

SCHOOL OF MATERIALS AND MINERALS RESOURCES ENGINEERING
UNIVERSITI SAINS MALAYSIA

MODIFIED POLY (LACTIC ACID) (PLA) FILAMENT FOR 3D PRINTING WITH
IMPROVED THERMAL PROPERTIES

By

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DECLARATION

I hereby declare that i have conducted, completed the research work and written the dissertation entitled: “Modified Polylactic acid (PLA) filament for 3D printing with improved thermal properties. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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Equation 3.1: Degree of crystallinity

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LIST OF ABBREVIATIONS

ASTM	American Society For Testing and MAterials
CO ₂	Carbon dioxide
DSC	Differential Scanning Calorimetry
FDM	Fused deposition Modelling
FTIR	Fourier Transform Infrared
Mw	Weight average Molecular weight
PCL	Polycaprolactone
PE	Polyethylene
PEG	Poly (ethylene glycol)
PEO	Polyethylene oxide
PGA	Polyglycolic acid
PHB	Poly (3-hydroxybutyrate)
PLA	Poly (lactic Acid)
PS	Polystyrene
UTM	Universal Testing Machine
XRD	X-Ray Diffraction

LIST OF SYMBOLS

$^{\circ}$	Degree
$^{\circ}\text{C}$	Degree celcius
Min	Minutes
E_b	Elongation at break
mm	Milimiter
cm	Centimeter
cm^3	Cubic meter
W_f	Weight fraction
MPa	Megapascal
KJ/m^2	Kilojoule Per square Meter
g	Gram
Mg	Miligram
g/cm^3	Gram per cubic centimeter
%	Percent
wt%	Percent by weight
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
ΔH	Melting enthalpy
T_{m1}	Melting peak 1
T_{m2}	Melting peak 2
rpm	Revolution Per minute

FILAMEN ASID POLYLAKTIK(PLA) DIUBAHSUAI UNTUK PERCETAKAN 3D DENGAN MENAMBAH BAIK SIFAT TERMAL

ABSTRAK

Dalam kajian ini, matlamat utama adalah untuk mengetahui kesan pemplastik dan penyepuhlindapan kepada sifat mekanik dan terma kepada struktur PLA. Gabungan PLA dengan pemplastik seperti polietilena glikol (PEG) disediakan dengan nisbah gabungan yang berbeza 100/0, 95/5 dan 90/10. Penyemperitan skru tunggal telah digunakan untuk menggabungkan komposisi untuk menghasilkan bahan-bahan untuk membentuk mampatan dan filamen untuk percetakan 3D. Diameter dai lain dihasilkan. Keputusan mendapati bahawa meningkatkan kandungan PEG akan mengurangkan kekuatan tegangan dan modulus tegangan dengan meningkatkan pemanjangan pada patah disebabkan oleh kesan pemplastik memberikan kelenturan kepada struktur PLA. Untuk sifat terma, analisis DSC menunjukkan penurunan suhu T_g dan suhu penghabluran sejuk (T_{cc}) apabila kandungan pemplastik meningkat yang membantu kepada peningkatan pergerakan rantai. Untuk meningkatkan sifat-sifatnya, proses penyepuhan telah dilakukan pada suhu 70 °C, 90 °C dan 120 °C selama 90 minit. Untuk pencetakan 3D, suhu katil telah digunakan untuk mengkaji pemindahan haba dari satu lapisan ke lapisan yang lain. Untuk sifat-sifat mekanik, hasil menunjukkan bahawa penyepuhlindapan pada 90 °C adalah suhu optimum yang meningkatkan kekuatan tegangan, pemanjangan pada patah dan modulus tegangan untuk penyepuhlindapan dan sampel percetakan 3D. Untuk sifat terma, analisis DSC menunjukkan pengurangan T_g dan T_m dengan pembentukan dua puncak lebur yang menunjukkan process mencairkan semula. Analisis XRD menunjukkan puncak kristal dikesan pada $2\theta = 16.9$ dan $2\theta = 19.3$ yang menunjukkan kristal terbentuk di dalam PLA. FTIR Analisis memperlihatkan pengesanan C=O, -CH dan C-C dan C-O-H menunjukkan kehadiran PEG dalam PLA struktur.

MODIFIED POLYLACTIC ACID (PLA) FILAMENT FOR 3D PRINTING WITH IMPROVED THERMAL PROPERTIES

ABSTRACT

In this research, the primary objective is to study the effect of plasticizers and annealing on mechanical and thermal properties of the PLA structure. The blend of PLA with plasticizers namely Poly (ethylene glycol) (PEG) is prepared with different blend ratio 100/0, 95/5 and 90/10. Single screw extrusion has been used to blend the composition to produce the materials for compression moulding and filament for 3D printing. Different die diameter has been used to produce the filament. It was found that increasing the PEG content will decrease the tensile strength and tensile modulus with increase the elongation at break. This is due to the plasticizer effect which reduces the glass transition temperature (T_g) and impart flexibility to the PLA structure. For thermal properties, the DSC analysis shows the decrease of T_g and cold crystallization temperature (T_{cc}) results as the plasticizer level increased to enhanced chain mobility. XRD analysis shows the smaller peak detects at 10% PLA/PEG blends and other blends shows amorphous graph. To improve the properties, annealing process has been done at temperature of 70 °C, 90 °C and 120 °C for 90 minutes. For 3D printing, bed temperature has been used to study the heat transfer from one layer to another. For mechanical properties, results shows that annealing at 90 °C is the optimum temperature which increase the tensile strength, elongation at break and tensile modulus for annealing and 3D printing samples. For thermal properties, DSC analysis shows the decrease of T_g and T_m with formation of double melting peak result in melt-recrystallization occur. XRD analysis shows the peak detects at $2\theta = 16.9$ and $2\theta = 19.3$ which indicate the crystal formed inside PLA. FTIR is been conduct to detect the presence of PEG inside the PLA which result in detection of C=O, -CH and C-C and C-O-H indicate the present of PLA and PEG in the blend.

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

In recent years, biodegradable polymer has received much attention due to its wide application especially in packaging and medical equipment. These polymers bring a significant contribution to the sustainable environment by reducing the waste from synthetic plastic materials. Currently, synthetic polymer create massive problem to the environment pollution in landfill waste and poses a threat to wildlife when dispose it to the nature especially sea. Other advantage of using biodegradable polymer is it can reduce the greenhouse gas emission and the landfill space. Moreover, as it been contact with the seawater, it can be dissolve naturally without need to undergoes any process. Today, there are many biodegradable polymers such as polycaprolactone (PCL), polyethylene oxide (PEO), poly (3-hydroxybutyrate) (PHB), and polyglycolic acid (PGA) but the most popular and important biodegradable polymers are Poly lactic acid (PLA).

Poly (lactic acid) (PLA) is one of the common thermoplastic produced by lactic acid which come from renewable resources such as corn. PLA can be prepared either by condensation polymerization of the free acid or by ring opening polymerization of the lactide. PLA was discovered in 1932 by Carothers (DuPont) who produced a low molecular weight product by heating lactic acid under vacuum. According to Bouapao et. al., (2009), PLA has stereoisomers due to chiral molecule of the lactic acid which will produce different type of poly lactic acid such as poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA). Isotactic and optically active PLLA and PDLA are crystalline, whereas relatively atactic and optically inactive PDLLA is amorphous. PLA is a partially crystalline

polymer with a glass transition temperature (T_g) in the range of 65–70°C and a melting temperature (T_m) around 160 to 170°C.

Biocompatibility as well as the dissolvability in the human body makes PLA suitable to be used in medical application such as tissue engineering through hydrolysis of ester backbone during the contact with system inside human body (Hamad et. al., 2015). In addition, other properties such as high clarity and good mechanical properties make PLA more popular in medical application especially in drug delivery system and implant in human body. Hamad et. al., (2015) stated that in term of tensile strength, young modulus and flexural strength, PLA is much better rather than polystyrene (PS) and polyethylene (PE). In food packaging, PLA has better permeability performance against transfer of gases, water vapour, and aroma molecules when compare with PE however it still considered low and need modification (Siracusa, 2012).

Despite its advantage, PLA possess some drawback such as rigid and brittle with low deformation at break. According to Bergsma et al., (1995), PLA also has low degradation rate which take place in the ester backbone that will take several years for it to fully decompose. This will affect the packaging and medical application in term of waste and dissolvability during its service life. In some application that require plastic deformation at higher stress levels, the low strength and toughness of PLA is limited its usage. In addition, PLA is slow crystallization rates which the product (especially injection molding) will become amorphous and hence give lower thermal resistance and barrier properties that limit the used in certain application. (Nanthananon et. al., 2015). Currently, research is focus on modification of PLA to improve its hydrophobicity and low affinity towards cell that elicits inflammatory response to living host. Unless the properties is been improved, this drawback will holds the advance of PLA to used widely in other application.

To enhance the properties of PLA, it can be blend with certain plasticizers. By blending with plasticizers, it can decrease the glass transition temperature (T_g), increase ductility by increase the free volume and improve the processing thermal of the PLA. To blend with PLA, some criteria of the plasticizer need to be met which is low volatility, compatible and biodegradable and most important is non-toxicity (Hansen, 2004). There are many example of plasticizer from biodegradables and non-degradable such as glycerol and citrate ester but the most suitable one is polyethylene glycols (PEG), especially low molecular weight PEG (Vieira et. Al., 2011). It has been reported that PEG is most suitable material that can be blend with PLA due to its miscibility and biodegradability. Miscibility is one of the key factors for the successful increase of tensile properties and decrease of T_g . In addition, PEG is a hydrophilic, biocompatible polymer that has been used for many applications from industrial manufacturing to biotechnology (Zalipsky and Harris (1997), Inada et. Al., (1995).

3D printing is one of the most widely used technologies in making product based on polymer materials. Basically, 3D printing is one of the methods to produce a prototype or complicated product in term of design that will reduce a cost and time compared to conventional processing such as moulding. There are variety of 3D printing technologies have been developed such as Fused Deposition Modelling (FDM), Fused Filament Fabrication (FFF), Selective Laser Sintering (SLS) and polyjet (Prashanth et. al., 2017). FDM process consists of the use of thermoplastic filament. The advantages of FDM are easy operation, high material utilization, high automation and flexibility (Pan et. al., 2016). At the moment, there is two of the most popular filament used for FDM which PLA and Acrylonitrile Butadiene Styrene (ABS). These filament is made from extrusion process with the die diameter is around 1.75 mm. then, the filament is heated to the melting point of the

materials through the nozzle, extruded layer by layer at the heated bed and create a 3D dimension object based on the design insert.

Although PLA has advantage of good formability when be fused and deposited during printing, the processability of the FDM using blend is still limited. The properties of the product such as tensile strength is low due to weakness point between layers when printing (Dawood et. al., 2016). Decreasing in tensile strength also might contribute by low crystallization rate properties of PLA. It is postulated that blends could improve the rate of crystallization however, the compatibility between polymer blends will play a crucial role.

In this study, PLA and PLA blends (with PEG as plasticizer) were prepared using 3D printing and the properties were compared with conventional processing using extrusion and compression moulding. To improve the mechanical properties of PLA and PLA blends, annealing at different temperature were applied in both processes. In 3D printing, bed temperature was set at different temperature to allow annealing during printing. The properties of the materials such as mechanical strength, thermal and physical properties were analysed.

1.2 PROBLEM STATEMENT

Nowadays, the plastic waste problem become one of the main problem the world is facing due to the increasing of consumption of plastic product from petrochemical. Furthermore, the decreased of raw materials from fossil fuels has made researcher to use a bioplastic as sustainable approach to reduce the waste and PLA has been used as it is biodegradable and environmental friendly (Potiyaraj, 2016).

A few issues arise when dealing with PLA. PLA is high brittleness and low heat distortion temperature which will decrease the mechanical and thermal properties of the PLA product. Furthermore, the potential thermal degradation at typical processing conditions that was also accelerated by the presence of ester groups that could be the potential transesterification reactions leading to a decrease of PLA molecular weights (Murariu et al., 2008). Nevertheless, the limitation in using FDM such as the printing part has weaker properties. Wang et. al., (2017) state that when comparing the injection molding and 3D printing which is FDM, the mechanical properties of FDM is weaker compare to injection molding due to the formation of void by incomplete diffusion at interfaces. In addition, the melt viscosity of PLA is not very shear-sensitive and the melt has relatively poor strength (Carlson et al., 1999). If the filament exhibits a low stiffness or high viscosity, buckling will occur just before the entrance to the liquefier, thus making FDM processing impossible. Filaments require a high stiffness and lower melt viscosity to a useable level (Masood et. al., 2005). In addition, PLA has low toughness and crystallization rates restrict its application especially in medical and packaging field.

The alternative approach has been used to overcome the drawback of PLA which is by blending with other materials to produce new materials with improved application. For example, the blending of PLA and thermoplastic polyurethane (TPU) will increase toughness (Li and Shimizu, 2007). In this experiment, plasticizer has been chosen to blend with PLA which is polyethylene glycol (PEG). The properties of PEG such as hydrophilicity and biocompatibility make its suitable candidates to be blend with PLA (Noori and Ali, 2014). PEG also increase the flexibility and ductility of the glassy polymer but the challenge is the miscibility between the material that can affect the mechanical, thermal and morphology of the blend. The most important thing is to used biodegradable polymer rather than non-degradable. According to Sin et. al., (2012), to maintain the biodegradables of PLA it must be

blend with renewable or degradable resources polymer. Another method is by annealing the PLA, annealing is heat treatment which is used to recrystallize the structure after the processing to increase its properties.

In this study, by blending with plasticizer such as poly (ethylene glycol) (PEG), PLA crystallization rate can be improved and chain mobility can be enhanced to become more flexible. Another method used which is annealing to increase the crystallinity and strength of the PLA. The aim of this study is to improve thermal properties of PLA by blending with other materials and annealing.

1.3 RESEARCH OBJECTIVE

The main purpose of this research is as follows:

- I. To produce modified PLA filament for 3D printing
- II. To determine optimum thermal parameter for obtaining satisfactory mechanical properties.
- III. To access the effect of Annealing temperature on sample of conventional method and 3D printing
- IV. To compare the processing properties of conventional method and 3D printing properties

1.4 THESIS OUTLINE

Chapter 1 begins by introducing general overview of research, including the problem statement, which motivated this research. Research objectives are inserted next, followed by flow and organization of the thesis.

Chapter 2 describes literature connected to this study, involving a number of previous publications and discoveries substantial to the research.

Chapter 3 outlines the materials involved in the research and methodologies in order to prepare and execute the research work.

Chapter 4 reports the findings and results on the research. After that, the findings are compared and discussed accordingly, covering from processing, tensile and thermal properties.

Chapter 5 summarises the conclusions of outcomes from previous chapters in this research

CHAPTER 2

LITERATURE REVIEW

2.1 FUSED DEPOSITION MODELLING (FDM)

2.1.1 INTRODUCTION

Fused deposition modelling (FDM) is one of the 3D printing types which can be classified as rapid prototyping. FDM is widely used in design and product development processes especially in medical equipment and the food packaging. Another type of 3D printing which is competitive with other FDM machine such as stereolithographic and selective laser sintering. Both type also applied in medical field that relate with scaffolds and hard or soft tissue (Drummer et. al., 2012). The concept of FDM is such as the process involve in making a product or prototype part by using the filament.

Yen et. al., (2016) state that 3D printer based on the FDM technology is divided into two layers: the host computer and the bottom control. The host computer mainly runs three-dimensional designing software, slicing software, printing control software and so on. The bottom control includes embedded microcontroller, main board, stepping motor, motor driver, limit switch, thermoplastic material extruder, printing platform, temperature sensor and so on. Filament will be in form of semi molten and shape like a wire. The main working parts of the FDM 3D printer such as the heater and liquefier that melt the filament so that it can be arrange according to the shape, the nozzle part will extrude or push out filament when in melt conditions, the platform act as a base for the filament to shape the part of the product, the wheels will drive the filament into the heater from the cartridge and the last one is the piston which will move the platform in z-axis easily for the filament to be draw (Liou, 2007).

Through the use of layer by layer accumulating of specific material to produce three-dimensional physical model, 3D printing is an innovative manufacturing technology which

takes advantage of the CAD model. There is no need to develop new mould in the entire product manufacturing process, and the mould obtained by three-dimensional solid modelling of computer can print products directly, so it is possible to achieve product rapid manufacturing. The FDM 3D printer which is a rapid prototyping printer based mainly on printing plastic with plasticity is the most rapid development and the most mature technology in the current 3D printing market, and it is also the most widely applied 3D printer currently.

2.1.2 PROCESSING

In the FDM process, parts are fabricated by extruding a molten filament through a heated nozzle in a prescribed pattern onto a platform. The filament wire consists of polymer or other materials that have been heated up at tip of the nozzle where the filament is been extrude out. As the material is deposited, it cools solidifies and bonds with the adjoining material. When one whole layer is deposited, the base plate moves down by an increment equal to the height of the filament and the next layer is deposited. The nozzle will move in x and y direction to printing the part or product layer by layer (Sun et. al., 2008). FDM prototypes can be viewed as composites structures composed of partially bonded filaments. The shaped of the prototypes or product can become simple or complexes depend on the 3D drawing applications. This process requires minimal manpower and is increasingly used to fabricate customized products for engineering as well as medical applications (Weng et. al., 2016).

Longwei et. al., (2006) explain about FDM process which begin in printing raw material of the FDM 3D printer where it gets into the feeding pipe through the wire feeder. Then, it enters the heating pipe through the transition pipe, and then the thermoplastic material is heated in the heating pipe which regulates heating temperature with feedback regulation via thermistor. Squeezed by the non-melting material, the material of heating and

melting parts squeezes out the thermoplastic filament of predetermined diameter from the nozzle. Another studies which is Too et. at., (2002) also state that fused deposition modelling process of 3D printing begin by deposits molten thermoplastic material such as PLA and ABS which common material used in FDM. The material will be extruded from nozzle head, fabricated or form the product layer-by-layer. They generally rely on some form of stepper-motor/belt drive system to move the print head in the x-y axis, as material is expelled, forming the particular shape desired. Another stepper-motor, with some form of direct drive gear or threaded rod serves to raise and lower the print bed, creating the desired layering of material. Another motor with a tensioning/drive system is used to move raw material in the form of a plastic filament through the hot-end, which heats the material to a liquid state, before it is expelled through a precisely machined nozzle (Hernandez, 2015).

The influence of the nozzle structure on the FDM printing is mainly the internal flow structure of the nozzle and the control of heating temperature of the nozzle and also the different pressure difference in each flow generated by flow fields in different flows. Longwei et. al., (2006) also state that the temperature of the nozzle affects various performance of material, such as cohesiveness, accumulation resistance, wire flow, extruded wire width and so on. For one thing, if the temperature is too slow, it will lead to partial solid material, as a result, too large viscosity of material will affect the velocity of wire and even the block nozzle. If the temperature is too high, it will lead to partial liquid material, as a result, the wire material appears sallow and increasing mobility and also too fast extruded speed, which can't control the wire precision accurately. In such a system, there are both theoretical device limitations on precision motor step size, nozzle width, hot-end temperature sensor accuracy as well as practical expectations for variation. Loose belts, inaccurate filament sizing, and nozzle clogging can all contribute to variation of the product during processing. The nozzle flow mainly applies Teflon material which has acid-base resistance

and various organic solvent resistance characteristics and even almost insoluble in all solvents (Pan et. al., 2016).

2.1.3 EFFECT OF BED TEMPERATURE

Heat beds are used because they dramatically improve print quality by keeping the extruded plastic warm and thus preventing warping. Warping is a common condition caused by plastic on the edges of the part cooling down at an uneven rate when compared to the plastic inside of the part. The result is that corners warp up and deform your model. Derived from the raft, mouse ears are a clever and effective technique to make sure that the corners of your prints are well secured to the platform and do not lift. Although they offer greater adhesion by increasing the surface area for your part to grip onto the bed, they are not 100% effective without a heat bed. Sometimes the warping forces are simply too great and can overcome the mouse ears. Heat beds work to prevent this warping effect by keeping your part warm during the whole printing process which keeps the material at or above heat-deflection temperature (the temperature at which it is malleable). Keeping the parts in the heat-deflection range ensures that the part remains flat on the print bed. Heat beds, in combination with other tools to increase adhesion, and improve the printing quality.

Shafer et. al., (2016) suggest that to improve the adhesion of the first layer to the printing bed, several things can be done:

- Clean the printing surface to remove grease and residues from the bed;
- Levelling the printing bed so that the first layer is in close contact with the printing bed;
- Cover the printing surface with polymeric films or tapes like polyimide (PI) or blue painters tape;

- Slightly increase the tape surface roughness by sanding it;
- Apply water-soluble glues, hair sprays or special coatings;
- Print on a plate or film of the same material that is being printed;
- Print on cleated surfaces and increase the temperature of the printing bed to a recommended value for a given material

Spoerk et. al., (2018) studies about the adhesion forces for both PLA and ABS which show a strong dependence on the printing bed temperature. In the case of PLA printed on both bed materials up to a bed temperature of 60°C a steady rise in the adhesion force is observed. This increase can be attributed to an enhanced chain mobility of the deposited filament with higher temperatures (Forrest et. al., 1997). A point to highlight is the strong increase in the adhesion force as the temperature of the printed bed augments from 60 to 70°C. This is related to the glass transition temperature (T_g) of the printing material (60.6°C for PLA). Around the T_g , the segmental mobility of macromolecules is the highest for a material, which might result in enhanced adhesion between polymeric surfaces and other materials (vinogradov et. al., 1970), (Zeng et. al., 2006)). When the segmental mobility is increased, segments of the polymer chains can diffuse into the interface and the amount of adhesion is dependent on the extent of inter-diffusion and chain interpenetration into the interface. Spoerk et. al., (2018) also state that as the temperature keeps increasing beyond 70 °C, the adhesion forces drop independent of the printing bed material to roughly 50–60% of the forces for a bed temperature of 70 °C. The described decrease can be attributed to the changed interaction between the molten polymer and the printing surface.

The adhesion behaviour of ABS printed onto the glass or PI film exhibits a similar trend to that of PLA. The adhesion forces increase with rising temperature in a non-linear fashion with a maximum slightly above the T_g . As it was not possible to measure at temperatures

higher than 120 °C due to limitations of the printer bed heaters (Spoerk et. al., 2018). Another studies from Choi et. al., (2016) about the influenza of bed temperature on ABS material. It shows that the heat shrinkage of the ABS material substantially increased when the temperature of the bed was 40 °C or lower, which hindered the inter-layer adhesion. As the layers were separated from one another, the specimen manufacturing failed. When the temperature of the bed was 90 °C or lower, in comparison to 110 °C, the shape errors due to the heat shrinkage remarkably increased. Given the ABS' softening point being 104 °C, the bed temperature of 110 °C paralleled the ABS's softening point, which left a small temperature gap between the ABS material and the bed during the process, resulting in little heat shrinkage. By contrast, when the bed temperature was below 90 °C and much lower than that of the softening point, the significant temperature gap between the ABS material and the bed during the process seemed to increase the heat shrinkage to a great extent.

2.2 MATERIALS USED IN FDM

2.2.1 ACRYLONITRILE BUTADIENE STYRENE (ABS)

The name ABS polymer is derived from the initial letters of three main monomers – acrylonitrile, butadiene and styrene, used in its preparation. ABS is not a random terpolymer of acrylonitrile, butadiene and styrene. Industrially important ABS polymers are two-phase polymer systems that consist of dispersed polybutadiene (or a butadiene copolymer) rubber particles and a matrix of styrene acrylonitrile copolymer (SAN). The rubber particle is grafted with styrene and acrylonitrile to enhance their compatibility with the matrix. The fraction of rubber content in ABS is varies from 10-25% for common commercial grades and special grades, e.g. for blending with poly (vinyl chloride) can even contain over 45% rubber. The higher rubber content and the different type of polymer forming the continuous phase result

in the ABS polymers having a number of properties better than common grades of high-impact polystyrenes (Hashim et. al., polymer).

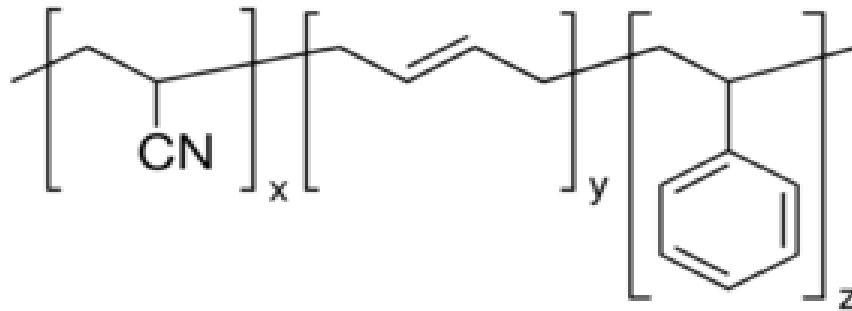


Figure 2.1: The structure of ABS polymer (Chanda and Roy, 1993)

There are two most important ways of producing ABS polymers which is (1) blend of styrene-acrylonitrile copolymer with butadiene-acrylonitrile rubber and (2) inter-polymers of polybutadiene with styrene and acrylonitrile which is now the most important types. A typical blend would consist of 70 parts styrene-acrylonitrile with ratio of (70:30) copolymer and 40 parts butadiene-acrylonitrile (65:35) rubber (Chanda and Roy, 1993).

ABS resins are composed of over 50% styrene and varying amounts of butadiene and acrylonitrile. Kulich et. al., (2002) state that there are three commercial processes for manufacturing ABS which are emulsion, mass, and mass-suspension. Styrene provides rigidity and ease of processability, acrylonitrile offers chemical resistance and heat stability, and butadiene supplies toughness and impact strength. ABS having high rubber content possesses higher impact strength than those with low content of rubber. Increase in rubber content results in greater ductility of these blends. Large-volume applications for ABS resins include plastic pipe and automotive and appliance parts. Although ABS has many desired properties as engineering thermoplastic, it's still has some limitation for example, easily burn with high flammability value and poor resistance to outdoor UV light (Chanda and Roy,

1993). It can be further blended with other materials to introduce new and improve resin grades.

According to Kulich et. al., (2002), the presence of SAN grafted onto the elastomeric component, usually polybutadiene or a butadiene copolymer, compatibilizer the rubber with the SAN component. Property advantages provided by this graft ter-polymer include excellent toughness, good dimensional stability, good processibility, and good chemical resistance. The system is structurally complex. This allows considerable versatility in the tailoring of properties to meet specific product requirements. Numerous grades of ABS are available, including alloys and specialty grades for high heat, flaming-retardant, or static dissipative product requirements. Good chemical resistance combined with the relatively low water absorptivity (<1%) results in high resistance to staining agents.

The critical thermal properties for ABS are heat distortion, coefficient of linear thermal expansion, thermal endurance, thermal conductivity, and specific heat. In general, plastics have significantly higher thermal expansion coefficients than metals. Consequently, in applications where parts are constrained, thermal stresses must be accommodated in part design or expansion may induce failure in the part. This property is especially important in ABS products designed for electroplating (Moh et al., 1997). Svec et al., (1990) state that the thermal properties of ABS polymers are characterized mainly by the glass transition temperature, T_g . An increase in temperature of the material leads to a decrease in the tensile strength and an increase in the ductility and toughness. However the modulus of elasticity in tension decreases. Kim and Kang (1995) have studied the glass transition temperature after reprocessing three ABS polymer five times using an extruder. The glass transition temperature of the SAN phase did not change after repeated extrusions. Other mechanical properties such as strain to failure, tensile strength and hardness changed slightly but impact

resistance of all materials decreased due to degradation of the polybutadiene component of ABS.

ABS can be processed by compression and injection molding, extrusion, calendaring, and blow molding. Post-processing operations include cold forming, painting, and adhesive bonding. As a “bridge” polymer between commodity plastics and higher performance engineering thermoplastics, ABS has become the largest selling engineering thermoplastic. Thus, the scope of possible applications is broadened and resulting in overall demand growth for ABS (Jin et al., 1998).

2.2.2 POLYLACTIC ACID (PLA)

According to Auras (2010), Poly (lactic acid) (PLA) polymers are biodegradable polyesters derived from lactic acid (LA) or 2-hydroxy propionic acid, which is generally obtained by bacterial fermentation of carbohydrates from agricultural crops such as corn, potato, and cassava. PLA is the best known polymer and belongs to the family of aliphatic polyesters commonly made from acids, which include polyglycolic acid or polymandelic acid, and are considered biodegradable and compostable. Garlotta (2001) state that PLA can be synthesized by two polymerization routes, poly-condensation of lactic acid or ring opening polymerization of lactide. Lactic acid is been used as a feedstock for PLA production. Figure below shows the chemical structure of Polylactic acid (PLA):

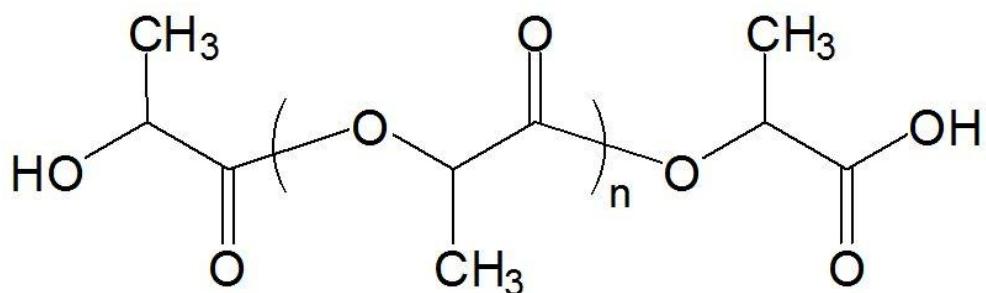


Figure 2.2: The chemical structure of Polylactic acid (Garlotta, 2001)

The production of lactide from lactic acid as well as in catalyst become of economic interest since recent advances have been achieved through the development for ring-opening polymerization in bulk to form PLA (Hartmann, 1998). Lactic acid can exist in two main optical configurations which is *L* or *D*. PLA polymers can be produced with varying degrees of *L* or *D* lactic acid. According to Saeidlou et. al., (2012), lactic acid has two active forms which is *L*-lactic acid and *D*-lactic acid which is due to the asymmetric carbon atom. Pure *L*- or *D*- referred to as PLLA and PLDA respectively. PLA can be named as poly (XY-lactic acid), in which X and/or Y are the amount of *L*- and *D*-lactic acid, respectively. *D*-lactic acid mainly comes from the racemic lactic acid (LD configuration). So, a PLA polymer's label as poly (96% *L*-lactic acid) will be composed of 96% *L*-lactic acid and 4% *D*-lactic acid (Auras, 2010). PLA resins containing more than 93% *L*-lactic acid are semi crystalline while PLA resins with 50–93% *L*-lactic acid are strictly amorphous. Furthermore, all these varies lactic acid are mainly targeted for particular application such as injection moulding, biaxial oriented films, injection stretch blow moulded bottles, fibre melt spinning, and spun bond items depend on degree of *L*- and *D*-lactic acid that depend on the application.

PLA can be a well-behaved thermoplastic with a reasonable shelf life for most single-use packaging applications and when disposed of properly will hydrolyse to harmless natural products. It could be a technical and economic solution to the problem of the eventual of the

very large amount of plastic packaging used around the world. Garlotta, (2001) also state that due to it high strength, high modulus and good clarity. Nowadays, consumer and companies are interested in bio-friendly packaging materials for food packaging applications because of their compostability, recyclability, and sustainability. They becoming more aware of waste problems come from the plastic product itself and demand the use of bio friendly packaging materials for example the food packaging. The selection of food packaging polymers not only depends on the evaluation of polymer standard properties, but also on the recyclability and sustainability of these polymers to be able degrade and become more eco-friendly. As a consequence, PLA have received increased attention in the last decade due to its natural biodegradability.

Since the 1970, PLA has been used extensively for medical applications because of its bioresorbable and biocompatible properties in the human body and made it suitable choice for drug delivery system. Auras et. al., (2003) state that PLA is highly hydrolysable in the human body can be made from annually renewable resources to yield the structure for use in either the packaging field or the biocompatible /bio absorbable medical device market. PLA is degraded by simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyse this hydrolysis. The rate of degradation is dependent on the size and shape of the structure, the isomer ratio, and the temperature of hydrolysis Auras (2010). In particular, polylactide and copolymers of polylactide with other aliphatic polyesters have been widely examined for their use in biomedical application. Furthermore, it also has high potential to replace the petroleum-based polymer in making a plastic product due to good optical, physical, mechanical, and barrier properties (Saeidlou et. al., 2012).

PLA is a comparatively brittle and stiff polymer with low deformation at break. By modify these properties, PLA is able to compete with other more flexible commodity polymers such as polyethylene, polypropylene, PET or PVC. PLA closely resembles to

polystyrene, being characterized by a high modulus and low elongation to break (Dorgan et. al., 2000). That is to say, PLA is a relatively brittle plastic but possesses good strength which from applications perspective, PLA should be able to compete with polystyrene. The barrier properties of PLA against organic permeants, such as ethyl acetate and d-limonene, are comparable to PET (Auras et. al., 2006). Lim et. al., (2008) state that semi crystalline PLA exhibits T_g and T_m which is similar to many thermoplastic polymers. Above T_g which is around 58 °C. PLA is rubbery while below T_g , it becomes a glass which is still capable to creep until it is cooled to its transition temperature at approximately (-45 °C), below which it behaves as a brittle polymer. The T_g of PLA is dependent on both the molecular weight and the optical purity of the polymer. Auras et. al., (2005) state that un-oriented PLA is quite brittle, but possesses good strength and stiffness. Oriented PLA provides better performance than oriented PS, but comparable to PET. Mechanical properties such as tensile and flexural modulus of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and PS, but the Izod impact strength and elongation at break values are smaller than those for these polymers (Dorgan et. al., 2000).

2.3 POLYLACTIC ACID (PLA) BLENDS

The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. For packaging and hygiene applications, only nontoxic substances approved for food contact and personal care can be considered as plasticizing agents. There are numerous other demands put on the plasticizers, but the following ones are especially important. The plasticizer should be miscible with PLA, 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 et al., 2006). Furthermore, the plasticizer should not be prone to migration because this would cause

contamination of the materials in contact with the plasticized PLA. It would also cause the blended material to regain the brittleness of pure PLA. It is well-known that for instance the monomer, lactide itself, is considered as one of the best plasticizers for PLA (Sinclair, 1993, Jacobsen and Fritz, 1999), but it has the disadvantage to migrate very rapidly at the polymer surface. Therefore, different plasticizer systems have been studied to find out other alternatives: glucose monoesters and partial fatty acid esters (Sheth et al., 1997), glycerol esters (Ljungberg and Wesslen, 2002), citrates (Baiardo et al., 2003) and even higher molecular weight plasticizers like poly(ethylene glycol) (Kulinski and Piorkowska, 2005, Pillin et al., 2006, Shuichi Tanoue et al., 2006).

2.3.1 PLASTICIZER

Reinecke et. Al., (2011) state that plasticizer is an additive that is mixed with a polymer in order to reduce polymer–polymer chain secondary bonding to make it more flexible, durable, and processable. Furthermore, plasticizers also provide mobility for the macromolecules by lowering the second-order transition temperature of the macromolecule which result in a softer and more easily deformable Polymer. Reinecke et. Al., (2011) also state that Plasticizers are generally low molecular weight (M_w) liquids that is added to a material (usually a resin or elastomer) that will make the material softer, more flexible. Plasticizers are incorporated in the amorphous parts by forming secondary bonds to polymer chains and spread them apart which increase the free volume and decrease the glass-transition temperature (T_g) of the polymer. According to Godwin, (2011), free volume is measure of internal space available within a polymer. When increased the free volume, molecule or polymer chain will have high movement due to more space provided that will make polymer system more flexible while structure and size of any crystalline part remains unaffected.

Rosen (1993), state in her studies about the primary role of all plasticizers in the processing method. When incorporated into a polymeric material, a plasticizer improves the workability and flexibility of the polymer by increasing the intermolecular separation of the polymer molecules. Plasticization efficiency can be seen in the amount of plasticizer presence in polymer structure that will reduce the T_g (Senichev and Tereshatov, 2004). Lowering the glass transition temperature (T_g) will improve the flexibility and processability of polymers as plasticizer is low molecular weight non-volatile additives. Moreover, polymer toughness and flexibility is improved and lower thermal processing temperatures can be employed (Zhu et al., 2002).

Plasticizers are also used with other polymer types due to the uprising development of plasticizer parallel with commodity polymer for example polyvinyl chloride (PVC) which

most widely used plasticized polymer. PVC is a synthetic resin made from the polymerization of vinyl chloride. At its pure form, PVC is lightweight and rigid plastic. PVC can be divided into two categories which are un-plasticized PVC and plasticized PVC. For un-plasticized PVC, free volume arises from the movement of polymer end groups, side chain and internal movement. Because of its excellent plasticizer compatibility characteristics, PVC can be modified through the polymer backbone such as adding more side chains or end groups or incorporate small molecule with flexible end groups that can move and rotate to make it plasticized polymer (Godwin, 2011). The amount of plasticizer added to a polymer varies depending on the effect required and small addition of plasticizer may improve the workability of the polymer melt. Un-plasticized PVC (U-PVC), is used in applications such as pipes, siding, and window profiles while plasticized PVC used in automotive interior trim, jacketing, cable insulations, and PVC floorings (Godwin, 2011).

2.3.2 FUNDAMENTAL

According to Immergut et. al., (1965), there are two main groups of plasticizers which are internal and external plasticizers.

i. Internal Plasticizer

Internal Plasticizers involve in the change or alteration of polymer or monomer chemical structure which is called copolymerization. By modify the chemical structure of the polymer, the flexibility of the polymer may be increased. This can be done either by random copolymerization or side chain grafting. Immergut et. al., (1965) state that internal plasticizers is where the second monomer is copolymerized into the polymer structure and thereby making it less ordered, more difficult for the chains to fit closely together and softens the polymer by lowering the glass temperature (T_g) or the modulus. From Vieira et. al

(2011) studies, Internal plasticizers generally have bulky structures that provide polymers with more space to move around and prevent polymers from coming close together. Polymer molecules and become part of the product, which can be either co-polymerized into the polymer structure or reacted with the original polymer. Therefore, polymer softer due to low T_g and elastic modulus

Internally plasticized systems consisting of simple random copolymers, designed for use in flexible plastic articles, which more ordered copolymerization would imbue a higher degree of crystallinity thereby giving polymer tendency to increase the flexibility. The latter lowers the glass transition temperature (T_g), and reduces crystallinity by disrupting physical interactions between the chains. Internal plasticizers generally have an unsatisfactorily narrow use temperature range, since they soften more sharply than analogous externally plasticized systems or polyblends (mixtures of two or more polymers). Usually the internal plasticizer is a monomer whose polymer has good low temperature properties. Another type of internal plasticization involves the introduction of side chains (either substituents or grafted branches) that can be caused by lowering of the forces between the polymer chains owing to the bulkiness of the substituent groups. Another example of internal plasticization is the alkylation of polyamides which gives elastic fibres by lowering crystallinity and T_g through reduction of intermolecular forces (Immergut et. al., 1965).

ii. External Plasticizers

The external plasticizers are the most important as far as commercial application is concerned. External plasticizers are low volatile substance that added into the polymer where the plasticizer molecule interact with polymer chains but not chemically attach to them by primary bond and can be lost by evaporation, migration or extraction (Vieira et. al, 2011). This chemical interacts with the polymer only physically, via its solvent capabilities. This type of

plasticization is usually done at elevated temperatures. This is because they provide more satisfactory combinations of properties and allow the manufacturer more formulating flexibility than if the plasticizer were added during the polymerization process. From Immergut et. al., (1965) studies, External plasticizers are compounds of low vapour pressure which without chemical reaction, interact with the polymer, mainly at elevated temperature, by means of their solvent, or swelling power. A distinction should be made between solvent plasticizers and non-solvent plasticizers.

There are two groups of external plasticizers, primary and Secondary. A primary plasticizer, when added to a polymer, causes elongation and softness to be increased. These changes are brought about by mechanisms described where under suitable conditions the polymer would eventually dissolve in the plasticizer. With a crystalline or semi crystalline polymer, there are some compounds which enter both the crystalline (ordered) and the amorphous (disordered) regions. Vieira et. al, (2011) also state that primary plasticizer is sole plasticizer that used as main element in processing with the polymer. The plasticizer will gel the polymer rapidly in normal processing temperature and the polymer will soluble at high concentration of the plasticizer.

A secondary plasticizer, when added to the polymer alone, does not bring about these changes and may have limited compatibility with the polymer. Immergut et. al., (1965) state that only the amorphous regions are penetrated and compound may be considered as a non-solvent plasticizer However, when added to the polymer in combination with a primary plasticizer, secondary plasticizers enhance the plasticizing performance of the primary plasticizer. This is because it has lower gelation capacity and limited compatibility with the polymer (Vieira et. al, 2011). Secondary plasticizers are also known as extenders or softener. Such softeners are used sometimes as diluents for the primary plasticizer. The benefit of using external plasticizers, compared to internal ones, is the chance to select the right