal process parameters were 100% infill density, 20mm/sec printing speed, 220 ^{o}C nozzle temperature, to produce biomedical components with better mechanical properties using FDM 3D printing process.

Although, 3D printing process is present since 40 years, but still AM technology is far beyond than traditional manufacturing processes i.e. formative and subtractive manufacturing processes. However, 3D printing technology is becoming an increasingly popular manufacturing technology. The demand for fully automated miniaturize is increasing due to their versatility and speed in fabrication. With the ability to produce customized columns and stationary phases through print-to-order production and continuously development of new printing materials, this technology can help in the creation of more sensitive and selective printing platform. In addition, by using multi-material printers, various components like stationary phases, columns, and flow connectors can be produced using materials with different properties. Furthermore, the advent of AM technology has opened new opportunities in CH sector, paving the way for novel applications and avenues of explorations. These technologies allow for the cataloguing and study of both physical and virtual

models, that form the base for the display and analysis of the shape and metrics of every artistic and historical artefact of interest. Latest 3D modeling and printing experiences have shown the need to introduce a new professionalism in support of an architect, engineer, archeologist, conservator and restorer, that need the need of digital technologies related to the instrumental survey, to 3D modeling and solid printing. Despite rapid advancement in 3D printing technology, there are still many constraints to obtain above goals. Most of those hurdles have been mentioned above and will hopefully be addressed in near future, so that AM technology could compete traditional manufacturing processes in every manufacturing sector. The rate at which AM technology is developing is impressive, and continuous improvement in the resolution of commercial 3D printers and constantly increasing variety of printing materials will help in overcoming the current limitations in near future with increasing the potential of AM to great extent [46, 47].

2.1 Scope of this research work

Polylactic acid (PLA) is an aliphatic polyester made up of monomers called lactic acid. It is a biodegradable polymer and is produced from renewable sources. This characteristic makes it beneficial as compared to other polymers that are toxic to the environment. Polybutylene adipate-co-terephthalate (PBAT) is a synthetic biodegradable polymer and its bio-degradation rate is much faster than PLA.

One of the major limitations with PLA is high brittleness. Despite of being biodegradable in nature, PLA is still not used to its full capacity because of high brittleness. Many attempts to improve the properties of PLA, especially elongation capability, have been reported in the literature [32, 33, 48, 49]. Since PBAT is a soft material, therefore, increasing its weight percentage has decreased tensile and flexural strength. However, little or no effect was seen on thermal degradation, crystallinity and degradation rate [30, 38, 50].

Based on the previous work, it has been concluded PBAT will have impermissible negative impacts on the properties of PLA, if wt.% of PBAT is increased from 10%. Some previous works have recommended PBAT less than 10 wt.%. Therefore, with the purpose to enhance the elongation capacity of PLA without damaging its tensile and flexural strengths, we have prepared a PLA-PBAT blend FDM filament with a composition of 8 wt.% PBAT. In addition, pure PLA

filament was also extruded under same processing parameters. The extruded filaments were then used in FDM 3D printer to check their printability. Furthermore, their properties were compared with properties of commercial pure PLA filament available in the market. Currently, PLA is not being prepared locally in Pakistan, and PLA filaments available in the market have been imported from other countries. Therefore, this work will also act as a pioneer step in term of local preparation of PLA filament.

Chapter 3 Materials

3.1 Poly Lactic Acid (PLA)

Polylactic acid (PLA), is composed of monomers called lactic acid, that are connected together by ester bond, and has got interesting properties. Biodegradable polymers have recently attracted researchers, because of their applications and usage in the protection and maintenance of the environment. Since aliphatic polyester polymers are susceptible to biological attack, and therefore, are being considered very important by the researchers. PLA is also an aliphatic polyester and it is being generated or produced from the sources which are renewable and that is why PLA has received too much attention. Some of its mechanical properties like flexural strength, tensile strength, young modulus, are considered superior or ideal mechanical properties. These properties are even higher than those of PE, PS, PP and other polymers. Unfortunately, PLA is very brittle material, having less than 10% elongation at break, with low toughness, and this limits its applications in the areas where plastic deformation under high stress is needed. However, its elastic modulus and tensile strength are comparable to other polymers. This high brittleness results in poor processability as well. Figure 4 shows the life cycle of PLA or the stages PLA undergoes, from very initial stage to the final stage [48, 51-53].

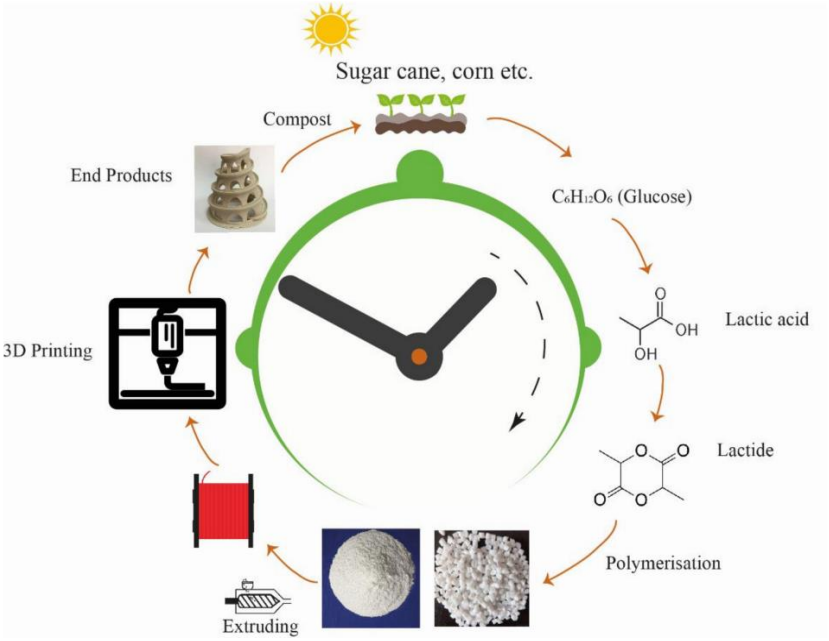

Figure 4. Life cycle of biodegradable polylactic acid

3.2 Polybutylene Adipate-Co-Terephthalate (PBAT)

Polybutylene adipate terephthalate (PBAT) is an aliphatic-aromatic co-polyester that is obtained from poly-condensation between butanediol (BDO), adipic acid (AA) and terephthalic acid (PTAA). PBAT is a synthetic and 100% biodegradable polymer, that is prepared from fossil fuel. It has an excellent elongation at break and is very flexible polymer. Its degradation rate is much faster than PLA and degraded in some weeks, but, its biodegradation is dependent on environmental degradation conditions and chemical structure. Sometimes micro-organisms i.e., algae, bacteria, fungi, carry out the degradation process. Biodegradation also happens by a combined depolymerization process, where PBAT chains are broken down by non-enzymatic reactions like thermal degradation, chemical hydrolysis and also by metabolization of these microorganisms [54-56]. Table 1 shows some of the properties of PLA and PBAT [51, 56].

Table 1. Characteristics of PLA and PBAT

S.No	Characteristics	PLA	PBAT
1	Molecular weight (g/mol)	≈ 100.000 g/mol	≈ 40.000 g/mol
2	Melting point (^{0}C)	168 ^{0}C	120 ^{0}C
3	Glass transition temperature (^{0}C)	62 ^{0}C	-30 ^{0}C
4	Density (g/cm^3)	1.25 g/cm^3	1.25 g/cm^3

Chapter 4 Application of PLA-PBAT filament

As discussed in the beginning that, PLA is a biodegradable polymer and that is why, it is being preferred over other petroleum based plastic materials, which are being considered harmful for the environment. The world is moving rapidly using toward sustainable and environmentally friendly products and this trend shows that PLA will have pivotal role, when we talk about plastic consumption. PLA can be used to manufacture products by using different manufacturing processes i.e. injection molding, extrusion etc., but the trend of using PLA in AM technology is also increasing exponentially. Among different types of AM techniques, PLA is frequently used in FDM 3D printing process, and is being considered one of the main FDM materials. Some years ago, FDM was being used to print prototypes, but now FDM is being used to print PLA functional parts as well. Following are some areas, where PLA is currently being used to print end user products.

4.1 Prototypes:

Prototype is something that acts as a model for the actual product. It is preliminary version of a product that helps to test your ideas and communicate the purpose of a feature or the overall design concept to user prior to committing resources toward development. FDM is effective printing process for manufacturing prototypes, because it is a cost effective and fast printing method that can produce complex geometries with ease. PLA is preferred to print prototypes because, it is very easy to work with and produce products with good quality finish. It is also durable and strong, making it good choice for creating functional prototypes that can withstand testing and experimentations. Additionally, PLA is an environmentally friendly choice, and it is prepared from renewable resources and is biodegradable. In a nutshell, using PLA for printing prototypes is a smart choice that provides a number of benefits for both the user and the environment. Adding PBAT with PLA will further increase its importance by toughening it.

4.2 Aerospace industry:

3D printing is an ideal choice for many prototyping and functional use applications within the aerospace and aviation industry. Components manufactured through 3D printing can be stronger and light and lighter than components made by using traditional manufacturing. Variety of

aerospace components are being made using 3D printing process for example, jigs and fixtures, surrogates, mounting brackets, high details visual parts and cabin parts, lights holders and many more. PLA is an excellent material for these applications, because it is a light weight material with low density, and such high strength materials with low weight, are considered ideal materials for aerospace industry, because it will allow for more fuel-efficient flights, which can save millions of dollars in fuel cost over the life of an aircraft. Additionally, PLA is highly resistant to temperature and thus aerospace parts made from PLA can perform their functions properly in extreme environments. Also, aircrafts are made from many complex components, and PLA is an ideal material to print or manufacture such complex shapes. Overall, PLA is a versatile and reliable material that plays an important role in the aerospace industry.

4.3 Healthcare industry:

PLA has emerged as a versatile biopolymer and is being used in bioengineering. Its medical applications vary from regenerative medicine, tissue engineering to orthopedic, dental and cardiac use. Since 3D printing is best option to print customized products, therefore, by using PLA in 3D printing, patients specific tissue engineering scaffold, or rapidly manufactured medical equipment, and personnel protective equipment (PPEs) can be generated. It is commonly used in surgical implants, drug delivery system, and tissue engineering because it is safe for human use and can be broken down by body over time. Also, PLA has the ability to maintain its strength and integrity in high-stress environment, making it reliable material for medical devices. In a conclusion, PLA has revolutionized the medical industry by providing a sustainable and affective solutions for a wide range of medical needs.

4.4 Electronic industry:

The application of PLA has recently gained popularity in the electronics industry. PLA is being used to produce various components like casings for electronic devices, circuit boards etc. The application of PLA in the electronics industry is expected to continue growing as more companies embrace sustainable practices and seek alternative material to traditional plastics. With its unique combination of properties, PLA offers a promising solutions to meet the growing demands for sustainable electronics.

4.5 Figurine:

Figurines and statuettes are three dimensional sculptures that often show the human form. They are being created to celebrate or commemorate high-profile people or events. Most of them are being made from plastic. Since their designs are highly customized and complex, therefore 3D printing technology can be considered ideal choice to make them. Using PLA in figurine making will produce smooth and glassy finish. Also, PLA has low melting point, therefore it would be easy to make complex shapes and designs, because of the ease to handle it. PLA is also durable and can resist wear and tear, making it ideal for creating figurine that will be used often or displayed over a long period of time.

4.6 Automotive industry:

Automotive industry is one of the huge industries in today's world and is still rapidly growing. It is contributing significantly, i.e., 3.65% of global GDP. Automotive industries are heading rapidly toward incorporating 3D printing processes in their manufacturing system. Till now, 3D printing has been used to print 70% of a whole and car and efforts are underway to increase this capacity to 90% and even beyond if possible. However, only prototypes are being created currently and not a road worthy vehicle. Plastic is the most used 3D printing material in automotive industry as compare to metal or ceramic. Among other plastics, PLA and PBAT are being preferred because of their biodegradable and eco-friendly nature and therefore, PLA has a wide range application in automotive industry. PLA is used to create parts such as dashboard, interiors, and even car bodies. This is because PLA is a lightweight and durable material, that is able to withstand high temperature and pressure. Apart from that, there are various other application of PLA in the automotive industry, for example, production of lubricants, adhesive and coatings. Although, PLA is being printed at low temperature and does not need a highly heated platform, but, it is harder to manipulate than other materials. Overall, PLA is an innovative material that can help to reduce the environmental impact of the automotive industry, while still maintaining high level levels of performance and durability.

Figure 5. Applications of PLA as a 3D printing material

Figure 5 shows some of the functional parts, that are being made of PLA through FDM 3D printing process. As discussed above, PLA is not used in wide applications due to its brittleness, that could lead to sudden failure with causing catastrophic damages. Therefore, many efforts have been made to address such issues with PLA and enhance its capability for different applications. Since, PBAT is also biodegradable material, therefore, its addition would not affect the biodegradability of PLA and thus PBAT is an excellent choice as a PLA additive. It has been proved from mechanical and thermal testing results, that by adding 8 wt.% PBAT has enhanced the flexibility and thermal properties of PLA. Similarly, it has been proved previously, that addition of PBAT has enhanced durability and impact resistant of PLA. This makes it suitable for wider range of applications, such as packaging, 3D printing and textiles. Thus, addition of PBAT will improve the intrinsic limitations of PLA and will make it more suitable for the applications mentioned above.

Chapter 5 Methodology and Experimentation

5.1 Materials and Filament Extrusion

PLA pellets used in this experiment with commercial grade (H8000-5D), and PBAT pellets (virgin material) were obtained from Orinko Advanced Plastic Co Ltd.

Extrusion process was carried out in collaboration with Waseem Enterprises Lahore. Prior to blending, both PLA and PBAT pellets were dried up to remove in the oven at 80 ^{0}C for 6 hours to remove moisture and achieve better performance in the extrusion process. After removing the moisture, pellets were blended using mixer. The blend was then poured into the hopper of a single-screw extruder. Filaments were extruded at 170-180 ^{0}C by keeping an average diameter of 1.75 ± 0.02 mm. Figure 6 illustrates the schematic of single screw extruder, which is widely used mixing device in the industry especially in plastic industry. Plastic is heated and other components are distributed through the viscous liquid. Hopper is used to load material that is to be melted and extruded. Single material or a mix of materials can be loaded into the hopper and in our case we had heated pure PLA pellets as well as blend of PLA pellets and PBAT pellets. After feeding the material into the extruder, barrel is heated up to the melting point of that material. Pressure is inserted on the thermopolymer melt, so that molten material can be extruded through the nozzle. Screw is used to continuously push plastic through a constant profile. Heaters are used to heat up the material inside the barrel until it gets converted to molten state. Nozzle is placed at the end of the extruder which is used to extrude the filament. Size of the extruded filament depends on the diameter of the nozzle. In our case we had used nozzle with 1.75 mm diameter and had extruded filament with 1.75 ± 0.02 mm. Cooling fans are acting as a cooling agent and help in maintaining the barrel temperature in the acceptable range to avoid any kind of damages [57].

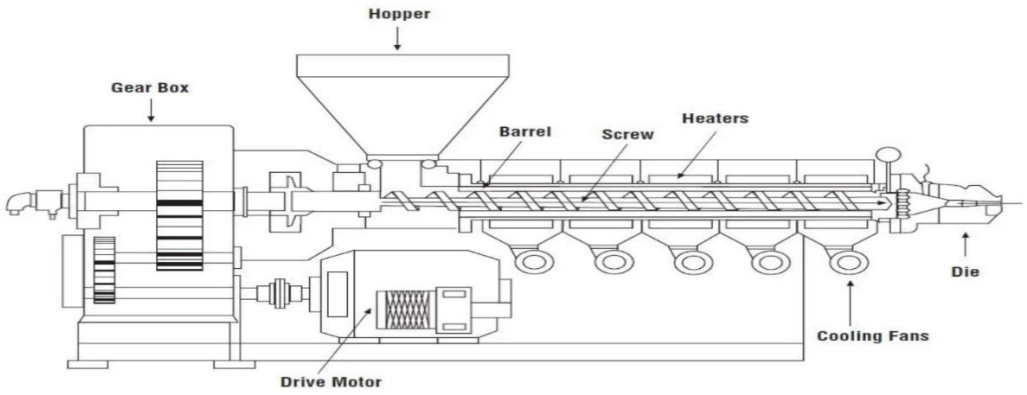

Figure 6. Schematic of single screw extruder (Ref: AZO materials)

In the single screw extruder, molten material flows through a channel of rectangular cross sections. The surfaces are called trailing and leading surfaces of the flight, the bottom is the screw root and top is the inside surface of the barrel. Fluid is pushed forward because of the relative motion of the channel and the barrel. Viscous drag force is transmitted to the fluid in the channel from the barrel surface and all fluid motion derives from it. That force builds pressure and the molten metal is then pushed toward the nozzle and filament is extruded according to the required specifications. In general, main function of extruder is to supply well-mixed homogenous polymer melt at specified uniform pressure and temperature. This objective is achieved by making extruder fully equipped with an efficient feed system, drive, a screw-designed to melt and pass the polymer and devices such as pressure, temperature sensor that are needed to monitor the system for control and troubleshooting. Although, considerable improvements have been incorporated in polymer extrusion over the last five decades, but still thermal monitoring and control is a problem and needs to be addressed. Many parameters and steps are considered important during extrusion process, but, accurate and continuous monitoring of the major variables along with the use of advance process control strategies are invaluable to form good quality extruded product, either in the form of filament or other extruded product [58].

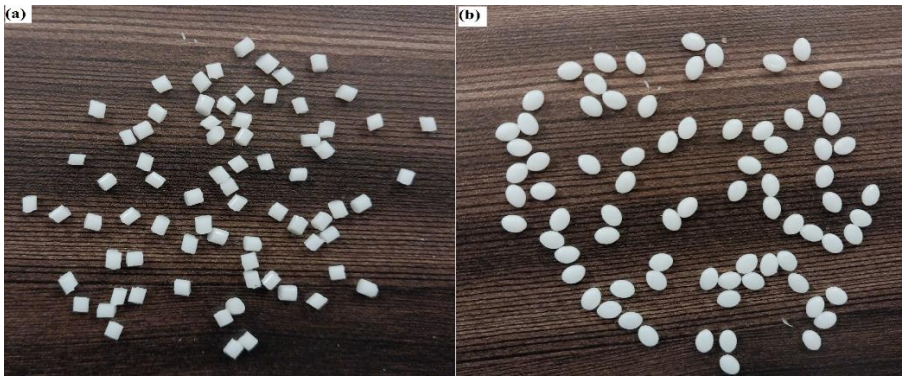

Figure 7. Pellets used for filament extrusion: (a) PLA pellets, (b) PBAT pellets

Figure 7 (a) represents the PLA pellets with circular cross section and spherical PBAT pellets (b) that were used to extrude the pure PLA filament and PBAT-reinforced PLA filament respectively. These are biodegradable pellets obtained from natural resources, such as starch extracted from sugar beet, corn and wheat and have been bought from Orinko Advance Plastic Co Ltd. Similarly, PBAT pellets are shown in Figure 7 (b), which are spherical in shape. PBAT pellets are prepared from fossil sources and have got significant importance being completely biodegradable with high elongation capability.

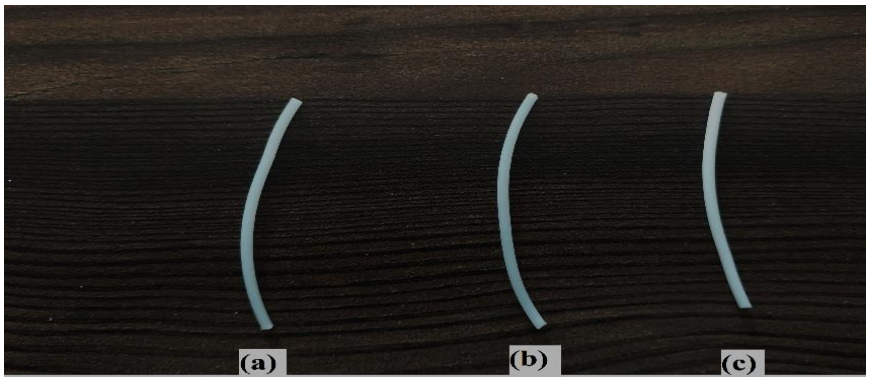

Figure 8. FDM filaments: (a) Lab developed pure PLA filament, (b) Lab developed PLA-PBAT filament, (c) Commercial PLA filament

Figure 8 shows the images of (a) extruded pure PLA filament, (b) extruded PLA-PBAT filament, and (c) commercial filament which was brought from the market. Commercial PLA filament was bought from the market to conduct a comparison of properties, especially tensile and flexural

properties. All the above three filaments were then used in FDM 3D printer to print ASTM D-638 tensile specimen and ASTM D-790 flexural specimen.

Figure 9. Extruded PBAT-reinforced PLA filament

Figure 9 shows the extruded spool of PLA-PBAT filament. Similar spool was also prepared for pure PLA filament. These spool of filaments were heated before using them in the printer in order to remove moisture content from them.

5.2 Design of Experiment (DOE)

Design of experiment (DOE) is a branch of applied statistics, that deals with planning, conducting, analyzing and interpreting controlled test the assess the factors that control a value parameter of a group of parameters. Ronald Fisher, introduced four persisting principles of DOE in 1926, i.e. the factorial principle, randomization, replication and blocking. Randomization refers to the order, in which the trails of an experimental run are performed, while blocking, let you restrict randomization by carrying out all the trials with one setting of the factors and then all the factors with other setting and is being carried out, when randomizing a factor is impossible or too close. Similarly, replication is a repetition of experimental treatment, including the set up. It is a powerful data collection and analysis tool and can be applied in variety of experimental situations. It allows to manipulate multiple factors and identify their impacts on the desired outputs also called as responses. This manipulation helps in identifying most important and less important and then prioritize them on the basis of their importance for upcoming experimental trials. DOE is used, when more than one input factor is supposed to influence the output or response. Furthermore, it

helps in to run trials that span the potential experimental region for our factors and also enabling us to understand the combined effect of the factors. [59, 60].

Full factorial design gives combination of all experimental trials or all possible combination of the factors, that are used to determine the response or output. Full factorial is represented by L^k, where "L" number of factor level, while "k" represents total number of factors. And then experimental runs are carried out according to that combination. Therefore, there are some alternatives, which are being used to minimize the number of trials or experiments, with almost same output. Taguchi is on the top among the alternatives, that are being used to replace full factorial design. Taguchi DOE was used to design the experiment and print samples accordingly. It is a popular approach for quality optimization and reduces the variation of defects in the process or product. In addition, Taguchi DOE minimizes the total number of experiment as compared to full-factorial design with giving nearly same results [33]. Orthogonal array (OA) is selected based on the degree of freedom (DOF) as shown in Eq. (1) .

$$DOF = 1 + (\text{no of factors}) \times (\text{factor level} - 1) \quad (1)$$

$$DOF = 1 + (3) \times (3-1) = 7$$

Therefore, for three factors i.e. type of material, temperature and layer thickness, and three levels, L9 OA was selected to print the samples with 01 repetitions for each setting as shown in sign to 36 with one repetitions.

Table 2 generated by Minitab® software. There are total three number of factors i.e material type, layer thickness and temperature, and, three levels of each factor. The selection of L9 OA reduced the number of experiments from 108 in full factorial design to 36 with one repetitions.

Table 2. Taguchi orthogonal L9 array

S.No	Materials	Temperature (^{0}C)	Layer Thickness (mm)
1	Lab Developed PLA (LPLA)	210	0.1
2	Lab Developed PLA (LPLA)	215	0.15

3	Lab Developed PLA (LPLA)	220	0.2
4	Lab Developed PLA-PBAT (PLA-PBAT)	210	0.15
5	Lab Developed PLA-PBAT (PLA-PBAT)	215	0.2
6	Lab Developed PLA-PBAT (PLA-PBAT)	220	0.1
7	Commercial PLA (CPLA)	210	0.2
8	Commercial PLA (CPLA)	215	0.1
9	Commercial PLA (CPLA)	220	0.15

5.3 ASTM Standards and Specimen Design

Various standards are being used for tensile and flexural specimen. Two standards, that are commonly being used are American society for testing and materials (ASTM) standard and international organization for standardization (ISO) standard. For this experimental work, we printed tensile and flexural specimens according to ASTM standard. Specimen were designed using Solidworks® 3D Computer Aided Design (CAD) software. ASTM D-638 dog-bone sample is chosen to print tensile specimen, while ASTM D-790 is chosen for flexural specimen. Figure 10 represents schematics of the testing specimen, while Table 3 represents the dimensions of tensile and flexural specimens [33].

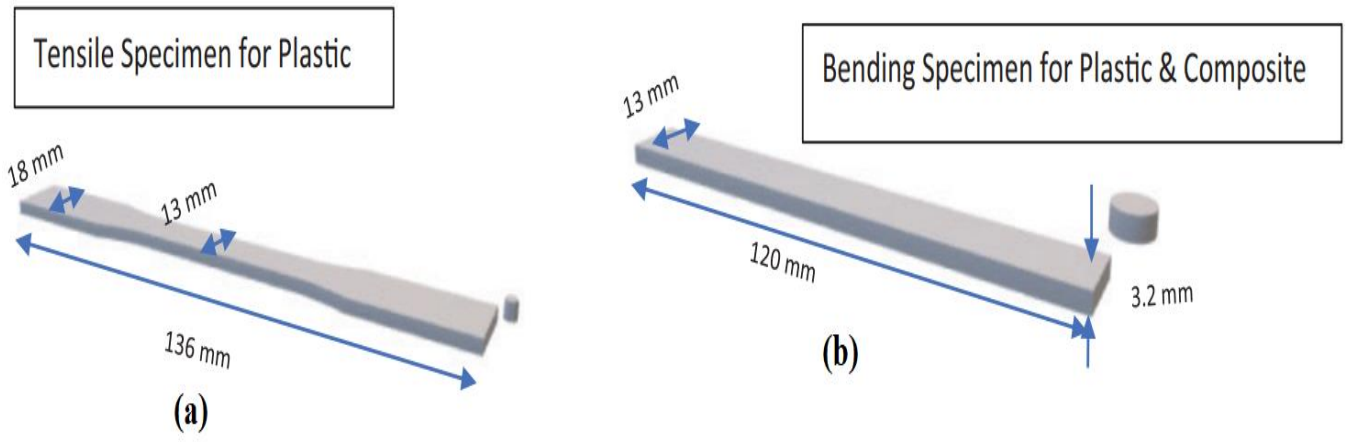

Figure 10. Testing specimens: (a) ASTM D-638, (b) ASTM D-790

Table 3. Dimensions of ASTM D-638 and ASTM D-790 specimens

Characteristics	Tensile Specimen	Flexural Specimen
Specimen Type	Dogbone	Rectangular cross-section
Grip/ Overhang	30 mm	10 mm
Gauge/Support Span	50 mm	100 mm
Width at Grip	18 mm	13 mm
Width at Gauge	13 mm	13 mm
Thickness	3.2 mm	3.2 mm
Total Length	136 mm	120 mm
Rate of crosshead motion for testing	2 mm/min	2 mm/min

5.4 FDM 3D Printing

After designing the specimen, they were saved in standard tessellation language (STL) file. An STL file stores information about 3D CAD model and represent the model with small triangles. STL file is then transferred to slicing software to slice the model. Ultimaker Cura®; an open source slicing software for FDM 3D printers, was used for slicing and creating G-code. It is powerful and easy to use 3D printing slicing software and allows users to slice CAD model for printing, as well as customize and optimize print setting according to the material that is being used to print the product. Although, it offers limited setting options for the novices, which are also called basic and very crucial parameters of FDM 3D printer. However, for experts, there are over 200 settings, which can be used by the experts to get best results for their products. Ultimaker Cura® is most widely used slicing software, and is useful tool for wide range of users like professionals, students, industries, hobbyists etc. It can import 3D model in STL format and allow users to scale, orient

and rotate model on the build plate or platform. It has also got built-in 3D model viewer, that allows users to envisage and manipulate their models in real time. It is considered to be good tool to enhance the quality and reliability of the print and allows for greater control and customization of print. Its interface is user friendly and easy to understand and has both paid and free version.

After slicing the CAD model, geometric code (G-code) is generated. That G-code is basically a language which human tell a machine to carry out the assigned task and print the object. This code consists of the all the information and commands that are needed to move parts within the printer and print the product layer-by-layer until it gets completed.

In our case, all the filaments were reheated, using Nabertherm (Model N41/M) at 50 ^{o}C for 2-3 hours before starting the printing process in order to remove the moisture and ensure that dry filaments are being used to print the sample. Table 4 provides summary of the parameters that were selected and fixed to print the samples. These parameters were selected using Ultimaker Cura® software and then STL file of the CAD model is sliced. The printer is then started to print the samples, under room temperature and normal humidity. Two samples were printed against each test.

Table 4. Selected parameters of FDM

S.No	Parameters	Selected Value
1	Build plate temperature	60 ^{0}C
2	Printing speed	50 mm/s
3	No of top and bottom layers	5
4	Raster angle	45^{0}
5	Part orientation	Horizontal
6	Infill density	100%
7	Infill pattern	Lines
8	Build plate adhesion	Brim
9	Fan speed	100%

The G-codes were used to print the samples using ANET A-8M dual extruder machine with build

plate size 220 x 220 x 240 mm. Figure 11 represents the preview of Cura at 45^{o} and actual printing by FDM.

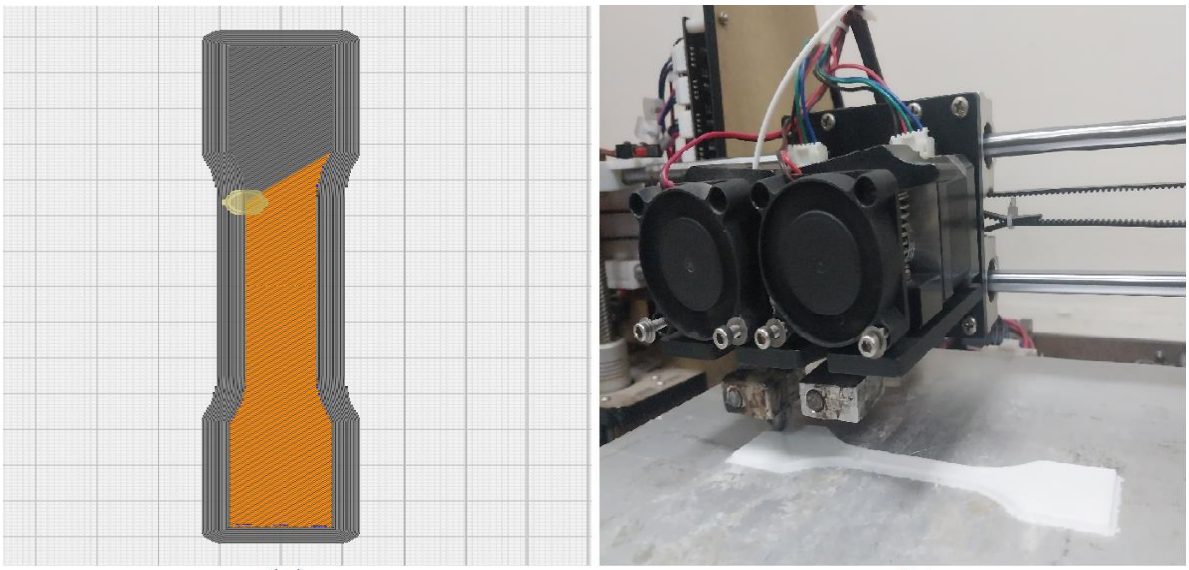

Figure 11. (a) Ultimaker Cura® preview, (b) FDM printing process

5.5 Mechanical Testing

In order to evaluate the mechanical properties of lab developed pure PLA and PBAT-reinforced PLA filaments, tensile and flexural testing were performed. Tensile strength is the capacity of any material to resist stretch or tension, while flexural strength is the ability of a material to resist deformation under bending movement or bending force. In addition, a commercial PLA filament was purchased from the market (3dworld.pk) in order to compare its properties with lab developed filaments.

Mechanical tests were performed using Haida (ID-8607-S) double column universal testing machine (UTM). Tensile and flexural specimen are shown in Figure 12.

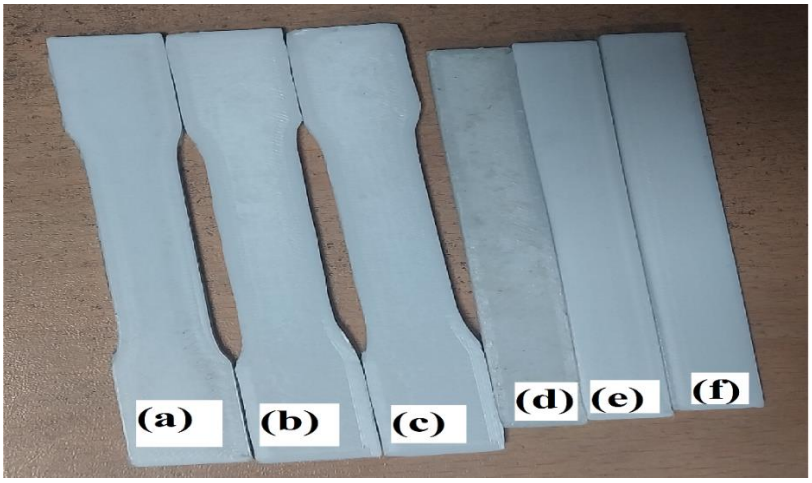

Figure 12. Printed samples: (a&d) Lab developed PLA, (b&e) Lab developed PLA-PBAT, (c&f) Commercial PLA

5.5.1 Tensile Testing

Tensile testing is a destructive testing, that gives information about the tensile strength, yield strength and ductility of any material. It also measures the force that is needed to break a polymer or any other material and the extent to which material can be stretched or elongate till breaking point, also called as elongation at break and usually represented in the form of percentage. Various tensile standards are being used to perform tensile testing for example ISO 527-4, ISO 527-5, ASTM D-3039, ASTM D-638, and ASTM D-297 [61]. Since, tensile test is used to determine various properties as mentioned above, but, here in this work we will be using ultimate tensile test (UTS) value in MPa and elongation at break (%).

Ultimate tensile strength (UTS), is actually the maximum stress that specimen is exposed to during the test. UTS value may differ, depending upon the type of fracture i.e. brittle or ductile or both. These properties are depending upon the environmental conditions, which that either testing is being performed in extreme hot or cold conditions. The accurate value of UTS is very important, because, it plays important role in balancing between weight and safety of the material [62]. UTS value is being calculated by dividing the cross section of the area of the specimen, by the stress placed on the material. It is dependent on the preparation of the specimen, presence of surface defects, and temperature of the test environment [63].

Similarly, Elongation at break, also known as fracture strain, is the ration between change in length

and initial length after the breaking of the specimen. It shows that how much a material can be stretched in term of percentage as compared to its original dimensions, before it breaks. The final length of the material is compared with its initial or original length to determine the materials ductility. This property is an important property, because, it measures how much shaping and bending a material can withstand without breaking and also defines the ductility of a polymer. It tells about the capacity of any material to absorb energy by plastic deformation. It is effected by various factors like temperature, filler content, orientation level and velocity of testing [64-66].

The Ultimate tensile strengths of the specimen are measured using Haida UTM. Figure 13 (a) displays the testing setup employed for tensile testing, while Eq. (2) is used to calculate ultimate tensile strength mathematically. ASTM D-638 Specimen is placed between the chunk and load is applied at the rate of 2mm/min until its breaking point.

$$\sigma_u = \frac{P_{max}}{A_0} \qquad (2)$$

Whereas P is the maximum load applied, while A is the original cross sectional area of the specimen.

5.5.2 Flexural Testing

Flexural testing is performed to identify the flexural behavior of the specimen and for determining the flexural modulus, flexural strength and other aspects of the flexural stress/ strain relationships. Results of the flexural test depend on different conditions. Flexural properties can only be used for engineering designing purposes for the materials having linear stress/strain behavior, while for the materials with non-linear behavior such properties are only nominal. Flexural test for highly brittle material is preferred, because it is too difficult to conduct their tensile test [67].

This method is used to probe the flexural behavior and to calculate flexural strength of the specimen. There are basically two types of flexural test i.e 3-point flexural test and 4-point flexural test. In 3-point flexural test, testing specimen is placed on two supporting pins and external load is applied at the center of the specimen, while in 4-points flexural test, the specimen is placed on

two supporting pins and external loads are applied at two points. Specimen is deformed to the point of maximum deflection, and maximum bending stress is called flexural strength [68, 69]. The same Haida (ID-8607-S) UTM is employed to carry out the 3-point bend test to calculate the flexural strength of PLA specimen. Both tensile and flexural tests were performed under normal room temperature and humidity. The sample prepared as per ASTM D-790 standard, is placed on two supporting pins. A load rate of 2mm/min is applied to the specimen. The testing setup employed for the 3-point bend test of 3D-printed PLA specimen is shown in Figure 13 (b) and can be calculated using Eq. (3).

$$\sigma_f = \frac{3FL}{2wt^2} \tag{3}$$

Whereas F is the maximum applied force, L is length, w is width and t is thickness of the specimen.

(a) (b)

Figure 13. Haida UTM set-up: (a) Tensile set-up, (b) Flexural set-up

5.6 Thermal Testing

5.6.1 Differential Scanning Calorimetry (DSC) testing

Differential scanning calorimetry (DSC) is a thermoanalytical technique and is used to measure the energy transferred to or from sample that is undergoing or has gone physical or chemical change. It detects exothermic and endothermic transition and also enthalpy of the material as a function of temperature. A sample is placed inside an isolated chamber called calorimeter. A reference sample is placed in another pan inside the chamber and heat of the both pans are maintained constant. Once the sample undergoes any kind of transition i.e., melting, glass transition, crystallization etc., peaks are generated either in upward direction or downward direction. Since, the temperatures of both pans are to maintained constant, therefore, if any endothermic process is taking place, then specimen will require more external heat to balance temperature with the reference material. To achieve this, heat flow will be more toward the sample pan. The opposite will happen in case of exothermic transition. Peaks above the centerline represent exothermic transition e.g., crystallization phenomenon, while peaks below the center line represent endothermic reaction [70, 71].

Similarly, degree of crystallinity is determined using DSC curve. Crystallinity, represents the fraction of ordered molecules in a polymer. The more crystalline a polymer is, the more ordered or regularly aligned its chains will be. The usual procedure to measure degree of crystallinity is by drawing a linear arbitrary baseline from the first onset of melting to the last trace of crystallinity and determines the enthalpy of fusion or enthalpy of melting from the area under this endothermic peak [72].

Differential scanning calorimeter (DSC2-01128) available in USPCASE NUST was used to evaluate thermal properties of PLA-PBAT material. Glass transition temperature, melting temperature and cold crystallization temperature were identified. A sample weighing 5.6 mg was heated at 10 ^{o}C/min heating rate in a nitrogen environment at temperature 25 ^{o}C to 250 ^{o}C. Furthermore, degree of crystallinity was calculated by finding the area under melting curve using Origin® 2022 software. Eq. (4) is used to find degree of crystallinity of a component in a composite.

$$X_c = \frac{\Delta H_f}{\Delta H_f^0 \times W_{PLA}} \quad (4)$$

Where X_c is the degree of crystallinity, ΔH_f is heat of melting or fusion of the sample, ΔH_f^o represents heat of fusion of 100% crystalline material and W_{PLA} is the weight fraction of PLA in PLA-PBAT composite. Heat of fusion of 100% crystalline PLA (ΔH_f^o) is around 93.6 J/g, which is measured at equilibrium temperature [39].

5.6.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA), also known as thermogravimetry (TG), where mass of the material is being monitored or observed as a function of time or temperature. The sample is subjected to controlled rising temperature inside controlled environment. The environment is normally controlled by any inert material, nitrogen gas in our case. The purpose of maintaining such environment, is to avoid any kind of reaction i.e., oxidation, reduction etc. With increasing temperature, material starts to loss its mass and the point at which this thermal degradation starts, is called onset temperature, denoted by T_{onset}. Mass of the materials is reduced due to decomposition, evaporation, volatility etc.

Thermobalance is thought to be the heart of thermogravimetric analyzer, that measures the sample mass as a function of time and temperature. The mass of the material will may increase or decrease upon heating, and thermobalance detect that change in mass with respect to time and temperature. Sample is placed in the pan inside the furnace and mass of the sample is monitored during the experiment. For weight loss, TGA has curve in descending direction from left to right. After onset temperature, mass of the material is constantly reduced until a stage, after that mass will not reduce further and TGA curve will move straight toward right. Temperatures at various percent loss in material can be identified using TGA curve. In our case, we have calculated temperature at 5%, 10% and 50% reduction in the mass of the material.

In this research work, thermal decomposition of PLA-PBAT filament was assessed using thermogravimetric analyzer (TGA 5500-0304). The sample was heated from 25 ^oC to 550 ^oC at a heating rate of 10 ^0C/min under nitrogen atmosphere. The data points were then used in Origin® software to plot TGA curve and then temperatures at various percent weight loss have were identified. PLA-PBAT filament was analyzed using above thermogravimetric analyzer in

USPCASE NUST and then results were compared with the TGA value of pure PLA in the literature.

5.7 Morphological Characterization

The cross sections of PLA-PBAT filament and pure PLA filament were characterized using Olympus digital microscope (Model: DSX1000 and Objective lens: DSX10-XLOB20X). The surfaces were observed and analyzed in 3D view at 280x magnification in order to differentiate between ductile fracture and brittle fracture.

Chapter 6 Results

6.1 Tensile and Flexural Properties

Mechanical testing of the lab developed filament and commercial filament were performed to validate the properties of lab developed filaments. Table 5 represents tensile and flexural properties, and elongation at break obtained by mechanical testing.

Table 5. Average tensile and flexural strengths, and elongation at break of the filaments

S.No	Material Type	Temperature (^{0}C)	Layer Thickness (mm)	Average Tensile Strength (MPa)	Average Flexural Strength (MPa)	Elongation at Break (%)		
						E_1 %	E_2 %	E_{Avg}
1	LPLA	210	0.1	51.17	104.185	9	9	9
2	LPLA	215	0.15	52.51	108.31	9	9	9
3	LPLA	220	0.2	47.505	99.22	9	8	8.5
4	PLA-PBAT	210	0.15	47.825	107.295	11	11	11
5	PLA-PBAT	215	0.2	45.97	96.67	10	10	10
6	PLA-PBAT	220	0.1	48.34	101.73	12	11	11.5
7	CPLA	210	0.2	49.375	102.78	9	9	9
8	CPLA	215	0.1	51.625	106.395	10	10	10
9	CPLA	220	0.15	53	109.705	11	10	10.5

Ultimate tensile strength (UTS) is the maximum stress that a material can withstand while being pulled or stretched without breaking. Table 5 represents average UTS of lab developed PLA (LPLA), lab developed PBAT reinforced PLA (PLA-PBAT) and commercial PLA (CPLA). It can be seen that commercial PLA specimen printed at 220 ^{0}C with layer a thickness 0.15mm has shown the highest value of 53.00 MPa. PBAT-reinforced PLA filament has exhibited highest UTS around

48.34 MPa, which is closer to the values shown by pure PLA. While discussing the impact of layer thickness on the tensile strength, Tymrak and others have stated that increasing the layer thickness will result in a decrease in tensile strength [73]. This pattern can be seen in Table 5, where the printed specimen with 0.2mm layer thickness have least tensile strength value as well as flexural strength value. Specimen printed with small layer thickness are closely joined together with better inter-layer bonds when compared with the specimen with larger layer thickness. Since PBAT is a soft material and has potential to decrease tensile strength of PLA, but, will have negligible minimum negative impact on the tensile strength of PLA when the amount of PBAT is less than 10% in PLA-PBAT blend [34]. By looking at Table 5, it can be seen that tensile strength of lab developed pure PLA is slightly higher as compared to PLA-PBAT component. However, on the other hand, elongation capability of PLA-PBAT has improved enough compared to lab developed pure PLA filament. Elongation capacity of PLA-PBAT blend at maximum load has surpassed commercial PLA filament and that can be considered as one of the beneficial findings of this research work. Although, commercial filament is being sold in the market as a pure PLA filament, but we do not know about its exact composition and the way it has been extruded, for example extrusion parameters i.e. barrel temperature, speed, environment etc., or possible addition of any solubilizer. Despite all the possibilities, tensile properties of the filaments prepared for this study are comparable with commercial filament and can be used for various practical applications.

Similarly, Table 5 also represents flexural strength of the filaments. Like tensile strength, commercial PLA specimen printed at 220 ^{o}C with layer thickness 0.15 mm has highest flexural strength of 109.705 MPa, while PBAT-reinforced PLA filament printed at 215 ^{o}C with layer thickness 0.2 mm has least flexural strength of 96.67 MPa. Expecting the effect of PBAT in PLA as per the previous work [34], a decrease in the flexural strength can be seen when compared with the properties of lab developed pure PLA filament (LPLA), but this reduction has given an advantage with enhancing the ductile nature of PLA; a highly-brittle material. Here it must be noted that, samples printed with layer thickness of 0.15mm have shown highest value for flexural strength across all the three types of material. Therefore, 0.15mm layer thickness can be considered as an optimal layer thickness to print PLA products through FDM 3D printing. Furthermore, highest flexural strength of LPLA is 108.31 MPa and that is close to the highest flexural strength

of commercial PLA i.e 109.71 MPa. This means that LPLA filament can be used an alternative to CPLA filament available in the market.

6.2 Differential Scanning Calorimetry (DSC) testing

DSC analysis tool is used to explore the thermal properties of PLA-PBAT. The DSC second heating curve in represents peak values of glass transition temperature T_g, cold crystallization temperature T_c and melting temperature T_m. According to the curve shown in Figure 14 T_g, T_c and T_m are observed at 62.07 ^oC, 97.298 ^oC and 162.38 ^oC. Similarly, the degree of crystallinity (X_c) for PLA –PBAT appeared 38.7% that is higher than degree of crystallinity reported by H. Ismail et al. [39]. A number of works have been carried out, discussing the effect of PBAT on the degree of crystallinity of PLA with mixed type outcomes. However, Noreen et al. [74] have discussed that little quantity of PBAT will increase the degree of crystallinity of PLA, but, if the quantity of PBAT is increased too much, then it will effect in the opposite direction. In our case, PBAT has also increased the degree of crystallinity (X_c) of PLA up to 38.7%, when compared with X_c of pure PLA 30.9% reported in [39]. The reason behind this increase in degree of crystallinity could be, PBAT has acted as a nucleating agent, enhancing the degree of crystallinity of PLA. T_g and T_m values of PLA-PBAT have also increased as compared to T_g and T_m of pure PLA presented in [39]. Such increase in temperatures could be because of higher degree of crystallinity.

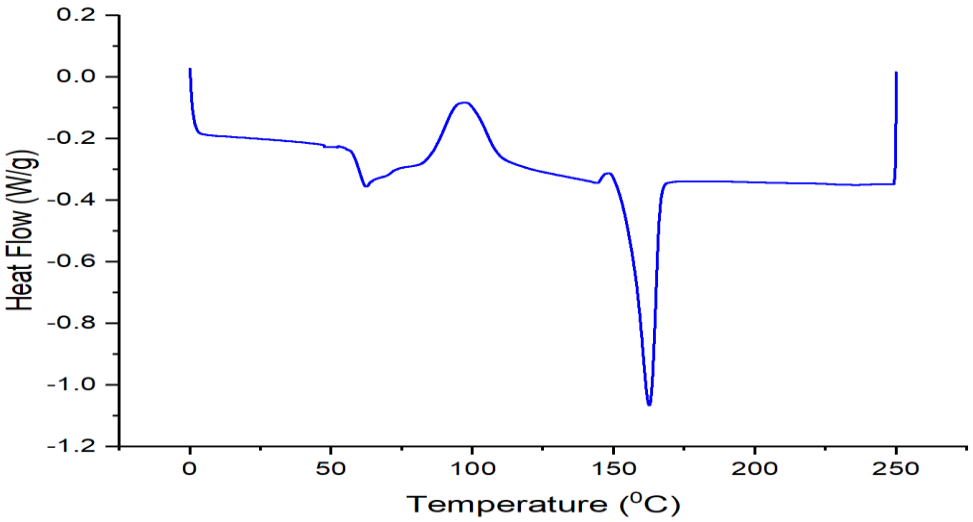

Figure 14. DSC curve of PLA-PBAT filament

6.3 Themogravimetric Analysis (TGA)

Thermogravimetric analysis is carried out to investigate thermal decomposition of PLA-PBAT FDM filament. Mass is changed due to oxidation, combustion, degradation or evaporation. The weight loss of substance after degradation is monitored as a function of temperature. Figure 15 represents the degradation of PLA-PBAT filament with respect to temperature. The degradation starts, (also known as onset temperature T_{onset}) at 281.82 ^{o}C. Similarly, 5% ($T_{5\%}$), 10% ($T_{10\%}$) and 50% ($T_{50\%}$) thermal degradations are 323.7 ^{o}C, 335.78 ^{o}C and 360.42 ^{o}C respectively. According to the TGA values reported for pure PLA in [38], T_{onset} , $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ are 282 ^{o}C, 319.6 ^{o}C, 329.6 ^{o}C and 352.2 ^{o}C. When compared with thermal degradation of PLA-PBAT, it can be seen that T_{onset} is almost unchanged for both i.e pure PLA and PLA-PBAT filaments. However, addition of PBAT has improved thermal degradation of PLA-PBAT filament with an increase in temperature. The reason behind this could be, the miscibility and compatibility of PLA and PBAT are improved. Furthermore, residue % of PLA-PBAT is 2.13% at 550 ^{o}C as compared to 0% residue for pure PLA at 600 ^{o}C. It proves that thermal stability of PLA-PBAT filament is higher than pure PLA filament.

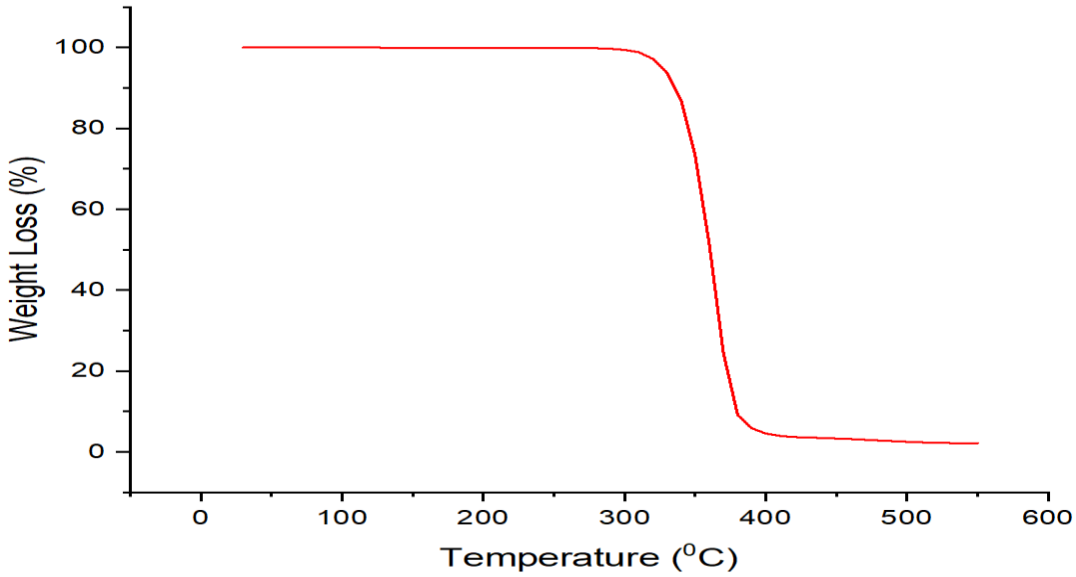

Figure 15. TGA curve of PLA-PBAT filament

6.4 Morphological Characterization of Pure PLA and PLA-PBAT Specimen

Figure 16 shows the morphological characteristics of the cross sections of pure PLA and PLA-PBAT specimen. It was documented using digital microscopy. Based on the morphological data from digital microscope, the 3D reproduction of the surfaces was generated, which gives 3D view of the cross sections. The surfaces in Figure 16 (a) represent pure PLA FDM printed specimen while the surfaces in Figure 16 (b) represent PLA-PBAT FDM printed specimen. By closely observing 3D view of the surfaces, it can be seen that the surface of pure PLA is flat, while on the other hand PLA-PBAT has bumpy surface with peaks. These peaks show that the specimen had undergone necking before breaking and had experienced more ductile fracture as compared to pure PLA specimen which has flat surface with no peak, showing that it had experienced brittle fracture. Therefore, it can be concluded that addition of PBAT has enhanced the ductility of PLA.

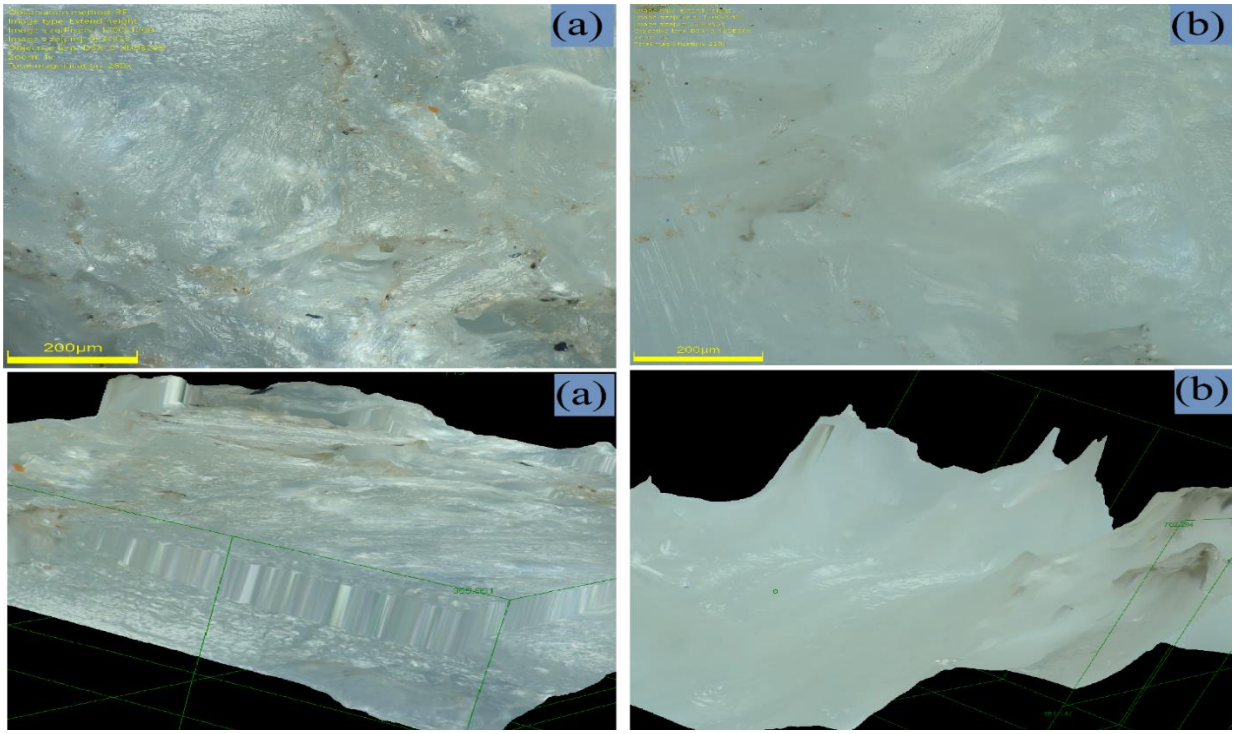

Figure 16. Images of surface topography (up) and 3D production of surface topography (down), (a) Pure PLA FDM printed specimen, (b) PLA-PBAT FDM printed specimen

Chapter 7 Analysis

Minitab® software was used to carry out statistical analysis based on the data presented in Table 5. The results obtained are represented in Table 6, that includes signal to noise ratio (SNRA) and mean value of the specimen for "larger is better" given by Eq. (5).

$$\frac{s}{N}\text{ratio} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \quad (5)$$

Table 6. Calculation of S/N ratio, MEAN values of the replicates of testing specimens (Tensile strength mean = MEAN 1, Flexural strength mean = MEAN 2)

S. No	Material Type	Temperature	Layer Thickness	UTS-1	UTS-2	SNRA1	MEAN 1	FS-1	FS-2	SNRA 2	MEAN 2
1	LPLA	210	0.1	52.25	50.09	34.1745	51.17	121.23	87.14	40.00573	104.185
2	LPLA	215	0.15	49.22	55.8	34.35366	52.51	89.58	127.04	40.30169	108.31
3	LPLA	220	0.2	49.4	45.61	33.51405	47.505	85.5	112.94	39.68204	99.22
4	PLA-PBAT	210	0.15	47.55	48.1	33.59267	47.825	110.89	103.7	40.59696	107.295
5	PLA-PBAT	215	0.2	44.35	47.59	33.23331	45.97	104.44	88.9	39.62157	96.67
6	PLA-PBAT	220	0.1	47.53	49.15	33.68247	48.34	106.84	96.62	40.11609	101.73
7	CPLA	210	0.2	47.75	51	33.85603	49.375	119.48	86.08	39.89261	102.78
8	CPLA	215	0.1	53.3	49.95	34.24348	51.625	94.97	117.82	40.38789	106.395
9	CPLA	220	0.15	53	53	34.48552	53	129.23	90.18	40.38951	109.705

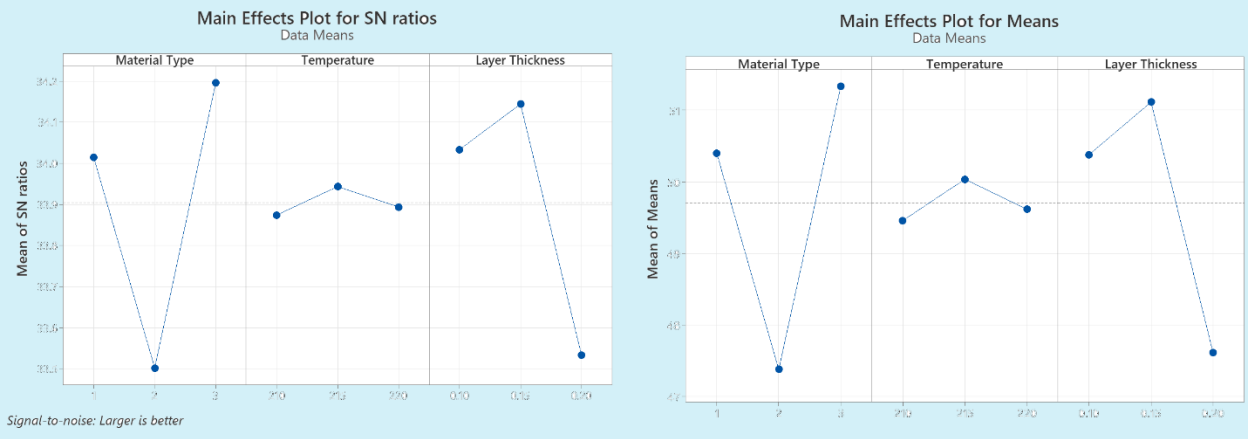

Figure 17. Main effect plots for SN ratio and Means of tensile strength

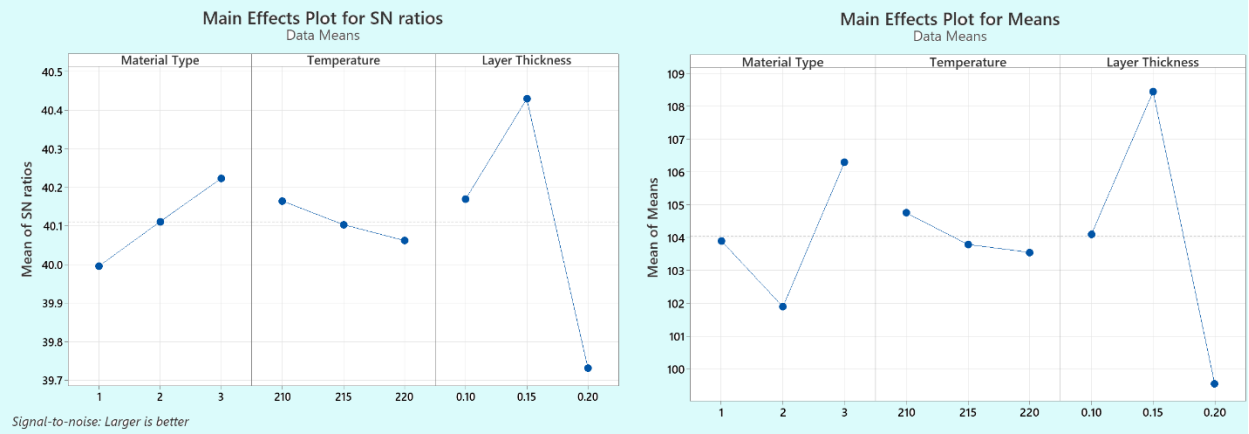

Figure 18. Main effect plots for SN ratio and Means of flexural strength

It can be seen clearly in the main effect plots that temperature has little effect on both tensile Figure 17 and flexural strengths Figure 18, while the other two factors i.e type of material and layer thickness have shown great positive or negative impacts. Commercial PLA filament has shown superior mechanical properties followed by lab developed pure PLA filament. The effect of PBAT on mechanical properties is consistent in main effect plot like it was during mechanical testing i.e have reduced tensile strength and flexural strength slightly at the cost of an increase in the elongation capacity of PLA as shown in Table 5. In addition, it can be observed from the main effect plots, that both tensile and flexural properties will decrease when layer thickness is increased beyond 0.15mm. Since, specimen have shown highest tensile strength printed at 215 ^{o}C with 0.15

mm layer thickness, and highest flexural strength printed at 210 ^{o}C with 0.15 mm layer thickness. Therefore, these were considered as optimal parameters and samples were printed at optimized parameters to confirm the properties of material and experimental procedure.

Furthermore, Table 7 and Table 8 represent the responses for tensile and flexural testing. This ranking is based on the difference generated in S/N ratio and mean for each level of a factor. Thus, factor with largest delta has the highest impact on the outcome and is ranked first [33]. Based on the value of rank, it can be figure out that material type has greatest impact on tensile strength followed by layer thickness, while temperature has the least impact with being the third in the rank order. Similarly, layer thickness has shown greatest impact on flexural strength followed by material type and temperature. It must be noted here that both material type and layer thickness have come out as important factors. Since, material type does not offer that much freedom to change, therefore, mechanical properties can be highly improved by selecting proper layer thickness.

Table 7. Response tables for tensile strength obtained from Minitab®

Level	Response table for Means			Response table for S/N ratio (Larger is better)		
	Material type	Temperature	Layer thickness	Material type	Temperature	Layer thickness
1	50.40	49.46	50.38	34.01	33.87	34.03
2	47.38	50.03	51.11	33.50	33.94	34.14
3	51.33	49.62	47.62	34.20	33.89	33.53
Delta	3.96	0.58	3.50	0.69	0.07	0.61
Rank	1	3	2	1	3	2

Table 8. Response table for flexural strength obtained from Minitab®

Level	Response table for Means			Response table for S/N ratio (Larger is better)		
	Material type	Temperature	Layer thickness	Material type	Temperature	Layer thickness
1	103.91	104.75	104.10	40.00	40.17	40.17
2	101.90	103.79	108.44	40.11	40.10	40.43
3	106.29	103.55	99.56	40.22	40.06	39.73
Delta	4.40	1.20	8.88	0.23	0.10	0.70
Rank	2	3	1	2	3	1

Table 9. ANOVA results for tensile testing

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Material Type	2	25.6228	52.45 %	25.6228	12.8114	11.06	0.083
Temperature	2	0.5359	1.10 %	0.5359	0.2680	0.23	0.812
Layer Thickness	2	20.3796	41.72 %	20.3796	10.1898	8.80	0.102
Error	2	2.3160	4.74 %	2.3160	1.1580		
Total	8	48.8544	100.00 %				

Table 10. ANOVA results for flexural strength

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value	P-Value
Material Type	2	29.047	19.24 %	29.047	14.5234	24.57	0.039
Temperature	2	2.426	1.61 %	2.426	1.2132	2.05	0.328
Layer Thickness	2	118.304	78.37 %	118.304	59.1522	100.09	0.010
Error	2	1.182	0.78 %	1.182	0.5910		
Total	8	150.960	100.00%				

Table 9 and Table 10 summarize analysis of variance and tell about the significance of each selected factor. These values have been calculated by selecting 90% confidence interval (CI) i.e α

= 0.1. Based on the data, it can be seen that material type has highest 52.45% contribution followed by layer thickness 41.72% in determining tensile strength. Similarly, layer thickness has highest contribution of 78.37 % followed by material type with 19.24 % in calculating flexural strength. Furthermore, P-value is an important factor in defining the significance of any factor. For 90 % CI or $\alpha = 0.1$, material type is a highly significant in case of tensile testing, while both layer thickness and material type are significant factors in 3-point bend test to determine flexural strength. Temperature has turned out as an insignificant factor in both tensile and flexural test with larger value.

Moreover, Minitab® is used to find following regression equations for tensile and flexural strength.

$$\text{Tensile strength} = 49.5 + 0.47\ \text{Material Type} + 0.016\ \text{Temperature} - 27.6\ \text{Layer Thickness} \quad (6)$$

$$\text{Flexural strength} = 134.3 + 1.19\ \text{Material Type} - 0.120\ \text{Temperature} - 45.5\ \text{Layer Thickness} \quad (7)$$

We used Minitab® software to develop regression equations for tensile and flexural strengths. Equation *(6*) is used to determine tensile strength and Equation *(7*) is used to calculate flexural strength. We have determined tensile and flexural strength values at three random points and have compared them with the actual values obtained from experimental works. Predicted and actual values are shown in Table 11, where both predicted and actual values are close to each other with minimum error. We have got mixed outcomes, i.e., in some cases predicted values are higher than actual values, while in other cases actual values are slightly higher than predicted values. Since, both predicted and actual values closely match with each other, therefore, the accuracy of experimental work can be confirmed by comparing the predicted values with the actual values and the experimental work can be validated by these results.

Table 11. Experimental values and predicted values at random points using regression equation

Test No	Factors			Tensile Values (MPa)			Flexural Values (MPa)		
	Mat_Type	Temp (^oC)	Layer (mm)	Predicted *(P)*	Actual *(A)*	Error *(A-P)*	Predicted *(P)*	Actual *(A)*	Error *(A-P)*
1	LPLA	210	0.1	50.57	51.17	0.6	105.74	104.185	-1.555
2	PLA-PBAT	220	0.1	50.73	48.34	-2.39	104.54	101.730	-2.81
3	CPLA	215	0.1	50.65	51.625	0.975	105.14	106.395	1.255

7.1 Optimal Parameters and Confirmatory Experiments

As discussed above, one sample from each material was printed at optimal parameters and mechanical testing were conducted. Table 12 represents the mechanical results of the specimen printed at optimal parameters.

Table 12. Testing results of the specimens printed at optimal parameters

S. No	Material Type	Temperature ^0C	Layer Thickness	Tensile Strength (MPa)	Flexural Strength (MPa)	Elongation at break (%)
1	LPLA	215	0.15	49.55		9
2	PLA-PBAT	215	0.15	47.80		12
3	CPLA	215	0.15	51.92		10.5
4	LPLA	210	0.15		107.96	
5	PLA-PBAT	210	0.15		105.99	
6	CPLA	210	0.15		112.02	

Results of the specimen printed at optimal parameters are inconsistent with the results of the samples printed before. This also authenticate the work done before and quality of the materials used.

Chapter 8 Conclusion and Future Directions

Followings are the major findings of this work.

- By extruding pure PLA pellets and PLA-PBAT pellets, we were able to prepare pure PLA filament and PBAT-reinforced PLA filament successfully. These filaments were then used in FDM 3D printer to print tensile and flexural specimens with encouraging results as compared to commercially available PLA.
- Based on the suggestions of previous studies, we incorporated 8 wt.% PBAT into PLA. This was done to prevent a significant decrease in tensile and flexural strengths of PLA, which can occur if PBAT content exceeds 10 wt.% thus enhancing ductile behavior of the material.
- The addition of 8 wt.% PBAT to PLA resulted in an increase in elongation at break from 8% to 12% for PLA-PBAT filament, while maintaining the tensile and flexural strengths at comparable levels to pure PLA.
- The degree of crystallinity (X_c) of PLA-PBAT filament increased remarkably, i.e., 38.7% which is notably higher than the reported X_c of pure PLA in the literature, which is 30.9%. Additionally, glass transition temperature and melting temperature of PLA-PBAT were found to be 62.07 ^oC and 162.38 ^oC.
- Both PLA and PLA-PBAT have same onset temperature T_{onset} of thermal degradation i.e. around 282 ^oC, while $T_{5\%}$, $T_{10\%}$ and $T_{50\%}$ for PLA-PBAT were 323.7 ^oC, 335.78 ^oC and 360.42 ^oC, higher than for pure PLA. These indicate that adding 8 wt.% PBAT has improved has improved the thermal stability of PLA.
- Upon examining optical micrographs, it can be observed that the surface of the cross section of PLA-PBAT has a bumpy appearance with peaks, in contrast to the flat fractured surface of pure PLA. These peaks are a result of necking of the specimen prior to fracture. Based on this evidence, it can be concluded that PLA-PBAT specimens have undergone

ductile transition before fracture, whereas pure PLA specimens have experienced brittle fracture.

- Based on the results obtained from ANOVA and SNRA, it has been proven that material type and layer thickness are the significant factors in determining tensile and flexural strengths, whereas the printing temperature does not seem to have a significant impact.
- The regression equations used to determine the tensile and flexural strengths yielded predicted values that closely match the actual or experimental values. These outcomes confirm the validity of experimental works and results.
- In future research, more combination ratios of PLA with Polyhydroxyalkanoates (PHA), Polybutylene succinate (PBS), Polycaprolactone (PCL), Starch, Cellulose, can be prepared.

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