EFFECTS OF ACCELERATED WEATHERING ON THE PROPERTIES OF POLYLACTIC ACID TOUGHENED WITH AN ETHYLENE COPOLYMER AS AN IMPACT MODIFIER

by

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Thesis submitted in fulfillment of the

requirements for the degree of

Master of Science

May 2013

ACKNOWLEDGEMENT

Firstly I would like to express my deep and sincere gratitude to my main supervisor, Associate Professor Dr. Razaina Binti Mat Taib as wel as co-supervisor Associate Professor Dr. Chow Wen Shyang for their guidance, inspiration, devotion and perpetual encouragement till the completion of this work at Universiti Sains Malaysia (USM).

I wish to express my warm and sincere thanks to Professor Dr. Radzali Othman, Chairman of AUN/SEED-Net program at USM, who was constantly taking a good care of me as well as all other AUN/SEED-Net students. I would also like to gratefully acknowledge Professor Dr. Hanafi Ismail, Dean of School of Materials and Mineral Resources Engineering, all of lecturer and technicians for their kindness and support.

I am grateful to JICA-AUN/SEED-Net program for the opportunity to undertake this work and financial support. I would like to thank you to AUN/SEED-Net officers as well as Ms. Nutthanun and also all of my friends from USM for their active supports and assistance through my study.

I am greatly indebted to Department of Mechanical Engineering, National University of Laos (NUOL), Laos, especially to Associate Professor Korakanh pasomsouk for granting permission to conduct my higher studies in USM.

Finally, I would like to thank my family and all of my friends at the Universiti Sains Malaysia (USM) especially in the School of Materials and Mineral Resource Engineering for their constant support, encouraging and inspiration.

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LIST OF SYMBOLS

a	The initial crack length
A	Cross-section area of the fracture specimen
E	Tensile modulus
EB/ε	Elongation at break
F_{max}	Maximum load applied
h	Hour
IS	Impact strength
K_c	Fracture toughness
mg	Milligram
min	Minute
mL	Milliliter
mm	Millimeter
M_n	Molecular weight number
M_w	Molecular weight
rmp	Round per minute
T_c	Crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
wt %	Weight percentage
X_c	Percentage of crystallinity
ΔH_c	Enthalpy of crystallization
ΔH_m	Enthalpy of fusion

ΔH_m^o	Enthalpy of fusion for 100% crystalline of polymer
σ_c	Critical stress
°C	Degree Celsius
°C/min	Degree Celsius per minute

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials
ATBC	Acetyl tri-*n*-butyl citrate
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetric
EAC	Ethylene Acrylate Copolymer
EPM	Ethylene Propylene Monomer
FTIR	Fourier Transformation Infra-red
GPC	Gel Permeation Chromatography
HDT	Heat Deflection Temperature
PCL	Poly Caprolactone
PEG	Poly Ethylene Glycol
PDLA	Poly(D-lactic acid)
PLA	Poly-lactic Acid
PLLA	Poly(l-lactic acid)
PP	Polypropylene
PS	Polystyrene
SEM	Scanning Electron Microscopy
TGA	Thermo-gravimetric Analysis
UV	Ultra Violate

KESAN CUACA DIPERCEPATKAN TERHADAP SIFAT-SIFAT POLILAKTIK ASID DIPERKUAT HENTAMAN OLEH KOPOLIMER ETILENA SEBAGAI UBAH-SUAI HENTAMAN

ABSTRAK

Polilaktik asid (PLA) dilebur-campurkan dengan jumlah yang berbeza (0 hingga 30 wt%) kopolimer etilena terubah-suai hentaman yang didapati secara komersial. Adunan PLA/kopolimer etilena disediakan dengan penyemperit skru tunggal dan acuan mampatan untuk menghasilkan spesimen ujian. Kesan cuaca dipercepatkan yang melibatkan pendedahan UV dijalankan terhadap adunan adalah mengikut ASTM D 154. Perubahan dalam ciri-ciri mekanikal, termal dan morfologi ditentukan selepas 250, 500, 750, and 1000 jam pendedahan. Ciri-ciri mekanikal adunan PLA/kopolimer etilena dikaji melalui ujian tegangan, lenturan, patah keliatan dan hentaman. SEM digunakan untuk menyiasat morfologi permukaan patah bagi sampel tegangan dan hentaman serta morfologi permukaan PLA dan adunan PLA/kopolimer etilena selepas pendedahan UV. Ciri-ciri termal ditentukan menggunakan DSC dan TGA untuk menyiasat perilaku termal PLA dan adunan PLA/kopolimer etilena sebelum dan selepas pendedahan UV. Permukaan sampel yang terdedah kepada UV diperiksa menggunakan FTIR dan SEM sementara GPC digunakan untuk memeriksa berat molekul PLA sebelum dan selepas pendedahan UV. Keputusan menunjukkan bahawa penambahan kopolimer etilena meningkatkan keliatan dan hentaman. Penambahan 20 wt% kopolimer etilena mengurangkan kekuatan tensil dan kekakuan tensil sebanyak 51.2 dan 41.2%. Pada kandungan ubah suai-hentaman yang sama kekuatan fleksural dan kekakuan fleksural menurun sebanyak 39.6 dan 37.3%. Kekuatan kentaman pula meningkat sebanyak 125%. Penambahan ubah-suai hentaman mengurangkan darjah kehabluran PLA. Sifat-sifat tensil, fleksural dan hentaman adunan PLA/kopolimer etilena merosot selepas pendedahan kepada cuaca dipercepatkan disebabkan oleh foto-degradasi yang berlaku terhadap PLA di bawah sinaran UV serta degradasi hidrolitik berpunca daripada kehadiran lembopan semaja ujian di jalankan. Penurunan sifat-sifat mekanik ini adalah disebabkan oleh degradasi berat molekul PLA seperti yang ditunjukkan oleh análisis GPC. Sampel juga menunjukkan ketidakstabilan dimensi, rapuh dan berubah warna menjadi sedikit kekuningan selepas pendedahan.

EFFECTS OF ACCELERATED WEATHERING ON THE PROPERTIES OF POLYLACTIC ACID TOUGHENED WITH AN ETHYLENE COPOLYMER AS AN IMPACT MODIFIER

ABSTRACT

Polylactic acid (PLA) was melt-blended with different amounts (0 to 30 wt%) of a commercially available ethylene copolymer impact modifier. PLA/ethylene copolymer blends were prepared via a single-screw extruder and compression moulded into test specimens. Accelerated weathering which involved UV exposure was carried out on the blends following ASTM D 154. Changes in the mechanical, thermal properties and morphology were determined after 250, 500, 750, and 1000 hrs of exposure. The mechanical properties of PLA/ethylene copolymer blends were studied through tensile, flexural, fracture toughness and impact test. SEM was used to investigate the morphology of the tensile and impact fracture surfaces as well as the surface morphology of PLA and PLA/ethylene copolymer blends after the UV exposure. The thermal properties were determined using DSC and TGA to investigate the thermal behaviour of PLA and PLA/ethylene copolymer blends before and after the UV exposure. The exposed surface was examined using FTIR and SEM while GPC was used to investigate the molecular weight of neat PLA before and after the UV exposure. The addition of ethylene copolymer showed significant increased in the elongation at break and impact resistance of PLA. This is due to the toughening effect of ethylene copolymer. The addition of 20 wt% ethylene copolymer decreased the tensile strength and tensile modulus by 51.2 and 41.2% respectively. At the same impact modifier content, the flexural strength and flexural modulus decreased by 39.6 and 37.3% respectively. Impact strength of the blend however, increased by 125%. Addition of impact modifier decreased the degree of crystallinity of PLA. Tensile, flexural and impact properties of PLA/ethylene copolymer blends decreased after the accelerated weathering due to the photo-degradation of PLA under the UV exposure as well as hydrolytic degradation of PLA due to the presence of the moisture during the weathering condition. Decreased in the mechanical properties was due to molecular weight degradation of PLA. This was confirmed by the GPC analysis. The samples too exhibited dimensional instability, became brittle and turned slightly yellow after the exposure.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Commodity plastics such as polypropylene (PP), Polystyrene (PS), Polyethylene (PE) and Polyvinyl chloride (PVC) in the forms of film, flexible bags and rigid containers are being used in the packaging industry. Unfortunately, once these materials are discarded they continue to exist in the environment without being degraded resulting in a multitude of ecological and environment concerns (Mohanty et al., 2002). These petroleum-based plastics or non-biodegradable materials and alternative disposal methods are limited. Incineration of plastic wastes always produce a large amount of carbon dioxide and create global warming and sometimes produced toxic gases, which can contribute to global pollution (Tachibana et al., 2009). Satisfactory landfill sites are also limited.

Increasing awareness on the impact of plastic materials on the environment the industries consider biodegradable polymer for their products. Polylactic acid (PLA) is a biodegradable thermoplastic which is derived from renewable resources.. PLA can be produced via direct condensation polymerization of lactic acid or by ring opening polymerization of cyclic lactide dimer, a diester of lactic acid which is obtained from the fermentation of sugar feed stock (Martin and Avérous, 2001, Ren, 2011). PLA has good mechanical properties that are similar with those of commodity plastics such as polyethylene (PE), polypropylene (PP) and polystyrene (PS) (Sudesh and Iwata, 2008). PLA can be processed with standard plastic processing equipments for a variety of applications (Garlotta, 2001). The glass transition temperature of PLA is high and is above room temperature. PLA is fully compostable in municipal/industrial facilities and can be disposed by traditional waste management methods such as incineration, landfill and mechanical recycling. PLA will completely degrade in commercial compost in roughly 30 - 45 days (Kale et al., 2007b). Figure 1.1 shows the completely degradation process of PLA.

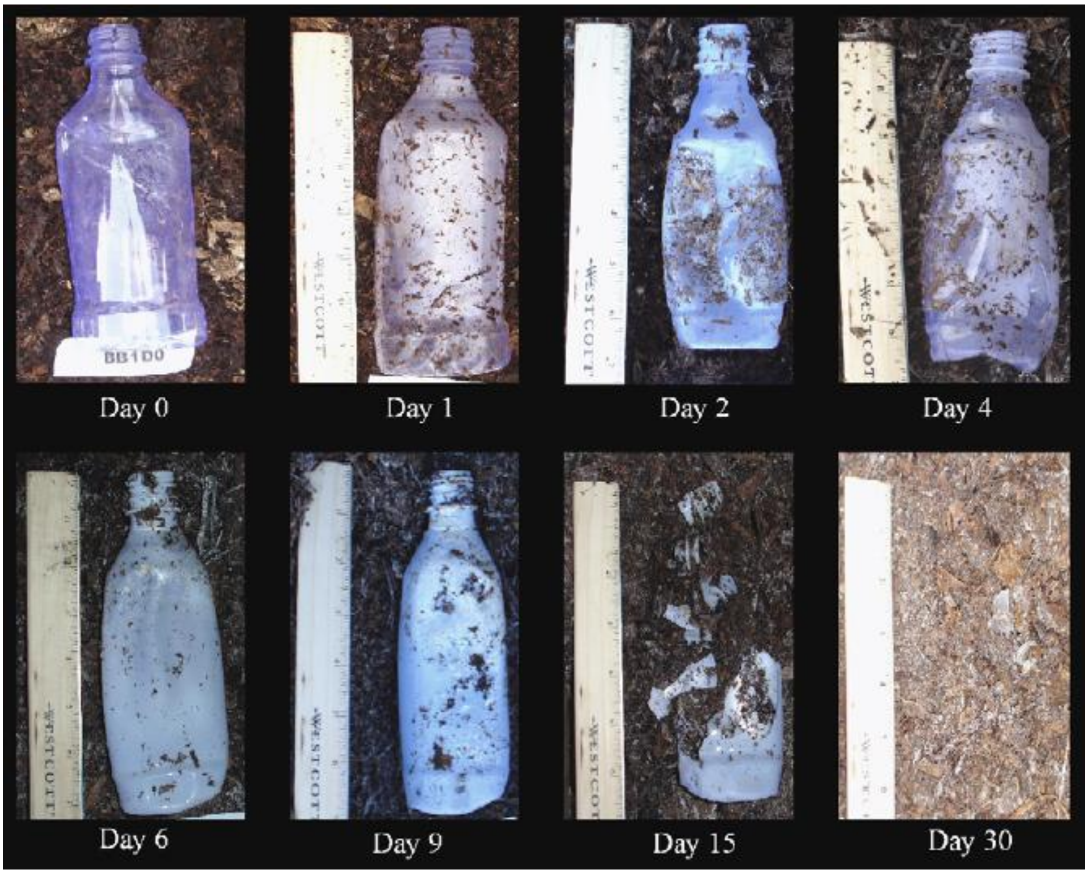


Figure 1.1 Biodegradation of PLA bottles in actual composting conditions (Kale et al., 2007a)

However, PLA has several unsatisfactory characteristics, including poor elongation at break, thermal stability and impact resistance which limits its broad commodity applications. In order to improve properties of PLA such as the elongation at break and impact resistance numerous efforts, such as copolymerization, plasticization and blending of PLA and fabrication of PLA-based composites and nanocomposites have been attempted to modify the properties of PLA (Grijpma and Pennings, 1994, Martin and Avérous, 2001, Zhang and Sun, 2004, Sinha Ray and Bousmina, 2005, Zhang J.W et al., 2006, Bhardwaj R., 2007). Blending of PLA with non-biodegradable polymer has been conducted to overcome the drawbacks of PLA properties such as brittleness, low heat deflection temperature (HDT), fragility, and poor barrier properties. Balakrishnan et al. (2010) were found that, blending of linear low density polyethylene (LLDPE) into PLA improved the impact strength but slightly decreased the strength and stiffness of PLA. The elongation at break was gradually decreased with the increase in LLDPE content. Addition of plasticizers such as polyethylene glycol (PEG) into PLA may also overcome the brittleness of PLA matrices (Pluta et al., 2006).

An impact modifier, ethylene copolymer (Biomax® strong 100) from DuPont is designed to modify PLA and enhance its performance in packaging and other industrial applications. The additive is used to improve the toughness of PLA without the reduction of product transparency. The additive can also act as processing aid to improve PLA performance particularly in thermoforming process. Taib et al. (2012) studied the effect of adding ethylene copolymer into PLA. Improvements of elongation at break and impact resistance of PLA were observed.

The study of degradability of materials is an important area from scientific and industrial point of view to estimate service of the materials. Most of synthetic thermoplastic polymers as well as biodegradable polymers are susceptible to degradation and undergo loss of physical properties or colour changes to varying degrees when exposed direct to UV and visible light (Singh and Sharma, 2008, Yew et al., 2009). The effect of exposed to the moisture, heat, and ultra-violet (UV) radiation and more importantly a combination of these parameters may degrade the properties of the materials (Islam et al., 2010). PLA will undergo photo-degradation and the degradation proceeds via Norrish II mechanism at ester group and ethylene group adjacent to the ester oxygen (Balakrishnan et al., 2010, Tsuji et al., 2006b). The presence of moisture will accelerate the photo-degradation process (Ahmad Thirmizir et al., 2011).

1.2 Problem statement

There are many studies on blending of PLA with biodegradable and non-biodegradable polymers as to improve the impact properties and toughness of PLA. Studies on the effect of adding plasticizers are also available in the literature. Very limited information however, can be found from these studies on durability of PLA when it is exposed to UV. Studies on the effect of UV as well as moisture on PLA and impact modified PLA is important to estimate the service life of these materials for outdoor applications.

1.3 Objectives

This study focused on the preparation and characterization of PLA and PLA/ethylene copolymer blends. Properties of these materials before and after subjected to accelerated weathering condition were determined for the durability study. The objectives of this study:

(i) To determine the effect of adding impact modifier on the morphological, thermal and mechanical properties of PLA.

(ii) To characterize the effect of accelerated weathering on the properties of PLA/ethylene copolymer blends.

1.4 Thesis overview

Chapter 1: Starts with a brief introduction on biodegradable materials with some specific issues that are concern. The problem statement, objectives and general flow of the whole research works are also carefully outlined.

Chapter 2: Various literature reviews that are related to biodegradable polymers and the degradation mechanisms of PLA material. Their definition, classification, blends, characterization of the blends and applications are discussed in this chapter.

Chapter 3: Focussed on the explanation of the raw materials used in the present study such as PLA resin and ethylene copolymer. Fabrication methods of the PLA blends and characterization of the samples are explained in this section.

Chapter 4: Result and discussion on the effect of adding ethylene copolymer the properties of PLA/ethylene copolymer blends. The effects of the accelerated weathering on the properties of PLA and PLA/ethylene copolymer blends were also discussed.

Chapter 5: Concluding remarks on the present research study as well as some suggestions for further research.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable polymers

Biodegradable polymers are materials obtained completely from renewable resources that can be completely degraded by microbial attack under appropriate environment conditions. Biodegradable materials offer an answer to maintaining sustainable development of materials within limited of the fossil residues and increasing environmental pollution from non-degradable polymers. These polymers are set to solve both problems by providing a renewable resource for degradable green polymers with minimal environmental repercussions. In addition, due to their biodegradability and biocompatibility, some of these polymers are also useful for new emerging in several applications such as medical applications, agriculture, packaging or commodity applications. Many previous reports discussed different type and properties of these polymers (Chiellini and Solaro, 1996, Akaraonye et al., 2010, Grabow et al., 2010, Hay et al., 2010, Sato et al., 2010, Thomson et al., 2010, Wang et al., 2010, Yunos et al., 2010, Sungsanit, 2011).

According to the *American Society for Testing and Materials*, biopolymers are degradable polymers in which degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae (Shimao, 2001). The degradation process involved chain scission leading to photo-degradation, oxidation and hydrolysis which can affect the polymer properties and/or microstructure. As for the present, concerns over the limiting availability of landfill site, environmental regulations, and also increasing the oil prices are reviving interest in these materials (Amar et al., 2005). Another definition states that biodegradable polymers capable of undergoing decomposition primarily through the enzymatic action of microorganisms to form carbon dioxide, methane, inorganic compound, or biomass in a specified period of time (Kolybaba et al., 2003). Biodegradable Plastic Society Japan (BPS, Japan) reported that, most of biodegradable plastics can be degraded in soil and climate conditions and their biodegradation, due to changed in molecular structure of the polymers can result in the weight loos and decreased in mechanical properties (Hoshino et al., 2002).

The definition of biodegradable polymer varies greatly among scientists, manufacturers, and consumers. Biodegradable polymers are defined as those that undergo microbially induced chain scission leading to the mineralization. Specific conditions in term of pH, humidity, oxygenation, and the presence of some metals are required to ensure the biodegradation of such polymer. Biodegradable polymers which are obtained from bio-sources like corn, wood cellulose or can also be synthesized by bacteria and other biodegradable polymers can be derived from the petroleum sources or may be obtained from mixed sources of biomass and petroleum. The most commonly studied of biodegradable polymers are biodegradable polymers made from renewable resources like Polylactic acid (PLA) which are attracting much more attention because of more eco-friendly to the environment (Sinha Ray and Bousmina, 2005). Biodegradable polymers are typically produced from 100% of renewable resources, therefore they can be biodegraded eventually by microorganisms in the natural environment into carbon dioxide (CO_2) and water (H_2O) (Funabashi et al., 2009). Concerns with environmental issues will impose the additional requirement for properly designed biodegradable materials of the complete "mineralization" or disappearance of the degradation products into CO_2, H_2O, CH_4, or biomass without the production of harmful intermediates. The time frame required for biodegradation will be mandated by the disposal method and condition. The increase in compositing and anaerobic bioreactor technology will produce specific environmental conditions and lead to specific requirements for biodegradable plastics packaging (McCarthy, 2005).

Figure 2.1 shows classification of biodegradable polymers, these are obtained from four families. Only three families of biodegradable polymers are obtained from renewable resources or biomass. The polymers are derived from biomass such as agro-polymers which from agro-resources (e.g. starch, cellulose) by fractionation. The microorganisms and biotechnology families are polyesters, obtained respectively by fermentation from biomass or from genetically modified plants and by synthesis from monomers obtained from biomass. The petrochemical product families are also polyesters, but totally synthesized by petrochemical process (John and Thomas, 2008). Therefore, these different biodegradable polymers into two main groups; the first is agropolymers and second is the biodegradable polyesters or biopolyesters (Averous, 2004).

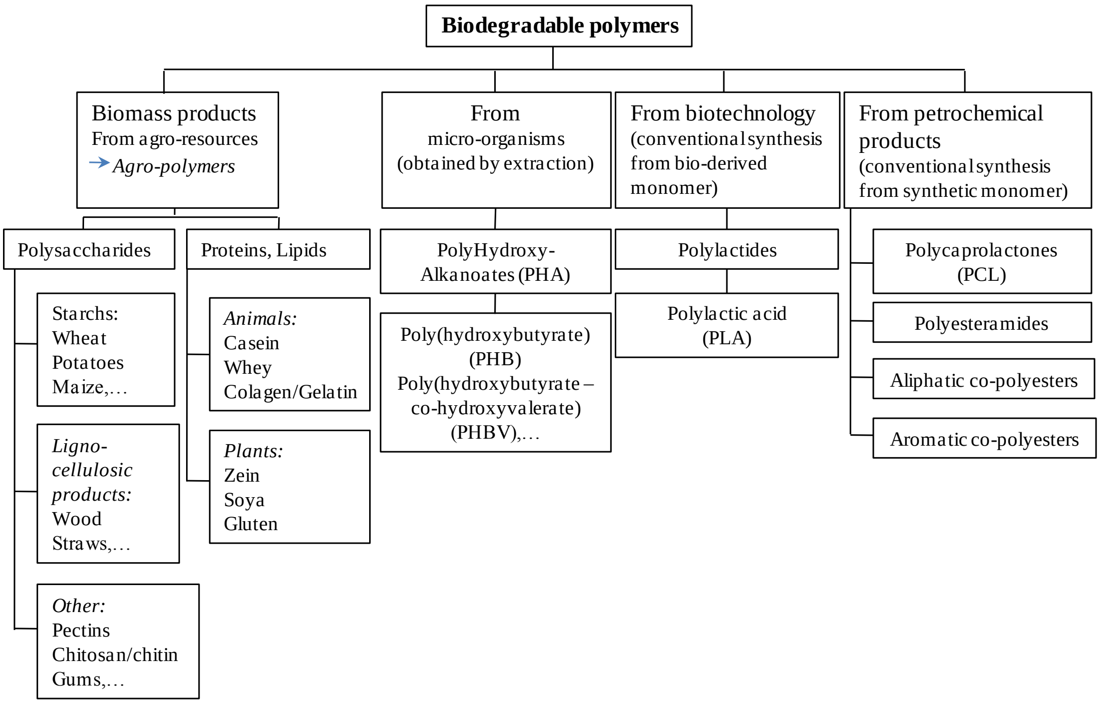


Figure 2.1 Classification of the biodegradable polymers (Averous, 2004)

Natural biodegradable polymers are normally produced in nature by all living organisms as they presented certainly from renewable resources. The most abundant natural polymers are polysaccharides such as cellulose and starch. Other important classes of natural polymers are polyester such as polyhydroxy-alkanoates, proteins such as silk and others (Li and Shimizu, 2007a).

Table 2.1 Application of biodegradable plastics (Shah et al., 2008)

Plastics	Uses
Polyglycolic acid (PGA)	Specialized applications; controlled drug releases; implantable composites; bone fixation parts
Polylactic acid (PLA)	Packaging and paper coatings; other possible markets include sustained release systems for pesticides and fertilizers, mulch films, and compost bags
Polycaprolactone (PCL)	Long-term items; mulch and other agricultural films; fibers containing herbicides to control aquatic weeds; seedling containers; slow release systems for drugs
Polyhydroxybutyrate (PHB)*	Products like bottles, bags, wrapping film and disposable nappies, as a material for tissue engineering scaffolds and for controlled drug release carriers
Polyhydroxyvalerate (PHBV)	Films and paper coatings; other possible markets include biomedical applications, therapeutic delivery of worm medicine for cattle, and sustained release systems for pharmaceutical drugs and insecticides
Polyvinyl alcohol (PVOH)	Packaging and bagging applications which dissolve in water to release Products such as laundry detergent, pesticides, and hospital washables
Polyvinyl acetate (PVAc)**	Adhesives, the packaging applications include boxboard manufacture, paper bags, paper lamination, tube winding and remoistenable labels

*http://en.wikipedia.org/w/index.php?title=Polyhydroxybutyrate&oldid=189442759. Accessed February 14, 2008.

**http://www.chemquest.com/store/polyvinyl-acetate-european-adhesives.html, 2006

Polymers from renewable resources or bio-based thermoplastics which they not only biodegradable or compostable, but also considered advantage to the environment. These polymers have increasingly attracted many researchers for two major areas: firstly the opportunity to close the carbon cycle by eventually returning plant-based carbon to the soil through biodegradation or composting and therefore reducing environmental impacts, and secondly to use less of fossil energy and reduced carbon dioxide emissions over the manufactured product life cycles (Plackett, 2011). Bio-based polymers generally focuses on bio-based thermoplastics which are not only biodegradable, or compostable, but are considered advantaged to the environment. The mainly points that attracted to using those of biodegradable polymers are based on: (1) the opportunity to close the carbon cycle by eventually returning plant-based carbon to the soil through biodegradation or composting and thereby reducing environmental impacts; (2) less use of fossil energy and reduced carbon dioxide emission over manufactured product life cycle. Figure 1 below is illustrated the schematic life cycle of bio-based product.

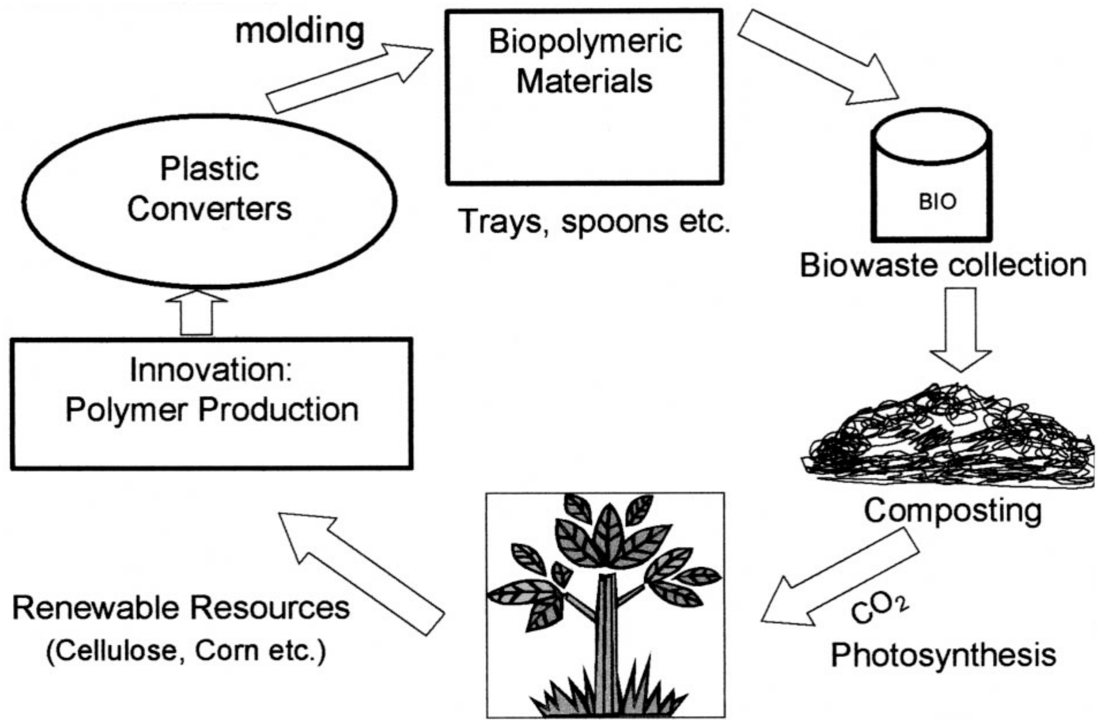


Figure 2.2 Life cycle of bio-based product in composting condition (Mohanty et al., 2002)

Biopolymers are novel materials of the twenty-first century and further be great importance to the world materials, not only as solution to growing the environmental threat, but also solution to uncertainty of petroleum supply. Biodegradable polymers are nowadays moving into main-stream use and are competing with commodity plastics which results in commercial demands more than 30% per year in 2002 (Mohanty et al., 2002).

On the other hand the main reason for initial interest in biodegradable polymers is because of non-biodegradable commodity presents a major waste disposal problem. As consequence there has been development of biodegradable polymers suitable for food packaging applications, several performance criteria need to be fulfilled such as strength and flexibility, non-toxicity, impermeability to oxygen, good moisture resistance, stability during storage over a wide temperature range and low cost for both the starting materials and the processing technology. Therefore, the focus has shifted towards the zero-emission concept largely because of global climate change due to increasing the greenhouse gas emissions. This has given a very strong push for the development of biodegradable plastics that can be produced from renewable resource such as Polylactic acid (PLA) and other biodegradable materials (Sudesh and Iwata, 2008).

2.1.1 Polylactic acid (PLA)

Polymers based on lactic acid (PLA) are a most promising category of polymers derived from 100% renewable resources. They are not only compostable and biocompatible, but also processability with most standard plastic processing equipments (Almenar et al., 2010). PLA can be produced via direct condensation polymerization of lactic acid or by ring opening polymerization of cyclic lactide dimer, a diester of lactic acid which is obtained from the fermentation of sugar feed stock. PLA is a chiral molecule and existed in two optically active forms; L-lactide and D-lactide, and the formation of semi-crystalline can be produce by depolymerization of both monomers, in addition of its stereo-chemical structure can be easily to modified by polymerizing, a controlled mixture of both isomers to yield amorphous or semi-crystalline polymers (Smith, 2005, Nair and Laurencin, 2007).

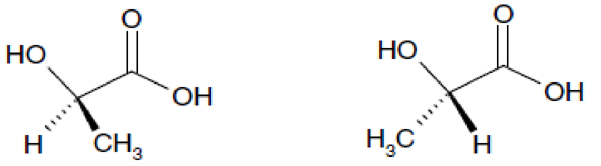
The properties of lactic acid based polymers very to a large extent depending on the ratio between, and distribution of the two stereoisomers and other comonomers (Tsuji and Ikada, 1996, Huang et al., 1998, Södergård and Stolt, 2002). The polymer can be manufactured by different polymerization routes. High molecular weight of PLA is most commonly made by ring-opening polymerization (ROP) of the ring-formed dimer, dilactide (lactide; 3,6-dimethyl-1,4-dioxane-2,5-dione), which is made by deploymerisation of the polycondensed lactic acid (LA; 2-hydroxypropanoic acid) (Södergård and Stolt, 2010). This route is a two step reaction that usually involves additional purification steps and is therefore related to costs affected. 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 polymer with a high molecular weight. Solvent assisted polycondensation is one way to overcome this problem and melt polycondensation followed by solid-state polycondensation is another one (Moon et al., 2001, Lim and Tsuji, 2010). The third approach to achieve high molecular weight LA based polymers is to utilize the terminal group of the prepolymer in linking processes where a liking agent is employed (Hiltunen et al., 1996). Such prepolymers can be composed of only one stereoisomer, combination of D- and L-lactoyl units in various ratios, or di, or multifunctional comonomers.

Generally, commercial PLA grade are copolymers of L-lactide and D-lactide. The optical purity depending on (L and D%), strongly affects the properties. Optically pure PLA is isotactic and highly crystalline. Decreasing the optical purity reduces the degree of stereoregularity and crystallinity. Poly(L-lactide) (PLLA) with more than 15% D-lactide is amorphous (Hu et al., 2003). PLA can be produced totally amorphous or with up to 40% crystalline. PLA resins containing more than 93% (L-lactide) are semi-crystalline (Avérous, 2008). Poly(L-lactide) (PLLA) which derived from pure L-lactide, has a high melting temperature (175°C), poor processability and crazes easily because of its high crystallinity. Poly(D, lactide) is an amorphous polymer with the glass transition temperature to 60°C. This polymer has low mechanical properties to be used in packaging applications. Properties such as melting point, mechanical strength and crystallinity are determined by the polymer architecture (by different proportion of L, D) and molecular mass. The time taken for degradation is affected by the degree of crystallinity and molecular mass of the polymer; high values of both PLA will require longer time for degradation. On the contrary, poly(D, L-lactide) (PDLLA) is amorphous polymer due to the random distribution of L- and D-lactide units and has a T_g of 55-60°C (Garlotta, 2001, Gupta and Kumar, 2007). In these review are used PLA as a general term indicating either amorphous or crystalline polymer, whenever necessary the specific structure is indicated as PLLA, PDLA or PDLLA.

2.1.1a Polymerization

Polylactic acid is one of the extensively studied biodegradable thermoplastic polymer because they can be obtained from renewable feedstock (Ren et al., 2006). PLA belongs to the family of aliphatic polyester commonly made from α-hydroxy acids. PLA can be produce from lactic acid (2-hydroxy propionic acid) through fermentation of renewable resources such as corn starch and sugarcane (Bax and

Müssig, 2008). Lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom and exists in two optically active configurations L(-) lactic acid and D(+) lactic acid, L-isomer is produced in humans and other mammals, Figure 2.3 (Garlotta, 2001, Gupta and Kumar, 2007). It is a high water-soluble, three carbon chiral acid that is naturally occurring and is most commonly found in L(-) form (Huang et al., 1998). Both D(+) and L(-) enantiomers are produced in bacterial system, commonly of the commercially produced lactic acid can be obtained by fermentation of carbohydrates, selecting suitable micro-organisms, e.g. homo-lactic organisms such as various optimized or modified strains of lactobacilli are used to produce stereoregular L-lactic acid. However lactic acid obtained by the chemical process is a racemic mixture of D- and L-isomers (Garlotta, 2001, Gupta et al., 2007).



L - Lactic acid D - Lactic acid

Figure 2.3 Different isomeric forms of lactic acid (Gupta and Kumar, 2007)

Lactic acid is produced commercially by fermentation, as chemistry routes, or via petrochemical feedstock, which is illustrated in Figure 2.4. The lactic acid produced by this route is optically inactive racemic mixture of L- and D-ennantiomers, therefore nowadays the most popular route is fermentation, in which corn starch is converted into lactic acid by bacterial fermentation using an optimized strain of lactobacillus. Like all biological lactic acid and the lactic acid produced is existing more than 99.5% of L-isomer. Which is the reason that favouring production from renewable resource rather than petrochemical.

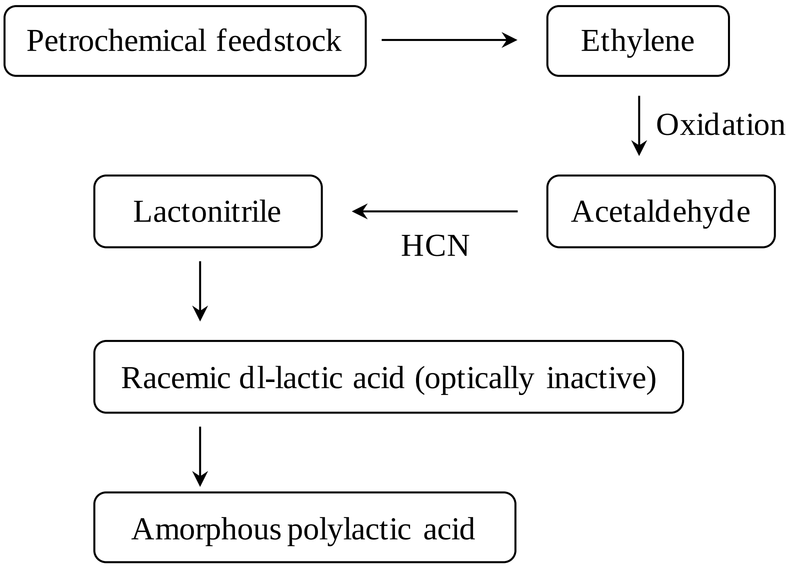


Figure 2.4 Petrochemical route of PLA (Gupta et al., 2007)

Two different routes of polymerization can be followed to produce PLA from lactic acid monomers, as an illustrated in Figure 2.5. Lactic acid is condensation polymerized to yield low molecular weight, brittle, glassy polymer, which for most part is un-useable for any application unless external coupling agents are used to increase the molecular weight of the polymer (Garlotta, 2001). Polymer obtained by this direction condensation is low molecular weight due to difficulty to removing water from highly viscous reaction mixture (Gupta and Kumar, 2007). The back biting equilibrium reaction of these resulting low molecular weight forms the six members lactide ring (Garlotta, 2001).

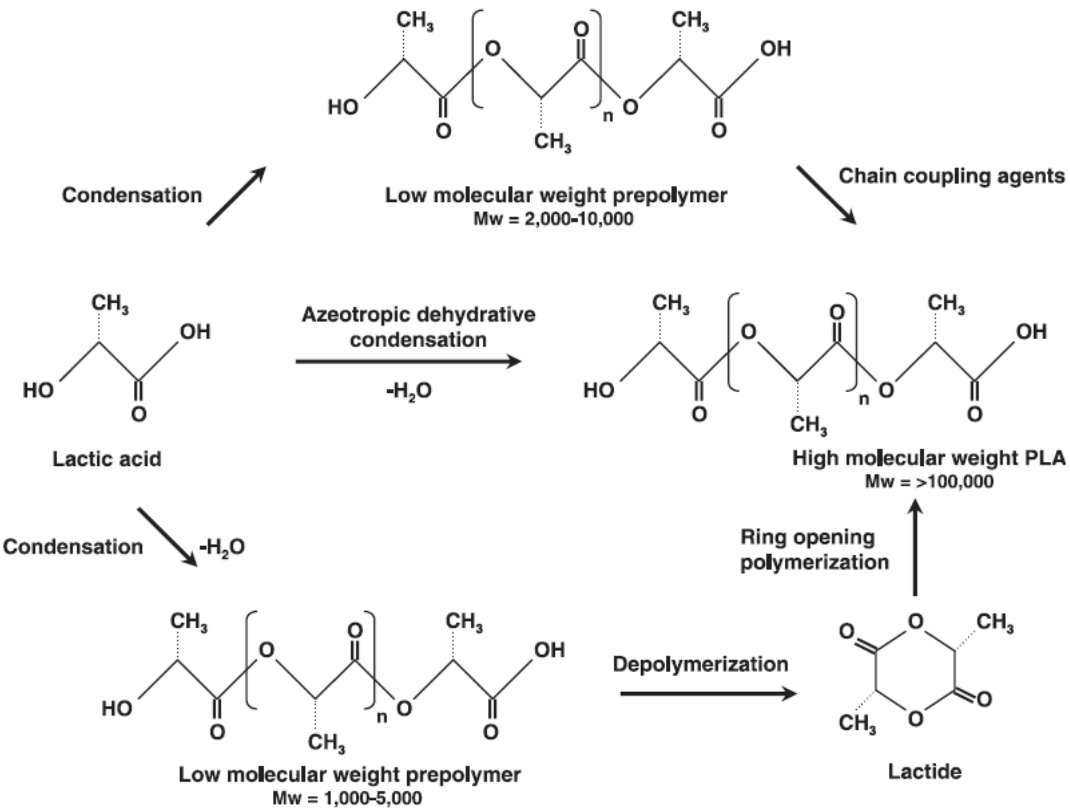


Figure 2.5 Synthesis method for high molecular weight PLA (Gupta et al., 2007)

Controlled polymerization of low molecular weight polymer can be done to produce crude lactides which have to be purified and undergo to ring opening polymerization (in the presence of catalyst) to yield high molecular weight polymer. Since lactic acid is found in two stereoisomerism forms, therefore lactides are found in three stereoisomerism forms, which are DD-lactide, LL-lactide and DL-lactide/meso-lactide as shown in Figure 2.6. Ring-opening polymerization can be divided into two, which cationic and anionic ring opening polymerization. Purification of crude lactides is essential in order to remove impurities such as water, lactic acid and oligomers which could interfere with polymerization reaction, resulting in low molecular weight polymer with high degree of polymerization. This ring opening polymerization technique is a solvent free process adapted by Cargill

Dow, the present major producer of PLA. This method was producing only pure, high molecular weight PLA until Mitsui Toatsu Chemical commercialized a process wherein lactic acid and catalyst are azeotropically dehydrated in a refluxing, high-boiling, aprotic solvent under reduced pressure to obtain PLA with weight average molecular weight greater than 300,000 (Lunt, 1998, Garlotta, 2001, Gupta and Kumar, 2007).

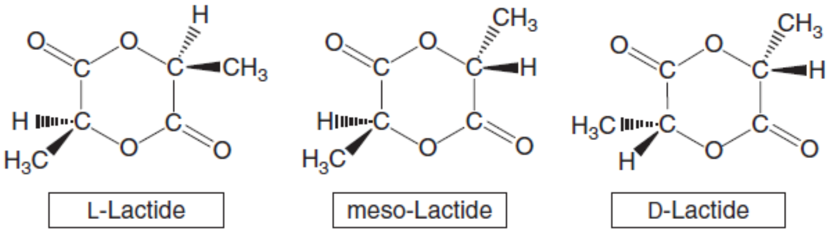


Figure 2.6 Chemical structures of L-, meso- and D-lactides (Avérous, 2008)

2.1.1b Processing and mechanical properties

Polylactic acid is an aliphatic thermoplastic material which can be processed similar to any thermoplastic materials. The polymer can be melted and form into fibres, rods and moulds parts, and final parts can be extruded, injection moulded, compression moulded or solvent spun, or casts. Complication during processing can occur, due to hydrolytic sensitivity of the polymer bonds. The presence of moisture during processing can reduce the molecular weight and alter the final properties of the polymer. Therefore, to avoid hydrolytic degradation during processing, the polymer need to be dried before processing (Middleton and Tipton, 2000). Different processing methods are needed to broaden the application areas of PLA. Example of different processing method include injection moulding, hot press moulding, spinning, blow moulding, foam moulding and electro spinning (Ren, 2011).

Injection moulding is the most widely used converting process for thermoplastic articles, especially for those that are complex in shape and require high dimensional precision. Most injection moulding machines for PLA are based on the reciprocating screw extruder, although two-stage systems, which integrate a shooting pot and extruder in a single machine, have also been deployed for injection moulding of preforms for PLA bottles. Figure 2.7 is illustrated the schematic of injection moulding machine.

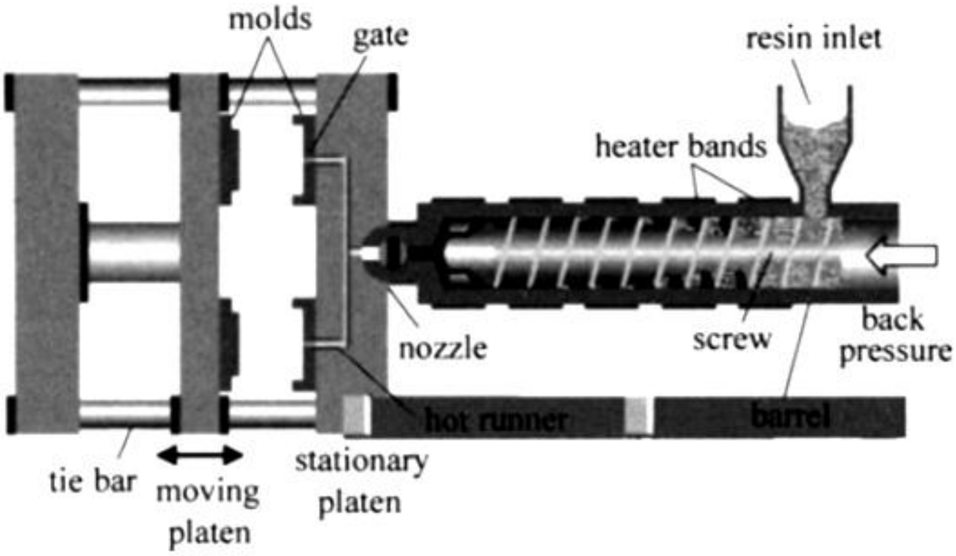


Figure 2.7 Components of an injection moulding machine (Ren, 2011).

The production of PLA bottles is based on injection stretch blow moulding (ISBM) technique. This process produces biaxial orientated PLA bottle with much improved physical and barrier properties compared to injection moulded amorphous PLA. The molecular orientation induced during the ISBM process decreases the effect of aging by stabilizing the polymer free volume. The crystallites produced during strain-induced crystallization also reduce the aging effect since they can act as physical crosslink to stabilize the amorphous phase, thereby reducing its brittleness (Lim et al., 2008). Similar effects have been reported for semi-crystalline PET

(Mukherjee and Jabarin, 1995). Figure 2.8 shows injection stretch blow moulding (ISBM) technique to produces plastic bottle from the first until finished product.

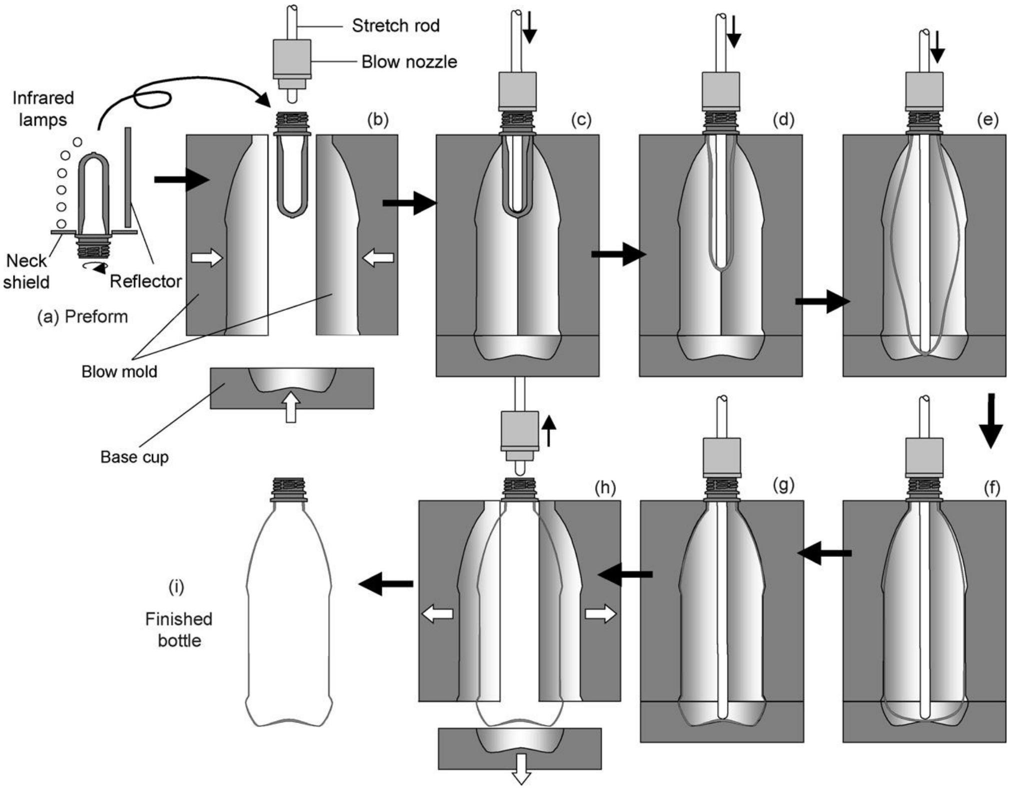


Figure 2.8 Injection stretch blow molding (ISBM) of PLA bottle (Lim et al., 2008)

PLAs are strong but brittle. The comparison on mechanical properties of PLA (96% of optical purity) with some thermoplastics is given in Table 2.2. It was found that the mechanical properties of Polylactic acid are slightly better than polystyrene. The physical and mechanical properties of Polylactic acid are affected by the molecular characteristic, highly ordered structure and materials morphology (Tsuji. H., 2002).

Table 2.2 Comparison of polylactic acid (96% optical purity) with thermoplastics (Bastioli, 2005)

	Tensile modulus (MPa)	**Notch Izod impact (J/m)**	**Flexural modulus (MPa)**	**Elongation at break (%)**
Polylactic acid	3834	24.6	3689	4
Polystyrene	3400	27.8	3303	2
Iso tactic polypropylene	1400	80.1	1503	400
High density polyethylene	1000	128.16	800	600

Molecular weight is an important parameter to determine mechanical properties of PLA. The increase in molecular weight will lead to the increase in the number of entanglements and therefore lead to increase in mechanical properties of Polylactic acid. In addition, it was proved that increase in crystallinity (X_c) and crystalline thickness (L_c) increase the tensile strength and modulus, but decrease the elongation of PLA (Tsuji. H., 2002). The thermal properties of PLA may be determined by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical Analysis (DMA). The glass transition temperature T_g of PLAs around 60–70°C and this is followed by melting between 150 and170°C. PLA is normally processed at 185–190°C (Garlotta, 2001). PLA properties are greatly dependent on the optical purity of L-isomer ratios. Table 2.3 represented the optical purity of PLA and properties.

Table 2.3 Optical purity of PLA and properties (Bastioli, 2005)

% L form of PLA	**T_g, °C, (DSC)**	**T_m, °C, (DSC)**	**ΔH_f, J/g**	**Density, g/m^3**
100	60	184	-	-
98	61.5	176.2	56.4	1.26
92.2	60.3	185.5	35.8	1.26
87.5	58	ND	ND	-
80	57.5	ND	ND	1.26
45	49.2	ND	ND	1.27

ND: Amorphous

2.1.1c Degradation and hydrolysis

Degradation of polymer is any physical or chemical change as related to the environmental factors such as light, heat, moisture, chemical conditions or biological activity. Degradation affects in polymer properties because the chemical, physical or biological reactions involved results in bond. Degradation has negative effect on material properties such as mechanical, optical or electrical characteristics, and facilitate cracking, crazing, erosion, discoloration, phase separation, or delamination of the PLA (Shah et al., 2008). The changes include bond scission, chemical transformation and formation of new functional groups (Yagi et al., 2010, Pospisil J & Nespurek S., 1997). The degradation either be photo, thermal or biological (Table 2.4).

Table 2.4 Various polymer degradation routes (Shah et al., 2008).

Factors (requirement/activity)	Photo-degradation	Thermooxidative degradation	Biodegradation
Active agent	UV-light or high-energy radiation	Heat and oxygen	Microbial agents
Requirement of heat	Not required	Higher than ambient temperature required	Not required
Rate of degradation	Initiation is slow. But propagation is fast	Fast	Moderate
Other consideration	Environment friendly if high-energy radiation is not used	Environmentally not acceptable	Environment friendly
Overall acceptance	Acceptable but costly	Not acceptable	Cheap and very much acceptable

Photo-degradation is related to the ability to absorb the harmful part of the tropospheric solar radiation. This includes the UV-B terrestrial radiation (~295-315 nm) and UV-A radiation (~315-400 nm) which are responsible for the direct photo-degradation (photolysis, initiated photo-oxidation). Visible part of sunlight (~400-760 nm) accelerates polymeric degradation by heating. Infrared radiation (~760-2500 nm) accelerates thermal oxidation (Pospisil J & Nespurek S., 1997). Most plastics tend to absorb high-energy radiation in the ultraviolet portion of the spectrum, which activates their electrons to higher reactivity and causes oxidation, cleavage, and other degradation (Shah et al., 2008). Photo-degradation causes PLA materials a decrease in molecular weight and the formation of C=C double bonds through the Norrish II mechanism (Singh and Sharma, 2008, Tsuji et al., 2012).

Thermal degradation of polymers is ‘molecular deterioration as a result of overheating’. At high temperatures the components of the long chain backbone of the polymer can begin to separate (molecular scission) and react with one another to change the properties of the polymer. The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include; reduced ductility and embrittlement, chalking, colour changes, cracking and general reduction in most other desirable physical properties (Olayan et al., 1996).

Oxo-biodegradation process uses two methods to start the biodegradation. These methods are photo-degradation (UV) and oxidation. The UV degradation uses UV light to degrade the end product. The oxidation process uses time, and heat to break down the plastic. Both methods reduce the molecular weight of the plastic and allow it to biodegrade (Shah et al., 2008).

Biodegradation is the process by which organic substances are broken down by living organisms. The term is often used in relation to ecology, waste management, environmental remediation (bioremediation) and to plastic materials, due to their long life span. Organic material can be degraded aerobically, with oxygen, or an-aerobically, without oxygen. A term related to biodegradation is bio-mineralisation, in which organic matter is converted into minerals (Shah et al., 2008). Plastics are biodegraded aerobically in wild nature, an-aerobically in sediments and landfills and partly aerobically and partly an-aerobically in composts and soil. Carbon dioxide and water are produced during aerobic biodegradation and carbon dioxide, water and methane are produced during anaerobic biodegradation (Khaladkar, 2011). Generally, the breakdown of large polymers to carbon dioxide (mineralization) requires several different organisms, with one breaking down the polymer into its