SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

EFFECTS OF ACRYLONITRILE-BUTADIENE LATEX POWDER ON THE IMPACT AND THERMAL PROPERTIES OF POLY(LACTIC ACID)

By

NURUL FARIHAH BT KAMAL

Supervisor: Professor Dr. Chow Wen Shyang

Dissertation submitted is partial fulfilment

of the requirements for the degree of Bachelor of Engineering with Honours

(Polymer Engineering)

Universiti Sains Malaysia

JULY 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled **“Effects of acrylonitrile-butadiene latex powder on the impact and thermal properties of poly(lactic acid)”**. I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or university.

Name of student: Nurul Farihah Bt Kamal Signature:

Date: 4 July 2017

Witness by

Supervisor: Professor Dr. Chow Wen Shyang Signature:

Date: 4 July 2017

ACKNOWLEDGEMENTS

Alhamdulillah, thanks to Allah to the almighty god because with his blessings and strength, I can successfully finish my final year project thesis right on time, although I have faced some obstacles while doing this research.

Then, I would like to thank to Prof Dr Chow Wen Shyang as my supervisor for this project, for his useful guidance and advices while assisting me in completing my Final Year Project. Without his moral supports, patience and encouragement, I may lose the hope to finish this project.

I also want to express my sincere gratitude to the technical staffs for helping me to do research by supplying the apparatus and materials, and also teaching me how to use some machine.

It is almost impossible for me to finish me research alone. I would like to thank to my family and all my friends because of their support and encouragement towards me. Without the help and effort that had been contributed by everyone, this project will not be successfully completed. I really thankful and appreciate for all of their kindness.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

ASTM	American Society for Testing and Materials
DSC	Differential Scanning Calorimetry
ENR	Epoxidized natural rubber
LDPE	Low-density polyethylene
NBR	Acrylonitrile-butadiene rubber
NR	Natural Rubber
PCL	Poly(caprolactone)
PDLLA	Poly(DL-lactide)
PEG	Poly(ethylene glycol)
PHA	Poly(hydroxyalkanoate)
PLA	Poly(lactic acid)
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
SBR	Styrene butadiene rubber
SEM	Scanning electron microscope

SYMBOLS

%	Percentage
^{o}C	Degree Celcius
g	Gram
g/cm^3	Grams per centimetre cube
kg	Kilogram
mm	Millimetre
Mw	Molecular Weight
MPa	Megapascals
min	Minutes
rpm	Revolution per minutes
T_{cc}	Cold crystallization temperature
T_g	Glass transition temperature
T_m	Melting temperature
wt%	Weight percentage
X_c	Degree of crystallinity

EFEECTS OF ACRYLONITRILE-BUTADIENE RUBBER LATEX POWDER ON THE IMPACT AND THERMAL PROPERTIES OF POLY(LACTIC ACID)

ABSTRACT

Polylactic acid (PLA)/acrylonitrile butadiene rubber (NBR) latex blends were prepared using internal mixer followed by compression molding. The blending ratio of PLA/NBR are 95:5, 90:10, 85:15, 80:20, 75:25 and 70:30. The objective of this research is to study the effect of NBR latex powder on the impact and thermal properties of PLA. The NBR latex powder was prepared by NBR latex compounding followed by drying and grinding process. The mechanical and morphological properties of PLA/NBR blends were characterized by Charpy impact test and Scanning Electron Microscopy (SEM). The thermal properties of PLA/NBR blends were determined using Thermogravimetric Analyzer (TGA) and Differential Scanning Calorimeter (DSC). Fourier Transform Infrared (FTIR) Spectroscopy was used to determine the intermolecular interactions of the PLA/NBR blends. It was found that the impact strength of PLA was increased by addition of NBR latex powder. This is due to the elastomeric behaviour of NBR latex powder itself. The glass transition temperature of PLA was reduced by the incorporation of NBR latex powder, which indicates the increased flexibility of PLA/NBR blends. Nevertheless, from the TGA measurement, the results showed that the addition of NBR latex powder reduced the thermal stability of PLA.

KESAN SERBUK LATEKS GETAH AKRILONITRIL BUTADIENA KE ATAS SIFAT HENTAMAN DAN TERMA POLI(ASID LAKTIK)

ABSTRAK

Adunan poli(asid laktik) (PLA)/lateks getah akrilonitril butadiena (NBR) telah disediakan dengan menggunakan pengadun dalaman diikuti oleh pengacuanan mampatan. Nisbah campuran PLA/NBR ialah 95:5, 90:10, 85:15, 80:20, 75:25 dan 70:30. Objektif kajian ini adalah untuk mengkaji kesan serbuk lateks NBR ke atas sifat hentaman dan terma bagi poli(asid laktik). Serbuk lateks NBR telah disediakan dengan menggunakan penyebatian lateks diikuti dengan pengeringan dan proses pengisaran. Sifat-sifat mekanikal dan morfologi adunan PLA/NBR telah dicirikan dengan ujian hentaman Charpy dan mikroskopi elektron imbasan (SEM). Sifat terma PLA/NBR telah dikaji dengan menggunakan penganalisis termogravimetrik (TGA) dan kalorimeter imbasan pembezaan (DSC). Spektroskop inframerah jelmaan Fourier (FTIR) telah digunakan untuk menentukan interaksi antara molekul adunan PLA/NBR. Adalah didapati kekuatan hentaman PLA telah meningkat dengan penambahan serbuk lateks NBR. Hal ini adalah disebabkan oleh tingkah laku elastomer serbuk lateks NBR. Suhu peralihan kaca PLA telah dikurangkan dengan kehadiran serbuk lateks NBR, ini menunjukkan peningkatan kelenturan adunan PLA/NBR. Walaubagaimanapun, keputusan TGA menunjukkan bahawa penambahan serbuk lateks NBR menurunkan kestabilan terma PLA.

CHAPTER 1

INTRODUCTION

1.1 Background

In recent year, biobased materials have attracted much attention in order to reduce environmental impact and sustainability issues. Biobased material is defined as the materials that are derived in whole or part from biomass resources which are alternative to conventional products. Biomass resources are developed from organic materials that are available on a renewable and sustainable basis such as crop residues, wood residues, grasses, and aquatic plants (Christoph et al., 2016). As interest in using biobased materials derived from renewable resources have become popular day by day, therefore biobased materials replacing the existing commodity and industrial products. One such biobased material is poly(lactic acid) (PLA), a well-known biodegradable polyesters which is nontoxic compounds in landfill (Rasal et al., 2009).

PLA , a polycondensation material of lactic acid, is one interesting biobased material owing to its ability breaking down by hydrolytic scission to its monomeric form, lactic acid (Agrawal et al., 2001). Because of its excellent in biocompatibility, mechanical properties and transparency, PLA exhibits great potential for application in many fields, such as biomedical devices, packaging and automotive industry (Zhao et al., 2013).

Although PLA exhibits biocompatibility, mechanical strength and processibility, it has drawbacks as well, which limit its use in certain applications. Some weakness also exist which do not allow replacing commodity polymers in large scale applications. Its inherent brittleness with less than 10% elongation at break (Hiljanen et al., 1996). According to Auras(2004) its tensile strength and elastic modulus are different than poly(ethylene terephthalate) (PET), the poor toughness limits its use in the applications that need plastic deformation at higher stress levels. Thus PLA can be modified for improve the toughness for wider applications. Many approaches was developed for toughening PLA such as copolymerization of lactide with other monomers, blending PLA with a variety of elastomers or rubbers, and the addition of rigid fillers. Among these strategies, blending PLA with flexible polymers or rubbers is the most common and effective one (Broz et al., 2003).

Rubber has been used as a second phase polymer to toughen brittle thermoplastics. The rubber particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately results in a material with improved toughness. Natural rubber (NR) and epoxidized Natural Rubber (ENR)are renewable resource that exhibits a unique combination of toughness, flexibility, biocompatibility and biodegradability with its low cost makes it was an alternative to improve the toughness of PLA (Bitinis et al., 2011). Nevertheless there is no studies on using acrylonitrile-butadiene rubber (NBR) in the form of latex reported. In fact, improvement thoughnessof PLA can be done by blending with NBR latex due to the excellent in toughness properties.

1.2 Problem statement

Poly (lactic acid) (PLA) is biodegradable and biocompatible thermoplastic. Unfortunately, the brittleness of PLA is major drawback that restrict its applications. In this study, in order to reduce the brittleness, PLA is blended with NBR latex which is elastomer has commonly been considered because elastomer particle behave as stress absorber enhancing fracture energy absorption of brittle polymer (Han et al., 2011).

Based on research conducted by Thongpin and coworker et al. (2014), blended PLA with NR and ENR with compositions from 0-30% by weight. However, the partially compatible between PLA and ENR was responsible for coarse surface, i.e. very fine particles of ENR dispersion. Incorporation of NR would enhance the crystallization ability of PLA better than ENR but thermal stability was decreased with both rubbers. The ductility of PLA has been significantly improved by blending with NR. The amount of NR at 10 % weight seems to give optimum property. At high content of NR, it seems to suffer tensile properties. In the case of the addition of ENR, it reduced crystallization ability, thermal resistance and tensile properties of the blend.

Acrylonitrile-Butadiene Rubber (NBR) latex is an emulsion copolymer of acrylonitrile and butadiene. Polarity in NBR is introduced by copolymerization with the polar monomer i.e. acrylonitrile. NBR has higher polarity than NR and should be more compatible and suitable for toughening PLA. This research was aimed to prepare PLA blended with NBR latex. The research focuses on the mechanical properties, thermal properties and morphology of PLA/NBR blend.

1.3 Objectives

a) To determine the feasibility of the preparation of NBR latex powder.

b) To investigate the effects of NBR latex powder on the impact strength of PLA.

c) To study the thermal properties of PLA/NBR blends.

1.4 Scope of work

In this study, acrylonitrile-butadiene rubber (NBR) latex was first prepared and grounded into powder form. Pure PLA and PLA/NBR blends (NBR loading from 5 to 30 wt%) were prepared using internal mixer followed by compression moulding. NBR latex was added to improve the impact strength of PLA. Impact, thermal and morphological properties of PLA and PLA/NBR blends were studied. The impact strength of the PLA and PLA/NBR blends were characterized by charphy impact tester. Thermal properties of PLA and PLA/NBR blends were characterized by using differential scanning calorimeter (DSC) and thermogravimetric analyzer.

1.5 Structure of thesis

Chapter 1 covers brief introduction about research background, problem statements, objectives and structure od thesis.

Chapter 2 discusses the literature review of this study. It covers literature regarding polylactic acid and NBR.

Chapter 3 provides the information about the material and method used in this study. The method and characterization methods such as impact, FTIR, DSC, TGA, and FESEM are given in this chapter.

Chapter 4 focuses on the experimental results and discussion. Further elaboration on the effect of NBR latex loading on impact, thermal and morphological properties of PLA .

Chapter 5 summarizes the significant findings in this study. Suggestions for future studies are also recommended.

CHAPTER 2

LITERATURE REVIEW

2.1 Biobased polymers

Recently, interest in using the concept of sustainable development have attracted much attention because of considerably improved environmental awareness of society and concerns about the depletion of petrochemical based materials . The most widely accepted definition of sustainable development is “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”. For a transition to a higher level of sustainability development it is important to make a number of changes in technological and social, and one of these is to develop alternative resources of raw materials.

Bio-based polymers offer important contributions by reducing the dependence on fossil fuels and through the related positive environmental impacts such as reduced carbon dioxide emissions. The legislative landscape is also changing where bio-based products are being favoured through initiatives such as the Lead Market Initiative (European Union) and Bio Preferred (USA). As a result, there is a worldwide demand for replacing petroleum derived raw materials with renewable resource-based raw materials for the production of polymers.

The first generation of bio-based polymers focused on deriving polymers from agricultural feedstocks such as, potatoes, and other carbohydrate feedstocks. However, the focus has shifted in recent years due to a desire to move away from food-based resources and significant breakthroughs in biotechnology. Bio-based polymers similar to conventional polymers are produced by bacterial fermentation processes by synthesizing the building blocks (monomers) from renewable resources, including lignocellulosic biomass (starch and cellulose), fatty acids, and organic waste. Natural bio-based polymers are the other class of bio-based polymers which are found naturally, such as proteins, nucleic acids, and polysaccharides (collagen, chitosan, etc.). These bio-based polymers have shown enormous growth in recent years in of technological developments and their commercial applications. There are three principal ways to produce biobased polymers using renewable resources:

(1) Using natural bio-based polymers with partial modification to meet the requirements (e.g., starch).

(2) Producing bio-based monomers by fermentation/conventional chemistry followed by polymerization (e.g., polylactic acid, polybutylene succinate, and polyethylene).

(3) Producing bio-based polymers directly by bacteria (e.g., polyhydroxyalkanoates).

2.2 Poly(lactic acid)

2.2.1 Introdution to PLA

Poly(lactic acid) (PLA) derived from an aliphatic polyesters commonly made from a-hydroxy acids, which include polyglycolic acid or polymandelic acid, and are biodegradable and biocompostable. PLA is a thermoplastic, excellent in mechanical strength,as a renewable resources that can yield articles for use in either the industrial packaging field or the biocompatible medical application including drug delivery system and tissue engineering. It is easily produced on standard plastics equipment to yield molded parts, film, or fibers (Rasal et al., 2010). It is one of the few interesting polymers in which the stereochemical structure can easily be modified by polymerizing a controlled mixture of the L or D isomers to yield high molecular weight amorphous or crystalline polymers that can be used for food contact (Bogaert et al., 2000). PLA is able to break down by simple hydrolysis of the ester bond and does not require the presence of enzymes to catalyze this hydrolysis. Its monomeric form which is lactic acid can be eliminated from the body through the incorporation into tricarboxylic acid cycle (Agrawal et al., 2001).

PLA can be processed on large-scale production lines to be used in various application whether by using injection molding, blow molding, thermoforming, and extrusion. The polymer must possess adequate thermal stability to prevent degradation and maintain molecular weight and properties. PLA undergoes thermal degradation at temperatures above 200°C by hydrolysis, lactide reformation, oxidative main chain scission, and inter or intramolecular transesterification reactions. PLA degradation is dependent on time, temperature, low-molecular-weight impurities, and catalyst concentration (Jashidi et al.,1988). Catalysts and oligomers decrease the degradation temperature and increase the degradation rate of PLA. In addition, the can viscosity and rheological changes, fuming during processing, and poor mechanical properties. Table 2.1 shows some of the most important physical and mechanical properties of PLA.

Table 2.1: Physical and mechanical properties of PLA (NatureWork, 2016).

Physical Properties	Cast
Specific Gravity	1.25
Melt Index, g/10 min (210ºC/2.16Kg)	10-25
Relative Viscosity	3.0-3.5
Crystalline Melt temperature	150-165
Glass Transition temperature	55-65
Clarity	Transparent
Mechanical Properties	
Tensile Yield Strength, psi (MPa)	7000 (48)
Tensile Elongation, %	2.5
Notched Izod Impact, ft-lb/in (J/m)	0.3 (0.16)
Flexural Strength (MPa)	12000 (83)
Flexural Modulus (MPa)	555000 (3828)

Different processing methodologies have been applied to control orientation and, hence, bulk properties of polymers. These approaches influence the bulk properties without altering the PLA chemistry or introducing additives. Injection molded samples of amorphous PLA showed higher tensile strength at break and notched Izod impact strength upon drawing. An injection molding process that applied an oscillating shear flow to orient the semi-solid melt improved the Charpy impact strength observed a substantial increase in elongation and tensile strength at break of PLA with different ratios of l-lactide to d,l-lactide upon biaxial orientation. For an l-lactide to d,l-lactide copolymer ratio of 80/20, elongation at break increased from 5.7 to 18.2% and tensile strength at break increased from 51.7 to 84.1 MPa upon biaxial orientation at 85◦C (Rahul, 2009).

PLA has been copolymerized with a range of polyesters in Figure 2.1, and other monomers either through polycondensation of lactic acid with other monomers, producing low molecular weight copolymers, or ring opening copolymerization of lactide with cyclic monomers like glycolide, caprolactone, valerolactone,trimethylene carbonate, etc. as well as linear monomers like ethylene glycol producing high molecular weight copolymers.

Poly(lactic acid) homopolymers have a glass-transition and melt temperature of about 55°C and 175°C, respectively. They require processing temperatures in excess of 185–190°C (Spinu et al., 1996). At these temperatures, unzipping and chain scission reactions leading to loss of molecular weight, as well as thermal degradations, are known to occur. Consequently, PLA homopolymers have a very narrow processing window. The most widely used method for improving PLA processability is based on melting point depression by the random incorporation of small amounts of lactide enantiomers of opposite configu- ration into the polymer by adding a small amount of D-lactide to the L-lactide to obtain PDLLA. Unfortunately, the melting point depression is accompanied by a significant decrease in crystallinity and crystallization rates (Spinu et al., 1996).

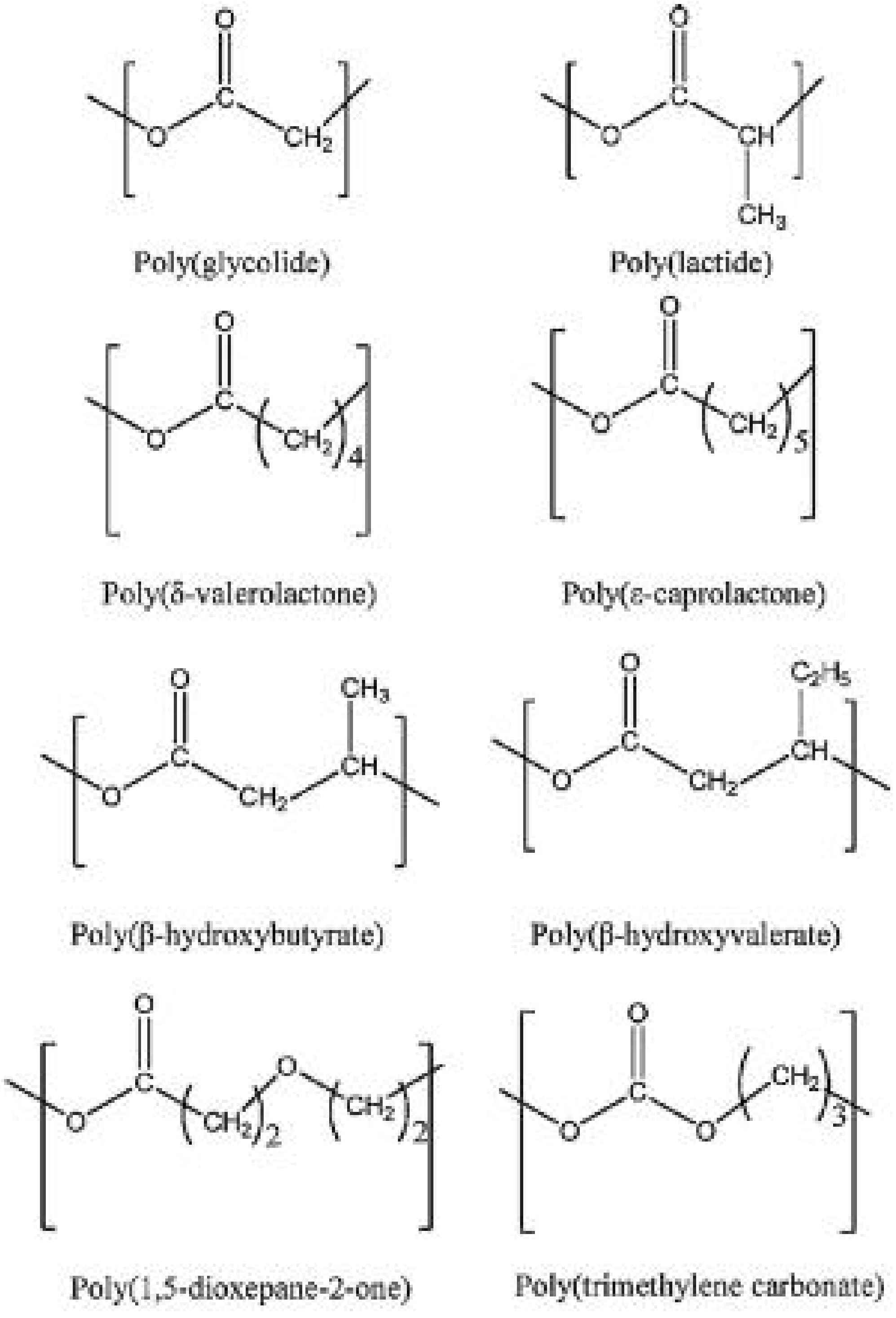

Figure 2.1: Common polyester repeat units of PLA based copolymers (Sodergad & Stolt, 2002).

2.2.1 Synthesis of PLA

The basic building block for PLA is lactic acid, which was first isolated in 1780 from sour milk by the Swedish chemist Scheele and first produced commercially in 1881. Food-related applications are the major use of lactic acid in the United States and account for 85% of the commercially produced product. It is used as a buffering agent, acidic flavoring agent, acidulant, and bacterial inhibitor in many processed foods. Lactic acid can be manufactured either by carbohydrate fermentation or chemical synthesis, although fermentation predominates (Benninga 1990).

Figure 2.2: Poly(lactic acid) (PLA) (ExtrusionBot, 2014).

Lactic acid (2-hydroxy propionic acid) is the simplest hydroxyl acid with an asymmetric carbon atom and exists in two optically active configurations. The L(1)isomer is produced in humans and other mammals, whereas both the D(2)- and L(1)-enantiomers are produced in bacterial systems. The majority of the world's produced lactic acid is made by the bacterial fermentation of carbohydrates, using homolactic organisms such as various optimized or modified strains of the genus Lactobacilli, which exclusively form lactic acid (Hartmann, 1998).

The synthesis of lactic acid into high-molecular weight PLA can follow two different routes of polymerization. Lactic acid is condensation polymerized to yield a low molecular weight, brittle, glassy polymer, which, for the most part, is unusable for any applications unless external coupling agents are used to increase the molecular weight of the polymer. 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 forms the six-member lactide ring. The second route of producing PLA is to collect, purify, and ring-open polymerize (ROP) lactide to yield high molecular weight of PLA. The lactide method was the only method of producing pure, high molecular weight PLA until Mitsui Toatsu Chemicals recently commercialized a process wherein lactic acid and catalyst are azeotropically dehydrated in a refluxing, high-boiling, aprotic solvent under reduced pressures to obtain PLA with weight-average molecular weights than 300,000 (Enomoto, 1994).

Synthesis method to produce to high molecular weight of PLA through condensation/coupling, azeotropic dehydrative condensation, or ring-opening polymerization of lactide . The condensation polymerization is the least expensive route, but it is difficult in a solvent free system to obtain high molecular weights, and therefore the use of coupling agents or esterification promoting adjuvants is required, adding cost and complexity (Cotarca, 1996). The self condensation of lactic acid results in a low molecular weight with an equimolar concentration of hydroxyl and carboxyl end group. To increase the molecular weight, chain-coupling agents must be added, and these will preferentially react with either the hydroxyl or carboxyl group, which leads to different kinetic reaction rates of coupling. The condensed PLA can be modified to produce either all hydroxyl or all carboxyl groups. Hydroxyl terminated PLA can be synthesized by the condensation of lactic acid in the presence of a small amount of multifunctional hydroxyl compounds such as 2-butene-1,4-diol, glycerol, or 1,4-butanediol, which leads to preferential hydroxyl end groups, or by the post condensation reaction of a monofunctional epoxide such as butyl glycidyl ether with the carboxylic acid to convert it to ahydroxyl group (Inata & Matsumura, 1986). This same concept can be used to synthesize an all-carboxyl-terminated PLA by the condensation reaction in the presence of multifunctional carboxylic acids such as maleic, succinic, adipic, or itaconicacid, leading to a carboxyl functional polymer (Bonsignore, 1985). The PLA can also be postreacted with acid anhydridessuch as maleic or succinic to convert the hydroxyl to a carboxylic end group (Jebay & Tenney, 1993).

The azeotropic condensation polymerization is a method to obtain high molecular weight polymer without the use of chain extenders or adjuvents. Copolymers using various diacids, diols, or hydroxyl acids are possible, with the use of solvents and residual catalyst the main drawbacks. A general procedure for this route consists of reduced pressure distillation of lactic acid for 2 to 3 hours at 130°C°C to remove the majority of the condensation water. Catalyst and diphenyl ether are added, then a tube packed with 3-A molecular sieves is attached to the reaction vessel. The refluxing solvent is returned to the vessel by way of the molecular sieves for an additional 30–40 hours at 130°C. The polymer can then be isolated as is or dissolved and precipitated for further purification (Ajioka et al., 1995).

This polymerization technique yields high molecular weight polymers, but with considerable catalyst impurities due to the high levels needed for acceptable reaction rates. This residual catalyst can cause many problems during further processing, such as unwanted degradation, uncontrolled or unreproducible hydrolysis rates, or, in the case of medical applications, catalyst toxicity and differing slow release properties. The catalyst can be deactivated by the addition of phosphoric or pyrophosphoric acid, and preferably two equivalents of acid to divalent tin catalyst are used. This provides a polymer with improved weathering resistance and heat and storage stability. The catalyst can also be precipitated and filtered out by the addition of strong acids such as sulfuric acid. Catalyst levels can be reduced to 10 ppm or less (Suizu et al., 1996).

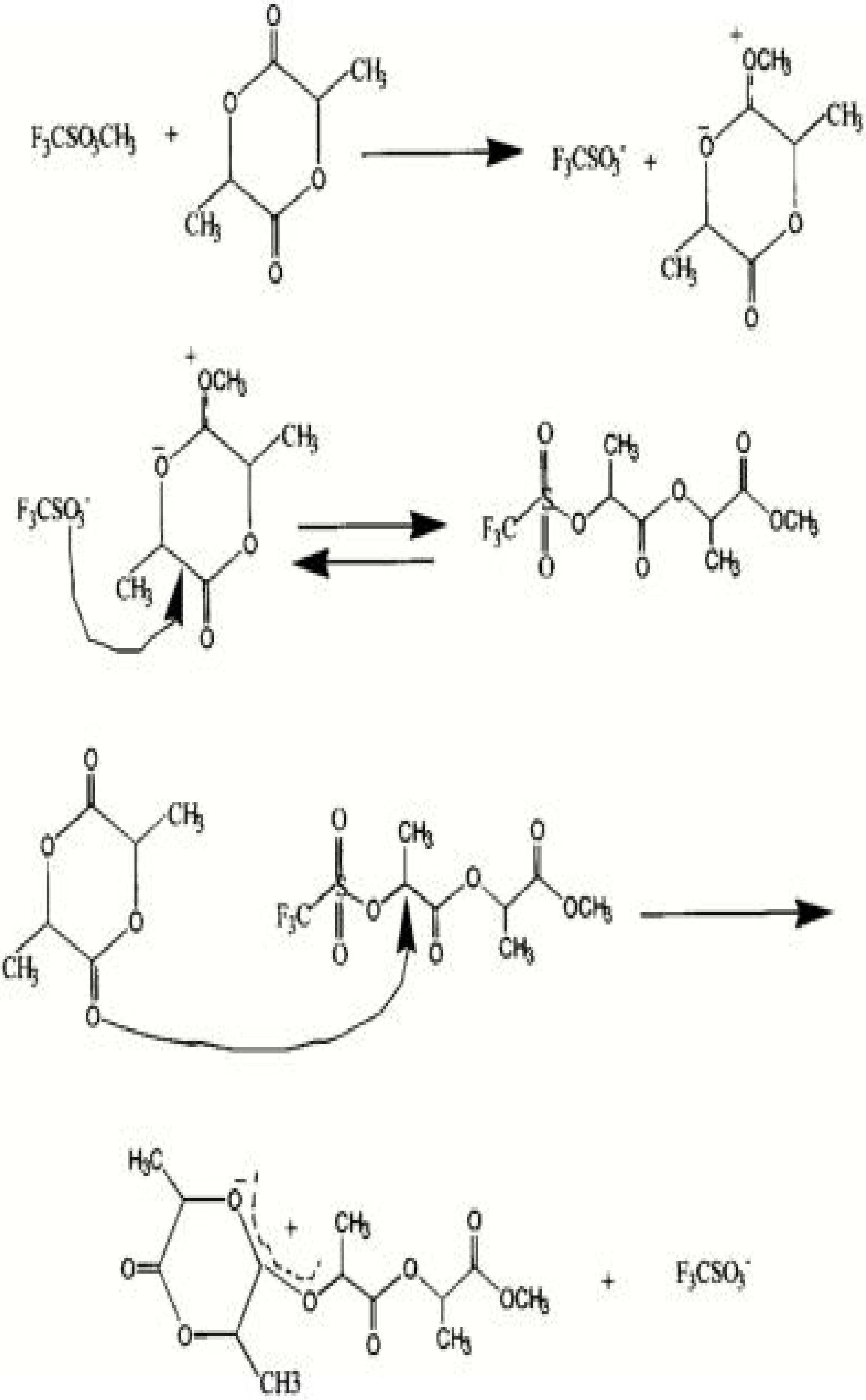

Figure 2.3: Cationic ring opening polymerization mechanism for PLA (Hartmann, 1998).

Poly(lactic acid) can undergo cationic ring-opening polymerization. It has been found that trifluoromethanesulfonic acid (triflic acid) and methyl trifluoromethanesulfonic acid (methyl triflate) are the only cationic initiators to polymerize lactide (Kricheldorf & Kreiser, 1987). The polymerization proceeds via triflate ester end groups instead of free carbenium ions, which yields, at low temperatures (<100°C), an optically active polymer without racemization. The chain growth proceeds by cleavage of the alkyl- oxygen bond. The propagation mechanism begins with the positively charged lactide ring being cleaved at the alkyl-oxygen bond by an S 2 attack by the triflate anion. The triflate end-group reacts with a second molecule of N lactide again in an S 2 fashion to yield a positively charged lactide that is opened. Then the triflate anion N again opens the charged lactide, and polymerization proceeds (Kricheldorf & Dunsing, 1986). The cationic polymerization mechanism is shown in Figure 2.3.

Anionic lactide polymerizations proceed by the nucleophilic reaction of the anion with the carbonyl and the subsequent acyl-oxygen cleavage. This produces an alkoxide end-group, which continues to propagate. The anionic polymerization mechanism is depicted in Figure 2.4. Jedlinski et al. (1995) has shown that the use of primary alkoxides such as potassium methoxide can yieldwell-defined polymers with negligible racemization, termination, or transesterification. Racemization of less than 5% was seen, starting with 99.9% pure L-lactide.

An extensive study of various anionic initiators for lactide polymerization was conducted. Kricheldorf et al. (1990) found that initiators of higher nucleophilicity are needed to initiate the lactide. Weaker bases, such as potassium benzoate, potassium phenoxide, or zinc stearate, do not initiate at low temperatures, but will initiate at high temperatures (1208°C). The high-temperature initiations occur in bulk but with considerable racemization and other side reactions, which hinder propagation. Initiators such as n-, sec-, or tert-butyl lithium and potassium tert-butoxide rapidly initiate the polymerization at low temperatures, but are plagued by side reactions, such as deprotonation of the lactide monomer. This deprotonation causes inconsistent polymerization, racemization, and, when done by the active chain end, termination, which thereby limits the molecular weights. Sipos et al. (1992) reported that the use of 18crown-6 ether complexes will yield higher molecular weights with narrow distributions, (PDI 5 1.1–1.2), but the slow the rate and give lower overall conversions. There are toxicity concerns with the use of lithium initiators, whereas the use of potassium or sodium metal ions yields polymers that are less toxic and are considered biocompatible.

The anionic and cationic initiations as described above are usually done in solvent systems and, due to their high reactivities, are susceptible to racemization, transesterification, and especially impurity levels. For practical, large-scale commercial use, it is preferable to do bulk melt polymerizations that use lower levels of nontoxic catalysts and are not plagued by these previous problems. The use of less-reactive metal carboxylates, oxides, and alkoxides has been extensively studied to correct these problems. It has been found that high-molecular-weight PLA is easily polymerized in the presence of tin, zinc, aluminum, and other heavy metal catalysts, with tin(II) and zinc yielding the purest polymers. These catalysts are favored because of their covalent metal oxygen bonds and free p or d orbitals.

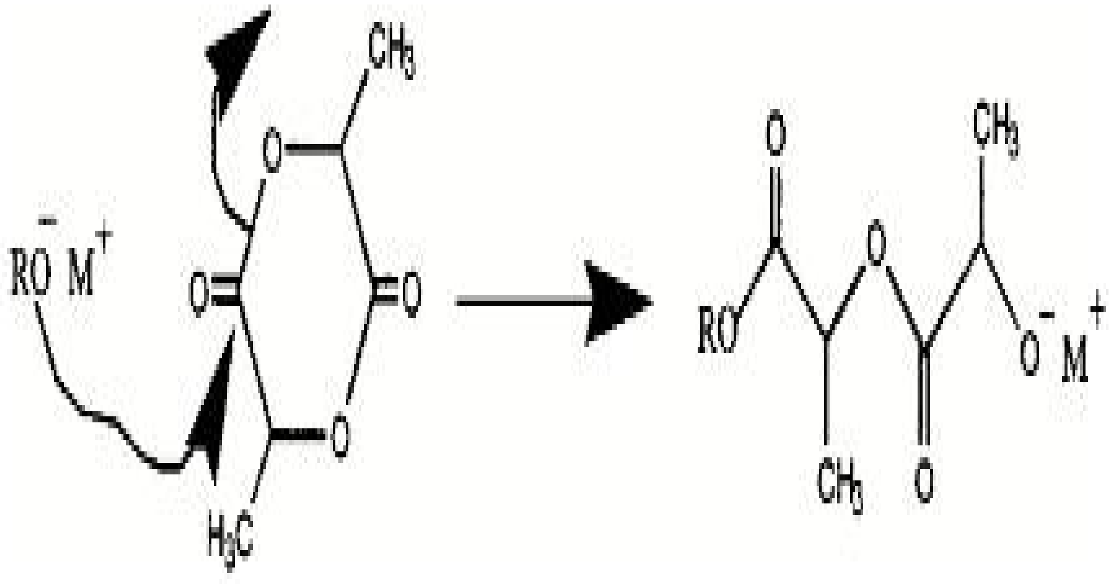

Figure 2.4: Anionic ring opening polymerization mechanism for PLA (Hartmann, 1998).

2.2.2 Advantages of PLA

Apart from being derived from renewable resources such as corn, wheat, and sugar beets, PLA is biodegradable, recyclable, and compostable (Sawyer, 2003). Its production also consumes carbon dioxide (Dorgan, 2001). These sustainability and eco-friendly characteristics make PLA an attractive biopolymer. Due to that PLA has potential to be used in food packaging, automotive parts, disposable tableware, sutures and drug delivery device (Martin el al., 2001).

The most attractive aspect of PLA, especially with respect to biomedical applications, is its biocompatibility. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. Also, the degradation products should not interfere with tissue healing. PLA hydrolyzes to its constituent hydroxy acid when implanted in living organisms including the human body. It is then incorporated into the tricarboxylic acid cycle and excreted (Athanasiou et al., 1996). Moreover, PLA degradation products are non-toxic (at a lower composition) making it a natural choice for biomedical applications (Eling et al., 1982

PLA has better thermal processibility compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), poly(ethyele glycol) (PEG), and poly(caprolactone) (PCL). It can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and film forming, with PLA resins for these methods commercialized by NatureWorks LLC (Auras et al., 2004). Vink et al. (2003) reported that PLA requires 25–55% less energy to produce than petroleum-based polymers and estimations show that this can be further reduced to less than 10% in the future. Lower energy use makes PLA production advantageous with respect to cost as well.

2.2.3 Disadvantages of PLA

Although PLA is an eco-friendly bioplastic with excellent biocompatibility, processibility, and less energy dependence, it has drawbacks as well, which limit its in certain applications. PLA is a very brittle material with less than 10% elongation at break (Hiljanen et al., 1996). Although its tensile strength and elastic modulus are comparable to poly(ethylene terephthalate) (PET) (Auras et al., 2004), the poor toughness limits its use in the applications that need plastic deformation at higher stress levels (Grijpma et al., 1992).

PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on the PLA crystallinity, molecular weight, weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content (Janorkar et al., 2004). The degradation rate is often considered to be an important selection criterion for biomedical applications (Tokiwa & Calabia 2006). The slow degradation rate leads to a long in vivo life time, which could be up to years in some cases.There have been reports of a second surgery almost 3 years after implantation to remove a PLA-based implant (Bergsma et al., 1995). The slow degradation rate is a serious problem with respect to disposal of consumer commodities as well.

PLA is relatively hydrophobic, with a static water contact angle of approximately 80. This results in low cell affinity, and can elicit an inflammatory response from the living host upon direct contact with biological fluids (Ratner, 1996). PLA is chemically inert with no reactive side-chain groups making its surface and bulk modifications a challenging task.

2.2.4 Approaches to enhance the properties of PLA

The brittleness of PLA can be modified to improve the toughness for various applications. Many approaches was developed for toughening PLA such as:

1. Copolymerization with other polymer
2. Blending with various additives
3. Surface modification
4. Blending with rubber

2.2.4.1 PLA surface modification

Surface-modification methods can be classified as non-permanent (non-covalent attachment of functional groups) or permanent (covalent attachment). While, undoubtedly, there has been work done to surface modify PLA for commodity applications (e.g., packaging films), there is a scarcity of data in the literature related to such things as friction modification, adhesion, and anti-fogging. However, there is abundant research reported in the literature, surface modification for biomedical applications, so this portion of the review will focus on those investigations with the notion that some of the approaches could also be suitable for other applications (Rahul et al., 2010).

Surface coating involves the deposition or adsorption of the modifying species onto the polymer surface. Typically, PLA has been coated with biomimetic apatite, extra cellular matrix (ECM) proteins like fibronectin, collagen, vitronectin, thrombospondin, tenascin, laminin, and entactin, RGD peptides, and PLA–PEG block, to control PLA–cell interactions (Rahul et al., 2010).

Chen et al (2006) produced PLA scaffolds coated with bonelike apatite or apatite/collagen composites. Saos-2 osteoblast-like cell compatibility of these scaffolds was greatly enhanced with these coatings. Atthof and Hilborn (2007) studied the collagen adsorption onto PLA discs. The adsorbed protein layer became structured showing clear fibrous networks on PLA. It was also demonstrated that the protein adsorption increased 3T3 mouse fibroblast cell attachment to the PLA surface. Quirk et al (2001) used poly(l-lysine)-RGD coatings to improve the spreading of bovine aortic endothelial cells on PLA. It was also demonstrated that the control over cell spreading inhibition could be achieved by altering the ratio of poly(l-lysine)/RGD components. Kubies et al (2003) deposited

Langmuir–Blodgett films of several AB and ABA type block copolymers on PLA film surfaces to improve hydrophilicity (where A= PLA and B = PEO, αmethoxy-ω-hydroxy PEO, α-carboxy-ω-hydroxy PEO, or poly(l-aspartic acid)). This study showed that the phase separation between the hydrophilic and hydrophobic was more favorable in the case of AB copolymers than ABA copolymers, resulting in more hydrophilic surfaces. Spatially selective adsorption of proteins and cells on PLA scaffolds is important with respect to biomedical applications such as medical implants, biosensors, and bioassays (Wang et al., 2005). Micro contact printed poly(oligoethyleneglycol methacrylate) (poly-OEGMA) on PLA film to create micron-size protein- or cell-resistant areas. Proteins or cells adsorbed only on the unprinted regions (Lin et al., 2005).

Although coating is a simple and convenient surface modification protocol, passive adsorption could induce competitive adsorption of other materials in the system and change the configuration of adsorbed species (Wang et al., 2005).

2.2.4.2 PLA copolymerization

PLA has been copolymerized with a range of polyesters and other monomers either through polycondensation of lactic acid with other monomers, producing low molecular weight copolymers, or ring opening copolymerization of lactide with cyclic monomers caprolactone,valerolactone, trimethylene carbonate, etc. as well as linear monomers like ethylene glycol producing high molecular weight copolymers.

Acid and hydroxyl groups present in the lactic acid make it feasible to copolymerize through polycondensation. According to Fukuzaki et al (1990) copolymerized l-lactic acid and ε-caprolactone without any catalyst to produce low molecular weight (M~6.8–8.8 kDa) copolymers for biomedical applications. These copolymers showed excellent in vitro (enzymatic) and in vivo degradation properties. l-Lactic acid and ε-caprolactone condensation copolymerization, using stannous octoate as a catalyst, was by crosslinking through reaction with diisocyanate to form biodegradable thermoplastic elastomers (Kylma & Seppala, 1997). l-Lactic acid has also been polycondensed with d,lmandelic acid (Fukuzaki & Aiba,1989) and other α-hydroxy acids such as d,l-α-hydroxybutyric acid, d,l-α-hydroxyisovaleric acid, and d,l-α-hydroxyisocaproic acid (Fukuzaki et al., 1989).

2.2.4.3 PLA blend with various additives

Blending is probably the most extensively used methodology to improve PLA mechanical properties. PLA has been blended with different plasticizers and polymers whether biodegradable and non-biodegradable to achieve desired mechanical properties. Lactide is a natural choice to plasticize PLA. Lactide plasticized PLA showed a significant increase in elongation at break but underwent stiffening with time due to low molecular weight lactide migration toward the surface Jacobsen & Fritz, 1999). Oligomeric plasticizers that would not tend to migrate toward the surface due to their relatively higher molecular have also been utilized. According to Martin and Avérous (2001) glycerol, citrate ester, PEG, PEG monolaurate, oligomeric lactic acid were used to plasticize PLA and found that oligomeric lactic acid and low molecular weight PEG (M∼400 Da) gave the best results while glycerol was found to be the least efficient plasticizer. Citrate esters (molecular weight 276–402 Da) derived from naturally occurring citric acid were found to be miscible with PLA at all compositions. For these blends with citrate esters, elongation at break was significantly improved accompanied with considerable loss of tensile yield strength (Labrecque et al., 1997).

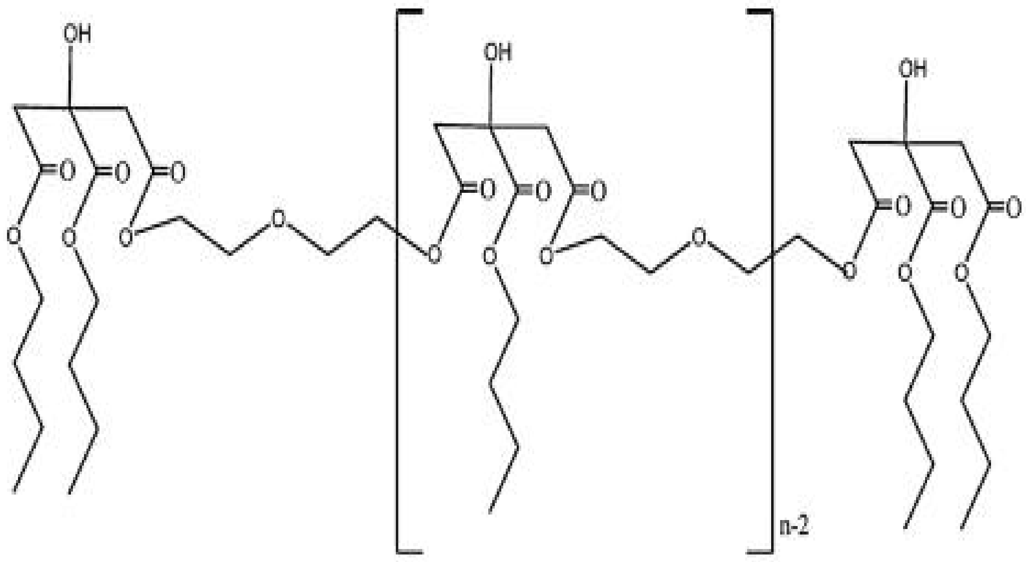

Figure 2.5: Chemical structure of oligomeric tributyl citatre (Ljungberg & Wesslén, 2003).

Ljungberg and Wesslén plasticized PLA using triacetine and tributyl citrate, successfully lowering Tg to ~ 10°C at 25 wt%, after which phase separation occurred (Ljungberg & Wesslén, 2002). Triacetine or tributyl-citrate-plasticized PLA films underwent crystallization, and plasticizer molecules migrated toward the surface with storage time due to their low molecular weight (Ljungberg et al., 2003). To overcome the aging problem, citrate oligomers (Fig. 2.5) were synthesized by trans-esterification of tributyl citrate and diethylene glycol. However, these oligomeric tributyl citratre plasticizers also underwent phase separation with storage time (Ljungberg & Wesslén, 2003). To achieve better stability, these researchers used diethyl bishydroxymethyl malonate (DBM) and its oligomer, synthesized through an esterification reaction between DBM and dichloride. When DBM alone was used as a plasticizer, it showed a tendancy to phase separate and migrate toward the surface. DBM-oligomer plasticized PLA demonstrated morphological stability with storage time (Ljungberg & Wesslén, 2004)