

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA**

**THERMAL AND RHEOLOGICAL PROPERTIES OF 3D PRINTED
POLYLACTIC ACID PLASTICIZED WITH POLYETHYLENE GLYCOL**

By

NOR FAZREENIZA BINTI NOR ASHIKIN

Supervisor : Dr Arjulizan Binti Rusli

Dissertation submitted in partial fulfillment
of the requirement for the degree of Bachelor of Engineering with Honours
(Polymer Engineering)

Universiti Sains Malaysia

JUNE 2018

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Thermal and Rheological Properties of 3D Printed Polylactic Acid Plasticized with Polyethylene Glycol Blends”. I also declare that it has not been previously submitted for the award of any degree of diploma or other similar title of this of any other examining body or university.

Name of Student: Nor Fazreeniza Binti

Signature:

Nor Ashikin

Date: 25 JUNE 2018

Witness by

Signature:

Supervisor: Dr Arjulizan Binti Rusli

Date: 25 JUNE 2018

ACKNOWLEDGEMENTS

First and foremost, I wish to thank God for giving me strength to complete my final year project and dissertation excellently within the provided time.

I would like to express my sincere appreciation to my project supervisor Dr Arjulizan Binti Rusli for her assistance and guidance throughout the entire project. She provided me a lot of useful resources and constructive ideas for my project. She also shared all the knowledge and patiently guides me whenever I was facing difficulties.

I also would like to thank all my lecturers in USM especially lecturers in Polymer Engineering section which gave me many valuable lessons and guidances since I was first year student. I am so grateful to School of Materials and Minerals Resources Engineering for this opportunity to do my degree of Bachelor of Engineering (Polymer Engineering) including my final year project which gave me benefits and satisfaction.

My special gratitude reach out to all staffs especially technical staffs in polymer section as they patiently and spending their valuable time to guide me along this study. I appreciated the knowledge and experience that I have gained during this four year of study.

Not to forgotten, all my friends and all polymer students who contributed in my project bit by bit.

Last but not least my precious parents, Mr Nor Ashikin Bin Mohamed Rashid and Mrs Yusnizah Binti Yahaya and my beloved siblings for their encouragement and patience in the course of doing my degree of Bachelor of Engineering (Polymer Engineering) in Universiti Sains Malaysia.

TABLE OF CONTENTS

CONTENTS	PAGE
DECLARATION	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF ABBREVIATIONS	xi
LIST OF SYMBOLS	xii
ABSTRAK	xiii
ABSTRACT	xv
CHAPTER ONE : INTRODUCTION	1
1.1 Overview	1
1.2 Problem Statement	4
1.3 Research Objectives	6
CHAPTER TWO : LITERATURE REVIEW	7
2.1 3D Printing	7
2.2 Polylactic Acid (PLA)	12
2.3 Poly(ethylene glycol) (PEG)	24
CHAPTER THREE : METHODOLOGY	26
3.1 Materials	26
3.1.1 Poly(lactic acid), (PLA)	26
3.1.2 Commercial PLA	26

3.1.3	Polyethylene Glycol (PEG)	26
3.2	Blend Preparation	29
3.3	Sample Preparation	30
3.3.1	Compression Moulding	30
3.3.2	3D Printing	31
3.4	Characterisation	31
3.4.1	Fourier Transform Infrared (FTIR)	31
3.4.2	Melt Flow Index (MFI)	32
3.4.3	Differential Scanning Calorimetry (DSC)	33
3.4.4	Parallel Plate Rheometer	34
3.4.5	Scanning Electron Microscopy (SEM)	36
3.4.6	Water Absorption test	36
CHAPTER FOUR : RESULTS AND DISCUSSION		38
4.1	Characterization of the samples	38
4.2	Melt Flow Index (MFI)	39
4.3	Differential Scanning Calorimetry (DSC)	41
4.3.1	DSC of hot press sample	41
4.3.2	DSC of 3D printed sample	45
4.4	Rheological Properties	49
4.4.1	Amplitude Sweep	49
4.4.2	Frequency Sweep	49
4.5	Morphology of fracture surface	61
4.6	Water Absorption	68

CHAPTER FIVE : CONCLUSIONS	71
5.1 Conclusion	71
5.2 Recommendations for future work	72
REFERENCES	73

LIST OF TABLES

Table 2.1: Selected physical and chemical properties of PLA.	17
Table 3.1: The physical, mechanical, thermal and optical properties of PLA.	27
Table 3.2: Material Data Sheet of Commercial PLA	28
Table 3.3: The properties of PEG.	28
Table 3.4: Compositions of plasticization PLA with PEG.	29
Table 4.1: Melt flow index of neat PLA, PLA/10 wt% PEG and commercial PLA at 170°C and 190°C.	40
Table 4.2: Thermal Properties of neat PLA, PLA/10 wt% PEG and commercial PLA for hot press sample determined by DSC.	42
Table 4.3: Thermal Properties of neat PLA, PLA/10 wt% PEG blend and commercial PLA for 3D printed sample determined by DSC.	46
Table 4.4: Water absorption of neat PLA, PLA/10 wt% PEG and commercial PLA for hot press and 3D printed samples.	68

LIST OF FIGURES

Figure 2.1: FDM along with sectional view of extruder (Ramya, 2016).	9
Figure 2.2: Life cycle of PLA (Sangeetha et al., 2018).	13
Figure 2.3: General structure of PLA	14
Figure 2.4: The stereoisomers of lactic acid (Xiao et al., 2012).	14
Figure 2.5: Synthesis of PLA from L- and D-lactic acids (Lim, Auras & Rubino, 2008).	15
Figure 2.6: Chemical structure of LL, DD and LD-Lactid	16
Figure 2.7: Mechanical properties of PLA compared to other common plastics (Dorgan, Lehermeier and Mang, 2000).	19
Figure 2.8: Structure of PLA.	24
Figure 3.1: Chemical structure of poly(lactic acid).	26
Figure 3.2: Chemical structure of polyethylene glycol	27
Figure 3.3: Brabender single screw extruder (lab scale size).	30
Figure 3.4: Compression moulding machine.	31
Figure 3.5: FTIR spectrometer.	32
Figure 3.6: Melt flow indexer	33
Figure 3.7: Differential scanning calorimetry machine.	34
Figure 3.8: Anton Paar rheometer.	35
Figure 3.9: FESEM machine.	36
Figure 4. 1: FTIR spectrum of PEG, PLA and commercial PLA.	39
Figure 4.2: Melt flow index of PLA, PLA/10 wt% PEG blend and commercial PLA at 170°C and 190°C.	41
Figure 4.3: DSC PLA	43
Figure 4.4: Thermograms for (a) cooling with a cooling rate 10°C /min and (b) second heating with a heating rate of 10°C /min for neat PLA, PLA/10 wt% PEG and commercial PLA of hot press sample.	44

Figure 4.5: Thermograms for (a) cooling with a cooling rate 10°C /min and (b) second heating with a heating rate of 10°C /min for neat PLA, PLA/10 wt% PEG blend and commercial PLA of 3D printed sample.	47
Figure 4.6: Storage and loss modulus as function of strain and temperature for (a) neat PLA and (b) PLA/10 wt% PEG.	50
Figure 4.7: Storage and loss modulus as function of frequency and temperature for (a) commercial PLA, (b) neat PLA and (c) PLA/10 wt% PEG hot press sample.	54
Figure 4.8: Damping factor vs. frequency of commercial PLA, neat PLA and PLA/10 wt% PEG blends for hot press sample at 170°C and 190°C.	54
Figure 4.9: Complex viscosity vs. frequency of commercial PLA, neat PLA and PLA/10 wt% PEG blends for hot press sample at 170°C and 190°C.	56
Figure 4.10: Storage and loss modulus as function of frequency and temperature for (a) commercial PLA, (b) neat PLA and (c) PLA/10 wt% 3D printed sample at 170°C and 190°C.	58
Figure 4.11: Damping factor vs. frequency of commercial PLA, PLA and PLA/10 wt% PEG blends for 3D printed sample at 170°C and 190°C.	60
Figure 4.12: Complex viscosity vs. frequency of commercial PLA, neat PLA and PLA/10 wt% PEG blends for 3D printed sample at 170°C and 190°C.	61
Figure 4.13: Fracture sample of neat PLA of (a) hot press and (b) 3D printed sample at 190°C with magnification 500x.	64
Figure 4.14: Fracture sample of PLA/10 wt% PEG of (a) hot press and (b) 3D printed at 190°C with magnification 500x.	65
Figure 4.15: Fracture sample of PLA/10 wt% PEG of hot press sample at (a) 170°C (b) 190°C with magnification 50x.	66
Figure 4.16: Fracture sample of PLA/10 wt% PEG of 3D printed sample at (a) 170°C (b) 190°C with magnification 50x.	67
Figure 4.17: Water absorption of PLA, PLA/10 wt% PEG blends and commercial PLA for 3D printed and hot press sample of (a) 170°C and (b) 190°C.	70

LIST OF ABBREVIATIONS

DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infrared
LVE	Linear Viscoelastic Region
MFI	Melt Flow Index
PE	Polyethylene
PEG	Polyethylene Glycol
PDLA	Poly(D-lactide acid)
PLA	Poly(lactic acid)
PLLA	Poly(L-lactic acid)
SEM	Scanning Electron Microscopy
TPU	Thermoplastic Polyurethane

LIST OF SYMBOLS

%	Percentage
°C/min	Degree Celcius per minute (unit for heating rate)
ΔH_c	Enthalphy for crystallization
ΔH_{cc}	Enthalphy for cold crystallization
ΔH_m	Enthalphy of melt
ΔH°_m	Enthalphy of fusion of PLA crystal to infinite size
η^*	Complex viscosity
g	Grams (unit for weight)
G'	Storage Modulus
G''	Loss Modulus
hrs	Hours
mm	Milimeter (mathematical unit)
Pa	Pascal
Pa.s	Pascal second
s	Second
$\tan \delta$	Damping factor
T_c	Crystallisation Temperature
T_{cc}	Cold Crystallisation Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature
X_c	Degree of Crystallinity

SIFAT-SIFAT TERMA DAN REOLOGI POLILAKTIK ASID DENGAN PEMPLASTIK POLIETILENA GLIKOL BERCETAK 3D

ABSTRAK

Dalam kajian ini, sifat-sifat terma, reologi dan morfologi Polilaktik asid (PLA) dengan 10 wt% poletilena glikol (PEG) selepas leburcampur pada dua suhu berbeza telah dikaji. Sifat-sifat tersebut telah dibandingkan dengan PLA tulen dan filamen PLA komersial yang digunakan untuk pencetak 3D. Campuran PLA/10 wt% PEG telah disediakan menggunakan ekstruder skru tunggal untuk menghasilkan pelet untuk penekanan panas atau filamen untuk percetakan 3D.

Peralatan pemprosesan yang berbeza mempengaruhi sifat-sifat terma secara berbeza di mana sampel penekanan panas menunjukkan suhu peleburan (T_m) dan suhu penghabluran (T_c) dengan perbezaan yang tidak ketara manakala adunan bercetak 3D menunjukkan pengurangan suhu peralihan kaca (T_g) dan T_m dengan kehadiran pemplastik. Kajian ini juga menunjukkan bahawa filamen PLA komersial mempunyai penghabluran yang lebih tinggi daripada PLA tulen yang digunakan. Indeks Alir Leburan PLA meningkat yang menunjukkan kelikatan berkurang dengan 10 wt% PEG atau peningkatan suhu. Sifat reologi menunjukkan modulus penyimpanan (G'), modulus kehilangan (G'') dan kelikatan kompleks (η^*) telah menurun dengan penambahan PEG tetapi η^* meningkat selepas percetakan 3D mungkin disebabkan pembentukan lapis demi lapis mengikut arah yang berbeza. Permukaan morfologi menunjukkan bahawa campuran PLA menjadi lebih mulur dengan penambahan PEG. Disamping itu, lapisan-lapisan untuk sampel bercetak 3D yang disediakan pada suhu 190°C membasahi dengan baik berbanding sampel pada 170°C mencadangkan bahawa 190°C suhu pemprosesan yang sesuai untuk pemplastik PLA. Ujian

penyerapan air menunjukkan peratusan penyerapan air yang lebih tinggi apabila PEG ditambah dan juga bagi sampel bercetak 3D berbanding sampel yang ditekan panas.

THERMAL AND RHEOLOGICAL PROPERTIES OF 3D PRINTED POLYLACTIC ACID PLASTICIZED WITH POLYETHYLENE GLYCOL BLENDS

ABSTRACT

In this work thermal, rheological and morphological properties of Polylactic acid (PLA) with 10 wt% polyethylene glycol (PEG) after melt blended at two different temperatures were investigated. The properties were compared with neat PLA and commercial PLA filament used for 3D printing. PLA/10 wt% PEG blend was prepared using single screw extruder to produce pellet for hot press or filament for 3D printing. The different of processing equipment affect thermal properties differently in which for hot pressed blends indicated insignificant changes of melting temperature (T_m) and crystallization temperature (T_c) while 3D printed blends showed reduction of glass transition temperature (T_g) and T_m in the presence of plasticizer. This study also suggested that the commercial PLA filament has higher crystallinity than the pure PLA used. The melt flow index of the PLA increased suggesting reduction of viscosity with 10w*% PEG or increase of temperature.

Rheological properties indicated that storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) decreased in the presence of plasticizer but the η^* increased after 3D printing process might be due to layer by layer formation at different directions. Morphology shows that the plasticized PLA becomes more ductile with the addition of PEG. In addition, the layers in 3D printed sample prepared at 190°C were wetted well than samples at 170°C suggesting that 190°C is suitable processing temperature for the plasticized PLA. The water absorption test showed higher percentage of water absorption as PEG was added and for 3D printed samples compared with hot pressed sample.

CHAPTER ONE

INTRODUCTION

1.1 Overview

3D printing is a process of making a three-dimensional (3D) object of virtually any shape from a digital model by adding material. 3D printing, which is additive manufacturing technology, is achieved using an additive process where successive layers of material are laid down in different shapes to form a 3D object. It has variety of uses since it known, greatly moving beyond prototyping or printing of designs draft to applications including medicine, jewelry and pharmaceuticals (Gonzalez and Benneth, 2016). Its automated nature allows individual experience to produce objects even though does not have experience to conduct the machine. Many 3D printing approaches reduce materials waste, hence the cost more save (Michael & Timothy, 2015).

Although 3D printing technology offers great potential, there are a few issues regarding 3D printer. The major issue is the limited capabilities of the 3D printers. It still lags behind optimal levels even though the processing speed, printing speed and printer resolution have increased vastly over the past years. Secondly, there are lack of diversity or limited materials could be used in 3D printer (Guvendiren *et al.*, 2016). It has limited materials with which they can print and many printers are limited to a single material (Michael & Timothy, 2015).

Usually the most common material type that used as filament in 3D printer is thermoplastic filament. It can be two varieties which are poly(lactic acid) (PLA) and acrylonitrile butadiene styrene (ABS) (Joe, 2015). It use pure material which is does not

have blend or plasticizer into it. The limited material makes it difficult to use when using 3D printer. Therefore, the requirement for material development for 3D printer application need to be improved such as improve the printing behaviour of the available materials, broaden the range of materials such as using polypropylene and polycarbonates and increase the properties of 3D printed objects.

Meanwhile, unmodified PLA is the most widely used material in 3D printer application. PLA is a biodegradable polymer that comes from renewable resources. It is belong to the aliphatic polyester group which is a product of the reaction among α -hydroxy acids (Wang, Gramlich and Gardner, 2017). It is produce from renewable resources like sugar beet, starch and corn and it is highlighted as “green” polymer due to its biodegradability (Ozdemir and Hacaloglu, 2017).

Besides, PLA can be recycled and starts to break down when exposed to industrial composting facilities. PLA is a non-petrochemical plastic; hence make it as an eco-friendly (Richard and Kalani, 2017). PLA is widely used in 3D printer because it is safe. Research said that it is safe even though it has strong odour when heated. It also considered safe to use to print objects that will contact in food and medical application (Cano, 2015).

PLA has a low glass transition temperature of 60°C. For melting point of PLA, the temperature is around 160°C. A temperature between 160 to 210°C is often used for 3D printing with PLA. PLA melts at low temperature which is around 160°C, although it bonds better around 180°C (Richard and Kalani, 2017). The characteristic of PLA also it has high strength, high modulus and transparency, compatibility and resorbability (Ozdemir and Hacaloglu, 2017). PLA has broad application in packaging and biomedical fields. PLA was being used because it worked very well and provided

the excellent properties at a low cost as compared to other traditional biodegradable polymers used in medical applications (Hamad *et al.*, 2015).

Unfortunately, at higher temperature, the PLA is too flexible for 3D printing and also starts to break down (Richard and Kalani, 2017). PLA has poor toughness because it is very brittle material, low thermal stability and limited barrier property (Ozdemir and Hacaloglu, 2017). Balakrishnan *et. al.* (2012) also said that PLA has weakness of stiffness with low deformation at break and low impact strength. Hence, it restrict from demanding mechanical performance applications unless it is suitably modified (Rasal & Hirt, 2009). The cost also expensive. PLA is use with natural fibre for composite, blend with other polymeric materials or adding plasticizer to reduce the cost. Besides, PLA is hydrophobic and can affect the inflammatory response because of its low affinity with cells when it is used as a tissue engineering material (Xiao *et al.*, 2012).

However, to overcome the toughness problem, a lot of researchers studied incorporation of various materials to the PLA to improve the impact and toughness properties. Among them, polyethylene glycols (PEG) is the most efficient plasticizer for PLA because it has low molecular weight (Serra *et al.*, 2014). The effect of PEG as plasticizer is to ease and optimize the fabrication process at low temperature. Incorporation of PEG into the PLA matrix led to different chain arrangements. The chain mobility is increases as the PEG is added. The thermal analysis of the different composition also showed a decrease trend of the T_g and an increase of the crystallinity values (Serra *et al.*, 2014).

1.2 Problem Statement

In this research experiment, the melt extrusion is the method for 3D printing. The technology based on extrusion principle is Fused Deposition Modelling (FDM). With FDM, thermoplastic material is extruded. The molten material is printed layer by layer, on top of the previous layer and fuses when the material hardens almost instantly after leaving the printing nozzle. The FDM method is one of the cheapest 3D printing methods (Van Wijik and Iris, 2015).

FDM process requires filament materials for printing models. In an extrusion process, a raw material usually a polymer or a polymer blend is forced to pass through a die, thus creating the desired cross sections. In melt extrusion, the polymer is melted by applying heat or pressure or both and is forced out through an orifice. Most of the filaments used in 3D printing are fabricated by melt extrusion using circular orifice to make long cylindrical filaments.

To be used as filament in 3D printing, the filament must possess uniform diameter and roundness. The usually diameter of filament for 3D printer is $1.75 \text{ mm} \pm 0.03 \text{ mm}$. The uniformity of the diameter and roundness will allow the filament to easy entrance into the nozzle, sufficient contact between the filament and the nozzle wall for efficient heat transfer and constant material flow.

Furthermore, different biodegradable as well as non-biodegradable plasticizers have been used to lower the glass transition temperature, increase ductility and improve processing of PLA. Among them, polyethylene glycols (PEG), especially low molecular weight PEG has been reported as one of the most efficient plasticizers for PLA (Serra *et al.*, 2014).

The modification of PLA with different biodegradable and non-biodegradable plasticizers, having a low molecular weight but a high boiling point and a low volatility, has been explored as a mean to lower the T_g and increase the ductility and softness of PLA. This has been achieved by varying the molecular weight, the polarity and functional groups of the plasticizers. Biocompatible molecules such as oligomeric lactic acid, oligomeric PEG, and glycerol are all plasticizers of choice for PLA (Martin & Averous, 2001; Ljungberg et al., 2005)

PEG can affect the thermal characteristics of PLA by disturbing the intermolecular forces. Both the molecular weight and the amount of the plasticizer influence the properties of PLA blends. Furthermore, there is a limit of miscibility and brittleness characteristics depending upon the plasticizer content and molecular weight. Plasticized PLA usually shows single T_g . The chain mobility of the PLA can be increase by increasing the amount of PEG. The increasing of chain mobility makes the chains to rearrange which can leads to decrease in T_g and improvement in crystallization (Ozdemir and Hacaloglu, 2017). Futhermore, PEG can play a role as polymeric plasticizer to lower the modulus and to increase flexibility of PLA (Tien and Sakurai, 2017).

The PLA will blend with these materials; PLA-PEG with several of composition. The best type of blend and composition of wt% is determined based on characterization and rheology of the materials.

In plasticized PLA, factors such as type and amount of plasticizer affect the properties of the blend. For example, amount of PEG plasticizer or other component could affect chemical structure, content or properties of the PLA. An optimum amount of plasticizer could impact differently on toughness properties of the blends.

In addition, knowledge on polymer properties is very important in order to optimize the polymer for 3D printing. Rheological analysis are very important in characterization of polymer for 3D printing application since it can be used as material characterization to determine processibility of a material and also can be used as input data for computer simulations. Thus, rheological properties are considered as one of the most important characterization for 3D printing application.

1.3 Research Objectives

The purpose of this research is to study the effects of poly(ethylene glycol) (PEG) into poly(lactic acid) (PLA) for 3D printing. PEG act as plasticization blend that will affect the properties of PLA and contribute to high ductility.

Therefore, the objectives of this research are:

- i. To produce a new filament of 3D printing based on PLA and PEG as a blend.
- ii. To determine of PLA/PEG in term of thermal and physical interaction.
- iii. To study the rheology of PEG plasticized PLA filament after 3D printing.

CHAPTER TWO

LITERATURE REVIEW

2.1 3D Printing

3D printing technology has increasingly progressed from just a rapid prototyping technology to the technology that used for production of final products intended for everyday use. The increasing in popularity has come with a proportionate increase in the study related to 3D printed techniques as it is very important to comprehend the properties and characteristics of the parts that are produced.

3D printing is an additive manufacturing process that allows fabrication of objects of virtually any shape directly from computer aided design (CAD) models. It will produce three-dimensional object from a package model that is largely additive in which successive layers of material are laid down in different shape (Soliman, Feibus and Baum, 2015).

3D printing consists of designing and printing part. Firstly, 3D printable model need to be designed first by using CAD software or via 3D scanner where a real life object is scanned to get a model and can be set to be printed. It is then converted into Standard Tessellation language (STL) file to the 3D printing software where the model is "slices" into digital cross section so that the machine could use them as a guide to print (Soliman, Feibus and Baum, 2015). Then, depending on the machine used, material or a binding material is deposited on the build bed or platform. It works by positioning the print head repeatedly in three directions which is x, y and z direction in order to print the material layer by layer until desired model is obtained (Ramya, 2016).

Some 3D printing techniques are capable of using a multiple materials during constructing parts and some may also utilize supports when building the part. Supports can be removed or dissolved in suitable media upon completion of the printing and the final object can be obtained. For some of the 3D-printed objects, post-processing may be need while for others, it may be not required. The biggest advantage 3D printer is that it can create and print almost any geometric shape (Soliman, Feibus and Baum, 2015).

Furthermore, 3D printing has been used in variety of applications such as in medical industries and tissue engineering, including craniofacial implants, dental molds, crowns and implants, prosthetic parts, on-demand medical equipment, surgical models, scaffolds for tissue regeneration such as skin and bone, organ printing and tissue models for drug discovery (Guvendiren *et al.*, 2016). The 3D printing technology also used for both prototyping and distributed manufacturing in industrial design, automotive industry and even used in production of food.

Besides, it has several types of 3D printing technologies such as stereolithography (SLA), fused deposition modeling (FDM), selective laser sintering (SLS), inkjet printing (Guvendiren *et al.*, 2016); laminated object manufacturing (LOM), direct metal laser sintering (DMLS) and poly-jet 3D printing (Ramya, 2016). The technologies are differing among them in the ways the layers are deposited to create parts and the materials that can be used in the production of the parts.

Among the additive manufacturing technique, FDM process seems to be more reasonable for basic use as it can be performed with the use of filament while other rapid prototyping forms the utilize resin based material. In addition, FDM is the second most widely used rapid prototyping technology after stereolithography (Ramya, 2016); (Soliman, Feibus and Baum, 2015). It is a low cost equipment, with variability in

material selection and easy operation (Wang, Gramlich and Gardner, 2017). FDM gives flexibility and improves creativity as complex shapes can be created effortlessly and quickly.

In FDM techniques, the main material that usually been used as the ink of the 3D printer to form products is solid plastic filament and it normally has 1.50 or 1.75 mm in diameter (Soliman, Feibus and Baum, 2015; Guvendiren *et al.*, 2016). Plastic filament material is extruded through a heated nozzle that traces the parts cross sectional geometry layer by layer. The nozzle is heated to melt the plastic to form individual lines that solidify onto a build plate (Ramya, 2016) and follows a predefined path to build up a 3D object layer-by-layer (Guvendiren *et al.*, 2016).

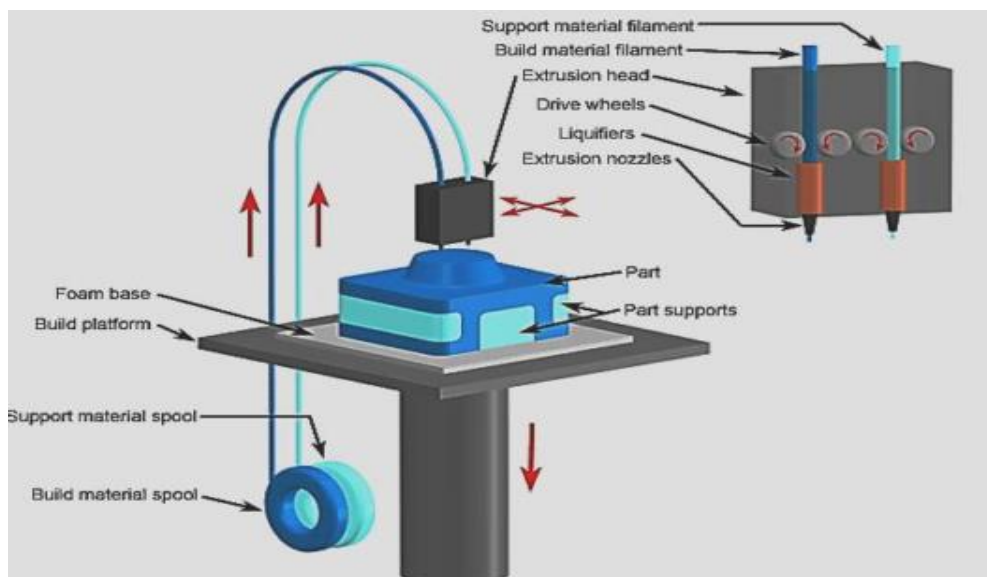


Figure 2.1: FDM along with sectional view of extruder (Ramya, 2016).

FDM process requires filament materials for printing models. Filaments can be prepared by several methods, among which, one method is melt extrusion. Most of the filaments used in 3D printing are fabricated by melt extrusion, using circular orifice to make long cylindrical filaments. In an extrusion process, a raw material, usually a polymer or a polymer blend is forced to pass through a die, thus creating the desired

cross sections. Based on the working temperature of the material being processed, extrusion can be cold extrusion or hot extrusion. In melt extrusion, the polymer is melted by applying heat or pressure or both and is forced out through an orifice.

FDM 3D printing procedure allows a product to be produced using only a filament. The materials that can be used for the production of the filament for the 3D printers mostly are thermoplastics, which can be prepared at relatively moderate temperature and pressure. Various thermoplastics are accessible for 3D printing with different strength and temperature properties including acrylonitrile butadiene styrene (ABS), nylon, polycarbonate (PC), high-density polyethylene (HDPE), polystyrene (PS) and polylactic acid (PLA). In addition, some of these materials can be used as a raw material for mixing with other materials to improve specific properties and functions but not much of these are available commercially. Among all of these, ABS and PLA are the most popular filament materials (Zhao *et al.*, 2018).

PLA is commonly used as a filament in 3D printing technology because it is one of the best and most used printable materials available for biological applications especially in FDM (Guvendiren *et al.*, 2016). PLA is derived from plant based origins which are renewable and degradable resources such as corn and rice (Xiao *et al.*, 2012). It belongs to the family of aliphatic polyesters commonly made from α -hydroxy acids, which include polyglycolic acid or polymandelic acid, and are considered biodegradable and compostable (Garlotta, 2002). PLA filament is a popular choice of filament for 3D printing also due to availability in wide range of colour including translucent colour. It is also available in glossy or other type of finishing. The application of PLA in 3D printing may not require the use of heating bed, could be printed at high printing speed and could be used to print product with sharp corner. The wide range of available colors and translucencies and glossy feel often attract those

who print for display or small household uses. Many appreciate the plant based origins and prefer the semisweet smell over ABS.

Meanwhile, ABS is a petrochemical-based, triblock copolymer that possesses good strength from the acrylonitrile and butadiene elements while gaining toughness from the styrene units, giving it an advantage over the somewhat brittle polyester materials such as PLA (Guvendiren *et al.*, 2016). However, ABS is produced from oil and considered toxic, and its production is not environmentally friendly (Zhao *et al.*, 2018) and not biodegradable which is a major detriment in an industry that is moving toward resorbable materials. ABS has seen limited use as a scaffold material outside of cartilage engineering because it generally performs the same or worse than PLA in areas of cell integration, processability and cost (Guvendiren *et al.*, 2016).

In comparison with ABS, PLA is a biodegradable plastic derived from renewable sources making it is a safer alternative to ABS (Zhao *et al.*, 2018). Due to its biocompatibility and biodegradability, PLA has been used in contact with mammalian bodies. Hence, it is widely used in biomedical such as surgical implant and pharmaceutical fields (Garlotta, 2002). PLA has been employed to manufacture tissue engineering scaffolds, delivery system materials, or covering membranes, different bioabsorbable medical implants, as well as in dermatology and cosmetics. It is because degradation of PLA products which is H₂O and CO₂ are neither toxic nor carcinogenic to the human body. As evident, PLA products have been approved by the US Food and Drug Administration (FDA) for direct contact with biological fluids (Xiao *et al.*, 2012).

PLA has good mechanical properties for a synthetic polymer but tends to be brittle and have a lower compressive strength (Guvendiren *et al.*, 2016). Eventhough a few polymers are commercially available, the number of materials available for 3D printing technology is limited. Therefore, the requirement for material development for

3D printer application need to be improved such as improve the printing behaviour of the available materials, broaden the range of materials such as using polypropylene and polycarbonates and increase the properties of 3D printed objects.

2.2 Polymeric Acid (PLA)

2.2.1.1 Introduction to PLA

PLA is a term referred to as polylactic acid or simply polylactide is a biodegradable thermoplastic made from lactic acid. It is an environment friendly polymer and usually produced from renewable sources, mainly from starch. They are naturally organic acid that can be produce in various ways of chemical synthesis or fermentation. Figure 2.2 shows the life cycle of PLA. It is categories among the biopolymers because of its renewability and degradability to nature. It has been found to exhibit similar properties with that petroleum based polymer. Besides, PLA has been used in wide range commodity applications due to its versatility. As examples, PLA is used in food, textile, pharmaceutical and chemical industries applications. They are naturally organic acid that can be produce in various ways of chemical synthesis or fermentation (Hakkarainen, Minna & Anna, 2011).

The history of PLA can be traced back to 1932 when a scientist from Du Pont, Wallace Carothers, heated lactic acid under vacuum and successfully fabricated a low molecular weight PLA (Lunt and Shafer, 2000). With an additional improvement, this process was patented by Du Pont in 1954 (Balkom, Welt and Berger, 2002). Then in 1988, Cargill Inc. planned to develop PLA to be a new commercialized product. Eventually with a joint venture of Cargill Inc. and Dow Chemical Company, Cargill Dow LLC was formed in 1997 and PLA was commercialized under the trade name of NatureWorks, nowadays as Ingeo™ (Vink *et al.*, 2003).

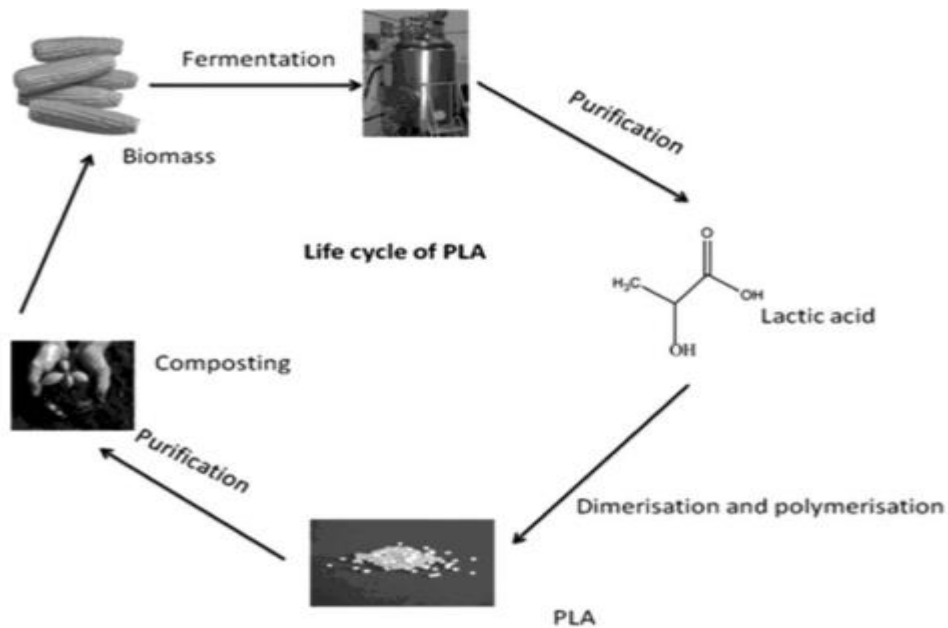


Figure 2.2: Life cycle of PLA (Sangeetha et al., 2018).

PLA material properties are good in comparison with many other bio-based materials. These properties depend on the processing temperature, component isomers, molecular weight, crystallinity, annealing time and glass transition (T_g). PLA is high strength and high modulus thermoplastic which can be processed by most conventional plastic processes like injection moulding, extrusion, blow moulding and even used as 3D printing filament.

PLA is a low energy consumption product with about 30-50% lower in energy consumption than the petroleum based polymers. In addition, PLA requires 25–55% less energy to produce than petroleum-based polymers. Lower energy use makes PLA production potentially beneficial with respect to cost. Hence, PLA is relatively low price and can replace the position of the petroleum based plastics in bioplastic industries. It is also able to maintain carbon dioxide balance after decompose thus is considered as the advantage of PLA rather than traditional petroleum-based plastics. PLA not produce toxic or carcinogenic effects (Sangeetha *et al.*, 2018).

2.2.1.2 Production of PLA

Figure 2.2 shows the structure of the PLA. It is a chiral polymer in which molecules containing asymmetric carbon atoms have a helical orientation. PLLA and PDLA are the two optical isomers of PLA.

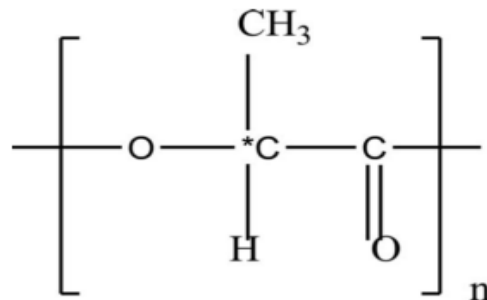


Figure 2.3: General structure of PLA

Furthermore, lactic acid (LA) has two isomers which are L-lactic acid and D-lactic acid (Figure 2.4). The two isomers of LA can produce four distinct materials which are Poly(D-lactic acid) (PDLA), a crystalline material with a regular chain structure; poly(L-lactic acid) (PLLA), which is semi-crystalline, and likewise with a regular chain structure; poly(D,L-lactic acid) (PDLLA) which is amorphous; and meso-PLA, obtained by the polymerization of meso-lactide (Xiao *et al.*, 2012).

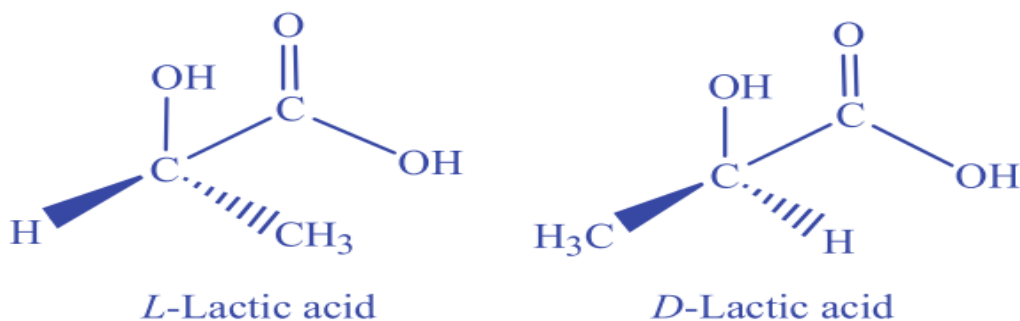


Figure 2.4: The stereoisomers of lactic acid (Xiao *et al.*, 2012).

Basically, the basic building block for PLA is lactic acid, which was first isolated in 1780 from sour milk by the Swedish Chemist Scheele and first produced commercially in 1881. Lactic acid can be manufactured either by carbohydrate, fermentation or chemical synthesis (Garlotta, 2002). Currently, the majority of lactic acid production is based on the fermentation route. PLA can be produced using several techniques, including azeotropic dehydrative condensation, direct condensation polymerization, and/or polymerization through lactide formation as shown in Figure 2.5.

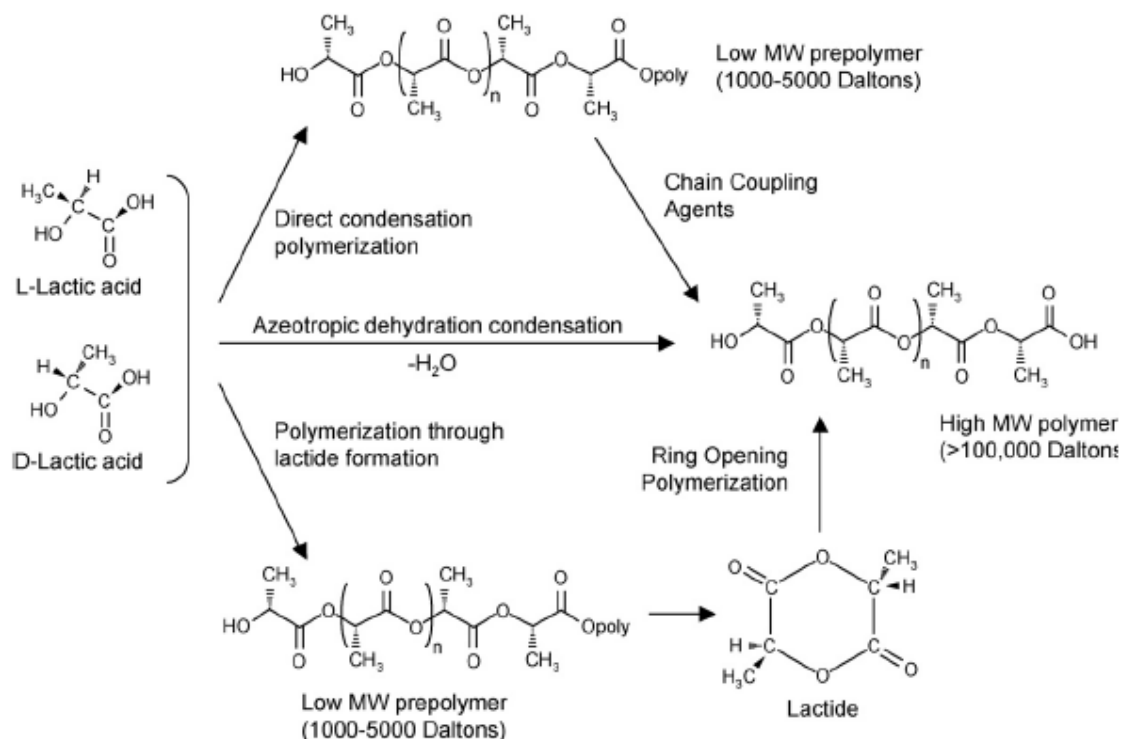


Figure 2.5: Synthesis of PLA from L- and D-lactic acids (Lim, Auras & Rubino, 2008).

Azeotropic dehydrative condensation of lactic acid is a method used to yield high molecular weight PLA (Garlotta, 2002). This method was commercialized by Mitsui Toatsu Chemicals in Japan. The general concept of this process involves removing water from lactic acid by reducing the distillation pressure in the vessel for 2-3 hours at 130°C. Then catalyst and diphenyl ester are added and a molecular sieve tube is connected to the vessel. The solvent is then refluxed through the sieve for 30 –

40 hrs at 130°C. After the process, the catalyst is removed and the polymer is then passed through a purification process (Auras, Harte and Selke, 2004; Garlotta, 2002).

In direct condensation, solvent is used under high vacuum and temperatures for the removal of water produced in the condensation. It is the least expensive method and has fewer processing steps. However, it is not easy to produce high molecular weight polymer with this method due to the presence of water and other byproducts (Auras, Harte and Selke, 2004; Vink *et al.*, 2003). The resultant polymer is a low to intermediate molecular weight material.

Meanwhile, ring-opening polymerization through lactide formation is the method that NatureWorks LLC uses to produce commercial PLA. This method was developed by DuPont in 1954 (Garlotta, 2002). In this process, lactic acid is polymerized into PLA pre-polymer with low molecular weight. Then the pre-polymer is depolymerized using a catalyst under low pressure and is transformed to lactide. Lactide, the cyclic dimer of lactic acid, is formed by the condensation of two lactic acid molecules as follows: L-lactide (two L-lactic acid molecules), D-lactide (two D-lactic acid molecules) and meso-lactide (one L-lactic acid and one D-lactic acid molecule) as in Figure 2.6. After lactide is sorted into a low D-lactide stream, and a high D-lactide and meso-lactide stream, high molecular weight PLA is produced by using ring opening of L-lactide (Garlotta, 2002).

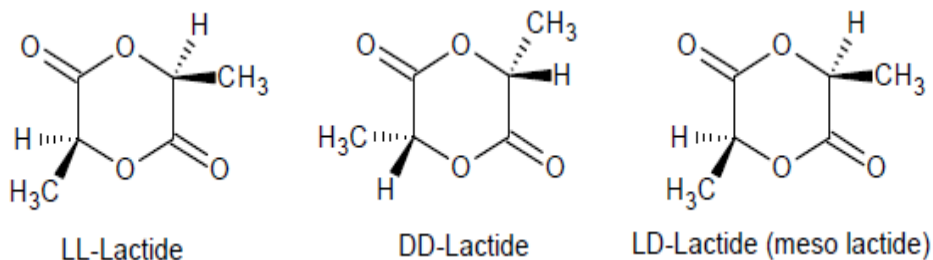


Figure 2.6: Chemical structure of LL, DD and LD-Lactid

2.2.1.3 Properties of PLA

2.2.1.3.1 Physical and Chemical Properties

PLLA is semi-crystalline polymer and PDLLA is an amorphous polymer. The best solvent for PLA is chloroform and other solvents also can be used such as chlorinated or fluorinated organic compounds, dioxane, dioxolane, and furan (Sangeetha *et al.*, 2018). Table 2.1 shows summary of some of the physical and chemical properties of PLA.

Table 2.1: Selected physical and chemical properties of PLA.

Properties	PDLA	PLLA	PDLLA
Solubility	All are soluble in benzene, chloroform, acetonitrile, tetrahydrofuran (THF), dioxane etc., but insoluble in ethanol, methanol, and aliphatic hydrocarbons		
Crystalline structure	Crystalline	Semi-crystalline	Amorphous
Melting temperature (T _m)/ °C	~180	~180	Variable
Glass transition temperature (T _g)/ °C	50-60	55-60	Variable
Decomposition temperature/°C	~200	~200	185-200
Elongation at break/ (%)	20-30	20-30	Variable

The homopolymer of PLA is a white powder at room temperature with T_g and T_m values of about 55°C and 175°C, respectively. High molecular weight PLA is a colorless, glossy, rigid thermoplastic material (Xiao *et al.*, 2012). It is degraded by

simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyze this hydrolysis (Garlotta, 2002).

2.2.1.3.2 Mechanical Properties

Mechanical properties reflect the cumulative effects of molecular weight, orientation of molecular chains and crystallinity that develop throughout the process. Depending on parameters such as crystallinity, polymer structure, molecular weight, processing and material formulation such as plasticizer, blends or composites, the mechanical properties of PLA can vary starting from soft and elastic materials to stiff and high strength materials (Sangeetha *et al.*, 2018).

PLA has great mechanical properties especially tensile Young's modulus, tensile strength and flexural strength contrasted to traditional polymers, such as polypropylene (PP), polystyrene (PS) and polyethylene (PE). Nonetheless, the elongation at break and the impact strength of PLA were lower than those of PP and PE (Hamad *et al.*, 2015).

PLA has the required mechanical properties for many applications. Figure 2.7 demonstrates a correlation of the mechanical properties of PLA to those of other common commodity plastics. It is clear from the figure that PLA most nearly looks like PS, being characterized by a high modulus and elongation at break. So that, PLA is a generally brittle plastic but however possesses good strength. Clearly, from an applications point of view, PLA should be able to compete with PS (Dorgan, Lehermeier and Mang, 2000).

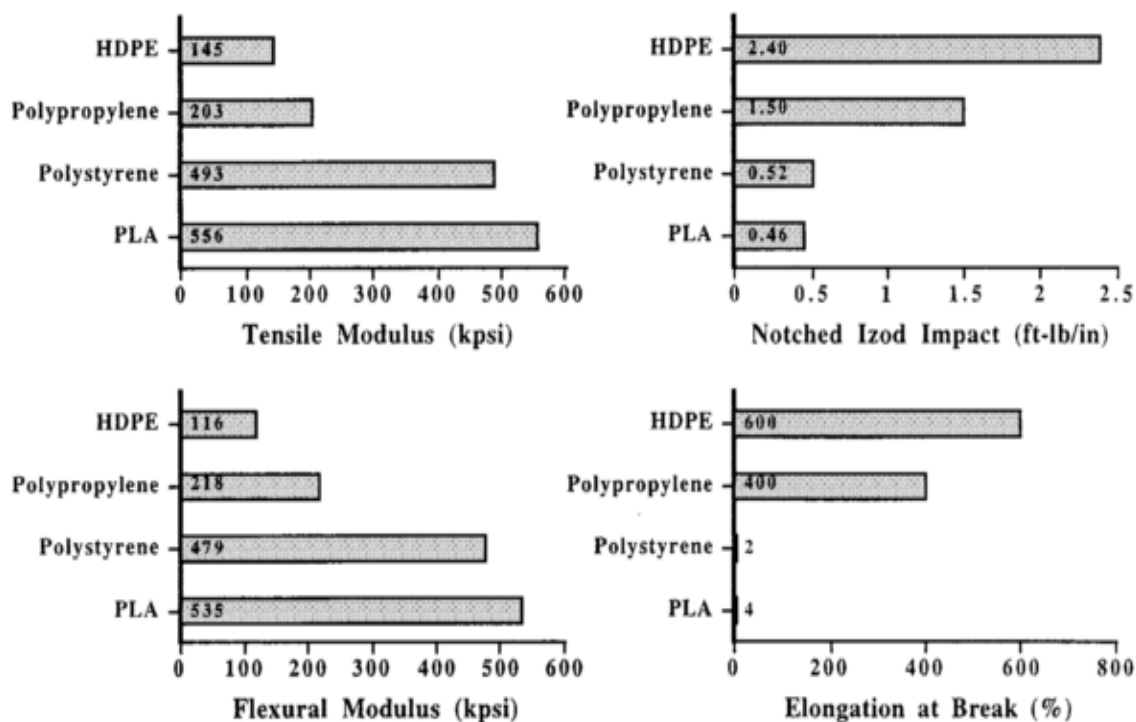


Figure 2.7: Mechanical properties of PLA compared to other common plastics (Dorgan, Lehermeier and Mang, 2000).

Additionally, additives such as plasticizer and impact modifier can help to modify the mechanical properties of PLA to meet the necessities for various applications. The additives should be non-toxic especially if it is intended to be used in medical or food contact. It is because of any additives used in PLA possibly soon leaks into environmental due to biodegradability and bio-compatibility of the PLA. Plasticizers are ordinarily employed modifiers to enhance the flexibility and decrease the cracking tendency of PLA product.

2.2.1.3.3 Thermal Properties

The thermal properties of PLA is rely upon its molecular characteristics, for example, crystalline thickness, crystallinity, spherulite size, morphology, and degree of chain orientation (Sangeetha *et al.*, 2018). PLA is a semi-crystalline or amorphous

polymer with a T_g and T_m of approximately 55°C and 180°C, respectively (Hamad *et al.*, 2015). They require handling or processing temperatures more than 185–190°C. However, PLA undergoes thermal degradation at temperatures above 200°C by hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intramolecular trans-esterification reactions. At these temperatures, unzipping and chain scission reactions leading to loss of molecular weight, as well as thermal degradations, are known to happen (Garlotta, 2002). PLA degradation is dependent on time, temperature, low-molecular-weight impurities, and catalyst concentration (Garlotta, 2002).

According to Baker *et al.*, (2008), the variety of the reported T_g of PLA due to the sample history, the technique used to observe T_g , the molecular weight of the polymer, the presence of plasticizers and polymer architecture. In addition, the T_g is sensitive to the tacticity of the PLA backbone, and for stereoregular polymers, it is sensitive to the degree of crystallinity. Furthermore, T_g is additionally controlled by the proportion of different lactides present. PLA resins containing over 93% of L-lactic acid are semi- crystalline, however when with 50–93% is completely amorphous (Sangeetha *et al.*, 2018). Hence, the values of T_g are different. These resulted in PLA polymers with a wide range of hardness and stiffness values.

2.2.1.4 Approaches to enhance properties of PLA

PLA is one of the important and the most promising commercially available. Generally, PLA possesses good mechanical and physical properties so that it is considered as an alternative in replacing petroleum-based plastics. However, there are some limitations of PLA such as brittleness, glassy polymer with poor elongation at break and low toughness that limits its applications (Xiao *et al.*, 2012).

The development or modification of PLA is needed to improve thermal and mechanical properties and hence can improve the flow properties such as viscosity. The approaches to improve mechanical properties and rheological properties and process-ability of PLA can be made such as (Ozdemir and Hacaloglu, 2017):

- 1) Blending of PLA to elastomer
- 2) Blending of PLA with impact modifier
- 3) Copolymerization with other polymer
- 4) Adding plasticizer

2.2.1.4.1 Blending of PLA with elastomer

Elastomers are polymers with low young modulus and high yield strain. If an amorphous polymer has a T_g below room temperature, it will have elastomer properties that consists of soft and rubbery segments. By introducing of elastomer to PLA, the PLA can enhance elastic and ductile properties (Kaavessina *et al.*, 2012).

Thermoplastic polyurethane (TPU) elastomer is an example of elastomer that recently used to be blended with PLA. TPU is made up of soft and hard segments. PLA/TPU blends has decrease the T_g and T_m . However, the crystallinity seems to increase with decreasing PLA content in the blends. Miscibility of the blends is increases with increasing polyurethane content (Jašo *et al.*, 2014).

2.2.1.4.2 Blending of PLA with impact modifier

Blending PLA with an impact modifier can be used to enhance and increase the toughness of PLA. Although some interesting and noteworthy results have been reported on toughening PLA, there are still some defects. For instance, some blends

were immiscible and compatibilizers were needed to increase compatibility to access the desired mechanical properties.

Besides, elongation at break was low as to limit other potential applications of PLA and high toughening modifier content increased the cost of blends. Furthermore, some PLA blends improved impact strength at the expense of reducing the strength and modulus. Therefore, a more economic and effective toughening modifier for PLA is still needed (Song et al., 2014).

Song et al. (2014) also reported that the stress-strain curves showed that the brittle behaviour of PLA changed to ductile failure with the addition of impact modifier. The brittleness of PLA was decreased while elongation at break increased with the incorporation of increasing amount of impact modifier. Thus, it can be concluded that the impact modifier have the ability to increase the toughness of PLA.

2.2.1.4.3 Copolymerization with other polymer

Various lactate copolymers have been developed thus far to tune the properties of PLLA and cope with different applications. Two synthetic approaches are available for the copolymerization. Firstly is ring opening of copolymerization of L-lactide with other monomers such as ϵ -caprolactone, glycolide and dipsipeptides and secondly is use of new cyclic monomers consisting of lactate and other monomer units.

Furthermore, there is an approach by blending PLA with poly(ethylene glycol) (PEG) multiblock copolymers with predetermined block lengths were synthesized by polycondensation of PLA diols and PEG diacids. The blending of these copolymers offers the chances to combine the hydrophilicity of PEG and biodegradability of PLA. It

is also can reduce the crystallinity of the copolymers and make a wide range of polymeric materials for medical applications (Luo et al., 2002).

2.2.1.4.4 Adding plasticizer

A plasticizer is a material incorporated in a plastic to increase its workability and its flexibility or elongation. The function of plasticizer on the molecular chain is to weaken or rupturing of selective bonds between molecules while leaving others strong to make processability of the material such as shaping or molding is possible. Free volume also will be increased as plasticizer added and hence the mobility of the chain becomes easier.

Moreover, flexibility and ductility of the PLA can be improved. The choice of plasticizer to be used for PLA is limited by the requirement of the application. In food packaging, only non-toxic substances were approved for food contact as plasticizing agents. The plasticizer should be compatible with the PLA and stable at the elevated temperature used during processing.

The presence of plasticizer will decrease the T_g of the polymer. Typical amounts of plasticizer that required are from 10 to 20 wt% to provide a substantial reduction of the T_g of the PLA matrix and adequate mechanical properties. The plasticizer and PLA must be miscible and thus creating a homogeneous blend. The plasticizer should not be too volatile because this would cause evaporation to occur at the elevated temperatures used at processing (Ren, Dong and Yang, 2006).

2.3 Poly(ethylene glycol) (PEG)

A lot of researchers studied incorporation of various materials to the PLA to overcome the impact and toughness problem properties of PLA. Among them, polyethylene glycols (PEG) is the most efficient plasticizer for PLA because it has low molecular weight (Serra *et al.*, 2014).

PEG is a hydrophilic, biocompatible polymer that has been used for many applications from industrial manufacturing to biotechnology (Serra *et al.*, 2014). PEG is also considered has good compatibility with PLA due to the terminal hydroxyl groups of PEG molecules can react with the carboxyl groups of PLA molecules as the structure of the PEG is depicted in Figure 2.8 (Li *et al.*, 2016).

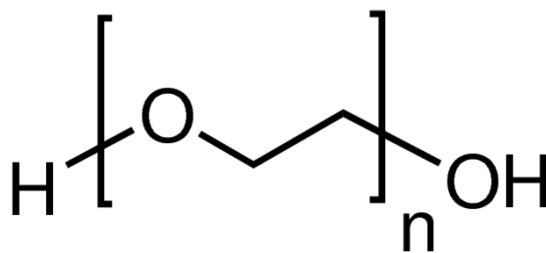


Figure 2.8: Structure of PLA.

PEG affects thermal characteristics of PLA by disturbing the intermolecular forces. Plasticized PLA usually shows single glass transition temperature (T_g) and increase the chain mobility and this segmental motion allows the rearrangement of chains which leads to decrease in T_g and melting temperature (T_m) and improve in crystallization (Barkoula *et al.*, 2008; Ozdemir and Hacaloglu, 2017; Serra *et al.*, 2014). Furthermore, the enhancement mobility of PLA can makes the tensile strength and elasticity modulus decrease and increasing in elongation at break by the addition of PEG to PLA (Barkoula *et al.*, 2008; Li *et al.*, 2016).