

**SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING**

**UNIVERSITI SAINS MALAYSIA**

**EFFECTS OF ANNEALING TREATMENT ON THERMAL AND  
MECHANICAL PROPERTIES OF POLY (LACTIC ACID)**

**By**

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "Effects of Annealing Treatment on Thermal and Mechanical Properties of Poly (lactic acid)". 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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## LIST OF ABBREVIATIONS

PLA	Poly (lactic acid)
XRD	X-ray Diffraction
DSC	Differential Scanning Calorimetry
TS	Tensile strength
EB	Elongation at break

## LIST OF SYMBOLS

$\text{kJ/m}^2$	Kilo Joule per meter square
MPa	Mega Pascal
$^{\circ}\text{C}$	Degree Celsius
%	Percentage
$T_m$	Melting temperature
$T_g$	Glass transition temperature

# **KESAN PENYEPUHLINDAPAN TERHADAP SIFAT TERMA DAN MEKANIKAL POLIASID LAKTIK**

## **ABSTRAK**

Tujuan kajian ini dijalankan adalah untuk mengkaji sifat terma dan mekanikal penyepuhlindapan poliasid laktik. Pelet PLA telah dikeringkan dalam ketuhar pada suhu 80°C sekurang-kurangnya selama 4 jam. PLA yang telah dikeringkan kemudiannya dibentuk menjadi kepingan ujian hentaman dan tegangan dengan menggunakan mesin pengacuan suntikan. Kemudian, penyepuhlindapan telah dijalankan terhadap sampel pada suhu 70°C, 80°C, 90°C, 100°C, 110°C, 120°C dalam ketuhar selama 90 minit. Selepas spesimen dikeluarkan daripada ketuhar, spesimen telah menjalani dua jenis teknik penyejukan yang berlainan. Teknik penyejukan yang pertama adalah pelindapkejutan di dalam bekas yang dipenuhi dengan kiub ais selama lima minit. Teknik penyejukan yang kedua adalah proses penyejukan pada suhu bilik dalam desikator. Kekuatan hentaman sampel diperolehi daripada ujian hentaman dengan menggunakan penguji hentaman. Tahap penghabluran dan sifat terma sampel penyepuhlindapan telah diuji dengan kalorimeter pengimbasan perbezaan (DSC). Selain itu, X-ray pembelauan sinaran dilakukan untuk menentukan perubahan dalam sifat-sifat selepas mengalami proses penyepuhlindapan. Didapati bahawa kekuatan hentaman berkurang dengan kenaikan suhu penyepuhlindapan. Penghabluran telah dipertingkatkan bagi sampel penyepuhlindapan dan menunjukkan sifat terma dan mekanikal PLA yang lebih baik.

# **EFFECTS OF ANNEALING TREATMENT ON THERMAL AND MECHANICAL PROPERTIES OF POLY (LACTIC ACID)**

## **ABSTRACT**

The purpose of this study is to investigate the thermal and mechanical properties of annealed PLA. PLA pellets has been dried in an oven at 80°C for at least 4 hours. The dried PLA were then moulded into impact and tensile test pieces using injection moulding machine. Then, the samples were subjected to 70°C, 80°C, 90°C, 100°C, 110°C, 120°C in oven for 90 minutes. After the specimens were removed from the oven, the specimens were undergone two different type of cooling techniques. First cooling technique was quenching into basin which filled with ice cubes for five minutes. Second cooling technique was cooling process at room temperature in desiccator. The impact strength of annealed samples was obtained from the impact test by using impact tester. The degree of crystallinity and thermal properties of annealed samples were characterized by Differential Scanning Calorimetry (DSC). Besides, X-ray Diffraction (XRD) analysis is done to determine the crystallinity changes after subjected to annealing process. It is found that impact strength decreased with increment of annealing temperatures. Crystallinity has been improved for annealed samples and exhibit better thermal and mechanical properties of PLA.

# CHAPTER ONE

## INTRODUCTION

### 1.1 Research background

Biopolymers or natural polymers can be defined as polymers formed under natural conditions during the growth cycles of all organisms. Whereas, petroleum based polymers are not degradable polymers due to the non-degradable behaviour of hydrocarbon plastic materials. This petroleum based polymers often used in daily life but it will end up as a plastic waste. Plastic waste are the main problems in providing pollutions. The invention towards degradable plastics helps to reduce the problems. The huge amount of plastic waste that resulted from dramatic increase in polymer production give rises to serious environmental concerns as plastic does not degrade. (Niaounakis, 2014)

Niaounakis (2014) added over-consumption of plastic around the world due to the advantages of plastic. Plastics are known as versatile, lightweight, flexible, moisture resistant and relatively inexpensive depends on their chemical structure. Plastic wastes discarded every year can vary in size from large containers, fishing nets or even microscopic plastic pellets. Most of these plastic wastes can be found everywhere including lands, rivers and oceans which polluting the environment. This phenomenon known as plastic pollution.

Marine life on shore and off shore including whale, sea lions, birds and microscopic organisms called zooplankton, are known to have suffered from entanglement and ingestion of plastic waste in the ocean. Some plastic pellets can be fragmented into particles which is thinner than the diameter of a human hair. As those pieces of plastic waste cannot be seen and floating around within the ocean, marine

animals and zooplankton could be affected as they are easily ingest those pieces of plastic wastes. (Martin et al., 2014)

Besides, petroleum based polymers are non-degradability, non-renewability, release the greenhouse gases and diminish petroleum resources during production and incineration of conventional synthetic petrol based polymers have restricted the versatility and applications of these polymers. In fact, the disposal of petroleum based plastics and the restricted availability of petrochemical resources are a global concern and it causes the biopolymers has been a focus of academic and industrial research in the context of sustainable development and reduced the impact on the environment. (Mohanty et al., 2002)

Polymer from renewable assets has gained world-wide interest and pulling in an increasing amount of attraction because of environmental concern and the fact that petroleum resources are depleting. Increasing society concern in terms of environmental aspects and sustainability along with addition of the strict governmental regulations in the non-degradable thermoplastics usage help to facilitate the development of biodegradable plastics. (Endres and Siebert-Raths, 2011)

The only sustainable solution is degradation of these plastic materials into small molecular weight fragment. Naturally, biodegradable polymers exist. Biodegradable polymers are characterized as those polymers that experience microbial induced chain scission prompting the mineralization. They act as renewable resources for polymer manufacturing as biodegradation process which eventually will be converted into carbon dioxide, methane, water, biomass and other natural substances. Besides, biodegradable polymers allow shorter time intervals to cycle and hence help in the reduction of waste volume of synthetic polymers which are not biodegradable. (Kaplan, 1998)



According to Chen et al (2003), the most common biodegradable polymers are poly (lactic acid), poly-caprolactone (PCL) and polyglycolic acid (PGA).

Poly (lactic acid) is one of the most semi-crystalline plastic with good properties that can be competing with recent commodity plastics as alternative materials. By having high molecular weight, PLA will consist high mechanical properties and melt strength during processing. PLA is relatively brittle and stiff material but possesses good strength. (Ahmed and Varshney, 2011)

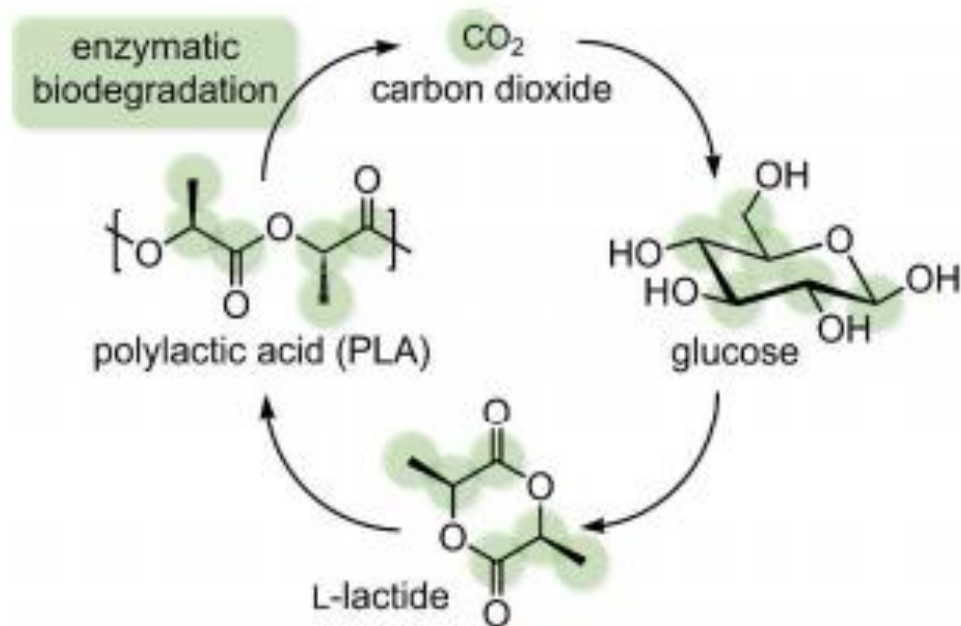
Majid et al (2010) stated that PLA offers good mechanical properties such as high tensile strength and elastic modulus, a high degree of transparency, good biocompatibility and excellent biodegradability. These factors allow it to replace conventional polymers in numerous applications such as packaging, extruded products and thermoformed containers.

In addition, PLA also can be used in biomedical applications such as medical implants, sutures and drug delivery system due to the biodegradability, biocompatibility and good mechanical properties. PLA becoming the most important bio-based polyester due to its favourable properties as support material for tissue generation. (Arshady, 1991)

However, similar with other polyester polymers, PLA inherently slow in crystallization to develop significant crystallinity. PLA could not crystallize and remained amorphous when the cooling rate is higher than 10°C/ min. In the processes such as injection moulding, where the cooling rate is high, it is much more difficult to develop significant crystallinity and thus modification is needed in order to increase the crystallization rate of PLA as well as the degree of crystallinity of PLA. (Zhang et al., 2012)

As a result, there are many approaches had been taken in order to increase the degree of crystallinity of PLA such as addition of nucleating agent, incorporation of plasticizer which increase the polymer chain mobility and enhance the crystallinity of PLA or modify the moulding condition for example like using lower cooling rate. (Vieira et al., 2011)

In this recent years, PLA is becoming increasingly popular due to the eco-friendly, biocompatible, process ability and energy savings of its characteristics. Besides, it is one of the bio-based polymers that can be easily compostable comes from derivation of renewable resources. The interest in using polymeric materials derived from renewable resources increases day by day because of the considerably improved environmental awareness of society and concerns about the depletion of petrochemical based material. (Majid et al., 2010) Figure 1 shows the full lifecycle of poly (lactic acid) generally relies upon enzymatic biodegradation.



**Figure 1 : The full lifecycle of poly (lactic acid) (Martin et al., 2014)**

## 1.2 Problem Statement

The term morphology in polymer often refers to crystallinity, dimensions, shape, distribution and orientation of the crystallites and amorphous phase. (Allin, 2001)

Morphology will occur during polymer processing like injection moulding. Macromolecules in injection-moulded parts will present an order due to the thermomechanical history. In injection moulding, a hot polymer melt rapidly fills a cavity to get desired product shape. During cooling stage, a thin section at cavity entrance will start to slowly solidify until it reaches the sufficient thickness before the product is injected from the mould. (Pantani et al., 2005)

According to Endres and Siebert-Raths (2011), most biopolymers exhibit slow crystallization during conventional processes like injection moulding. During conventional melt- processes, polymer crystals do not form at a sufficiently high rate to complete processing in a time similar to that of petroleum-based products. Currently, some polyesters, starch blends and cellulose derivatives are the only biopolymers that can be processed with similar cycle times by injection moulding as the comparative materials PP, PE-HD and especially ABS. Thus, PLA consume a large amount of time and energy due to PLA's slow crystallization during solidification. However, like other semi-crystalline thermoplastic, crystallinity of PLA can be improved by annealing process.

There is a critical issue concerning the slow crystallization rate of PLA. As a semi-crystalline polymer, it possesses almost no crystallization proceeds under the fast cooling such as a practical moulding condition. Without the usage of nucleating agent, PLA become amorphous even at a very low cooling rate. This low crystallization PLA exhibit poor heat resistance as well as mechanical properties that turns PLA into a much less competitive with the conventional polyolefins in the fibre and packaging applications. (Zhang et al., 2012)

Heat-treating is a term used to describe all of the controlled heating and cooling operations performed on a material in the solid state for the purpose of altering its microstructure and/or properties. Heat treatment involves the use of heating or chilling, normally to extreme temperatures, to achieve a desired result such as hardening or softening of a material. Proper heat treating requires precise control over temperature, time held at a certain temperature and cooling rate. (Salamone, 1996)

It is well known which semi-crystalline polymers generally change their physical properties when they are heated to elevated temperatures far below the melting point. These changes are related to alterations of the morphological structure and they indicate that in most cases, the polymeric sample is not in a state of thermodynamic equilibrium. Therefore the heat treatment results in a reorganization of the structure leading to a state of order with a lower free energy. (Lv et al., 2015)

Annealing is a secondary process which takes place after the formed part is produced. Parts that contain stresses or strains set up in the material during its fabrication will be removed. During annealing, moulded parts will be brought to a certain temperature and kept there for a time before cooling. By exposing plastic to elevated temperature, annealing process can improve the degree of crystallinity and dynamic mechanical properties by providing necessary energy and time for the molecular chains to be arranged in a more perfect crystal form. Annealing process may change the crystal structure, the degree of crystallinity, the perfection of the crystals, the orientation of both crystalline and amorphous phase, the contiguous structural morphology and the number of tie chains between the crystallites. (Srithep et al., 2013)

### **1.3 Research Objectives:**

Below are the several objectives of this research:

- i. To investigate the effect of annealing on the thermal properties of PLA.
- ii. To determine the effect of annealing on the mechanical properties of PLA.

### **1.4 Outline of Thesis Structure**

**Chapter One** presents a general introduction of biodegradable.

**Chapter Two** discuss on relevant literature review of on biopolymers, poly (lactic acid), annealing process and physical and mechanical characterization methods

**Chapter Three** covers the detail of materials, fabrication method, annealing process as a post treatment and analysis methods used to generate data.

**Chapter Four** has results and discussion on the effect of annealing process on thermal and mechanical properties of PLA. Besides, the effect of cooling medium on thermal and mechanical properties of annealed samples also were discussed.

**Chapter Five** presents the conclusion of research study with add-on some recommendation for future research.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Biopolymers

Polymers have made some positive impact by steadily replaced many conventional materials in various application. In automotive industry, for example, production process simplification, cost and weight reduction can be done by replacing metal with plastic. However, due to rising oil prices phenomena, has been urge researchers from all over the world to find ways for improvement. They do many researches on development of biopolymers. (Endres and Siebert-Raths, 2011)

According to Kaplan (1998), biopolymer are polymers that occur in nature including polyester. Those monomers of polyester are derived from renewable resources by chemical transformation. It can be synthesised from renewable feedstock like corn starch. Hydrolysis and fermentation process of feedstock will take place for bio-conversion into lactic acid. Through polymerization process, these lactic acids can be converted into poly (lactic acid).

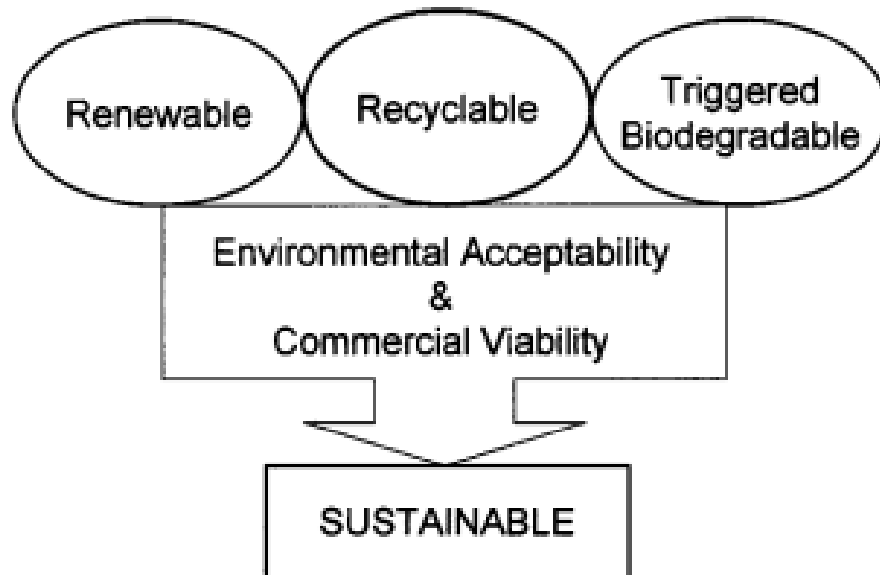
Besides, copolymer of PLA such as polycaprolactone (PCL), polyethylene oxide (PEO) and polyglycolic acid (PGA) also exhibit good biodegradability. (Chen et al., 2003) Table 1 shows properties and application of PGA, PLA and PLGA.

**Table 1: Properties and application of PGA, PLA and PLGA.****(Endres and Siebert-Raths, 2011)**

Polymer	Crystallinity	Tg (°C)	Degradation rate	Typical applications
PGA	Highly crystalline	35-40	2-3 months	Suture, Soft anaplerosis
PLA	Semicrystalline	60-65	More than 2 years	Fracture fixation, Ligament augmentation
PLA (L form)	Amorphous	55-60	12-16 months	Drug delivery system
PLGA	Amorphous	45-55	1-6 months	Suture, Fracture fixation, Oral implant, Drug delivery microsphere

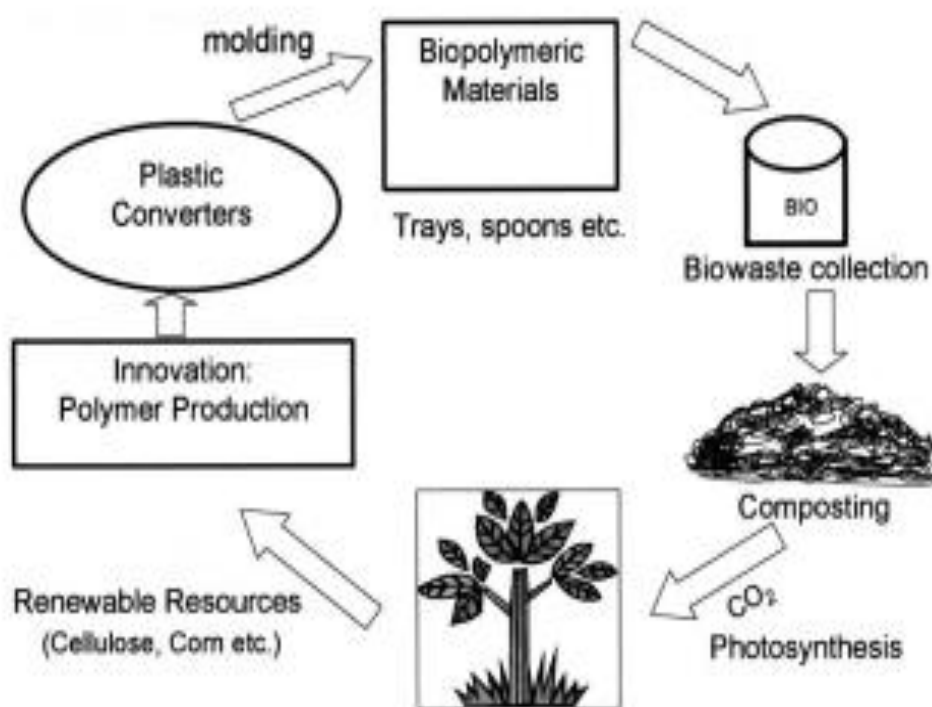
In order to compete with non-renewable petroleum-based polymers, Mohanty et al. (2002) said that, biopolymer must provide a great potential with their properties. Sustainability is the most crucial factor needed by the experts in industry. In this case, the best candidate to keep this sustainability is bio-derived thermoplastics. Made from renewable resources make them as environmental friendly materials since they are easy to degrade and recycle. The most common used aliphatic polyesters group are made

from hydroxyl acids which are compostable and biodegradable. Figure 2 shows concept of sustainability of biopolymers. Biopolymer products also maintain carbon dioxide neutrality as shown in Figure 3. (Mohanty et al., 2002)



**Figure 2: Concept of sustainability of biopolymers. (Mohanty et al., 2002)**





**Figure 3: Carbon dioxide sequestration. (Mohanty et al., 2002)**

## 2.2 Poly (lactic acid)

Poly (lactic acid) is a biodegradable polymer. PLA pellets were transparent, with a glass transition between 60°C until 65°C, a melting temperature 173°C-178°C and tensile modulus between 2.7 until 16 GPa. It is derived from biomass is a typical bio-plastic that can be made in a three-step process of fermentation, separation and polymerization. PLA can be processed like all other thermoplastic polymers with extrusion, injection moulding, blow moulding and thermoforming into various products like packaging. (Thomas et al., 2012)

Advantage of PLA is easy to degrade by simple hydrolysis of ester bond and does not require any assistance of enzymes to activate the degradation reaction. (Nascimento et al., 2010) Besides, it can be recycled and decomposed like all other organic matter. The recycled lactic acid can be reintroduced into the polymerization process of PLA. (Thomas et al, 2012)

Disadvantage of PLA is the poly (lactic acid) product does not suitable for the long term application because the natural matrix degrades over the time with the degradation of the ester bond unless it blend with other material for improvement. Low resistance to conditions of high heat and humidity and low heat distortion temperature (HDT) also the disadvantages of PLA. (Yu et al., 2006)

Thomas et al (2012) also discussed that although PLA is more expensive than many petroleum-derived commodity plastics, but the production is increased due to its biodegradable and biocompatible properties. The demand for corn is growing as corn is used for bioethanol and corn-dependent commodities.

PLA is quite brittle, low impact strength and elongation at break but it has good strength and stiffness compared to high density polyethylene. In contrast, PLA possess high modulus of elasticity that can be improved by increasing crystallinity, drawing and fibre reinforcement. PLA also excellent in odour and flavour barriers and heat stability. (Perego et al., 1996) Various properties of PLA were discussed in Table 2.

**Table 2: Properties of PLA (Technical Data Sheet of NatureWorks LLC)**

Property	Typical value
Specific gravity	1.24
Melt Flow Rate, MFR (g/10min)	14
Melting temperature, $T_m$ (°C)	145-160
Glass transition temperature, $T_g$ (°C)	55-60
Yield strength (MPa)	62
Flexural strength (MPa)	108
Notched Izod Impact strength (J/m)	16

PLA is widely used in medical application. Due to its ability to degrade by simple reaction of hydrolysis, it can avoid inflammatory reaction and transform into nontoxic sub-products to be eliminated by normal cellular activity and urine. Besides, its monomer lactic acid has a great worldwide demand due to its versatile applications. It can give a great advantage for metabolic function of cells. Its availability in small size help it to easily permeate through the lipid membrane and capable to enter the cells. This lactate will convert into glucose and serve as an energy substrate. (Farah et al., 2016)

Products of PLA can be easily recycled after use or hydrolysed back into its monomer. PLA is best for pharmaceutical, biological and medical applications as it is a

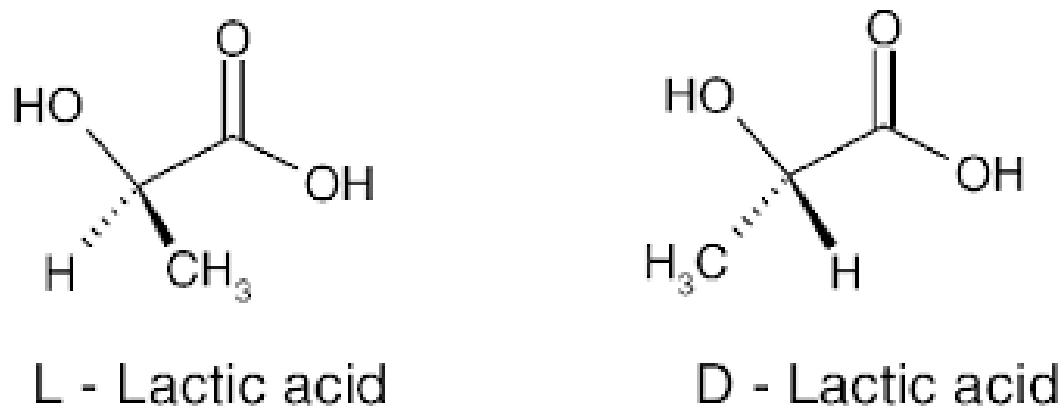
renewable, bio-compatible and biodegradable thermoplastic. Even though its application is good for environment, the price is high compared to others petrochemical synthetic polymer. High cost can be one of the factor that reduce the existence of PLA in market. ( Auras et al., 2011)

### **2.3 Synthesis of PLA**

Poly (lactic acid) is one of biodegradable polymer in this era globalization. It is a bio-derived polymer from renewable resources. Corn and sugar beets are currently utilized as feedstock in the commercial production of PLA resin. Basically, renewable resources will undergo fermentation process involve specific fungi before being polymerize into PLA through ring-opening polymerization. PLA has emerged as an alternative polymer to PE and PS as it has been found to have similar characteristics. (Perego et al., 1996)

Rathin and Michael (2006) stated that lactic acid (2-hydroxypropanoic acid), the monomer of PLA, exist with the presence of chiral carbon atom in two enantiomeric forms shown in Figure 10. L- and D- lactic acid provide different effect on polarized light. Variable of PLA material properties can be derived depends on the proportion of isomers. PLA structures with high L-lactide contents can be used to produce crystalline polymers while the higher D-lactide PLAs are more amorphous. Generally pure polylactides, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA), are crystalline polymers while atactic polymer, poly-(DL-lactide) is an amorphous material. Thus, the ratio between and distribution of L- and D- lactic acid will affect the properties of lactic acid based polymers.

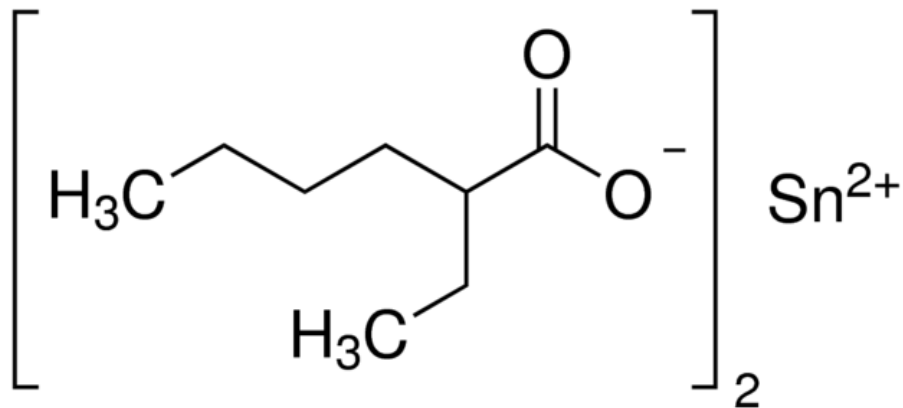
Ahmed and Varshney (2011) reported that L-lactic acid is a natural isomer while D- lactic acid is produced by microorganisms or by racemization. Figure 4 shows enantiomer of lactic acid structure.



**Figure 4: Enantiomer of lactic acid. (Cama et al., 2017)**

PLA can be synthesized with two different methods. First and the most common method used is the ring-opening polymerization (ROP). This is because high molecular weight of PLA can be produced by using this method. The mechanism involved in ROP can be ionic either is anionic or cationic or coordination-insertion, depending on the catalytic system. (Cama et al., 2017)

There are two common catalysts used in this polymerization method. They are aluminium and tin alkoxide. However, tin catalyst namely tin 2-ethylhexanoate, as shown in Figure 5 has been widely used in PLA synthesis. This is because it is more hydrolytically stable than aluminium catalyst and easier to handle during polymerization process. It is frequently used as initiator and co-initiator in PLA homopolymer synthesis. (Plackett and Vázquez, 2004)



**Figure 5: Tin(II) 2-ethylhexanoate. (Cama et al., 2017)**

Besides, Langford and Daniel (1996) discussed that polycondensation is a reaction between hydroxyl and carboxylic groups of lactic acid. Polycondensation used to produce low molecular weight of PLA. As a result, PLA will possess poor mechanical properties in brittle glassy condition which result a limitation for its applications unless improvement on molecular weight of the polymer is done with the help of external coupling agents.

The molecular weight of this condensation polymer is low due to the viscous polymer melt, the presence of water impurities, the statistical absence (low concentration) of reactive end-groups and the “back-biting” equilibrium reaction that form six-member lactide ring. Equilibrium needs to be shifted towards the product side by removal of water to produced high conversion and molecular weight. This polymerization requires long reaction times in combination with high temperatures. (Shin et al., 2011)

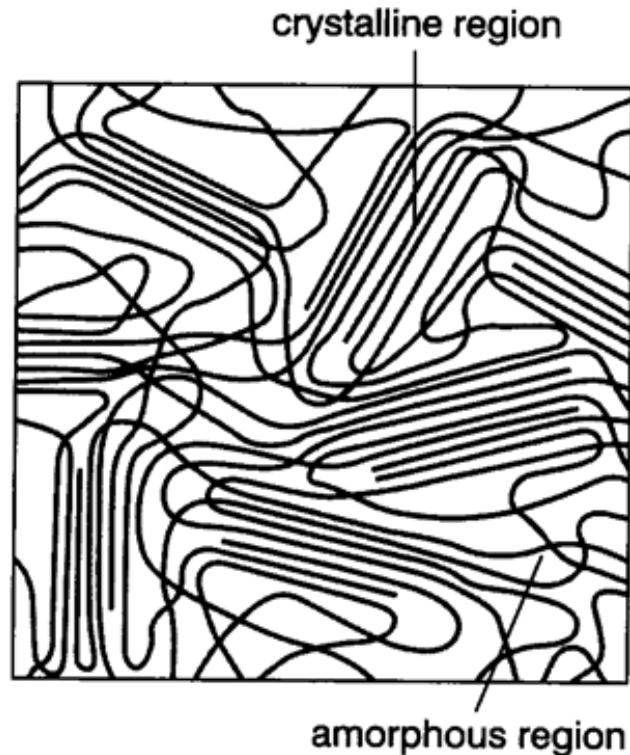
Nowadays, intensive research has been done to optimize PLA properties and to overcome the obstacles to engineering applications. High water vapor permeability is one of the obstacles for PLA application as a packaging material. Therefore, utilization of suitable coating is a successful method to increase the barrier properties. (Endres and Siebert-Raths, 2011)

The development of PLA based on molecular weight has been done to improve the properties. Further work by DuPont produced high molecular weight products that was patented in 1954 and Ethicon introduced high strength and biocompatible fibres for medical resorbable sutures in 1972. Now, NatureWorks LLC developed a continuous process for the high molecular weight of PLA from lactic acid. (Auras et al., 2011)

PLA prepared from polycondensation has low molecular weight and poor mechanical properties and therefore is not suitable for many applications. The commercial interest for solving this problem has increased because of the need of cost-effective approaches in the manufacturing of lactic acid based polymers with a high molecular weight. Solvent-assisted polycondensation is one way to overcome this problem. Besides, melt polycondensation followed by solid-state polycondensation and utilize the terminal groups of the prepolymer in linking processes with the help of linking agent. (Niaounakis, 2014)

## **2.4 Crystallinity of polymers**

Polymers exist both in crystalline and amorphous form called semi-crystalline polymers, as shown in Figure 6. Crystallization of polymers is a process for partial alignment of molecular chains to fold together and form ordered regions called lamellae. In liquid state, polymers composed of an irregular and entangled coil of long molecular chain. Some polymers retain such a disordered structure upon freezing and convert into amorphous solids. In other polymers, the chains rearrange upon freezing and form partly ordered and aligned regions. (Salamone, 1996)



**Figure 6: Crystalline and amorphous region in polymer. (Endres and Siebert-Raths, 2011)**

For semi-crystalline polymers, the degree of crystallinity is the most important characteristic. It affects hardness, Young's modulus, tensile strength and permeability. In particular, high degree of crystallinity of PLA has higher strength, good dimensional stability and chemical resistance. Less light can penetrate through the high degree of crystallinity polymer due to more aligned and ordered structure thus increase the opacity. (Auras et al., 2011)

#### **2.4.1 Crystallinity of PLA**

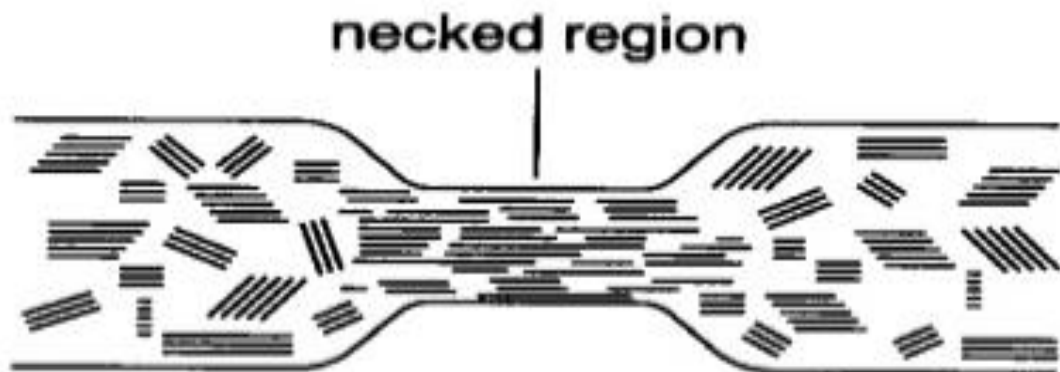
Crystallization rate of PLA is typically too slow to develop significant crystallinity unless the crystallization is induced by strain. In some process of PLA fabrication method, orientation is limited and the cooling rate is high bring a huge challenge to develop significant crystallinity. (Cipriano et al., 2014)



For example, injection moulding method. Most of previous study used annealing for injection moulded PLA specimen in order to induce the crystallization. Srithep et al. (2013) reported that crystallinity of PLA is influenced by different kind of factors. The significant factor is the relative amount of L-lactide acid to D-lactide acid.

#### 2.4.2 Crystallinity Improvement Techniques

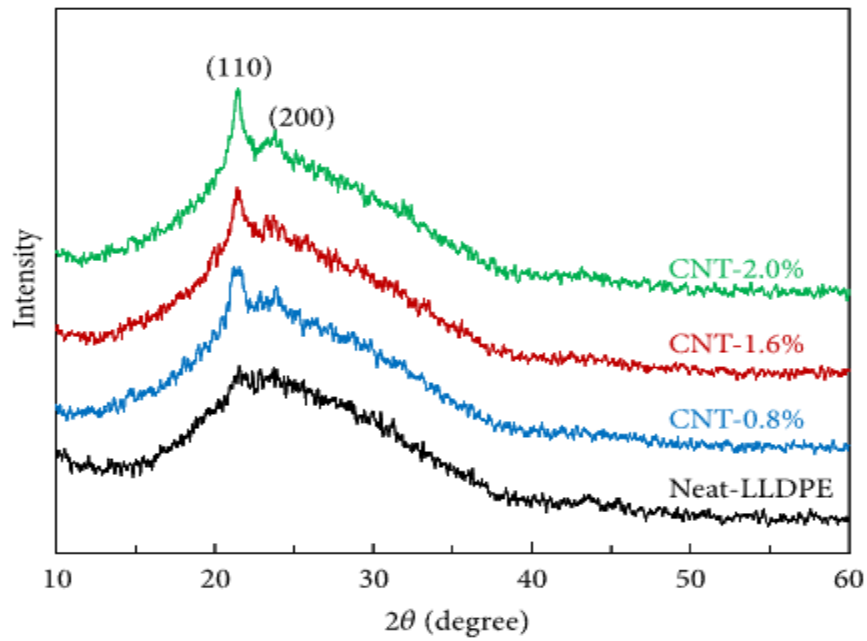
In polymer field, drawing usually refers to permanently deform the polymer in tension. It is corresponding to the neck extension process. During drawing, the molecular chains slip with each other and become highly oriented. As a result, degree of crystallinity will be increased. Drawing has been identified as an important stiffening and strengthening technique as it helps to improve mechanical strength and tensile modulus of polymer. However, it will depend on the extent of deformation of the material. For example, tensile modulus and strength values will be greater in the direction of deformation compared to other directions for materials drawn in uniaxial tension. Figure 7 shows neck formation during drawing process.



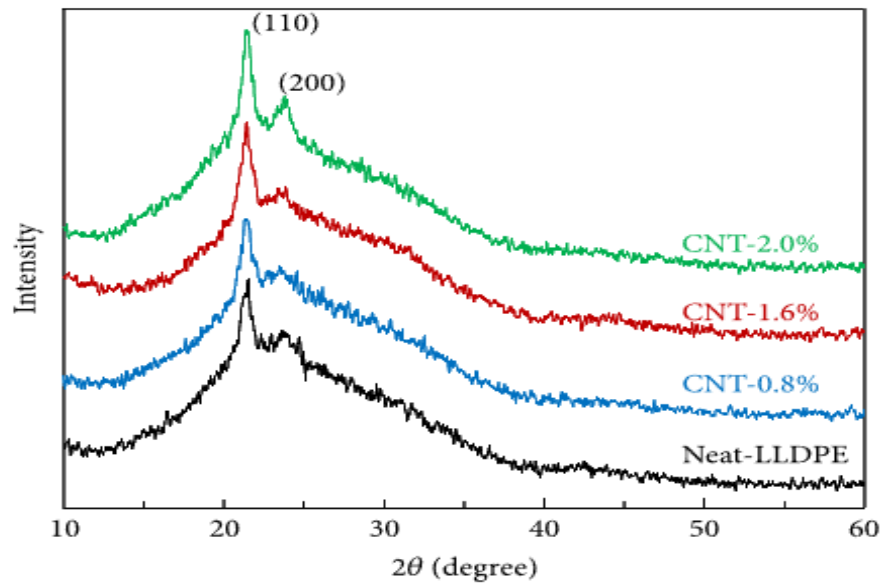
**Figure 7: Neck formation during drawing process. (Chung et al., 2001)**

According to Kim and Lee (2017), XRD pattern of LLDPE treated by heat drawing process as a function of the CNTs content shows increment in intensities of diffraction peaks compared to undrawn LLDPE fiber, as shown in Figures 8(a) and 8(b). This is

because the crystallinity was increased by orientation of polymer chain of LLDPE fiber due to the heat drawing process.



(a)



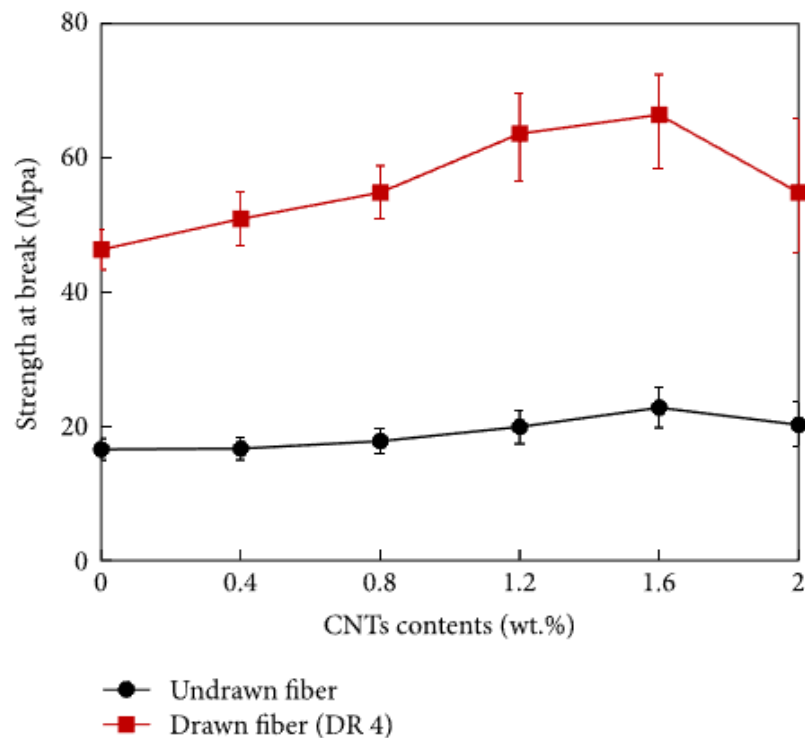
(b)

Figure 8: X-ray diffraction patterns of LLDPE fiber as a function of CNTs content:

(a) undrawn LLDPE fiber; (b) heat drawn LLDPE fiber.

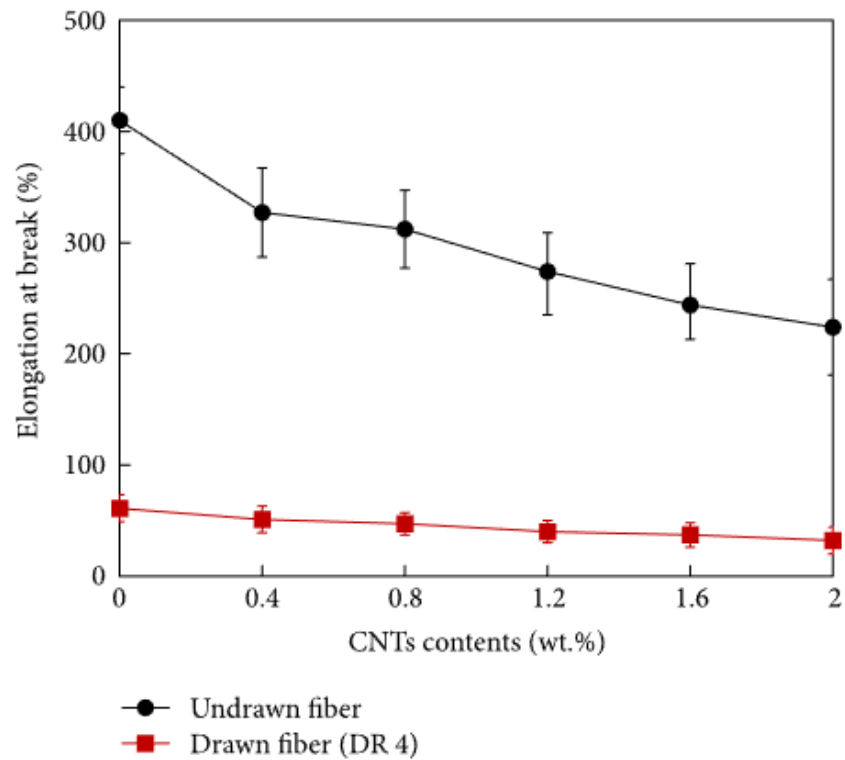
(Kim and Lee, 2017)

Kim and Lee (2017) added, heat drawing process improve mechanical strength and tensile modulus of LLDPE-CNTs fiber. Figure 9 shows tensile strength at break the neat-LLDPE fiber increased by 180% from 16.54 MPa to 46.33 MPa, whereas that of the LLDPE-CNTs 1.6 wt.% fiber increased by 191% from 22.78 MPa to 66.41 MPa after heat drawing process.



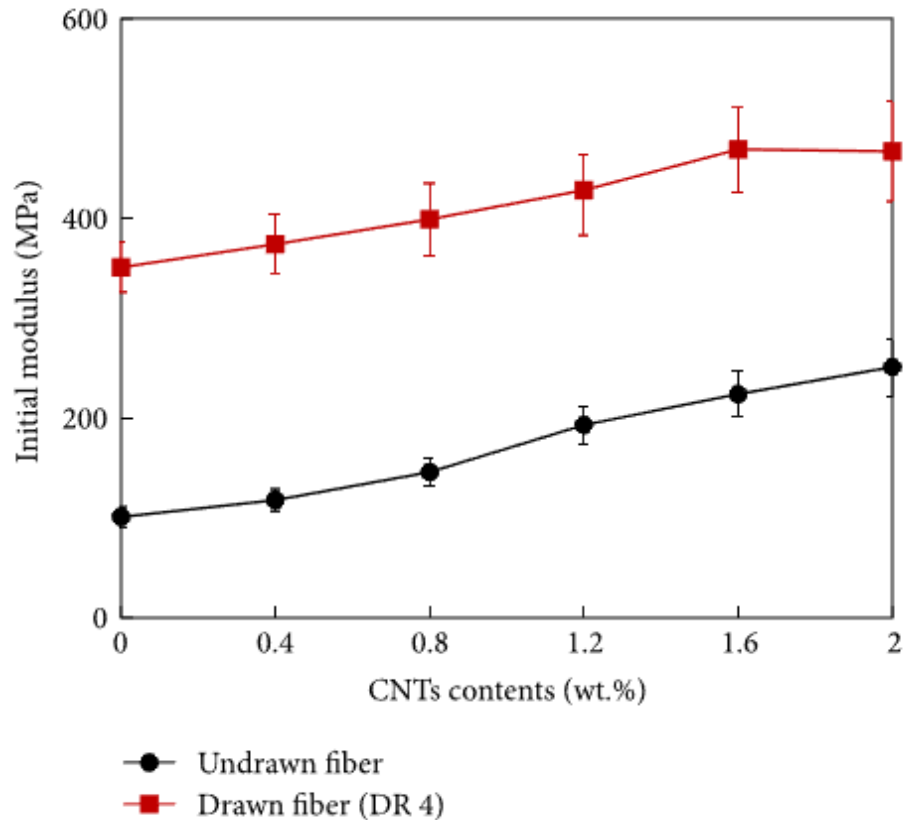
**Figure 9: Strength at break for undrawn and drawn LLDPE fiber as a function of CNTs content. (Kim and Lee, 2017)**

After heat drawing process, the plastic deformation of the LLDPE fiber decreased rapidly by comparing the elongation at break values of the undrawn and drawn fibers, whereas the neat-LLDPE fiber decreased from 410% to 61%, and the LLDPE-CNTs 2.0 wt.% fiber decreased significantly from 214% to 32%, as shown in Figure 10. (Kim and Lee, 2017)



**Figure 10: Elongation at break for undrawn and drawn LLDPE fiber as a function of CNTs content. (Kim and Lee, 2017)**

Besides, initial modulus of drawn fibers, as shown in Figure 11 higher than undrawn fiber shows the heat drawing process made the LLDPE fiber stiffer, results in straightening and sliding of the strained interfibrillar tie molecules, which allow easy alignment of the polymer segments to the crystals. (Kim and Lee, 2017)



**Figure 11: Initial modulus for undrawn and drawn LLDPE fiber as a function of CNTs content. (Kim and Lee, 2017)**

According to Lv et al (2015), other technique will be heat treatment (or annealing) for semi-crystalline polymers. Several benefits of this technique are increment in degree of crystallinity, crystallite size and perfection along with modification of spherulite structure.

Auras et al. (2011) discussed that tensile modulus of annealing for drawn material will be contrast with undrawn material. For undrawn material, tensile modulus will be higher with the increasing of annealing temperature. While decrement of tensile modulus will be showed by drawn material at higher annealing temperature. This is because the loss of chain orientation and strain induced crystallinity. The influence of annealing on tensile modulus of drawn material decreases with increment of annealing temperature.

Besides, initiation of crystallization process at high temperature upon cooling can be done with the help of nucleating agent. It is able to reduce the surface free energy barrier towards nucleation which result into higher degree of crystallinity. Talc is one of the most common used as a nucleating agent due to its excellent potential. Talc nucleates the crystallization of polymers through an epitaxial mechanism. (Li and Huneault, 2007)

According to Li and Huneault (2007), sodium benzoate and its derived salts has been used as an effective nucleating agent in PET. The mechanism starts with decomposition of the salt, followed by the reaction of sodium ions with the acid end-groups of the polyester in PET. As a result, it produced polymeric ionomers which then form clusters to act as a nucleating agent.

In addition, Vieira et al (2011) discussed that plasticizer can help to increase degree of crystallinity by enhancement of crystallization rate. It will increase the polymer chain mobility which reduced the energy during crystallization for the chain folding process.

Vieira et al. (2011) stated that, poly (ethylene glycol) (PEG) is the most suitable plasticizer for PLA. With the presence of PEG as a plasticizer in PLA, it will lower the glass transition temperature of PLA which shows increment of degree of crystallinity in PLA.

Li and Huneault (2007) discussed that, the effects of PEG or ATC plasticizer content on crystallinity developed for the PLA formulations with 1% talc in Figure 12. At 30°C of moulding temperature, the samples were all nearly amorphous. At 80°C of moulding temperature, the formulations developed substantial crystallinity. The crystallinity increased from 30 to 40 J/g, as the plasticizer content was increased to 5% and then reached a plateau. There was no obvious difference between the crystallinity developed with PEG or ATC plasticizers.