PROPERTIES OF POLY (LACTIC ACID) / POLYBUTYLENE ADIPATE TEREPHTHALATE REINFORCED WITH OIL PALM EMPTY FRUIT BUNCH COMPOSITES FOR FUSED DEPOSITION MODELING 3D PRINTING

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by

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LIST OF SYMBOLS

cm	Centimetre
℃	Degree Celsius
^{o}C/ min	Degree Celsius/ minute
GPa	Giga Pascal
g/cm^3	Gram/ centimetre cubic
g/10 min	Gram/ 10 minutes
J	Joule
J/g	Joule/ gram
J/m	Joule/ metre
J/m^3	Joule/ metre cubic
kg	Kilogram
kJ/m^2	Kilo Joule/ metre square
kN	Kilonewtons (Load cell)
MPa	Mega Pascal
mW	Megawatt
µm	Micrometre
mg	Milligram
mm	Millimetre
mm/ min	Millimetre/ minute
mm/s	Millimetre/ second
nm	Nanometre
-	Negative
%	Percentage
±	Plus-minus
+	Positive
rpm	Revolution per minute
s	Second
USD	U. S. Dollar
wt.%	Wight/ percentage

LIST OF ABBREVIATIONS

2D	Two-Dimensional
3D	Three-Dimensional
3DP	Three-Dimensional Printing
ABS	Acrylonitrile-Butadiene-Styrene
AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
BA	Butylene Adipate
BT unit	Butylene Terephthalate
CAD	Computer Aided Design
CM	Compression Moulding
CPKO	Crude Palm Kernel Oil
CPO	Crude Palm Oil
DLP	Digital Light Processing
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric
EBDM	Electron Beam Direct Manufacturing
EFB	Empty Fruit Bunch
FDM	Fused Deposition Modeling
FFB	Fresh Fruit Bunch
FRIM	Forest Research Institute Malaysia
IR 4.0	Industrial revolution 4.0
LOM	Laminated Object Manufacturing
MFI	Melt-Flow Index
MFR	Melt Flow Rate
MPOB	Malaysian Palm Oil Board
MPOC	Malaysian Palm Oil Council
NB	Not Break
OPF	Oil Palm Fronds
OPT	Oil Palm Trunks
PBAT	Polybutylene adipate terephthalate
PBS	Polybutylene Succinate

PCL	Poly (γ-caprolactone)
PDLA	Poly (D-lactic acid)
PDLLA	Poly (D, L-lactic acid
PE	Polyethylene
PEG	Poly (ethylene glycol)
PEO	Poly (ethylene oxide)
PHA	Poly (hydroxyl alkanoate)
PHB	Poly (hydroxyl butyrate)
PKS	Palm Kernel Shells
PLA	Poly (lactic acid)
PLLA	Poly (L-lactic acid)
PMMA	Polymethyl Methacrylate
POME	Oil Palm Mill Effluent
PORIM	Palm Oil Research Institute of Malaysia
PP	Polypropylene
PPF	Palm Pressed Fibres
PU	Polyurethanes
PVA	Poly (vinyl acetate)
ROP	Ring-Opening Polymerization
SEM	Scanning Electron Microscopy
SLA	Stereolithography
SLS	Selective Laser Printing
STL	Standard Tessellation Language
TGA	Thermogravimetry Analysis
UV	Ultraviolet

SIFAT KOMPOSIT (ASID POLILAKTIK) / POLIBUTILENA ADIPAT TEREFTALAT DIPERKUATKAN TANDAN KOSONG BUAH KELAPA SAWIT UNTUK PERCETAKAN 3D PERMODELAN PENGENDAPAN TERLAKUR

ABSTRAK

Asid polilaktik (PLA) adalah antara bahan pilihan yang digunakan dalam percetakan 3D kerana sifatnya yang unik seperti penampilan yang baik, ketelusan yang lebih tinggi, kurang ketoksikan dan pengembangan haba yang rendah yang membantu mengurangkan tekanan dalaman yang disebabkan semasa penyejukan. Walaubagaimanapun, PLA adalah rapuh dan mempunyai daya tahan dan ketahanan terma yang rendah yang mempengaruhi kemampuan cetaknya dan menyekat aplikasi perindustriannya. Oleh itu, dalam kajian ini, PLA diadun dengan pelbagai kandungan Polibutilena adipat tereftalat (PBAT) pada 20, 50 dan 80 % berat dalam skru kembar pemyemperit. Sifat tegangan, termal, morfologi dan kelakuan reologi filamen PLA/PBAT telah dicirikan. Kemudian, sifat PLA/PBAT (80 % PLA: 20 % PBAT) yang paling menjanjikan dan seimbang telah diperkuat dengan 10 % berat Tandan Buah Kosong (EFB) dan biodegradasi PLA/PBAT dan PLA/PBAT/EFB telah disiasat. Selepas itu, filamen PLA/PBAT dan PLA/PBAT/EFB yang dipilih telah dicetak menggunakan mesin pemodelan deposisi bercantum (FDM) percetakan 3D dan prestasi PLA/PBAT dan PLA/PBAT/EFB telah dibandingkan antara teknik percetakan 3D dan pembentukan mampatan. Sifat fizikal, mekanikal, termal dan morfologi PLA/PBAT dan PLA/PBAT/EFB telah dicirikan. Penambahan PBAT meningkatkan pemanjangan semasa patah PLA dengan linear peningkatan jumlah PBAT dan imej SEM yang menunjukkan pertumbuhan retak PLA/PBAT yang terlibat dengan perubahan bentuk mulur di hujung retak mereka. Walau bagaimanapun, 20 % berat PBAT telah dipilih sebagai sifat PLA/PBAT yang paling menjanjikan dan seimbang walaupun ia mempunyai sedikit peningkatan dalam pemanjangannya semasa retak tetapi mempunyai kekuatan tegangan tinggi dan modulus tegangan daripada 50 dan 80 % berat PBAT. Selain itu, kadar degradasi PLA bertambah baik apabila penampilan visual PLA/PBAT dan PLA/PBAT/EFB menunjukkan terjadinya pesuk, permukaan kasar, retak dan sampel pecah selama lima minggu dalam timbusan tanah di dalam keadaan makmal. Prestasi percetakan 3D 80PL20PB dan 80PL20PB10EFB adalah setanding atau dalam beberapa aspek mempunyai fizikal, mekanikal dan termal yang lebih baik daripada sampel yang dibentuk dengan mampatan. Kepadatan 80PL20PB-CM dan 80PL20PB10EFB-CM menyerap lebih sedikit air daripada struktur berliang sampel 3DP. Namun begitu, 80PL20PB-3DP mempunyai sifat tegangan dan hentaman yang lebih baik daripada 80PL20PB-CM. Kekuatan tegangan 80PL20PB10EFB-CM tidak menunjukkan peningkatan tetapi kekuatan tegangan dan modulus tegangan 80PL20PB10EFB-3DP menurun disebabkan oleh penyebaran EFB yang tidak sekata semasa proses pencampuran lebur yang menyebabkan berlakunya kekosongan dan pengagregatan. Terma kestabilan 80PL20PB-3DP adalah lebih baik daripada 80PL20PB-CM tetapi 80PL20PB10EFB-CM mempunyai kestabilan terma yang lebih baik daripada 80PL20PB10EFB-3DP. Pada masa akan datang, adunan polimer dan komposit daripada PLA, PBAT dan EFB dapat dikembangkan di mana sifatnya akan berdasarkan kajian kami. Kajian ini juga menjelaskan pentingnya pengaturan penyemperitan, adunan polimer dan formulasi komposit, dan faktor peneguhan semasa pembuatan filamen untuk percetakan 3D FDM.

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PROPERTIES OF POLY (LACTIC ACID) / POLYBUTYLENE ADIPATE TEREPHTHALATE REINFORCED WITH OIL PALM EMPTY FRUIT BUNCH COMPOSITES FOR FUSED DEPOSITION MODELING 3D PRINTING

ABSTRACT

Poly (lactic acid) (PLA) is amongst the preferable materials used in 3D printing because of its unique properties such as good appearance, higher transparency, less toxicity and low thermal expansion that help reduce the internal stresses caused during cooling. However, PLA is brittle and has low toughness and thermal resistance that affect its printability and restricts its industrial applications. Therefore, in this study, PLA is blending with various content of Polybutylene adipate terephthalate (PBAT) at 20, 50 and 80 wt.% in a twin-screw extruder. The tensile, thermal, morphology and rheological behaviour of PLA/PBAT filaments were characterized. Then, the most promising and balance properties of PLA/PBAT (80 wt.% PLA: 20 wt.% PBAT) was subjected to reinforced with 10 wt.% Empty Fruit Bunch (EFB) and the biodegradation of PLA/PBAT and PLA/PBAT/EFB were investigated. After that, the selected PLA/PBAT and PLA/PBAT/EFB filaments were printed using a Fused Deposition Modeling (FDM) 3D printing machine and the performance of PLA/PBAT and PLA/PBAT/EFB were compare between the 3D printing and compression moulding techniques. The physical, mechanical, thermal and morphology properties of PLA/PBAT and PLA/PBAT/EFB were characterized. The addition of PBAT increased the elongation at break of PLA with a linear increasing amount of PBAT. SEM images showed the crack growth of PLA/PBAT involved with a ductile deformation at their crack tip. However, 20 wt.% PBAT was selected as the most promising and balance properties of PLA/PBAT although it has a slight increment in its elongation at break but have high tensile strength and tensile modulus than 50 and 80 wt.% PBAT. In addition, the degradation rate of PLA was improving as the visual appearance of PLA/PBAT and PLA/PBAT/EFB shows the occurrence of dented, rough surface, cracking and sample breaking within five weeks in a soil burial in a laboratory condition. The performance of 3D printed 80PL20PB and 80PL20PB10EFB were comparable or in some aspects have better physical, mechanical and thermal than compression moulded samples. The compact 80PL20PB-CM and 80PL20PB10EFB-CM absorbs less water than that porous structure of the 3DP sample. However, 80PL20PB-3DP had better tensile and impact properties than that 80PL20PB-CM. The tensile strength of 80PL20PB10EFB-CM shows no improvement but the tensile strength and tensile modulus of 80PL20PB10EFB-3DP was decreased attributed to the inhomogeneous distribution of EFB during the melt-mixing process that led to the occurrence of voids and agglomeration. The thermal stability of 80PL20PB-3DP was better than 80PL20PB-CM but 80PL20PB10EFB-CM had better thermal stability than that 80PL20PB10EFB-3DP. In the future, the polymer blend and composite from PLA, PBAT and EFB can be developed where the properties will be based on our study. This study also shed light on the importance of polymer blend and composite formulations, and reinforcement factors during the manufacture of filament for FDM 3D printing.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Recently, the global market is moving towards the fourth industrial revolution (IR 4.0) and 3D printing is one of them. It is originated from a computer-aided design (CAD) program that prints an object layer-by-layer. It is a fast-emerging technology as it is good at reducing product development times between the sales and conception, maintain the production costs whether there are one or more units to be produced and no added cost for complexity hence, allow small businesses to operate as they do not have expensive funding to support their business and most importantly it can fabricate designs and features unmatched by other conventional manufacturing (Mohan et al., 2017). Nowadays, 3D printing is widely used in several areas such as healthcare and medicine, automotive, art, architecture and construction (Shahrubudin et al., 2019). Therefore, to preserve the fast technology worldwide, this research tries to explore the potential of polymer blend reinforced with natural fibres composite in 3D printing by producing polymer blend and polymer blend composite filament that can be fitted in the Fused Deposition Modeling (FDM) 3D printing machine.

Generally, a material extrusion-based 3D printing technology is widely used and the costs are very low (Melnikova et al., 2014). FDM is an example of a material extrusion technique that uses thermoplastic in the filament form. It is a process of joining materials directly from 3D computer model data by extruding the thermoplastic filament with temperature control units and depositing the semi-molten filament onto the bed platform in a layer-by-layer manner (Mohan et al., 2017). The types of filament used are limited to thermoplastic polymers with a suitable melt viscosity, have a low melting point and are limited to amorphous or low crystallinity polymers such as Poly (lactic acid) (PLA) (Mohan et al., 2017; Stoof and Pickering, 2018).

PLA is a commonly used material in 3D printing applications as it has a low degree of polymer shrinkage (Stoof and Pickering, 2018) and warping effect (Cardoso et al., 2020) that is crucial to the accuracy of components produced during 3D printing (Liu et al., 2019). Besides, 3D printed PLA with a low glass transition and melting temperature are widely used in 3D printing technology due to its low cost and weight, and have flexible process-ability (Iwata, 2015). In addition, PLA is one of the most promising thermoplastic materials with unique properties such as good appearance, higher transparency, glossy feel, good mechanical strength and less toxicity, and virtuous barrier properties (barrier or permeability performance against gases transfer, water vapour, and aroma molecules) (Farah et al., 2016, Mohan et al., 2016).

Unfortunately, PLA is relatively brittle, has a low impact strength and thermal stability thus limit its application in certain areas that require high-stress levels in plastic deformation (Bates-Green and Howei, 2017). Thus, extensive research has been done on the development of PLA. Recently numerous studies have been focused on polymer blending PLA with any other biodegradable polymer such as poly (butylene-adipate-co-terephthalate) (PBAT) to increase PLA’s ductility and thermal stability without compromising their degradability and thus expand its application. This is possible as PBAT is a copolymer made up of adipic acid, butanediol, and terephthalic acid. The terephthalic acid gives rise to high thermal stability and mechanical properties while adipic acid and butanediol impart flexibility and biodegradability (Singamneni et al., 2018).

Several types of research have reported the success-ability of polymer blending PLA with PBAT and the polymer blending can be used with natural fibres such as Empty Fruit Bunch (EFB) particles. EFB is one of the most valuable plants in Malaysia and it is an interesting cellulosic biomass to be utilized as a reinforcing material in the polymer composite into a beneficial and higher commercial value-added product because it has low density, real strength, relatively high toughness and most importantly it is biodegradable (Faizi et al., 2016). Besides, the reinforcement of EFB is a cost-effective method and can help solve the environmental issue regarding biomass waste by the oil palm plantation. In addition, EFB is a cost-effective method in polymer blending PLA with PBAT as the production costs of PLA and PBAT are witnessing a significant increase due to the higher costs of raw materials, transportation, energy consumed and chemicals which leads to a reduction in high end-user application prices.

1.2 Problem Statement

FDM is the most commonly used 3D printing methodology for its reliability, simplicity, affordability, minimal wastage and material availability. Poly (lactic acid) (PLA) is amongst the preferable materials used in FDM 3D printing because of its unique properties such as good appearance, higher transparency, less toxicity and low thermal expansion that help reduce the internal stresses caused during cooling. However, PLA is brittle and has low toughness and thermal resistance that affect its printability and restricts its industrial applications. Besides, the disadvantages of using pure polymer in 3D printing such as high cost, low strength, and easy distortion, restrict the application of FDM in cost-effective, functional, load-bearing applications as well as in large-scale production. Therefore, the development of a new polymer composite filament is expected to overcome the limitation in FDM 3D printing. Hence, polymer blending of PLA with PBAT is one of the approaches to improve the limitation of PLA because PBAT is ductile, flexible and have high toughness. However, both PLA and PBAT are considered expensive although PBAT is cheaper than PLA. The addition of natural fibres into the polymer blend is one of the approach that can reduce the cost of material production. Many research work has reported the utilization of various natural fibres in PLA filament. However, lack of study has been done on the utilization of EFB as filler/ reinforcement in PLA or PLA blend as 3D printing filament materials. The addition of 10 wt.% EFB is expected to lower the cost by 21% because EFB is cheap as it is available abundantly in nature. Moreover, EFB is considered to be potentially used in polymer composites because it has low density, real strength, high toughness and most importantly it is biodegradable. However, less amount of EFB should be added into PLA and PBAT to produce PLA/PBAT/EFB composite filament as the production of filament for 3D printing might facing difficulty in controlling the filament diameter during extrusion. This is because the filament diameter in 3D printing was limited to 1.75 mm (± 0.1 mm) and other than that, the filament cannot fit into the feeder.

1.3 Objectives

Following are the major objectives set for this research work:

1) To obtain the best formulation of PLA/PBAT blend based on the filament characterization such as mechanical, thermal and morphological properties
2) To analyze the biodegradation and rheological behaviour of PLA/PBAT blend and PLA/PBAT/EFB composite filament fabricated.
3) To evaluate the performance comparison of PLA/PBAT blend and PLA/PBAT/EFB composite on FDM 3D printing against the compression moulding techniques on their physical, mechanical, thermal and morphological properties.

1.4 Scope of Study

The primary goal of this research is to produce EFB particles reinforced PLA/PBAT composite in a filament form that can be used in an FDM 3D printing machine and compare its performance to that of the traditional compression moulding method.

Therefore, in this study, PLA is blending with various content of PBAT at 20, 50 and 80 wt.% and 10 wt.% EFB was reinforced into PLA and PBAT using a twin-screw extruder to produce a PLA/PBAT blend and PLA/PBAT/EFB composite filament for 3D printing. During the melt-blending, the filament diameter (1.75 mm ± 0.1 mm) must be control and achieve to avoid any printability issues later during 3D printing process. However, a consistent filament diameter was difficult to control as the filament produced from the extrusion was in a double filament attached together and the filament diameter was either too big or too small than 1.75 mm ± 0.1 mm.

Therefore, two important steps was implemented to achieve a consistent filament diameter for an easy and smooth printing process. First, the die nozzle of the twin-screw extruder was modified into single die nozzle to avoid entanglement of the double filament produced from the extrusion. Second, an electric spooling machine was custom-built to avoid producing an irregular filament diameter and the speed was controlled to get the consistent filament diameter that was suitable for 3D printing. Then, the filament was printed using FDM 3D printing machine.

Unfortunately, the melt-blending of EFB with PLA and PBAT was having an extra problems as the extrusion was jammed because the 20 wt.% EFB was stuck inside the screw and die nozzle. Hence 15 wt.% was melt-blending with PLA. 15 wt.% EFB into PLA and PBAT can be produced into 1.75 mm ± 0.1 mm filament diameter using twin-screw extruder, but the filament was stuck and causing clog even after changing the 3D printing die nozzle into 1.0 mm. Lastly, only 10 wt.% EFB was successfully melt-blending with PLA and PBAT using twin-screw extrusing and proceed into 3D printing.

1.5 Organization of Thesis

Each task was accomplished and compiled by chapters throughout this research work;

1) Chapter 1: Introduction

   Focused on introducing the overall research work and background, research gaps, the scope of study and objectives.

2) Chapter 2: Literature Review

   Focused on introducing and briefing on various aspects of polymer, polymer blend, natural fibres, biocomposite, 3D printing, conventional compression moulding and previously published works.

3) Chapter 3: Methodology

   Explains various materials used and experimental on process flow.

4) Chapter 4: Result and Discussion

   Deals with result and discussion of the PLA/PBAT blend, PLA/PBAT/EFB composite, filament, compression moulding and 3D printed samples on physical, mechanical, thermal, morphology, rheology and biodegradation, and its output related to previously published works.

5) Chapter 5: Conclusion and Future Recommendation

   Summarize the overall result and discussion, and recommendations for future research from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 3D Printing

Three-dimensional (3D) printing is a rapidly growing technology that has a revolutionary impact on products fabrication for applications in several areas including healthcare and medicine, aeronautics and space, automotive, food industry, art, textile and fashion, architecture and construction.

Recently, autonomous robots, simulated and augmented reality, the internet of things, cloud computing, cybersecurity, horizontal and vertical system integration, additive manufacturing (AM), and big data analytics are among the nine categories of digital transformation for the manufacturing industry that has recently gained traction in the global market, moving towards the fourth industrial revolution (IR 4.0). To persevere with the fast pace of technology, Malaysia is facing quite a challenge in trying to catch up with the other countries and undoubtedly Malaysia is still in an early development stage. Despite that, Malaysia stands out with and quickly boost its manufacturing industry in one of the IR 4.0 which is additive manufacturing (Mohd Ghazali, 2020).

In 2020, the universities in Malaysia work together along with the industries and community, to develop and produce equipment and products (face shield, COVID-19 swab test kit and ventilator) required by the frontlines to fight against the fatal invisible army also known as COVID-19. In 2015, the Global Agenda Council on Future of Software and Society, WEF forecast that the first production of the 3D printed car, 5 % of consumer product printed via 3D printers and the first transplant of the 3D printed liver are expected to occur in 2025. Thus, Malaysia should grasp and embrace the opportunity to become the next manufacturing hub in Southeast Asia and keep up with the global market in IR 4.0 (Mohd Ghazali, 2020)

In 1986, 3D printing was first described by Charles Hull (Wang et al., 2017). It is originally generated by a computer-aided design (CAD) program such as AutoCAD, AutoDesk, SolidWorks, or Creo Parametric. 3D printing is accomplished by converting an STL (Standard Tessellation Language or STereoLithography) file into a G-file using a 3D printer slicer software. The G-file then divides the 3D STL file into a series of two- dimensional (2D) horizontal cross-sections, allowing the 3D object to be printed, in consecutive layers of the desired material, starting at the base, essentially constructing the model from a series of 2D layers derived from the original CAD file (Gross et al., 2014).

In simple words, 3D printing is a process of joining materials from 3D computer model data layer by layer using filaments from various types and sizes to make objects. It is good at reducing product development times between the sales and conception, maintain the production costs whether there are one or more units to be produced and no added cost for complexity hence, allow small businesses to operate as they don’t have expensive funding to support their business and most importantly it can fabricate designs and features unmatched by other conventional manufacturing (Mohan et al., 2017).

In 3D printing, there are many types of 3D printers (Table 2.1), but all of them are additive and build the object layer by layer regardless of the technology involved, (Wijk and Wijk, 2015). All those techniques vary in terms of maximum space required cost, building layers and types of materials used.

Among those techniques, FDM and SLS are commonly used methods to print thermoplastic materials. Thus, for this project, FDM is used since it is the cheapest 3D printer developed for private use or small companies trying their first steps in the area of 3D printing (Melnikova et al., 2014). Furthermore, FDM is a material based extrusion 3D printing technique, mostly based on polymers in the filament form which is suitable to be used since the starting material produced to be print in the 3D printing machine is in a filament form.

Table 2.1 3D printing technology

Process (ASTM Process)	**3D Printing Technology**
Extrusion (Material Extrusion)	Fused Deposition Modeling (FDM) • Material is melted and extruded in layers, one upon the other (this technique is normally used in 3D printers at home)
Direct Energy Deposition (Direct Energy Deposition)	Electron Beam Direct Manufacturing (EBDM) • An electron beam melts a metal wire to form an object layer by layer.
Solidification of Powder (Powder Bed Fusion)	Selective Laser Sintering (SLS) • A bed of powder material is “sintered” (hardened) by a laser, layer upon layer until a model is pulled out of it.
Solidification of Powder (Binder Jetting)	3D Printing • The powder is bond by a binding material distributed by a movable inkjet unit layer by layer.

Photopolymerization (Vat Photopolymerization)	Stereolithography (SLA) • Concentrating a beam of ultraviolet light focused onto the surface of a vat filled with liquid photocurable resin. The UV laser beam hardening slice by slice as the light hits the resin. When a projector beams the UV light through a mask onto the resin it is called Digital Light Processing (DLP)
PhotoPolymerzation (Material Jetting)	Polyjet Process • A photopolymer liquid is precisely jetted out and then hardened with a UV light. The layers are stacked successively.
Sheet Lamination (Sheet Lamination)	Laminated Object Manufacturing (LOM) • Layers of adhesive-coated paper, plastic or metal laminates are glued together and cut to shape with a knife or laser cutter.

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2.1.1 Fused Deposition Modeling (FDM) 3D Printing

Fused Deposition Modeling (FDM) was first developed in the 1980s and was commercialised in the early 1990s by Scott Crump of Stratasys Inc., USA (Mohan et al., 2017). It is widely used in 3D printing technology for fabricating polymer composites because of its simplicity technique (Wijk and Wijk, 2015, Dudek, 2013), reliability and cost-effectiveness in producing 3D printed objects with good resolution (Mohan et al., 2017) yet, it can easily produce complex-shaped parts with no limitation due to the geometry complexity (Le Duigou et al., 2016).

In the process of fabrication in FDM (Figure 2.1), complex geometries components of a 3D model are produced by converting a file containing a 3D model into 3D stereolithography (STL) format using CAD software. The STL file is then imported into CAM software which produces a physical replica of the 3D model, which is then sliced into thin layers by a 3D printing machine comprised of tool paths to place a continuous feedstock filament onto a surface, layer by layer to build up the 3D components (Owolabi et al., 2016).

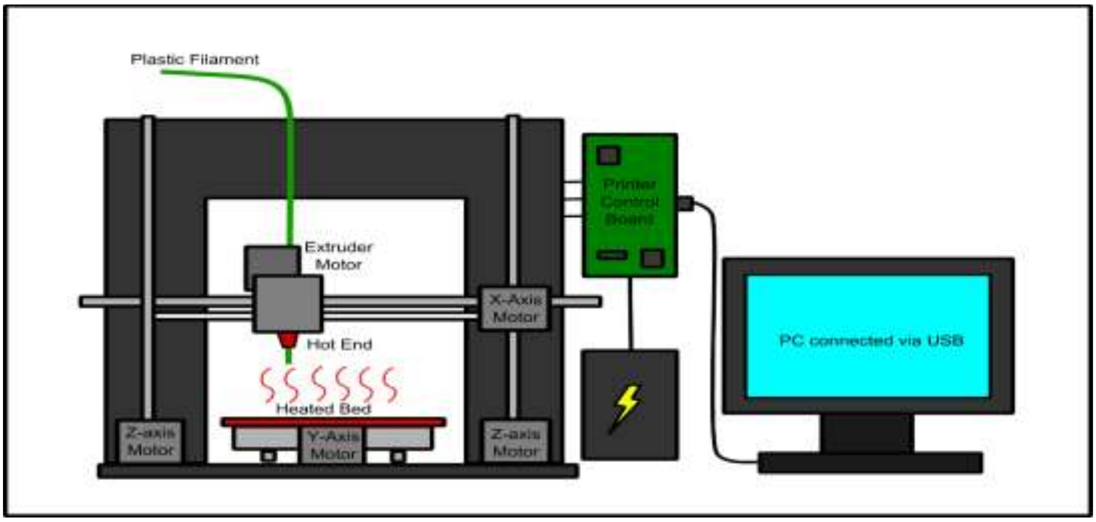

Figure 2.1 FDM 3D Printing machine

The materials used to create the 3D models are pushed down by two rollers to the nozzle tip of the print head’s extruder where they are heated to a semi-molten state by temperature control units. The semi-molten materials are extruded out of the nozzle tip and solidified in the desired areas when the print head traces the design of each defined cross-sectional layer horizontally. The stage is then lowered, and another layer is deposited in the same places and the process is repeated to fabricate a 3D structure in a layer-by-layer manner. Typically, the outline of the part is printed first, followed by layer by layer of the internal structures (2D plane).

2.1.1(a) Basic Requirement of Filament Fabrication in FDM

FDM is a material extrusion-based 3D printing technique that uses thermoplastic polymers in the filament form (Mohan et al., 2017). The filament used requires a specific diameter, strength and certain other properties (Dudek, 2013).

Usually, for an FDM 3D printer, a constant filament diameter of 1.75 mm (±0.1 mm) across the entire spool during the printing process is preferable. This is because a bigger filament diameter can cause a problem as the motor will have difficulty pushing the filament through or and the filament is unable to fit into the opening of the nozzle. Besides, the extruder gear may also shred the surface of the plastic, leaving it with nothing to grip and finally, stalling the extruder (Rahim et al., 2019).

Moreover, the feedstock material in the FDM machine is limited only to thermoplastic with suitable melt-viscosity and materials of a moderate melting temperature (Mohan et al., 2017). This is because the FDM machine has difficulty printing high melting point materials as its maximum operating temperature is around 300 ^{o}C (Mohan et al., 2017).

In addition, the thermoplastic used is restricted to amorphous polymer or low degree of crystallinity polymers. This is because the amorphous polymer easily solidified faster upon cooling as this behaviour is crucial to achieving a good piece of built print with successive addition of thin layers (Rahim et al., 2019). Besides, the polymer with a lower level of crystallinity exhibits a low degree of polymer shrinkage which is crucial to the accuracy of components produced (Stoof and Pickering, 2018).

2.1.1(a)(i) Selection of PLA over ABS in FDM

The most commonly used thermoplastic polymers in FDM are Acrylonitrile-butadiene-styrene (ABS) and Poly (lactic acid) (PLA). Yet, PLA is the most preferred polymer in FDM 3D printing since PLA come from renewable resources and is biodegradable (Prasong et al., 2020). Besides that, ABS also have an environmental issue due to the emission of volatile compounds such as styrene, as well as the discharge of unpleasant odours (Andrzejewski et al., 2020). Owing to the global environmental issues, PLA is considered as a possible alternative to replace the petroleum-based polymer making it an ideal choice for industrial. This is because the printable PLA creates no toxic gases while melting thus, no ventilation system is required when printing.

When compared to ABS, PLA is preferable for its wide range of available colours, translucencies, glossy feel and have a semi-sweets smell (Wijk and Wijk, 2015). In addition, PLA has a lower mechanical strength than ABS, but because it has a simple linear molecular chain structure, modified PLA can enhance its mechanical properties (Liu et al., 2019).

Aside from that, FDM machines are limited to amorphous polymers or low crystallinity polymers as they have a low degree of polymer shrinkage which is crucial to the accuracy of components produced (Stoof and Pickering, 2018). Having low thermal expansion help reduce the internal stresses caused during cooling and thus PLA is the most preferable compared to ABS because PLA has low glass transition, melting and printing temperatures than ABS. Therefore, the dimensional precision of printed PLA product is controllable and similarly to the original 3D model during printing (Wijk and Wijk, 2015, Liu et al., 2019) and thus, help reduce the warping effect (Cardoso et al., 2020, Andrzejewski et al. 2020).

During cooling, the materials stretch and slightly shrinking until the printed product start to stiffen at 110 ^{o}C and 56 ^{o}C for ABS and PLA, respectively based on their glass transition temperature and the remaining shrinking is resisted by the stiffness of the material. The stresses are internally stored instead of being relieved by the warmer material’s ability to flow thus, bending and warping occurring (Bates-Green and Howei, 2017).

In addition, more warping is likely to happen for ABS compared to PLA because of its high glass transition temperature. Thus, the printed PLA is relatively warm but cool for ABS. In other words, without the heated bed or closed chamber, the bottom layers of the printed product will get cool fast, shrinking and stiffening occur at the same time for the ABS printed product (Andrzejewski et al., 2020, Bates et al., 2017). Occasionally, PLA is the most popular polymer used among the home printers, hobbyists and universities other than the industrial section. Table 2.2 summarize the comparison between PLA and ABS in 3D printing.

Table 2.2 Comparison of ABS and PLA properties for 3D printing (Cale Rauch, 2018)

Polymer type	**ABS**	**PLA**
Extrude temperature	225-250 °C	190-240 °C
Bed temperature	80-110 °C	20-55 °C
Moisture	ABS with moisture will bubble and sputter when printed but easily dry.	PLA with moisture will bubble and sputter when printed. Not easily dry, can react with water and depolymerize at high temperatures
Heat	Less deformation due to heating	The product can deform because of heat
Smell	Plastic styrene smell	Corn like a sweet smell
Colour	Less colour brightness	Bright, shiny colours and smooth appearance
Hardness	Very sturdy and hard	Less sturdy than ABS
Fumes	Hazardous fumes	Non-hazardous fumes
Details	Higher layer height, less sharp printer corners, needs a heated printer bed for less warping.	Higher max printer speed, lower layer height, sharper printed corners, less part warping
Lifetime	Longer lifetime products	-
Environment	Non-biodegradable, made from oil	Biodegradable, made from sugar, corn, soybeans or maize

2.1.1(b) Printing Parameter in FDM

FDM is the most commonly used in producing conceptual models, prototypes and engineering components. The characteristics of the final product such as strength, surface finish, deformation, dimensional accuracy, porosity and energy consumption are mainly dependent on the printing process parameters (Rahim et al., 2019). Many researchers have performed studies on the effect of printing parameters such as slicing parameters, building orientation and temperature conditions on the printed product.

Filament diameter, layer thickness or height (Shuheng Wang et al., 2020), nozzle diameter, flow rate (Shuheng Wang et al., 2020), deposition speed, infill density and pattern, raster orientation or angle (Chockalingam et al., 2016, Shuheng Wang et al., 2020), air gaps (raster to raster, perimeter to raster), top or bottom thickness are the examples of slicing parameters. Meanwhile, the building orientation is the angle orientation of the printed product either vertically, horizontally or laterally and the temperature conditions are the environment, extrusion and bed or platform temperature (Popescu et al., 2018).

According to Popescu et al., (2018), only a few printing parameters have the same impact on the mechanical properties such as raster-to-raster air gap (recommendation being to set it at a negative value), raster angle, layer thickness, infill density and build orientation. The raster angle influences the anisotropy of the FDM parts and, therefore, their strength, being one of the most important process parameters impacting mechanical behaviour. When the printing angle is less than 45^o, the failure mode of the specimen trends to be an interlayer fracture, and conversely, the specimen's failure mode trends to be intra-layer fracture (Shuheng Wang et al., 2020). Shuheng Wang et al., (2020) also reported that the fill rate mainly affects the air gap inside the printed material. With the increase of the fill rate, the air gaps in the material decrease rapidly, which makes the material layers and the filaments more tightly bonded, hence, increases the resistance of the molecular chain for PLA materials. In addition, it is recommended to have a smaller layer thickness as it does not only strengthen the materials' interlayer bonding strength but also may have greater restrictions on the movement of adjacent polymer chains in PLA materials. It is supported by Liu et al., (2019), however, lower layer height might increase the additional printing time, but the better surface quality.

Meanwhile, the nozzle temperature mainly affects the fluidity of extruded material (Liu et al., 2019). This is because when the nozzle temperature is too low, the fluidity of the extruded material is poor resulting in weak interlayer bonding strength. However, the extruded material is almost liquid, and even partial thermal degradation will occur when the nozzle temperature is too high, which is not conducive to printing (Shuheng Wang et al., 2020). Therefore, the temperature must be precisely controlled considering the involvement of the material that might be causing overheated polymer swell and rapid degradation of properties (Dudek, 2013). In addition, increasing filament width enhances the porosity but lowers the cohesion of the material. This results in a reduction of tensile strength as well as fast and increased water uptake Le Duigou et al. (2016).

However, it is important to focus on evaluating their joint effect as this corresponds to real manufacturing conditions and the suitability of particular applications

2.2 Compression Moulding

Compression moulding is a common traditional that utilizes custom machined molds to form parts and products from uncured rubber or thermoset and thermoplastic polymer. The technique begins when a feeding material is placed between the heated mould cavity and parallel platens to consolidate the prepreg stack possibly using a picture frame mould to prevent resin overflowing from the edges of the laminate during compression. Then, it is compressed with a hydraulic press so that the material is in contact with all areas of the mould into the desired component (Rawi et al., 2013). It is widely used in industry, agriculture, transportation, electricity, chemical industry, construction and machinery.

The compression moulding technique is relatively simpler and straightforward compared to other moulding and manufacturing techniques. It is a cost-effective consolidation technique in terms of manufacturing and labour for small to medium production runs, less material wasted during the processing when handled carefully although it is a labor intensive process and it is an ideal technique for large manufacturing production, fairly complicated parts (Munsell, 2019). Moreover, the equipment and tools required for the production are much simpler attributed to the less typical investment.

However, compared to 3D printing, the compression moulding technique requires more time to cure the materials and this can affect the production rates and costs in higher volume projects. In addition, the material used in compression moulding technique may have flow restrictions inside the mould cavity. As a result, it may be unable to reach more intricate regions of the mould, necessitating tooling adjustments to fill some parts. For some complex part and product designs, this quality makes the procedure unsuitable. Besides, the part's size (projected area) and weight must be carefully calculated in proportion to the press force available to close and hold the mould closed throughout a moulding cycle. Even if this is ideal, expect additional parting line flash and control concerns, which may necessitate hand trimming or nitrogen de-flashing of the parts, which will add to the cost.

2.3 Biopolymer

Nowadays, a world without plastics or synthetic organic polymers seem impossible because it can be used in a wide range of applications such as packaging, building and construction, textiles, consumer products, electrical and electronics, transportation and industrial machinery. Several million metric tonnes of plastic are manufactured each year and recently in 2019, the total plastic production reached 368 million metric tonnes, worldwide.

A summary of the statistical analysis of global plastic production is shown in Figure 2.2. It has been documented that plastic production is expected to increase in the coming decades, thus it has become a serious concern worldwide since plastic waste are harmful to the environment. Though recently recycling has become more common, the plastics materials produced over the last 70 years have ended up in landfills, sometimes in water sources causing catastrophic environmental pollution.

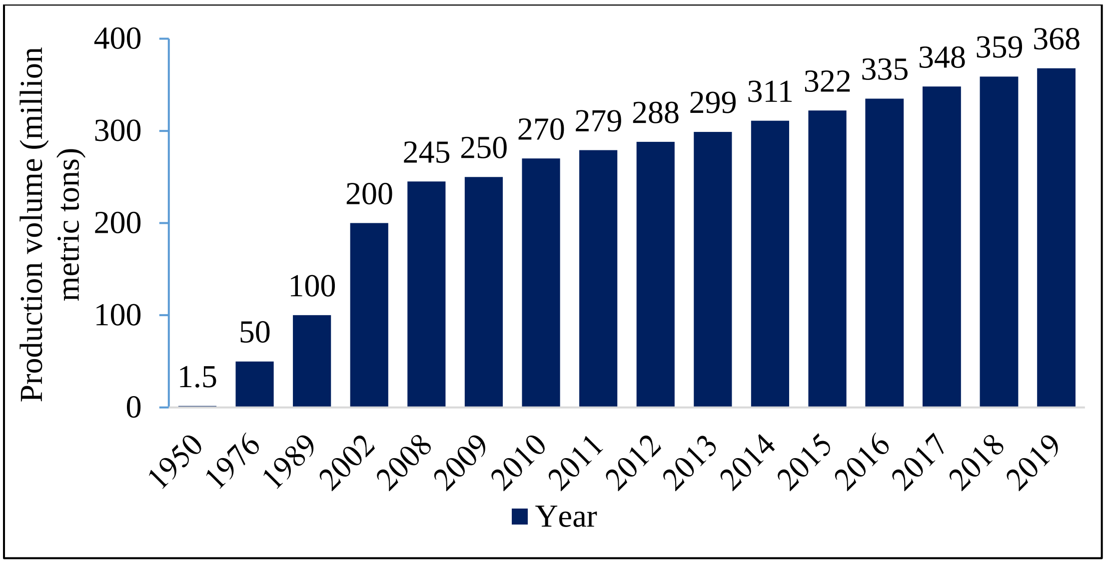

Figure 2.2 Statistic of global plastic production from 1950 to 2019 (Tiseo, 2021)

Biopolymers are biodegradable polymers made from renewable natural resources either chemically synthesized from a biological origin or fully biosynthesized by living organisms (Mohammad Rawi et al., 2013). Based on their origin, the biopolymer can be traditionally distinguished into natural, synthetic, and microbial biopolymers (Ibrahim et al., 2019).

The main property that distinguishes biopolymers from fossil-fuel-based polymers is their long-term viability or sustainability, which is enhanced by their biodegradability. The biopolymers are quickly decomposed when exposed to bacteria in soil, compost or marine sediment significantly reduce the emission of CO_2 compared to conventional incineration. Moreover, the biopolymers such as poly (lactic acid) (PLA), poly (3-hydroxy butyrate) (PHB) and poly (butyl succinate) (PBS) are thermoplastics with qualities similar to fossil-fuel-based plastics which is a significant advantage over the synthetic polymers (Mohan et al., 2016).

PLA on the other hand has the best tensile strength and is the least expensive among the biopolymers. Also, PLA appears to be a high potential candidate to replace polypropylene (PP) which is a thermoplastic polymer that has been commonly used in a broad range of applications including food packaging (Sritham et al., 2018).

2.3.1 Poly (lactic acid) (PLA)

PLA is a polyester of lactic acid bio-based or environmentally friendly biodegradable polymers. Lactic acid is a naturally occurring organic acid that is produced through the fermentation of feedstock from corn starch and sugarcane crops besides chemical synthesis (Deng et al., 2018). It is a hydroxyl acid with a carbon atom that is asymmetric and is widely used and exists in two optically isomeric forms which were D (-) and L (+) and – isomers as shown in Figure 2.3.

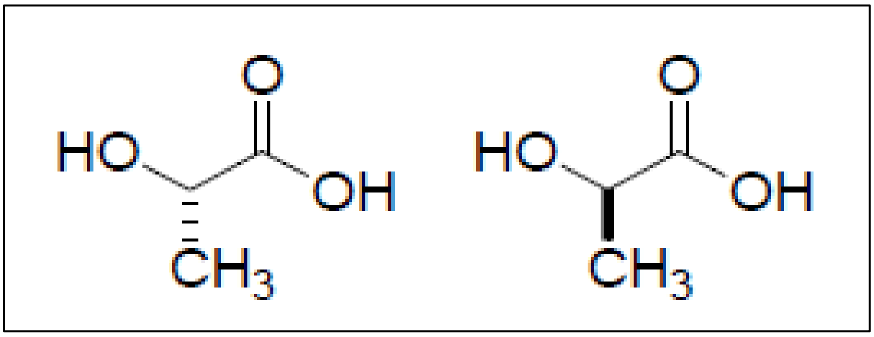

Figure 2.3 L- and D lactic acid (Xiao et al., 2012)

Figure 2.4 shows the lactide stereoisomers which were D-lactide, L-lactide, and meso-lactide that is needed for the synthesis of PLA. That two isomers of lactic acid can produce few distinct materials of PLA in stereochemical forms, for example, Poly (D-lactic acid) (PDLA) and Poly (L-lactic acid) (PLLA), and Poly (D, L-lactic acid) (PDLLA) is the copolymer produced from the L-lactide and D-lactide (Sarasini, 2017, Deng et al., 2018, Xiao et al., 2012, Farah et al., 2016). PDLA is a crystalline material with a regular chain structure, PLLA is a hemi-crystalline, and likewise, with a regular chain structure, PDLLA which is amorphous and meso-PLA are made by the polymerization of meso-lactide (Xiao et al., 2012).

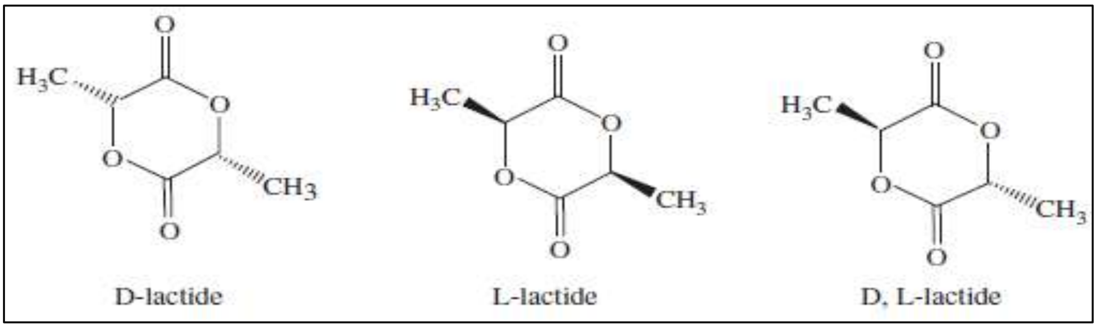

Figure 2.4 The diastreoisomers of lactide (a) D-lactide, (b) L-lactide and (c) meso-lactide (Ahmed & Varshney, 2011)

The lactide undergoes ring-opening polymerization (ROP) (Figure 2.5) to synthesize the high molecular weight PLA (Xiao et al., 2012, Farah et al., 2016). The ROP of lactide was first demonstrated by Carothers in 1932 but the high molecular weights were not achieved until Carothers at DuPont in 1954 improved lactide purification techniques (Jamshidian et al., 2010) and since then many companies have sprung up to commercialize PLA. In 2002, Cargill Dow LLC roughly used about 300 million USD to begin mass-producing their new PLA based plastic known as NatureWorks (Mohammad Rawi et al., 2013).

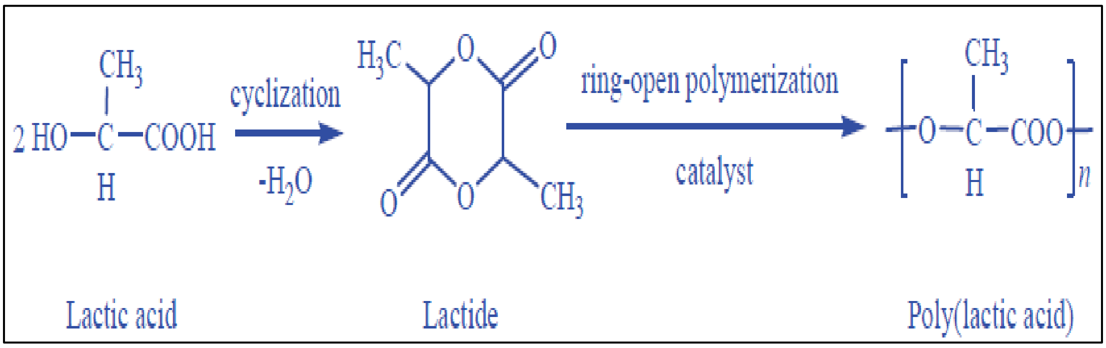

Figure 2.5 Ring-Opening Polymerization of PLA (Xiao et al., 2012)