SYNTHESIS AND CHARACTERIZATION OF POLYLACTIC ACID FROM BUTYL LACTATE

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SYNTHESIS AND CHARACTERIZATION OF POLYLACTIC ACID FROM BUTYL LACTATE

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master’s Degree.

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คำสำคัญ: พอลิแลคติกแอซิด (PLA)/แลคไทด์ (LT)/โพลิเมอไรเซชันแบบเปิดวงแหวน (ROP)/บิวทิลแลคเตท (BL)/สแตนนอส ออคโทเอท (SOC)

พอลิแลคติกแอซิด (PLA) เป็นพอลิเมอร์ที่ย่อยสลายได้ทางชีวภาพซึ่งมีความสำคัญมากในปัจจุบัน เนื่องจากคุณสมบัติหลักในการย่อยสลายทางชีวภาพและความเข้ากันได้ทางชีวภาพซึ่งผลิตได้จากทรัพยากรหมุนเวียน ในงานนี้มีการศึกษาการสังเคราะห์ PLA จากกรดแลคติค เพื่อเป็นผลการศึกษาเบื้องต้น โดยวัตถุประสงค์หลักเพื่อศึกษาการสังเคราะห์ PLA จากแลคไทด์ที่ได้จากบิวทิลแลคเตท เงื่อนไขการสังเคราะห์จะศึกษาเพื่อให้ได้ PLA ที่มีคุณสมบัติเหมาะสมเมื่อเทียบกับ PLA เชิงพาณิชย์ ซึ่งงานนี้จะแบ่งออกเป็นห้ากลุ่มการทดลอง

เครื่องปฏิกรณ์ที่มีขนาด 1 ลิตร ถูกใช้เพื่อศึกษาหาสภาวะที่เหมาะสมของการสังเคราะห์ PLA โดยศึกษาอุณหภูมิของปฏิกิริยา เวลาการเกิดปฏิกิริยาและปริมาณของตัวเร่งปฏิกิริยาที่ใช้ ในงานนี้มีการใช้สารซิงค์ออกไซด์ (ZnO) และทินคลอไรด์ ($SnCl_4$) เป็นตัวเร่งปฏิกิริยาสำหรับการสังเคราะห์แลคไทด์จากกรดแลคติกและบิวทิลแลคเตตตามลำดับ และใช้สาร Stannous octoate เป็นตัวเร่งปฏิกิริยาในการสังเคราะห์ PLA จากแลคไทด์ (LT) และมีการใช้พอลิกลีเซอรอล-10 ($C_{48}H_{94}O_{22}$) และ 1,4-บิวเทนไดออล ($C_4H_{10}O_2$) เป็นตัวริเริ่ม การเพิ่มตัวริเริ่มต่อการสังเคราะห์ PLA จะทำการศึกษาเพื่อตรวจสอบว่ามีผลต่อคุณสมบัติของ PLA อย่างไร และ ผลิตภัณฑ์ PLA ที่สังเคราะห์ได้จากกระบวนการจะถูกวิเคราะห์คุณสมบัติทางกายภาพและทางเคมี

ในการสังเคราะห์ PLA จากบิวทิลแลคเตท ประกอบด้วยขั้นตอนของโอลิโกเมอไรเซชัน (Oligomerization) ดีพอลิเมอไรเซชัน (Depolymerization) และพอลิเมอไรเซชันแบบเปิดวง (Ring opening polymerization) โดยในขั้นตอนแรกเป็นการสังเคราะห์แลคไทด์จากบิวทิลแลคเตท ผ่านขั้นตอนของโอลิโกเมอไรเซชันและดีพอลิเมอไรเซชัน พบว่าสภาวะที่เหมาะสมของกระบวนการของโอลิโกเมอไรเซชันเป็นดังนี้ อุณหภูมิของปฏิกิริยาคือ 180°C เวลาในการเกิดปฏิกิริยา 8 ชั่วโมง และปริมาณของตัวเร่งปฏิกิริยาคือ 0.1 %v/v และในขั้นตอนดีพอลิเมอไรเซชันเป็นดังนี้ อุณหภูมิของปฏิกิริยาคือ 210°C เวลาในการเกิดปฏิกิริยา 3 ชั่วโมง ตัวเร่งปฏิกิริยาเท่ากับ 0.1 %w/w ซึ่งได้ค่าร้อยละการผลิตได้แลคไทด์เท่ากับ 8% มีน้ำหนักโมเลกุลเฉลี่ย (Mw) คือ 124 g/mole อุณหภูมิหลอมเหลวคือ 127°C และอุณหภูมิการสลายตัวคือ 240°C สถาวะที่เหมาะสมในการสังเคราะห์ PLA เป็นดังนี้ อุณหภูมิของปฏิกิริยาคือ 180°C เวลาในการเกิดปฏิกิริยา 5 ชั่วโมง โดยใช้ตัวเร่งปฏิกิริยาเท่ากับ 0.2 %w/w และตัวริเริ่มคือ 0.02 %mole โดย PLA ที่ได้มีค่าร้อยละการผลิตได้เท่ากับ 35มีน้ำหนักโมเลกุลเฉลี่ยที่วัดจากความหนืดโดยวิธี Cannon-Fensk คือ 29000 g/mole

มีค่าอุณหภูมิสภาพแก้วเท่ากับ 60℃ อุณหภูมิหลอมเหลวคือ 150℃ และอุณหภูมิการสลายตัวคือ 335℃

สาขาวิชา<u>วิศวกรรมเคมี</u> ลายมือชื่อนักศึกษา..

ปีการศึกษา <u>2564</u> ลายมือชื่ออาจารย์ที่ปรึกษา..................................

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..............................

BEEVANG NYIAVUEVANG: SYNTHESIS AND CHARACTERIZATION OF POLYLACTIC ACID FROM BUTYL LACTATE. THESIS ADVISOR: SUPUNNEE JUNPIROM, Ph.D. 146 PP.

Keyword: POLYLACTIC ACID (PLA)/ LACTIDE (LT)/ RING OPENING POLYMERIZATION (ROP)/ BUTYL LACTATE (BL)/ STANNOUS OCTOATE (SOC)

Polylactic acid (PLA) is a biodegradable polymer that most important at the present due primarily to its properties as biological degradation and biocompatibility derived from renewable resources. PLA synthesis from lactic acid was synthesized as a preliminary result for this study. This work aims to investigate the PLA synthesis from lactide that derived from butyl lactate. The synthesis conditions were varied in order to obtain the PLA with the proper properties while compared to commercial PLA, the work was divided into five experimental series.

A 1 liter reactor was used to find the optimum condition of PLA synthesis by variation of reaction temperature, reaction time, and amount of catalyst. Zinc oxide and tin (IV) chloride were selected to use as a catalyst for lactide synthesis from lactic acid and butyl lactate, respectively. Tin octoate was employed as a catalyst in synthesis of PLA from produced lactide, then polyglycerol-10, and butanediol were used as an initiator. Effect of initiator addition on PLA synthesis was studied in one experimental series to examine whether it improve the properties of PLA. Yield of product as well as physical and chemical properties of the produced PLA were analysed.

PLA synthesis from butyl lactate was obtained from step of oligomerization, depolymerization, and ring opening polymerization. Lactide synthesized from butyl lactate through step of oligomerization and depolymerization, the optimum condition for variation of independent variables such as reaction temperature, reaction time, and amount of catalyst was 180°C, 8 h, and 0.1 %v/v, respectively, for the process of oligomerization and at 210°C, for 3 h, 0.1 %w/w, respectively, for depolymerization stage. This condition gave the purified lactide of 8 %yield with the average molecular weight (Mw) of 124 g/mole, melting temperature at 127°C, and decomposition temperature at 240°C. Synthesized PLA was obtained from the optimum condition of reaction temperature at 180°C, 5 h with amount of catalyst 0.2 %w/w, and initiator of 0.02 % mole. This condition gave 35 %yield, with a viscosity average molecular weight measured by Cannon-Fenske of 29000 g/mole.

The thermal stability for glass transition, melting, and decomposition temperature of this PLA sample was observed at 60, 150, and 335°C, respectively.

School of Chemical Engineering
Academic Year 2021

Student's Signature……………………………………
Advisor's Signature SUPUNNEE J. ………………………
Co-advisor's Signature…………………………………

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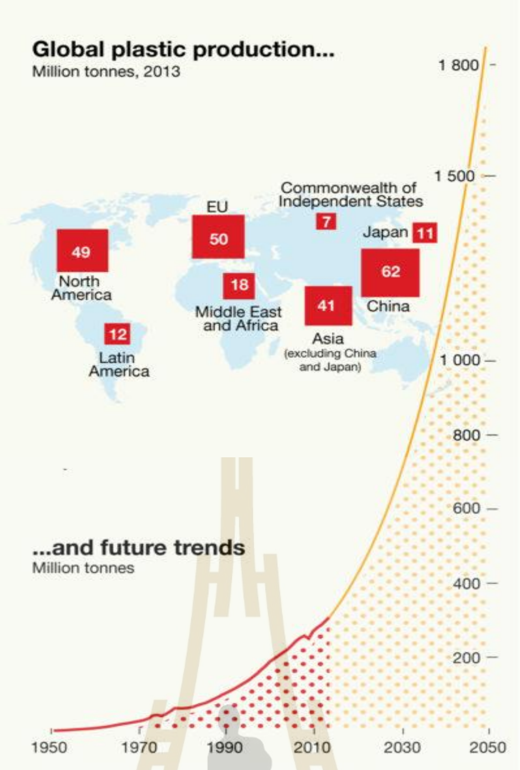
CHAPTER I

INTRODUCTION

1.1 Background and problem

Polymer materials are becoming increasingly significant in people's daily lives. However, there are a number of drawbacks, including rising consumption and the amount of polymer required while resources are depleting. The following are some of the drawbacks of petrochemical-based polymers: microplastic has emerged as a forward problem to humans and animals as an ecosystem from incomplete degradation material, uneconomical recycling costs, and the possibility of toxic migrating to edible materials when used for food packaging and medical applications. The diminishing oil and gas resources, environmental concerns about their degradation and incineration are the cause of climate change and global warming (Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010). Because of the high demand for plastic, these drawbacks have been steadily rising over time. However, plastics are utilized in a wide range of industries, including construction, packaging, electronics, electrical equipment, agriculture, and medical devices, to name a few ("Plastics – the Facts 2020. An analysis of Global plastic production, demand and waste data. ,"). The plastics sector is presently constantly rising all over the world, owing to increase demand and consumption of the materials, as seen by the ever-increasing number of plastic materials produced globally, as seen in Figure 1.1. This is a clearly important economic sector that will continue to grow, resulting in consumption increasing of plastic materials and the serious concern about each of the previously mentioned.



Source: Ryan, A Brief History of Marine Litter Research, in M. Bergmann, L. Gutow, M. Kiages (Eds.), Marine Anthropogenic Litter, Berlin Springer, 2015; Plastic Europe

Figure 1.1 Plastic worldwide production from 1950 to 2050 (in million metric tons)

Bioplastics, which are discussed in further detail in the following chapter, are currently another option that could provide a solution in the future of the plastic industry for dealing with these shortcomings. Polylactic acid is a well-known biodegradable polymer that is manufactured in small and big amounts and used in a wide range of industries. It is one of the most suitable polymers to replace non-biodegradable synthetic polymers based on fossil fuels due to its high mechanical qualities and environmental compatibility (Sungyeap Hong, 2014). Biopolymer development has risen in popularity in recent years as a result of its strategic nature and environmental motivations. Polylactic acid (PLA) is a biodegradable substance made from lactic acid derived from renewable resources such as garbage, potatoes, corn starch sugars, cassava or sugar cane, and glycerin waste from biodiesel and other agricultural products. PLA is increasingly being used in medical, pharmaceutical, and environmental applications due to its desirable features like as transparency, mechanical strength, compostability, and safety (Rahmayetty et al., 2018).

Polylactic acid (PLA) can be prepared by different ways from lactic acid such as direct condensation polymerization, ring opening polymerization and azeotropic condensation polymerization. Currently, PLA may be regulated by using various organometallic compounds as catalysts for aluminum, zinc, tin, and others. The most frequent catalyst for the manufacturing of high molecular weight polylactic acid is stannous octoate (Sn(Oct)$_2$). Recrystallization from ethyl acetate was used to purify all of the products (Yarkova, Novikov, Glotova, Shkarin, & Borovikova, 2015). The use of metal catalysts for PLA manufacturing has the disadvantage of contaminating the product with the metals employed. As a result, a thorough purification procedure is required, particularly when the polymer is intended for biomedical purposes (Rahmayetty et al., 2018). PLA is frequently utilized in the medical applications for tissue engineering, implants, and drug delivery systems, among other things. It's suitable for food packaging as well as textiles (Hans R. Kricheldorf & Weidner, 2019). PLA with a low molecular weight is suitable for medication delivery and has a lengthy track record of human safety (Y. Hu, Daoud, Cheuk, & Lin, 2016; Pivsa-Art et al., 2014).

Nowadays, two world manufacturers of PLA, Nature Works (USA) and Corbion (Netherlands), are using the lactic acid as raw material and it also has numerous studies and improvements. Furthermore, lactide is typically made from lactic acid, it always contains unconverted lactic acid as an impurity and must be purified through a number of technical difficulties, time-consumption and also excess solvent using. In a prior study, it was discovered that butyl lactate, which doesn't contain lactic acid, can be used to obtain lactide by simple purification process. Therefore, in this work aims to investigate the synthesis of PLA from butyl lactate. There are two main steps of PLA synthesis, first is the lactide synthesis from butyl lactate and PLA synthesis from produced lactide with stannous octoate as a catalyst. Since it is the new way of PLA synthesis that using butyl lactate as raw material and relatively hoping that it will be developed method in the future.

1.2 Objective

1) To investigate the optimum conditions to produce lactide from butyl lactate for further produced PLA.

2) To investigate the synthesis with and without initiator to produce PLA from produced lactide based butyl lactate.

3) To analysis the Energy index of PLA synthesis.

1.3 Scope of investigation

1) Study of PLA directly from butyl lactate as substrates by the ring-opening polymerization, whereas PLA was produced from lactic acid as the preliminary result.

2) The catalysts use on the stages are zinc oxide, tin(IV) chloride, stannous octoate.

3) The synthesized PLA was analyzed using: Fourier transform infrared spectrometer (FTIR), IR spectroscopy, Gel permeation chromatography (GPC), Differential scanning calorimetry (DSC), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), and Nuclear Magnetic Resonance (NMR)

1.4 Expected Benefits

1) The knowledge on PLA synthesis can be used to implement in the practical production.

2) The reduction of fossil-based resources and biodegradability of PLA lead to the reduction of climate change.

3) The increasing price of bio-based raw material it can be converted to high value products i.e. medical grade PLA.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Polymer

As polymers comprise thousands to millions of atoms in a huge molecule called macromolecules, a molecule has a collection of atoms that have strong interactions among themselves. Polymers are made by connecting a large number of small molecules called monomers. Monomers are simple organic compounds that have at least two active functional groups and a double bond.

2.1.1 Classification of polymer

Thermoplastic polymer and thermosetting polymer are the two forms of polymer as following described

1) **Thermoplastic:** When heated, these polymers soften and can be transformed into various shapes, which they can keep after cooling. The heating, reshaping, and retaining operations can all be done multiple times. Thermoplastic polymers are those that soften when heated and stiffen when cooled. (PLA, Ps, PE, etc.).

2) **Thermosetting plastic:** These polymers are heat-resistant plastics with specific features that make them resistant to temperature changes and chemical reactions. When exposed to high temperatures, it does not weaken and cannot be changed; however, it can be split or burned (polyester, phenolics, polyurethane).

Natural polymer and synthetic polymer are classification of polymer based on original source.

1) **Natural polymer:** Natural polymers are those obtained from natural materials. Rubber, silk, wool, cellophane, and other materials are examples.

2) **Synthetic polymer:** Synthetic polymers, such as polylactic acid, polyethylene, and others, are made from low molecular weight compounds.

Condensation polymer and addition polymer are two types of polymer based on the different mechanisms of synthesis produced from monomers.

1) **Condensation polymer:** Condensation polymers are polymers created by tiny molecules joining together and shedding water or methanol as byproducts during condensation.

2) Addition polymer: An addition polymer is one that can be made simply by joining monomers together without the use of any other coproducts. The most common type of addition polymer is one made from unsaturated vinyl monomer, and the process is usually carried out with the help of catalysts.

2.1.2 Polymerization

The process of linking numerous monomers as the basic building blocks together to produce polymers, which is the process of generating huge molecules from small ones. Polymerization occurs in chemical compounds though a variety of reaction pathways that vary in complexity depending on the functional groups present in the reactants. Step reaction polymerization (condensation), radical chain polymerization (addition), and ionic and coordination chain polymerization are all examples of polymerization (addition).

2.2 Biodegradable Polymer

Biopolymers have potential uses in almost all economic sectors. Biodegradable polymers are substances whose chemical and physical characteristics change and completely disintegrate. It is described polymers made from renewable resources, and decompose into natural byproduct as CO_2 and water. These polymers are made up mostly of ester, amide, and ether functional groups and can be found both naturally and synthetically. Their specific structure determines their characteristics and mode of breakdown. Condensation processes, ring opening polymerization, and metal catalysts are frequently used to make these polymers. Biodegradable polymers have a wide range of uses and applications.

Biodegradable polymer can be classified as:

1) Polymers that are inherently sensitive to microbial enzyme assault and have not been changed.

2) Polyesters and other synthetic polymers.

3) Polymers that have been changed with additives and fillers to make them more biodegradable. Biodegradable polymers that occur naturally are renewable. Some synthetic polymers are also sustainable since they are generated from renewable feedstocks. Poly lactic acid (PLA), for example, is derived from agricultural feedstocks. A flowchart depicting the production of biodegradable polymers shown in Figure 2.1.

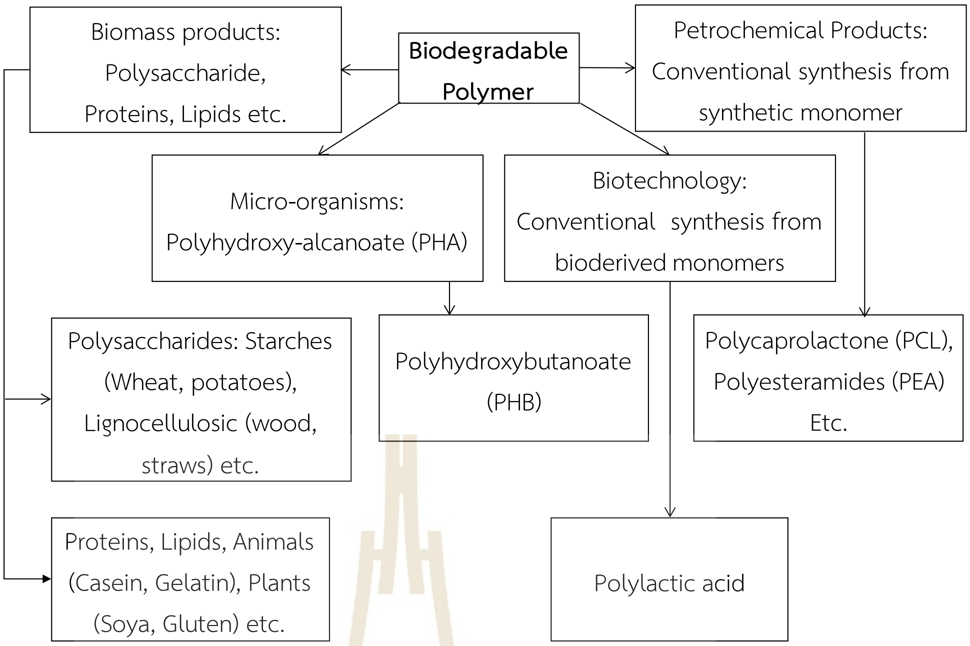


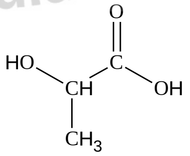
Figure 2.1 Biodegradable polymer classification

The purpose of this thesis is to describe PLA and its manufacturing procedures, as well as other independent variables and features that are suitable for combined cell scaffold.

2.2.1 Lactic acid

Lactic acid (LA), also known as CH_3-CHOHCOOH, is a nonvolatile acidic compound that is colorless and odorless. It's a low molecular weight organic acid that can be made synthetically or by fermentation which can be found in renewable resources such as maize starch sugars, cassava or sugar cane, and biodiesel glycerin waste, among others. Table 2.1 lactic acid the properties of lactic acid.

Table 2.1 lactic acid's physical properties (Davachi & Kaffashi, 2015).

Lactic acid	
Molecular formula	$C_3H_6O_3$
Molar mass	90.08 g/mole
Density	1.209 g/ml
Melting point	L: 53 ℃ D: 53 ℃ L/D: 16.8℃
Boiling point	122℃, at 15 mmHg
Viscosity (mPas)	28.5 (85.3% Solution in

Lactic acid manufacturing has recently seen a surge in demand due to its numerous applications in the textile, chemical, culinary, and pharmaceutical industries, as well as its use as a monomer in the production of biodegradable polymers (PLA). Lactic acid fermentation is based on the hydrolysis of lactic acid by a strong acid, yielding two forms of lactic acid: D(-) and L(+). Fermentative manufacturing, in which a suitable carbohydrate is transformed to lactic acid by microorganisms, has grown in popularity due to the advantages of environmental friendliness and the use of renewable resources, as previously stated. Lactic acid has an asymmetric carbon atom (chiral carbon) in its chemical structure, and it has two optically active enantiomers, L-lactic acid and D-lactic acid (Figure 2.2), which have different effects on polarized light. An equimolar (racemic) mixing of D(-) and L(+) isomers produces the optically inactive D, L, or meso form. Because it has both a carboxylic and a hydroxyl group, it is regarded the most viable monomer for chemical transformations (Lasprilla, Martinez, Lunelli, Jardini, & Filho, 2012). Lactic acid comes in two forms: L(+)- and D(-)-. The L(+)- form is the natural and most frequent, but the D(-)- form can also be created by microbes or though racemization (Zhang, Jin, & Kelly, 2007). Chemical synthesis and microbial fermentation processes for lactic acid generation are depicted in Figure 2.3.

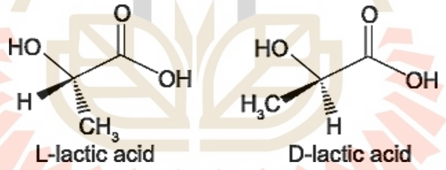


Figure 2.2 Two enantiomeric forms of lactic acid

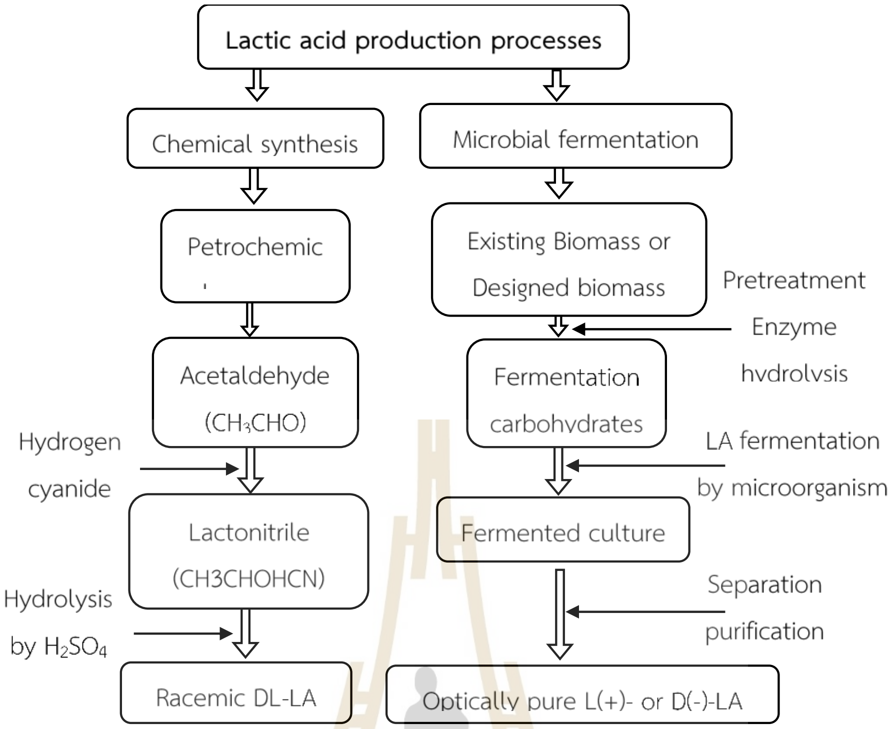
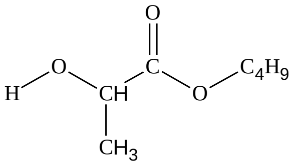


Figure 2.3 Chemical synthesis and microbiological fermentation are both used to make lactic acid (Tan, Abdel-Rahman, & Sonomoto, 2017)

2.2.2 Butyl lactate

Butyl lactate is an ester produced from lactate. For its hygroscopic, emulsifying, and exfoliating qualities, as an alpha-hydroxy acid ester, its use in cosmetic, food, and medicinal formulations has skyrocketed. By its flavorful effect, it is utilized as a food ingredient. It can be utilized as a solvent and chemical feedstock in industry. It can be utilized as an extractant for extracting 1-butanol from aqueous fermentation broth because it is a bio-based solvent. It can be made in a variety of ways using lipase from various sources (Kavčič, Knez, & Leitgeb, 2014). The lipase-catalyzed synthesis of these esters in low-water conditions offers substantial advantages over conventional chemical techniques, including lower energy consumption, easier downstream treatment, and reduced byproduct production (Domenico Pirozzi, 2006). Its properties are showing in Table 2.2.

Table 2.2 Butyl lactate's physical properties

Butyl lactate	
Molecular formula	$CH_3CHOHCOOC_4H_9$
Molar mass	146.19 g/mol
Density	0.9800g/mL
Melting point	-43.0℃
Boiling point	185.0℃ to 187.0℃
Viscosity	0.685cP (25 ℃)

Butyl acetate is usually made though Fischer esterification of butanol (or its isomer to make an isomer of butyl acetate) with acetic acid under reflux conditions in the presence of catalytic sulfuric acid, as shown in Figure 2.4.

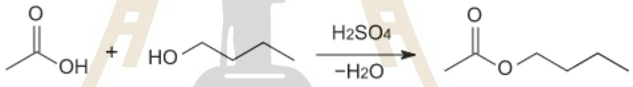
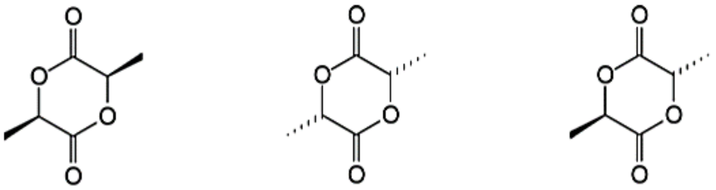


Figure 2.4 Production of butyl lactate

2.2.3 Lactide

The cyclic di-esters of lactic acid are known as lactide (3, 6-dimethyl-1, 4-dioxane-2, 5-dione) which contain in three stereoisomeric forms due to the two asymmetric carbon atoms in the molecule: L(-)-lactide (S,S), D(+)-lactide (R.R), and the optically inactive meso-lactide (R,S) (Figure 2.5) (Auras, Wiley, 2010).



(*R*,*R*)-Lactide
or D-lactide

(*S*,*S*)-Lactide
or L-lactide

(*R*,*S*)-Lactide
or *meso*-lactide

Figure 2.5 Structure of Lactides

D, L-lactide refers to the racemic 1:1 combination of L and D. Table 2 3 shows the physical and chemical properties of lactide.

Table 2.3 Lactide's physical and chemical properties

Properties	Value	Isomer
Molecular weight	144	D
	144	L
	144	meso
Melting temperature (℃)	90-97	D
	90-97	L
	53	meso
Boiling temperature (℃)	255	L
Optical rotation degrees	-260	L
	260	D

Methylene chloride, benzene, xylene, toluene, chloride, chloroform, tetrahydrofuran, isopropanol, acetone, ethyl acetate, methanol, and butanone are all miscible with lactide. To be able to carry out the ring-opening polymerization that results in PLA with high molecular weights, the lactide must be as pure as possible. Lactide is normally made in two steps: first, an oligomer of lactic acid is prepared, then a catalyst is added and the oligomer is heated under decreased pressure to produce the necessary lactide when the oligomer decomposes (Tyler, Gullotti, Mangraviti, Utsuki, & Brem, 2016). Figure 2.6 depicts the general lactide manufacturing process, including purification (Auras, Wiley, 2010).

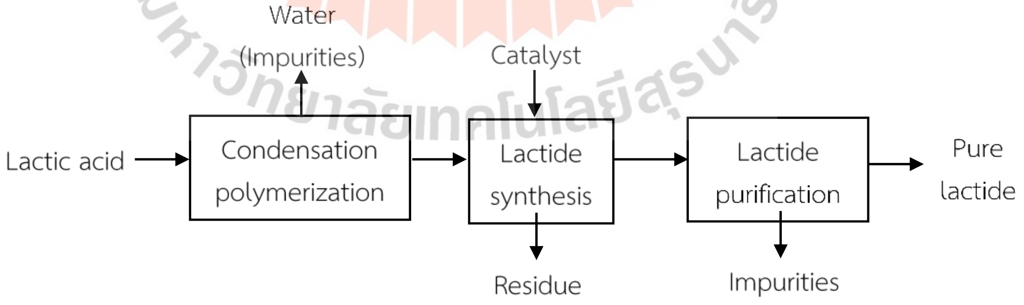


Figure 2.6 Lactide production and purification are depicted schematically

To get high purity, recrystallization from a mixture of toluene and ethyl acetate is a regularly used laboratory procedure for lactide purification. The reaction kinetics of lactide synthesis from alkyl lactate via a prepolymer pathway were compared to lactide synthesis from lactic acid. In order to generate the best feasible yield of lactide while still achieving L-isomer selectivity, a variety of different factors were examined. $Sn(Oct)_2$ was shown to be the most effective acid catalyst for L-lactide selectivity as well as providing a high oligomer yield from the alkyl lactate among the several acid catalysts evaluated. The findings demonstrate that alkyl lactate can be used to make high-quality lactide (Upare, Hwang, Chang, & Hwang, 2012). Table 2.4 shows the effect of alkyl group length on oligomerization and depolymerization and Table 2.5 shows newly developed lactide production methods in the laboratory.

Table 2.4 The effect of the length of the alkyl group on oligomerization and depolymerization (Upare et al., 2012)

Feed	Oligomerization				Depolymerization			
	Temp (°C)	Time (h)	Oligomer yield (%)	Mw (g/mol)	Temp (°C)	Time (h)	Crude lactide yield (%)	L- lactide (%)
Methyl	150	13	65	1918	180	5	49	98
Ethyl lactate	160	11	81	2346	180	5	46	98
Butyl lactate	185	19	71	1478	210	5	24	64

Table 2.5 Lactide synthesis methods that have recently been established in the laboratory

Catalyst	Temp (℃)	Pressure (kPa)	Time (h)	Yield (%)
Nano-ZnO (30-40 nm) aqueous dispersion (0.6	170-220	1-3	8	92
SnCl2 (0.1 %w/w)	210	10	8	79
zinc oxide (1.5 %w/w)	100-180	1-1.5	5	43-65
Stannous octoate (1 %w/w)	180–210	1	16	41.3
Stannous oxide (0.1 %w/w)	220	3	>8	77
Zinc oxide (1 %w/w)	230–240	1-3	-	72

2.2.4 Purification of lactide

Lactic acid, lactic acid oligomers, water, meso-lactide, and other contaminants are always present in a crude lactide stream produced by a lactide synthesis reactor. Lactide must meet strict standards for free acid content, water, and stereochemical purity. For lactide purification, two basic separation processes, distillation and crystallization, are being used:

1) Distillation: It takes a solid grasp of kinetics and vacuum equipment operation to separate the multicomponent combination of lactide, water, lactic acid,

and its oligomers into pure fractions. Although distillates and bottoms can be recycled, careful temperature and residence time changes are required due to the buildup of pollutants from the feed or the production of meso-lactide throughout the process. Meso-lactide is separated from lactide in the second column after the crude lactide from the synthesis has been distilled to remove the acids and water. Because the boiling temperatures of all compounds are between 200 and 300 °C, low pressures are used. The process of distillation is widely used (Auras, Wiley, 2010).

2) Solvent for crystallization: Recrystallization from toluene and ethyl acetate mixtures is a typical laboratory procedure for lactide purification. Lactide with an exceedingly high purity can be made by crystallizing it many times with varying toluene/ethyl acetate ratios. Several patents indicate the use of solvents in the crystallization of lactide, but melt crystallization without solvents is favored on a wide scale.

Melt Crystallization is a term that refers to the formation of crystals from Lactide crystallizes readily, and multiple patents detail how crystallization can produce lactide that meets specified lactic acid concentration, oligomers, meso-lactide, and water requirements. The lactide/lactic and lactide-meso-lactide thermodynamic equilibria, which define the highest yield as a function of these impurities in the feed, are described in an early patent. Different types of equipment are listed in patents, including static equipment, falling film crystallizers, a vertical column with a scraper to remove crystal mass from the cooled wall, and a scraped heat exchanger attached to a wash column. Large-scale crystallization equipment is difficult to design and scale-up due to the required heat transfer, as well as the possibility of increased viscosity of mother liquor due to oligomerization of lactide and residual acid. The desired stereochemical purity of the product determines whether to use distillation, crystallization, or new separation procedures such absorption or membrane separation. Crystallization produces highly pure lactide, which can be used to make high-melting PLLA homopolymers with a high molecular weight, for example. Because inexpensive distillation equipment does not completely remove all meso-lactide, ring-opening polymerization yields a lactide monomer mixture for PLA copolymers with different thermal characteristics. The kinetics of the reactive system, as well as the thermodynamic properties of the chemicals, are used to build the separation system. Advanced analytical procedures for lactic acid and its oligomers, lactides, and residues are required to obtain this knowledge. Lactide synthesis can produce impurities, similar to PLA degradation processes, and GC methods are required to detect these molecules and establish their destiny in the process.

2.3 Polylactic acid (PLA)

Polylactic acid (PLA) is a biodegradable and biocompatible substance that is made from LA monomer, which is obtained from 100 percent renewable resources such as cassava, sugar beets, rice, and corn. PLA is destroyed though simple ester bond hydrolysis, which does not necessitate the presence of enzymes to catalyze the process. The rate of degradation is determined by particle size and shape, isomer ratio, and hydrolysis temperature, as well as the PLA cycle in nature, which includes synthesis and hydrolysis shown in Figure 2.7 (Al-Mobarak, 2018).

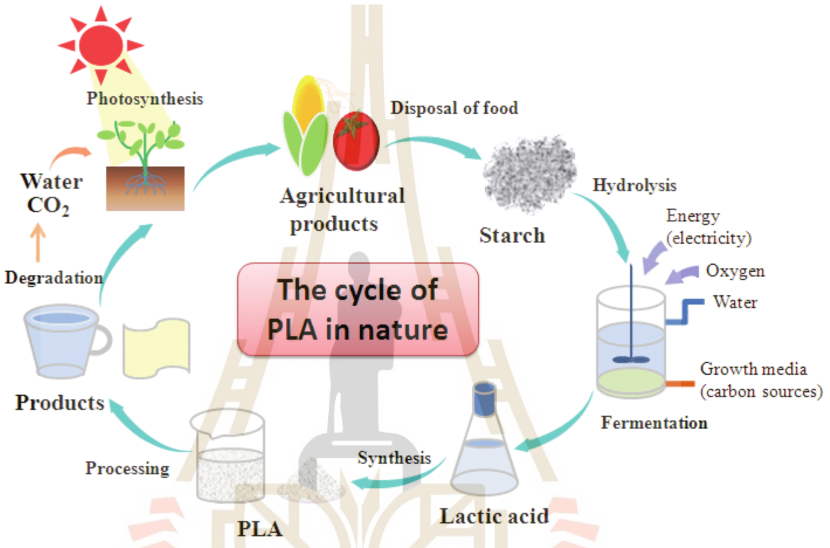


Figure 2.7 The cycle of PLA in nature

PLA degrades in the normal environment in around 6 months - 2 years, compared to 500 to 1000 years for traditional polymers like polystyrene (PS) and polyethylene (PE). Figure 2.8 shows images of PLA materials biodegrading in the normal environment. Rudnik et al. reported that the using "bioreactors," laboratory biodegradation investigations were conducted with burial in soil in Spata, Greece. The temperature of the soil was measured 30 cm below the surface and ranged from 16 - 21°C. After being buried in soil for a month, PLA films started to crack. The thin PLA sheet samples revealed several fissures. The beginning of the PLA film samples fragmentation is correlated with the rise in temperature. The degree of fragmentation and disintegration then advanced more quickly (Rudnik & Briassoulis, 2011).

Kale et al. studied PLA bottle biodegradation under actual composting conditions. The pile was sealed and the temperature reached the standard composting temperature after the compost had been applied to the packages. The performance of the composting process may be impacted by external atmospheric parameters such as temperature, relative humidity, and sun radiation, which were monitored. The PLA bottle can then decompose completely within 58 days (Kale, Auras, Singh, & Narayan, 2007).

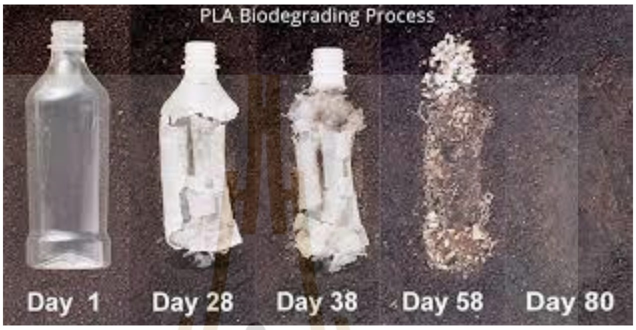


Figure 2.8 Biodegradation of PLA materials images

PLA has proven to be a viable replacement to petroleum-based polymers, with qualities comparable to HDPE, LDPE, PET, and other commonly used polymers. PLA, on the other hand, has greater production costs than its petroleum-based rivals, limiting its economic viability. Nowadays, the scarcity of fossil fuels is becoming a greater concern by the day, so industries and academics are rapidly shifting their focus to renewable sources to meet their needs, with PLA emerging as one of the finest options for current demands. PLA is a popular thermoplastic because it can be made from renewable resources and may decompose to lactic acid, a non-toxic and naturally occurring metabolite, without the use of enzymes. Because lactic acid has two stereoisomers, L-lactic acid and D-lactic acid, its polymer product can be made in a variety of ways, including pure Poly(L-lactic acid) (PLLA), pure Poly(D-lactic acid) (PDLA), and poly(D,L-lactic acid) (PDLLA) (Griffith, 2000; Lim, Auras, & Rubino, 2008). Lactic acid (2-hydroxypropionic acid) is the most basic hydroxy acid containing an asymmetric carbon atom. It comes in two optically active forms which humans and other animals create the L(+) isomer, whereas bacterial systems produce both the D(-) and L(+)enantiomers. The majority of commercially manufactured lactic acid is created by bacterial fermentation of carbohydrates, employing homolactic organisms such as various optimized or modified lactobacilli strains that only make lactic acid, lactobacilli amylophilus, lactobacillus bavaricus, Lactobacillus casei, lactobacillus maltaromicus, and lactobacillus salivarius are the organisms that produce the L(+)-isomer the most. D-isomer or combinations of both are produced by strains such as L. delbrueckii, L.

jensenii, or L. acidophilus. These bacteria are homofermentive, producing lactic acid via the Embden-Meyerhof route and converting up to 1.8 moles of lactic acid per mole of hexose (lactate yield from glucose >90%). At normal fermentation conditions, such as a low to neutral pH, temperatures around 40°C, and low oxygen concentrations, these strains produce high carbon conversions from feed sources. Figure 2.9 depicts the structural unit of PLA as well as the procedures involved in PLA production (Al-Mobarak, 2018).

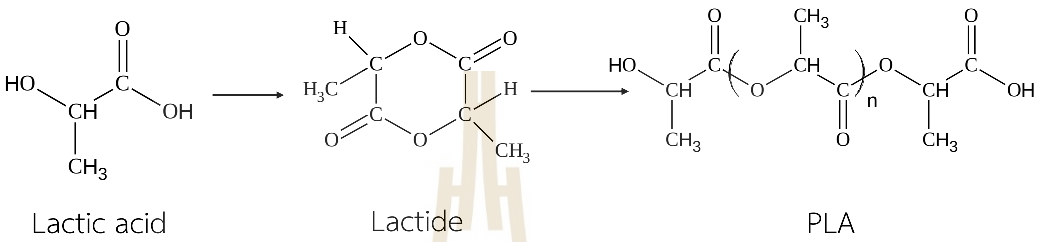


Figure 2.9 PLA structural unit and production steps

By copolymerizing mixes of L-lactide and D-, meso-, or rac-lactide (50 percent D- and 50 percent L-lactide), the stereochemical structure of each grade of PLA can be changed in high molecular weight semi-crystalline polymers. Polylactic acid is made by ring opening polymerization from lactic acid monomer as L(+) or D(-) enantiomers or DL racemic. Extensive research has lately been done to optimize the technique, with controlled architecture and mechanical properties, in high yield and molecular weights greater than 500,000 Da, for stringent medical and pharmaceutical needs (Choubisa, Patel, & Dholakiya, 2012). Tables 2.6 and 2.7 show the physical features of PLA, as well as its advantages and downsides.

Table 2.6 PLA's physical properties (Sungyeap Hong, 2014)

Lactic acid polymers	Tg, (°C)	Tm, (°C)	d, (g/cm^3)	Good solubility in solvents
PLLA	55–80	173–178	1.29	Chloroform, furan, dioxane and dioxolane
PDLLA	43–53	120–170	1.25	PLLA solvents and acetone
PDLA	40-50	120-150	1.248	Ethyl lactate, tetrahydrofuran, ethyl

Table 2.7 PLA's pros and cons (Davachi & Kaffashi, 2015)

Advantages	Disadvantages
Eco-friendly	Poor toughness
Biocompatibility	Slow degradation rate
Processability	Hydrophobicity
Energy savings	Lack of reactive side-chain groups

PLA synthesis necessitates precise control of parameters such as temperature, pressure, pH level, and the use of catalysts, as well as a long polymerization period and a lot of energy (Davachi & Kaffashi, 2015). The melting temperature (Tm) of polymeric crystals is influenced significantly by molecular weight. Figure 2.10 shows how the melting point temperature of PLA increases with the number average molecular weight (Mn) (Alaa, 2015).

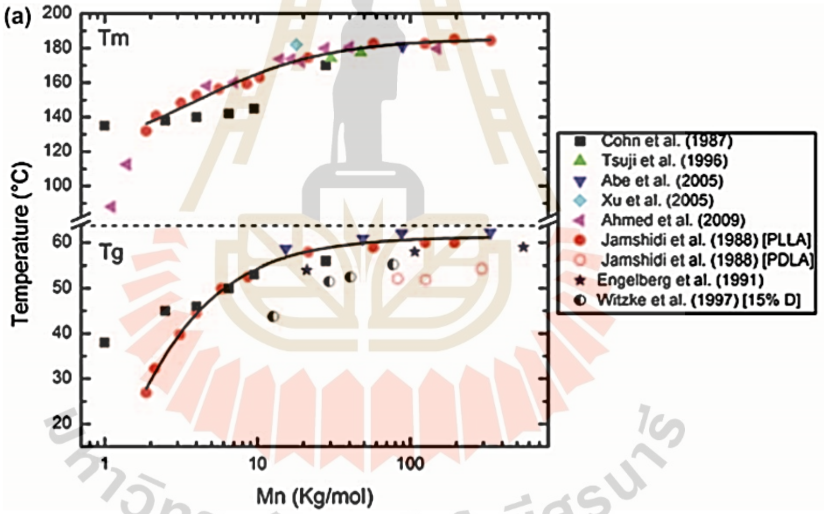


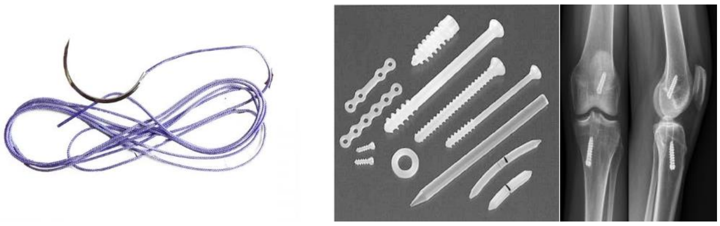
Figure 2.10 Temperatures of melting and glass transition vs. PLLA molecular weight (Alaa, 2015)

2.3.1 PLA applications

PLA is widely utilized in a variety of applications, including food packaging and containers, cold drink cups, flexible film, cutlery, bottles, disposable and compostable materials, the textile sector, and medicinal uses. PLA can be used to make drug delivery systems, scaffolds, surgical sutures, meshes, thin coatings, microcapsules, microspheres, bone fixation devices, and surgical screws in medical applications (Davachi & Kaffashi, 2015). Because unreinforced PLA has limits, several studies have been conducted to increase the possible applications of PLA composites, which range from biomedical to typical thermoplastics. The use of appropriate fiber or filler reinforcements opens up a world of possibilities for customizing product attributes for specific purposes. It has already been reported that employing natural fibers as reinforcements, it is possible to build totally biodegradable composite materials. PLA composites can also be effective in circumstances when matrix absorption is desirable, for as when exposing surfaces to tissues or releasing chemicals like antibiotics and growth hormones (Auras, Wiley, 2010). Tissue engineering is a broad term that refers to a variety of applications, although it is most commonly linked with applications that repair or replace parts or whole tissues (i.e. bone, cartilage, blood vessels, bladder, etc.) (Alaa, 2015). It is a branch of medicine that entails the use of cell fusion, engineering, and materials approaches, as well as appropriate biochemical and physiochemical elements, to enhance or substitute biological processes. It offers an option to the treatment of organ failure or loss. Patients are treated with their own cells grown on a polymer platform in order to repair a tissue portion from natural cells (Rajendra P. Pawar, 2014). Figures 2.11, and 2.12 shown examples of PLA-based products and PLA applications in the biomedical field, respectively.

garbage bags food

Green Table wares



sutures Surgical

Figure 2.11 PLA-based goods are available in a variety of shapes and sizes

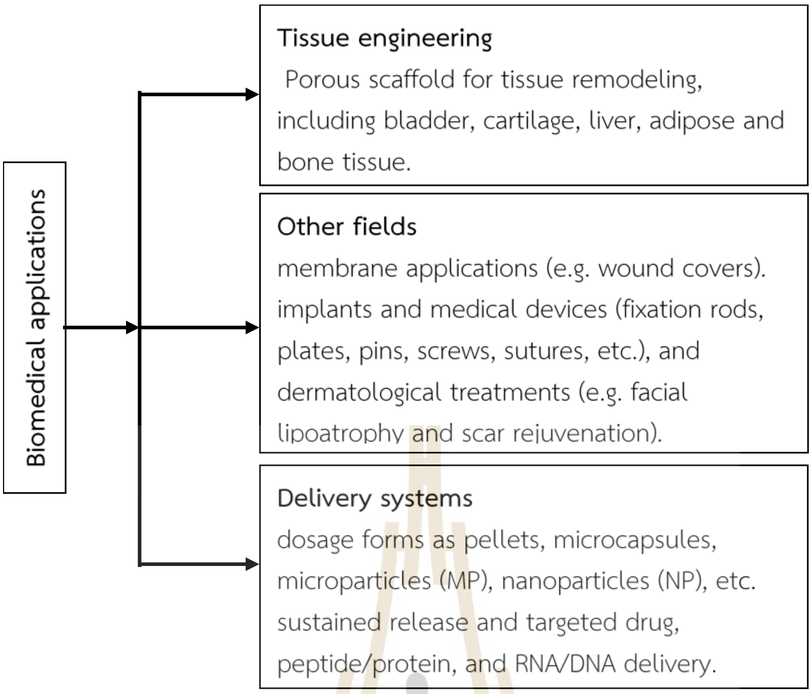


Figure 2.12 PLA applications in biomedical field

2.3.1.1 Tissue engineering applications

Tissue engineering is a fascinating medical method in which patients with organ deformities and malfunctions are treated with their own cells grown on polymer supports, resulting in the regeneration of a tissue portion from natural cells. It's a field dedicated to preserving and improving tissue function. Biodegradable materials are more appealing as transplantation supports because they can be removed from the transplantation site over time (M. Savioli Lopes, 2012). Surface qualities of materials have a role in deciding their applications, particularly in the case of biomaterials in biocompatibility. PLA has been used as an environmentally friendly material, as well as a material for surgical implants, medication delivery systems, and porous scaffolds for neotissue formation. (Madhavan Nampoothiri, Nair, & John, 2010). PLA has been approved by the US Food and Drug Administration (FDA) for use as a suture material due to its unique properties. PLA has recently been employed in tissue engineering, and it has proven to be one of the most advantageous matrix materials, as it performs well and provides outstanding qualities at a reasonable cost (M. Savioli Lopes, 2012). It's difficult to find materials that have all of the attributes needed for a given application, but PLA is a single polymer that can be used in a variety of applications because to its versatility in application due to simple physical-chemical structure alterations (Cheng, Deng, Chen, & Ruan, 2009). PLA porous scaffolds were developed specifically for culturing various cell types for use in cell-based gene therapy for muscle tissues, bone and cartilage regeneration, and other cardiovascular, neurological, and orthopedic diseases (Coutu, Yousefi, & Galipeau, 2009). The design and production of several bioabsorbable scaffolds for guided bone regeneration have been reported by Kellomaki et al. Tibial periosteal grafts used PLLA as a scaffold for bone growth in muscle. The bone had been created in predesigned patterns 6 weeks after reimplantation, when it was histologically mature (Kellomäki et al., 2000). The Polylactic acid scaffold for tissue engineering is presented in Figure 2.13

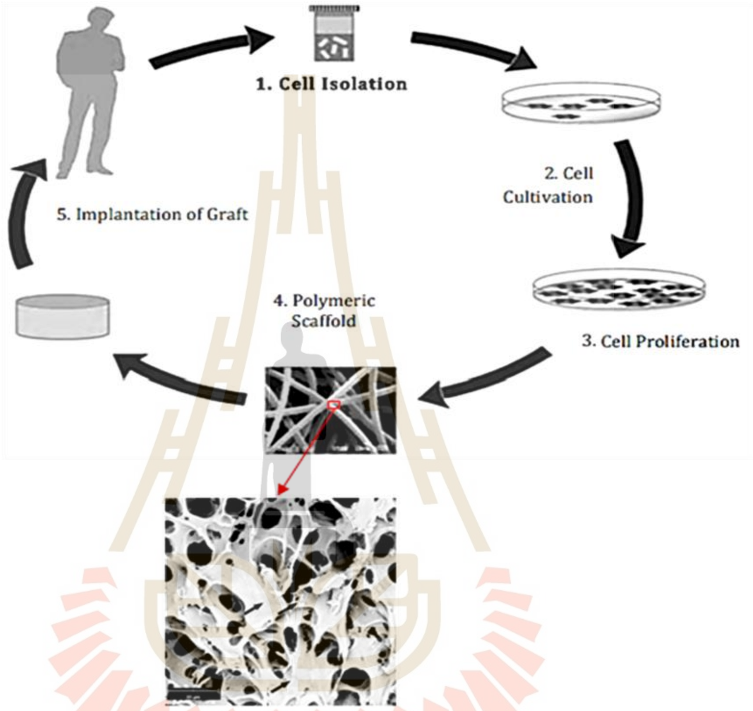
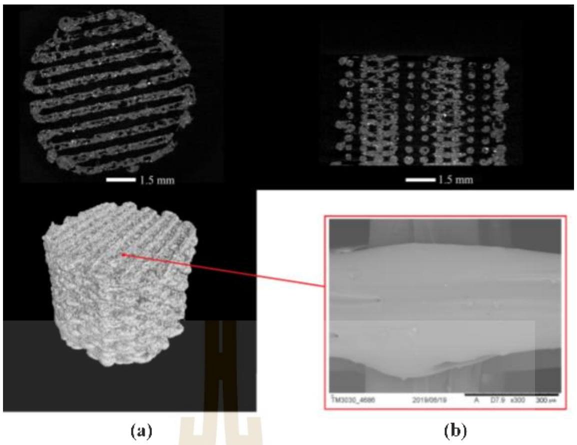


Figure 2.13 Representation showing tissue engineering principles (R. REVATI, 2015).

2.3.1.2 Advantages and disadvantages of PLA as base material for scaffold manufacturing

PLA has been widely employed as a basic material for scaffolds for bone, cartilage, tendon, neural, and vascular regeneration in tissue engineering applications. PLA is a biomaterial that has been certified by the Food and Drug Administration for interaction with biological fluids and can be made inexpensively from renewable resources. Its qualities are determined by the temperature at which it is processed as well as its molecular weight. The crystallinity ratio of PLA is an important feature that is controlled by the stereochemistry and thermal history of the polymer. The glass transition temperature, melting temperature, degradation rate, and mechanical properties of polymers are all influenced by crystallinity. The grass transition and melting temperatures both fall when the polymer's crystallinity rate decreases. The mechanical characteristics and degradation profile of a polymer, on the other hand, are affected by its molecular weight. The long time it takes for high molecular weight PLA to completely degrade in vivo has been identified as one of the factors contributing to the emergence of inflammatory reactions in the surrounding tissues. As a result, PLA with a low molecular weight is preferable for tissue engineering applications due to its faster breakdown rate, which should match tissue growth and give enough mechanical support in any scenario. PLA can also be processed using a variety of ways, and its degradation rate, physical, and mechanical qualities can be modified across a large range by changing the molecular weight or copolymer ratio, as previously described. For example, PDLA is primarily used in drug delivery systems because of its faster degradation rate, whereas PLLA is the preferred material for load-bearing applications due to its superior mechanical properties and higher biological activity, indicating greater potential for tissue engineering applications. PLLA has a Tg of 60–65 degrees Celsius, a melting temperature of 175 degrees Celsius, and a mechanical strength of 4.8 GPa. Because of its remarkable mechanical stability and biocompatibility in vivo, PDLLA has lately gained attention as a basic material for drug-delivery systems and scaffold construction. PLA has crucial properties for scaffold production since it is entirely destroyed by random hydrolytic chain scission, resulting in lactic acid monomers that are excreted from the patient's body via the tricarboxylic acid cycle. Another theory proposes that increasing PLA crystallinity enhances degradation rate by increasing hydrophilicity. Finally, the material qualities should be tweaked because the PLA-based scaffold will disintegrate entirely while providing mechanical support and without producing any undesirable tissue reactions until it is excreted from the human body via metabolic pathways. The slow disintegration rate of PLA (which can take many years) will result in accumulation due to poor removal of acidic degradation byproducts from the scaffold's environment, which could trigger a significant inflammatory response, impacting cell proliferation and tissue creation. This is the most significant drawback of using PLA as a foundation material for TE applications. Other significant disadvantages of PLA include: (1) its low toughness, as it is a brittle material with less than 10% elongation at break; (2) the lack of reactive sidechain groups, which makes it difficult to induce surface or bulk modifications to improve its properties; and, most importantly, (3) its low hydrophilicity, with a water contact angle of around 80 degrees. The latter flaw results in poor wetting qualities as well as a lack of cell adhesion and communication between the polymer and surrounding tissues. PLA bioactivity must be improved in order for it to be used in the intended tissue engineering application, taking into account all of these features

(Donate, Monzón, & Alemán-Domínguez, 2020). The 3D printed PLA-based composite scaffold shown in Figure 2.14.

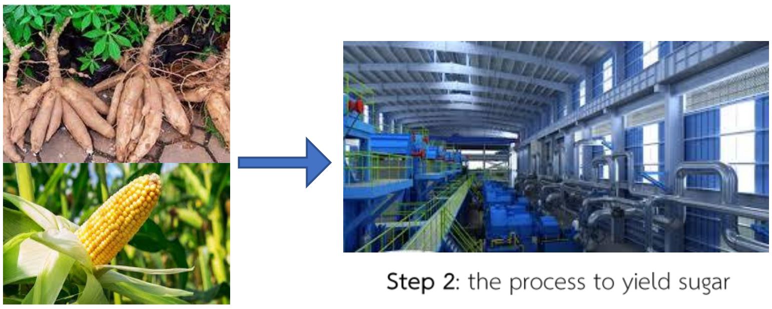


(a) (b)

Figure 2.14 β-TCP particles were used as an additive in a 3D printed PLA-based composite scaffold by (a) scanning electron microscopy (SEM; Hitachi TM 3030 at an acceleration voltage of 15kV) and (b) micro-computed tomography (micro-CT; Y. Cheetah, YXLON Ltd) [p0(Donate, Monzón, & Alemán-Domínguez, 2020)

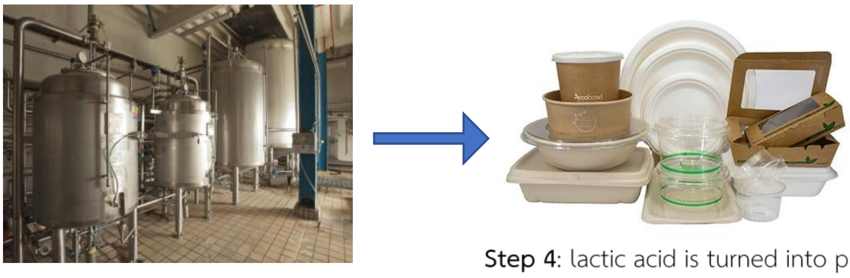
2.3.2 PLA synthesis

In general, there are three ways to make PLA such as Direct condensation polymerization is the initial step, which results in PLA with a low molecular weight. The second approach is azeotropic dehydrative condensation, which creates a product with a higher molecular weight by injecting organic solvents into the reaction mixture to remove water quickly. The third process is ring opening polymerization (ROP), which produces PLA with a high molecular weight by forming lactide by the depolymerization of lactic acid (Y. Hu et al., 2016). The Figure 2.15 and 2.16 shown the commercially manufacturing process of PLA and Routes of polylactic acid synthesis from lactic acid, respectively.



Step 1: renewable resource

Step 2: the process to yield sugar



Step 3: fermentation of sugar by bacteria to form lactic acid

Step 4: lactic acid is turned into plastic

Figure 2.15 PLA manufacture is an economically viable process

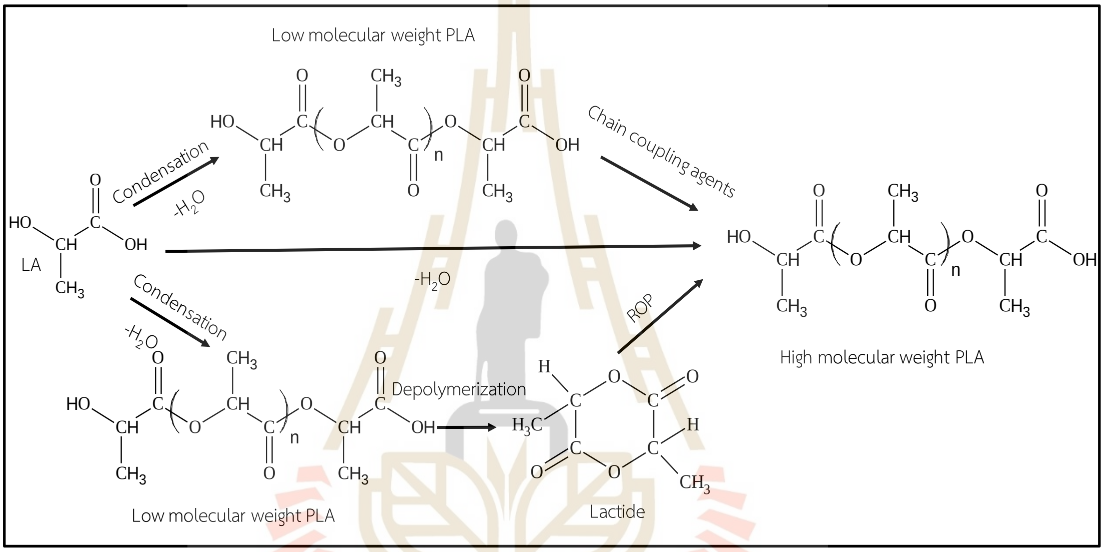


Figure 2.16 Polylactic acid synthesis routes from lactic acid

2.3.2.1 Direct condensation polymerization

Lactic acid polycondensation is a very straightforward process that involves the joining of tiny molecules (monomers) and the removal of byproducts (e.g., water and alcohols). In the case of PLA, the polycondensation of lactic acid by linking carboxyl and hydroxyl groups results in the simultaneous production of water as a byproduct. Direct polycondensation produces low molecular weight (50,000 g/mol) and low quality polymer due to the difficulties of completely eliminating byproducts from the excessively viscous reaction fluid (Y. Hu et al., 2016).

Condensation that occurs directly bulk (solution) polycondensation and melt condensation are two types of polymerization. To limit reversibility of the reaction, high temperatures and vacuum are employed to remove generated water from the bulk solution, although this frequently results in low molecular weight polymers, owing to the presence of water and contaminants. It's difficult to totally remove water from the highly viscous mixture, and the equilibrium between free acid, oligomers, and the water created is difficult to achieve (Rahul D. Sonwalkar, 2003). The method's biggest disadvantage is the low molecular weight polymer, which limits its application. Condensation polymerization produced oligomers with average molecular weights in the tens of thousands, and other side processes, such as transesterification, can result in the development of lactide-like ring structures. Furthermore, during the polymerization process, the stereoregularity cannot be controlled. Condensation polymerization is the cheapest method and is only used when a polymer with a low molecular weight is desired. However, chain coupling agents such as isocyanates, epoxides, or peroxide can be used to produce a high-molecular-weight polymer (Auras, Wiley, 2010). The coupling agent connects the low-molecular-weight polymer chain to the high-molecular-weight polymer chain indicated in Figure 2.17.

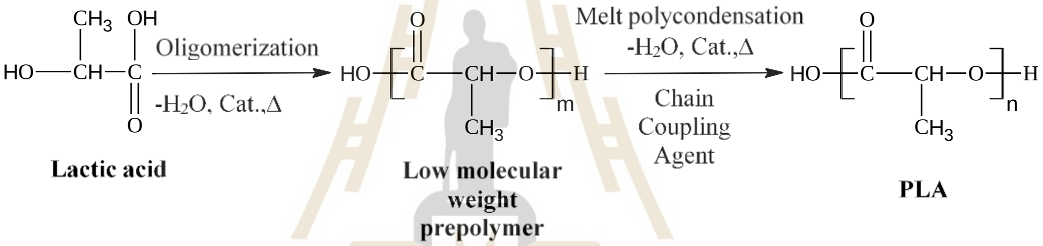


Figure 2.17 Polylactic Acid polymerization by direct condensation

Other drawbacks of this path include the need for relatively large reactors and considerable energy consumption to achieve the required high temperature and vacuum, resulting in an expensive final product. Furthermore, because LA is known to racemize at high temperatures, the end product may be of worse quality than expected (Hottle, Bilec, & Landis, 2013). The Figure 2.18 depicted the stages of the condensation polymerization process.

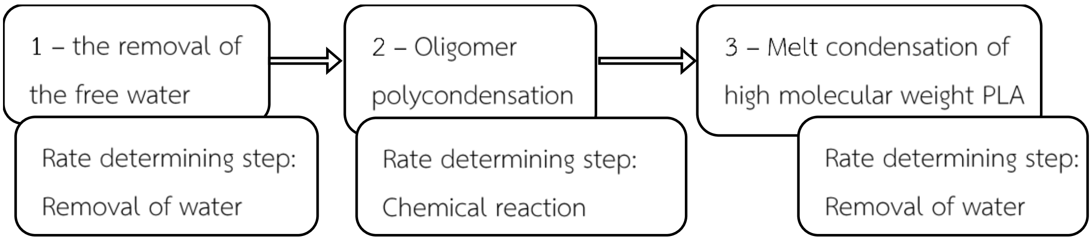


Figure 2.18 Condensation polymerization process phases

High evacuation, which is required to remove condensed water, is likely to remove L-lactide from the system, lowering polymer production. As a result, reaction conditions must be carefully monitored in order to create PLLA with a high molecular weight though direct polycondensation. Ordinary reaction conditions that could allow for successful water removal include: (1) a temperature range of 180–210°C; (2) a low pressure below 5 torr; and (3) a long reaction time in the presence of an adequate catalyst and, in certain cases, an azeotropic solvent (Masutani & Kimura, 2014).

The direct condensation method of producing PLA from lactic acid can be broken down into three stages:

(a) The content of free water is removed
(b) Polycondensation of oligomer
(c) High molecular weight PLA by melt polycondensation

2.3.2.2 Azeotropic dehydrative condensation

The same stages as in direct melt condensation of lactic acid are present in azeotropic dehydration, with the exception that the last high viscosity melt-polycondensation stage is skipped because the polycondensation is done in solution. As a result, removing the reaction water from the reaction medium becomes easier, allowing for a higher molecular weight of PLA to be achieved. The solvent, on the other hand, must be dried using a drying agent from the water created during the reaction (e.g., molecular sieve). The extracted solvent was dried and reintroduced back to the reaction mixture using molecular sieves, phosphorus pentaoxide, or metal hydrides, for example. An ion exchange resin was used as the drying agent in another similar application. Anisole and diphenyl ether were mentioned as possible solvents. In a total amount of 0.3 %mole, azeotropic dehydration of lactic acid containing impurities (e.g., chain terminators such as methanol, ethanol, acetic acid, and pyruvic acid) has also been recorded (Auras, Wiley, 2010). The azeotropic condensation polymerization method is a direct approach for producing high molecular weight PLA without the use of chain extenders or adjuvants, which has its own set of disadvantages. The removal of water from the reaction media becomes relatively easier in this approach, and a larger molecular weight of PLA can be achieved, as indicated in Figure 2.19. Mitsui Chemicals (Japan) has developed a process for producing high molecular weight PLA by azeotropically dehydrating lactic acid and a catalyst in a refluxing, high boiling, aprotic solvent under decreased pressures (Avérous, 2008). Because of the high concentration required to achieve an adequate reaction rate, this polymerization produces significant catalyst residues. This can result in a variety of problems during processing, including degradation and hydrolysis.

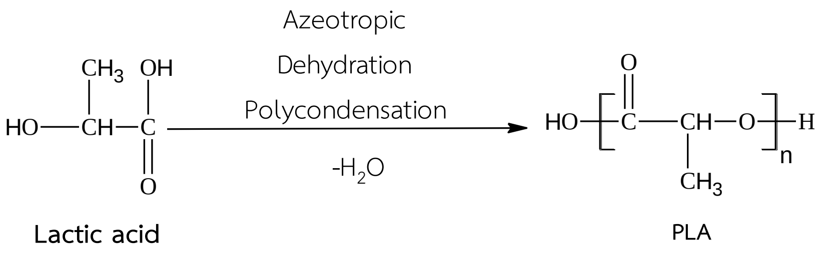


Figure 2.19 Azeotropic dehydration polycondensation of PLA

2.3.2.3 Ring-Opening Polymerization (ROP)

PLA is made by first forming lactide monomer and then converting it to the end product with the help of a catalyst. It enables the production of PLA with a regulated molecular weight, and the final product's qualities can be tailored to meet specific requirements (Y. Hu et al., 2016). Due to the possibility of precise chemical control, ring-opening polymerization is the most common approach to create high molecular weight PLA. The resulting polymers' varied characteristics make them more appropriate for use. (Maharana, Mohanty, & Negi, 2009). Polycondensation of lactic acid, depolymerization of oligomer, which is a cyclic dimer of lactic acid, and ring-opening polymerization of lactide of produced PLA are three different phases in the ROP method (Rahmayetty et al., 2018). The most common initiator is stannous octoate, which has a large molecular weight, a high rate of transformation, a high reaction velocity, and a relatively mild reaction condition (Mehta, Kumar, Bhunia, & Upadhyay, 2005). Because heavy metal catalysts are harmful, many nontoxic zinc, magnesium, calcium, and alkali metal catalysts have been created for the ring-opening polymerization technique of lactides to solve pollution problems (Köhn, 2003).

The mechanics of polymerization with a ring opening (ROP) of lactide, there are three reaction pathways: cationic, anionic, and coordination processes. Anionic polymerization becomes a source of undesired reactions such as racemization, decomposition reaction, and other side reactions due to the highly reactive anionic reactants that stifle chain grow/wh. Because of the nucleophile reaction to the active center, cationic polymerization can generate undesired side reactions or racemization. Metal catalysts, organic catalysts, cationic catalysts, and stereo-controlled polymerization are all used in the ring-opening reaction process. Melt polymerization, bulk polymerization, solution polymerization, and suspension polymerization have all been used to make PLA though ring-opening polymerization. Lactide ring-opening polymerization can be divided into three categories based on the reaction mechanisms and initiator types used: anionic polymerization, cationic polymerization, and coordination-insertion processes. A transition metal catalyst, such as tin or aluminum, is required for lactide ROP. Tin(II) 2-ethylhexanoate or stannous octoate ($Sn(Oct)_2$) is the most often used catalyst in the ring-opening polymerization of lactides shown in Figure 2.20. Because of its high catalytic efficiency, low toxicity, FDA approval for food and drug interaction, and ability to produce high molecular weight PLA with minimal racemization. For its solubility in molten lactide, stannous octoate is preferred for bulk polymerization. In the presence of stannous octoate, ROP is thought to happen though a coordination-insertion mechanism shown in Figure 2.21 (Alaa, 2015).

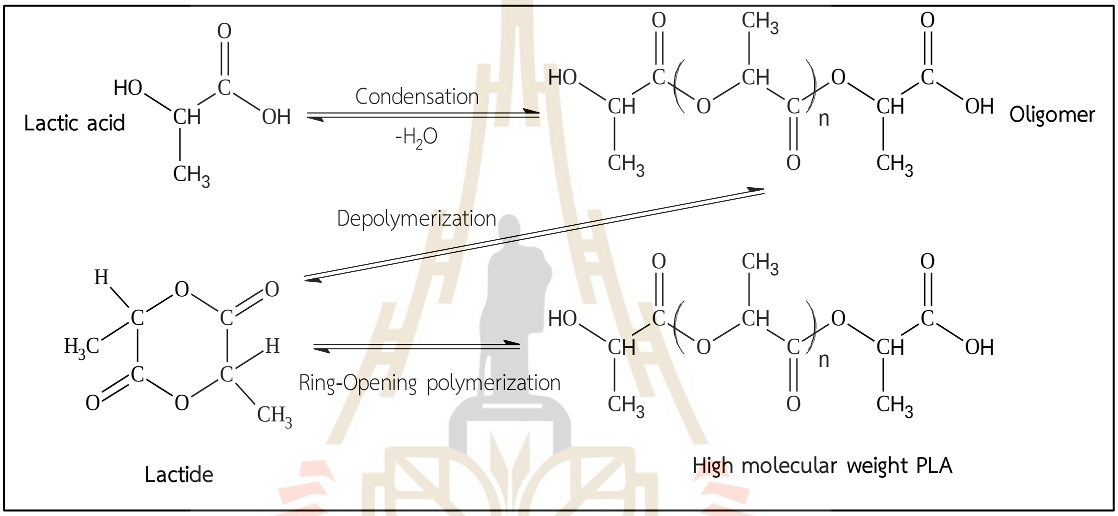


Figure 2.20 PLA manufacture from lactic acid via polycondensation and ring-opening polymerization

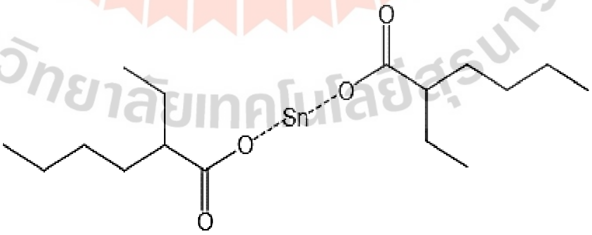


Figure 2.21 Stannous octoate ($Sn(Oct)_2$)

As indicated in Table 2.8, different methods for PLA synthesis, such as direct condensation polymerization, azeotropic polycondensation, and ring opening polymerization, each have advantages and disadvantages.

Table 2.8 Different polymer synthesis processes have pros and cons (Y. Hu et al., 2016)

Method	Advantages	Disadvantages
Direct condensation polymerization	High purity (suppression of side reactions)	Low yield
	High molecular weight	Long duration
	Moderate conditions	Complicated operation
Azeotropic polycondensation	Low cost	Low yield
	Basic equipment	Low purity (usually with residual solvent and byproducts in polymer)
	Moderate temperature (<180°C)	Solvent waste and pollution
Ring-opening polymerization	High purity	Low overall yield
	Wide range of molecular weight (2 x 104 to 6.8 x 105 g/mol	Long duration
	Availability in high molecular weight	Demanding condition
	Controlled polymer properties	Complicated operation

PLA synthesis from butyl lactate though the process called ring opening polymerization was combining in three stages such as the first oligomerization stage refers to the process of mixing monomers to react form polymers. The action is frequently followed by the release of a number of low-molecular weight (water, alcohol, salt) (Ehsani, Khodabakhshi, & Asgari, 2014; Masutani & Kimura, 2014). Butyl lactate oligomerization is a simple procedure that entails the combining of small molecules (monomers). Second, depolymerization stage is the breakdown of polymers (macromolecules) into their constituent monomers (smaller molecules). By treating polymer scraps in the presence of a chemical reagent, it allows the recovery of the initial monomer or oligomer from polymers having functional groups in the main chain (chemical depolymerization) (Castrovinci, Lavaselli, & Camino, 2008; Cunha et al., 2022). The breakdown of polymeric bonds, which can change a solid polymer into a sticky liquid containing monomers, dimers, and other lower-molecular-weight species, is known as depolymerization. Depolymerization is frequently accelerated by high temperatures and a confined atmosphere. Mechanism of oligomerization stage to obtain oligomer and depolymerization to obtain lactide are reported in the Figure 2.22, and 2.13, respectively (S. Rahmayetty, Bambang Prasetya, Misri Gozan, 2015; Sangroniz et al., 2020; Yarkova et al., 2015).

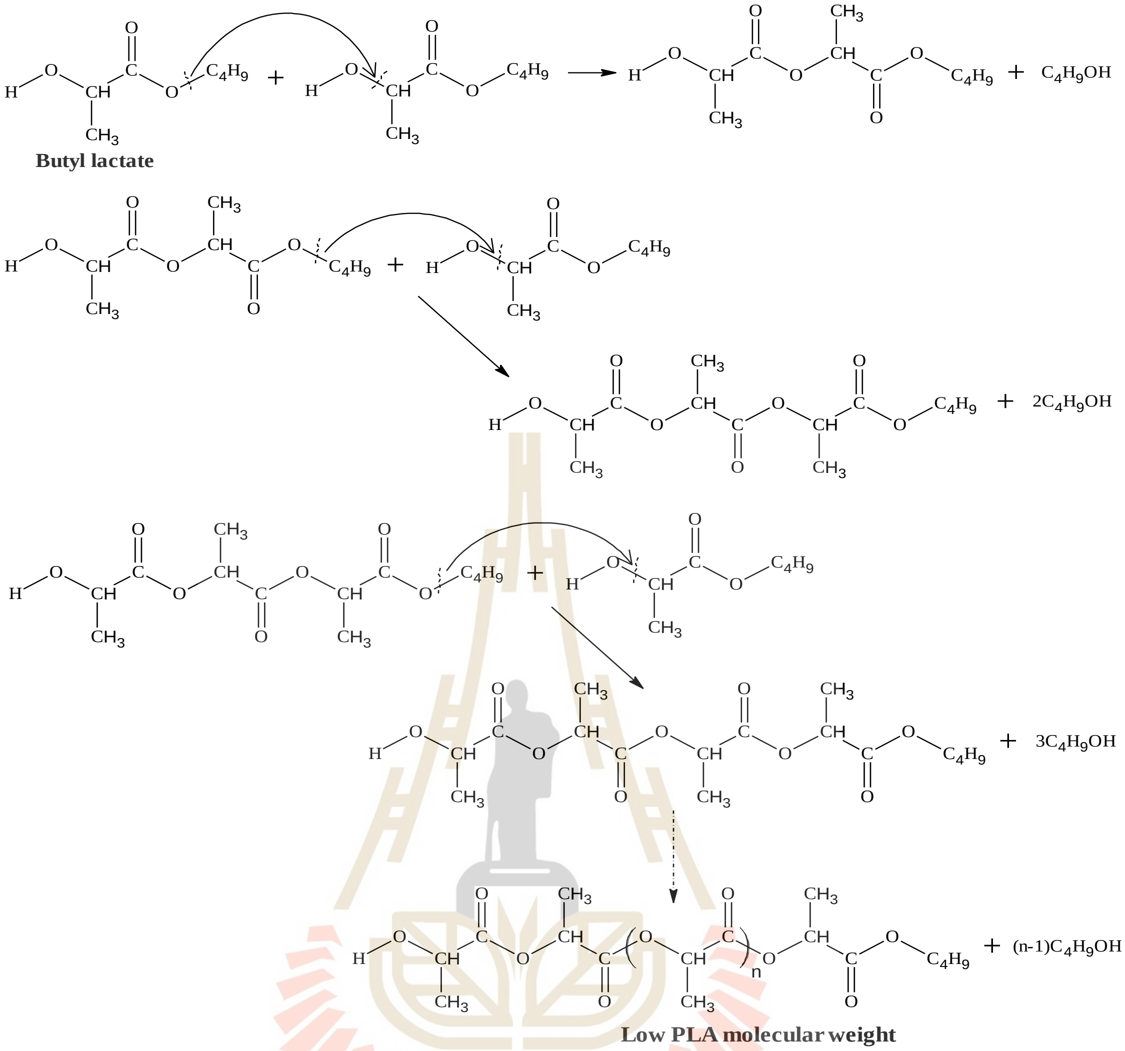


Figure 2.22 Obtaining oligomer from butyl lactate on stage of oligomerization

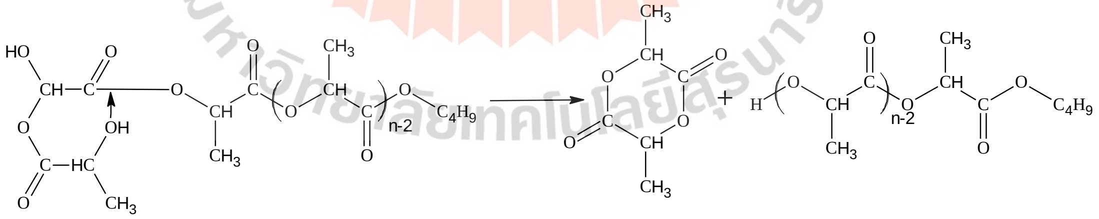


Figure 2.23 Back-biting reaction of OH group in Oligomerization chain to lactide on stage of depolymerization

The third method, ring opening polymerization (ROP), produces PLA with a high molecular weight. Purified and dried lactide (purity >99%) was used to start the polymerization process. In addition to the catalyst, initiators such as solvents or a trace amount of water must be employed to induce the ROP process.

Varied types of initiators cause different reactions, and they can be classified into three groups: Anionic polymerization, coordination–insertion mechanism, and cationic polymerization (Y. Hu et al., 2016). The chemistry of the polymerization stage, as well as the characteristics of the resultant polymer, can be precisely controlled using the ring opening polymerization (ROP) process for any additional application. The method yielded a high molecular weight PLLA of l-lactide from a low molecular weight PLLA. Before ring-opening polymerization (ROP) of lactide to generate high molar mass PLA, include lactic acid polycondensation followed by depolymerization to obtain lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) (Maharana et al., 2009). ROP of lactide with $Sn(Oct)_2$ as catalyst at a concentration of 100–1000 ppm yielded PLA with molecular weights up to 10^6 Da at 140–180°C in 2–5 h, according to Shimadzu and Dupont (Ray E. Drumright & Henton., 2000). PLA is made using polycondensation and ring-opening polymerization (ROP), with the latter being the most frequent route in contemporary PLA industrial production because it is the only way to make pure high molecular weight PLA ($Mw > 100{,}000$ g mol^{-1} (Yunzi Hu et al., 2017). As mentioned above, tin (II) 2-ethylhexanoate or stannous octoate ($Sn(Oct)_2$) is the most often used catalyst in the ring-opening polymerization of lactide since its high catalytic efficiency, low toxicity, FDA approval for food and drug interaction, and ability to produce high molecular weight PLA. The insertion-coordination mechanism was proposed to describe polymerization, as seen in Figure 2.24 (Sobczak & Kolodziejski, 2009). A hydroxyl compound (alcohol) or event water was added as a initiator in lactide polymerization catalyzed by $Sn(Oct)_2$. By ligand exchange, the alcohol initiator reacts with $Sn(Oct)_2$ to form a tin alkoxide bond. One of the lactide's exocyclic carbonyl oxygen atoms momentarily coordinates with the tin atom of the alkoxide catalyst in the next step. The nucleophilicity of the alkoxide component of the initiator as well as the electrophilicity of the lactide carbonyl group are both enhanced by the coordination. Next, acyl-oxygen bond in the lactide (between the carbonyl group and the endocyclic oxygen) is then broken, allowing the lactide chain to open and insert into the tin-oxygen bond in the catalyst (alkoxide). The transmission proceeds as more lactide molecules are introduced into the tin-oxygen bond, which is generated by the same mechanism reported (Kajsa M. Stridsberg, 2022; H. R. Kricheldorf & Damrau, 1998). Table 2.9 summarizes some of the researchers who looked into PLA synthesis under various conditions.

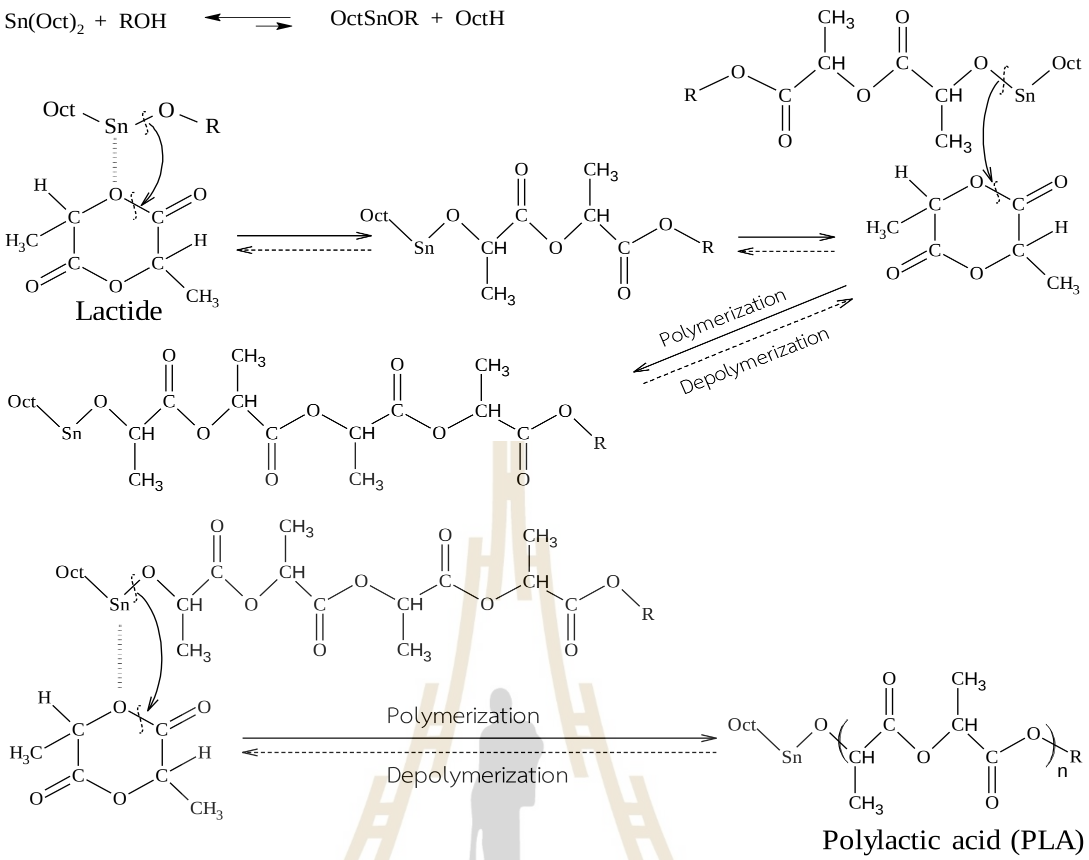


Figure 2.24 Synthesis of PLA though ROP of lactide with stannous octoate by coordination-insertion mechanism.

Table 2.9 Polylactic acid synthesis methods based on lactide product (Yunzi Hu, 2017)

Catalyst	Initiator	Temp (°C)	Pressure (kPa)	Time (h)	Yield (%)	Mw (g/mol)
Tin (II) 2-ethylhexanoate (0.1 wt%)	polyglycerol-10 (0.01 mol%)	200	atmospheric	25 min	81	151,127
Candida rugosa lipase (CRL) (2% w/w)	Nil	90	atmospheric	72	92	5,428
Tin (II) 2-ethylhexanoate (0.04 wt%)	Nil	170	atmospheric	2	91-93	125,942
Aluminum isopropoxide	Nil	130	Nitrogen gas	48	95	24,900
Potassium hexamethyl-disilazide	Toluene	25	-	20 min	100	98,400
Stannous octoate (0.03 wt %)	1-dodecanol	140	0.001	10	>95	100,000

2.4 Literature reviews

The second phase was warmed at 220°C for 4 h at a reduced pressure of 200 mmHg. The amount of catalyst (1w/w percent) was utilized as a catalyst for the third step (Ring-opening polymerization of lactide) at a temperature of 140°C for 2 h, after which PLA was generated.

Yunzi et al. (Yunzi Hu et al., 2017) used ring opening polymerization to create PLA fiber from lactic acid derived from food waste. Zinc oxide aqueous nanoparticles (30-40 nm) dispersion is an effective catalyst for polymerization and depolymerization with a wide surface area and rapid equilibrium. Lactide was synthesized at a rate of 91-92 percent in 8 h under ideal reaction conditions, which is a significant improvement over prior catalytic tin-based synthesis method. Rahmayetty et al. (Rahmayetty et al., 2018) investigated the role of Candida rugosa lipase (CRL) as a biocatalyst in PLA synthesis by ring opening polymerization. In L-lactide synthesis, the maximum CRL activity was found at a temperature of 90°C and a concentration of 2% (w/w) for 72 h. Differential thermal analysis (DSC), infrared spectroscopy (FTIR), gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), and X-ray diffraction were used to investigate the other qualities or characterization of PLA generated (XRD). Yunzi et al. (Y. Hu et al., 2016) found that the molecular weight of PLA did not necessarily rise with time, with the greatest value, 172,663 g/mol, achieved after 15 minutes at 170°C, followed by a reduction after 30 minutes and a tendency to be stable. This demonstrated that lactide polymerization might achieve a plateau in a short time, whereas prolonged heating could result in degradation. On average, tin(II)-2-ethyhexanoate is significantly less hazardous than tin(II)-2-ethyhexanoate made synthetically. Furthermore, the enzyme was used as a green biocatalyst to harvest PLA with a Mw of 37,800 g/mol without the possibility of organometallic contamination. Khlopov et al. (S. V. Khlopov Dmitry, Kozlovskiy Roman, Suchkov Yury and Otyuskaya Darya 2012) have described the use of butyl lactate as a substrate for lactide synthesis in two stages: oligomerization of butyl lactate and depolymerization of the oligomer for lactide production, and discovered that SnCl4 is the most efficient catalyst for both stages, because the lactide product obtained from lactic acid in case two stages of synthesis (oligomerization of lactic acid and depolymerization of oligomer to lactide) contains unconverted lactic acid as an impurity and requires several complicated and time-consuming purification stages to reach polymerization purity. Garlotta et al. (Garlotta, 2001) gave a talk about the synthesis of Polylactic acid and its physicochemical, chemical, and mechanical properties (PLA). Polylactic acid is a polymeric helix with a unit cell that is orthorhombic. PLA's tensile characteristics vary greatly depending on whether it is annealed or orientated, as well as the degree of crystallinity. The impacts of processing on PLA are also examined. Lim et al. (Lim et al., 2008) have done research on polymer processing methods (lactic acid). Polylactic acid (PLA) is an aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) building blocks, according to the researchers. It's also a compostable and biodegradable thermoplastic made from renewable plant materials like starch and sugar. PLA has traditionally been used primarily in biomedical applications due of its bioabsorbable properties. The development of new polymerization techniques that allow for the cost-effective manufacturing of high molecular weight PLA, combined with increased public awareness of environmental issues, has resulted in an increased use of PLA for consumer goods and packaging applications over the last decade. PLA has been proposed as one of the solutions to alleviate solid waste disposal issues and reduce reliance on petroleum-based plastics for packaging materials because it is compostable and sourced from renewable sources. Pawar et al. looked at the biomedical applications of Polylactic acid(Pawar et al., 2014) and Polylactic acid (PLA) is a biodegradable, biocompatible, non-toxic, and environmentally benign polymer, according to the research. Medical implants, tissue engineering, orthopedic devices, medication delivery systems, and other applications use PLA and its composites. Recent research and patents on the use of PLA-based polymers and their mixes in biomedical applications are highlighted in this study. Polylactic acid: manufacturing, uses, nanocomposites, and release studies were all covered by Jamshidian et al. (Jamshidian et al., 2010) The goal of this review is to introduce poly-lactic acid (PLA), a biodegradable, compostable thermoplastic manufactured from renewable resources. PLA characteristics and alterations via several ways are described, including the use of modifiers, blending, copolymerizing, and physical treatments; these are rarely discussed combined in previous publications. The industrial processing methods for making various PLA films, wrappings, laminates, and containers (bottles and cups) are discussed. PLA's potential as a powerful active packaging material in many applications requiring antibacterial and antioxidant properties is highlighted. As a result, the use of nanomaterials in conjunction with PLA structures to create new PLA nanocomposites with improved properties is also covered.

CHAPTER III

RESEARCH METHODOLOGY

This chapter describes the method of the thesis research, the work of PLA synthesis from butyl lactate as a raw material was carried out in a 1 liter reactor. The PLA synthesis process consists of two main steps. Firstly, lactide is produced from the butyl lactate which includes two stages oligomerization and depolymerization, then secondly, PLA was produced though ring opening polymerization of produced lactide. The produced lactide and PLA were characterized their physical and chemical properties. The diagram of the overview of this thesis work is as displayed in Figure 3.1. PLA synthesis contains main items of apparatus and instruments are shown in Figure 3.2. For the main items of apparatus and instruments for synthesis PLA size of 1 liter are shown in Figure 3.3.

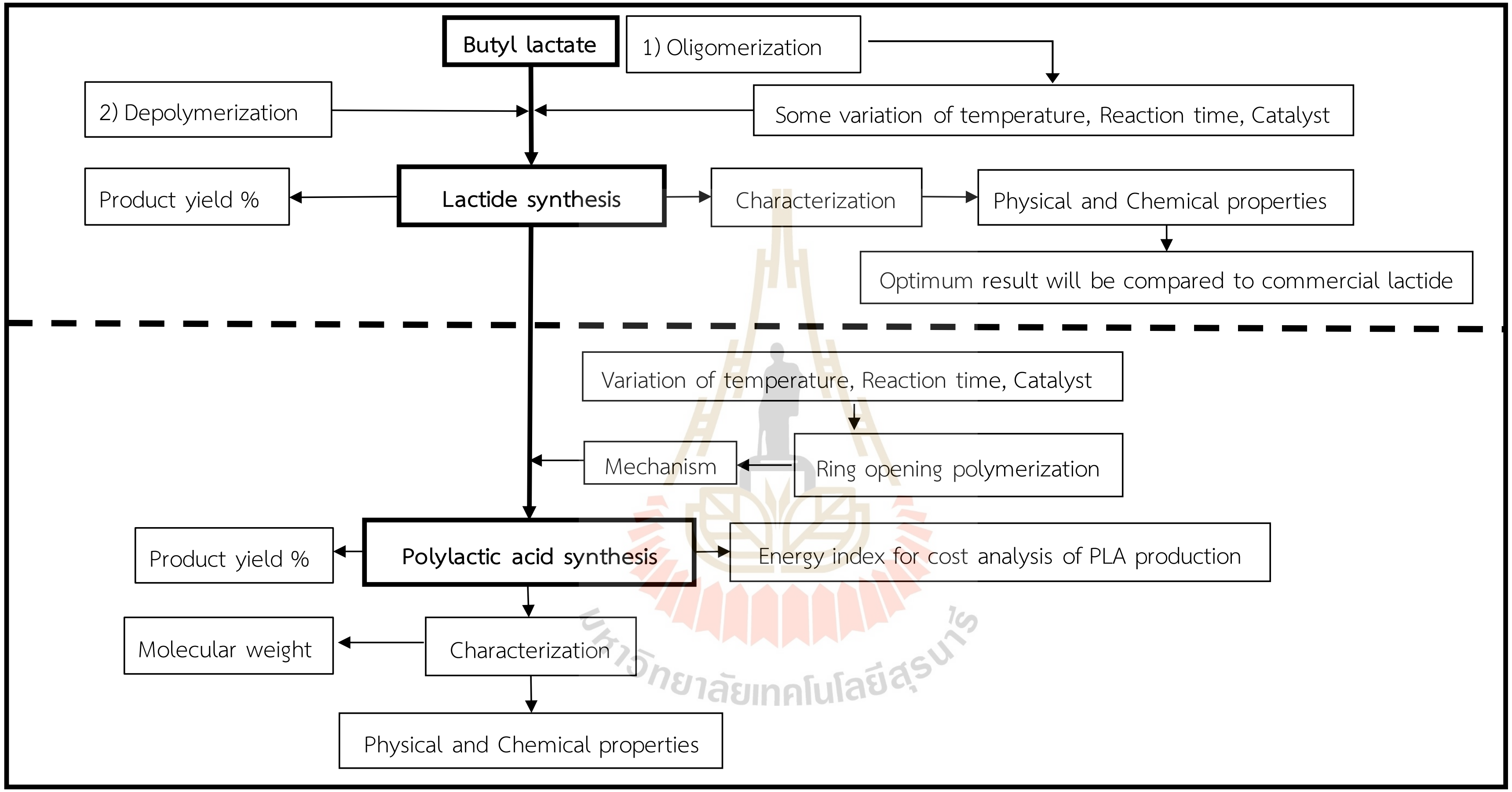


Figure 3.1 Overview of the research thesis including the lactide and PLA synthesis

3.1 Chemicals, apparatus and instruments

3.1.1 Chemicals

1) L-lactic acid (77.5-88.5%, $CH_3CHOHCOOH$)
2) Butyl lactate (95%, $C_7H_{14}O_3$)
3) zinc oxide (ZnO)
4) Stannous octoate or Tin (II) 2-ethylhexanoate ($C_{16}H_{30}O_4Sn$)
5) Methanol (CH_3OH)
6) Ethyl acetate ($C_4H_8O_2$)
7) Chloroform ($CHCl_3$)

3.1.2 Apparatus and Instruments

The main items of apparatus and instruments for synthesize PLA in this research project:

1) Three-neck round-bottom flask size 1 liter
2) Hotplate and magnetic stirrer C-MAG H7
3) Glass liebig condenser with 24/29 joint 300 mm jacket length
4) Round bottom flask 1-neck size 300 ml
5) Cooling circulator cater bath
6) BUCHI V-710 vacuum pump
7) RS pro type K thermocouple

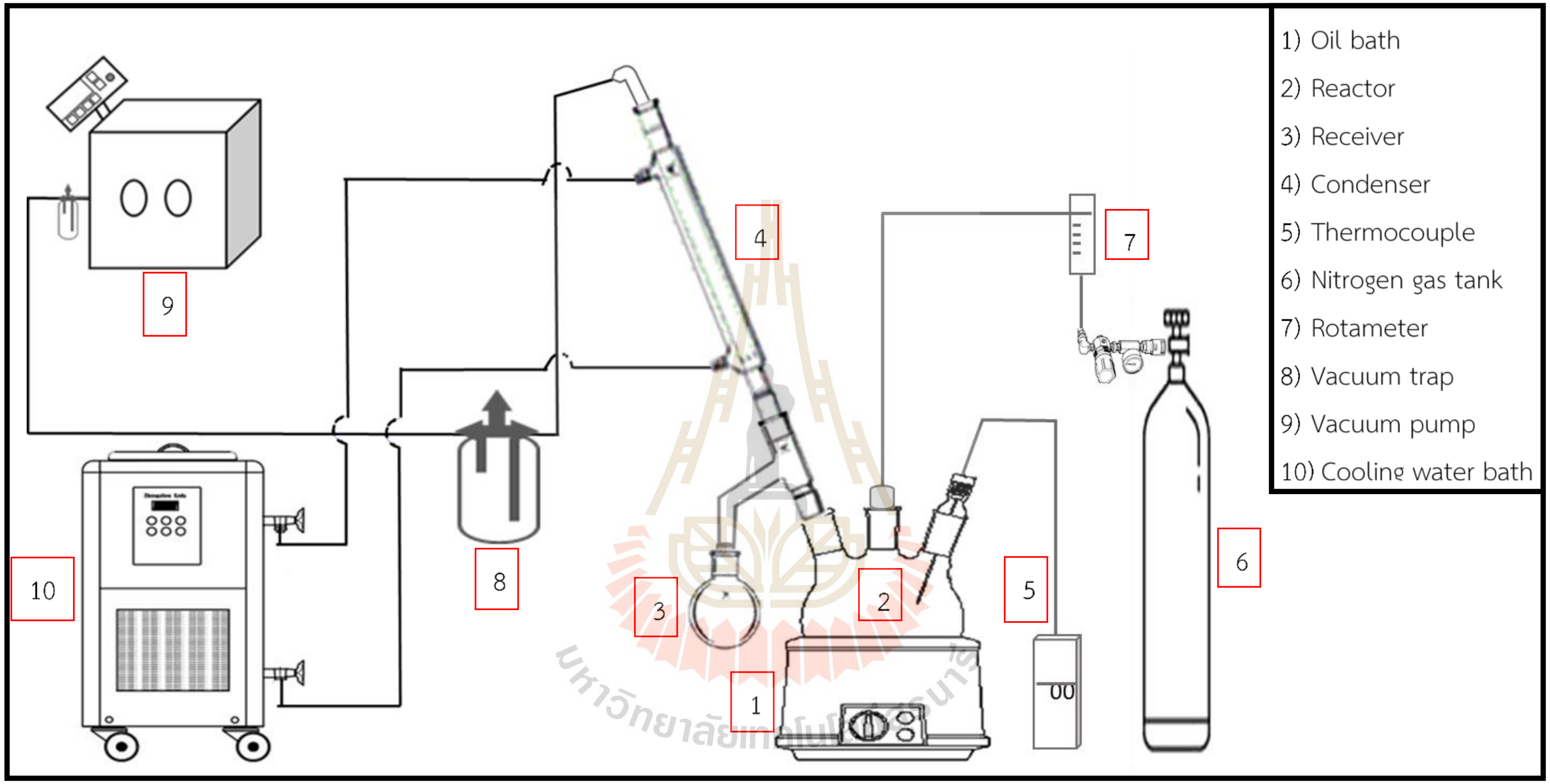


Figure 3.2 Main items of apparatus and instruments for 1 liter for PLA synthesis

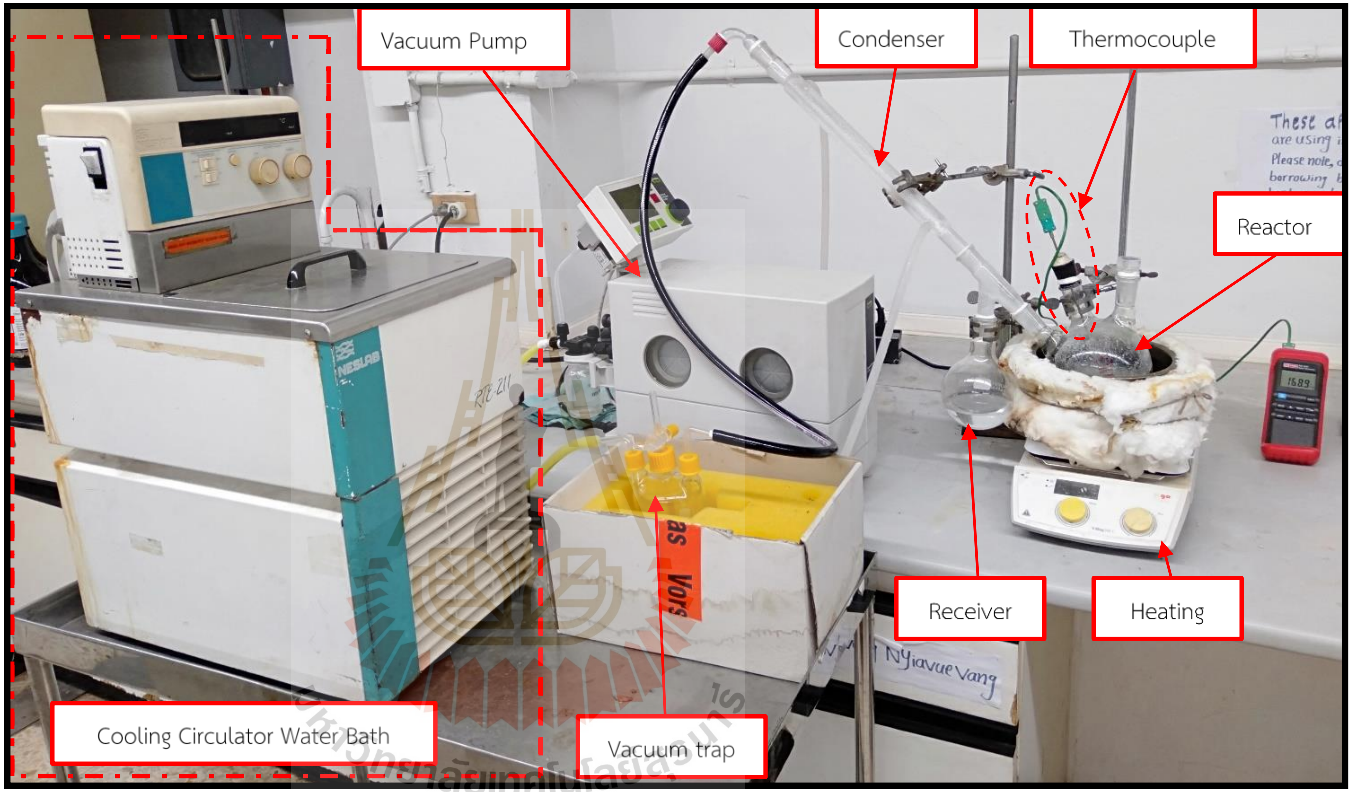


Figure 3.3 The main items of apparatus and instruments for 1 liter for PLA synthesis

3.2 Experiment

3.2.1 Lactide synthesis from L-lactic acid

1) Dehydration: L-lactic acid (liquid, 88%) (400 ml) with zinc oxide as a catalyst were added into a 1 liter three necked flask, which equipped with a magnetic mixer, a thermocouple and a condenser connected to a vacuum system. The process performed under pressure of 60 kPa at temperature 80°C for 2 h in order to remove water content.

2) Oligomerization: After dehydration, the product was further oligomerized by gradually increasing the temperature to 150-180°C under pressure of 20 kPa for 3 h without the addition of a catalyst.

3) Depolymerization: After 3 h of oligomer stage, lactide was produced though depolymerization, which carried out at 180-210°C, pressure 2 kPa and maintaining for 3 h without nitrogen gas flow. After the completion of the depolymerization process the crude lactide was cooled to room temperature. The lactide synthesis is summarized in Figure 3.4.

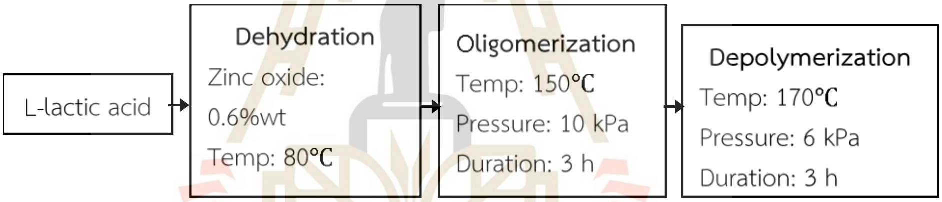


Figure 3.4 Lactide synthesis from L-lactic acid

3.2.2 Lactide synthesis from butyl lactate

1) Oligomerization: Butyl lactate (liquid, 88%) (300 ml) with tin(IV) chloride as a catalyst were added into a 1L three necked flask equipped with a magnetic stirrer, a temperature controller, and a distillation condenser. The reaction was carried out at 170 - 200°C for 5 - 27 h with continuous nitrogen gas flow (20 ml/min) to push evaporative alcohol continuously removed out from reactor into the condenser in atmospheric pressure. Afterwards, the condition changed to reduce pressure to 30 mbar, for 2 h so that the unreacted butyl lactate and alcohol was completely distilled out and collected in receiver from the produced oligomer.

2) Depolymerization: Oligomer synthesized from butyl lactate with tin(IV) chloride as a catalyst was transferred to the same setup apparatus on oligomerization stage, and a distillation column at 95°C. The reaction was carried out at 210°C under reduced pressure 5 mbar for 3 h. After the completion of the depolymerization process the crude lactide was cooled to room temperature.

For independent variable and dependent variable of lactide synthesis from both lactic acid and butyl lactate are shown in Table 3.1

Table 3.1 Independent variable and dependent variable for lactide synthesis

Independent variables	Dependent variables
1) Temperature (°C)	1) Yield (%)
2) Time (h)	2) Functional group
3) Amount of catalyst	3) Melting temperature

3.2.3. Lactide purification

The crude lactide was preheated at 80 - 90°C then dissolved in ethyl acetate (1:1.5 w/v) by stirring for 10 min. Vacuum filtration was used to separate the undissolved impurities, and the filtrate was cooled to ambient temperature before recrystallization at 4°C for 24 h. Vacuum filter was used to separate the recrystallized lactide from ethyl acetate, and the filtrate was subsequently dried in a vacuum oven at 40°C, pressure 100 mbar, for 24 h, as shown in Figure 3.5. After that, the lactide was purified and placed in the sample container. After completing the

process, the quantity of lactide was weighed and conversion yield of lactide was calculated by Eq. (3.1).

$$\text{Lactide yield (\%w/w)} = \frac{\text{Mass of purified lactide (g)}}{\text{Mass of butyl lactate (g)}} \times 100 \qquad (3.1)$$

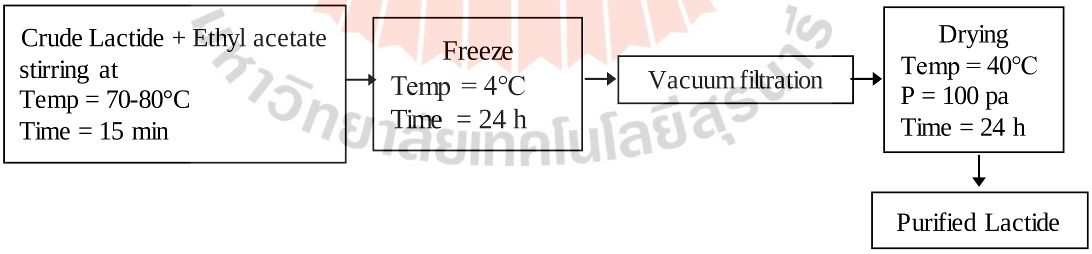


Figure 3.5 Purification of lactide

3.2.4 Ring-opening polymerization of lactide

Purified lactide was weighed then placed in a three-neck flask, which equipped with a magnetic stirrer, thermocouple with nitrogen gas flow at 20 mL/min. The process was conducted with and without initiator, and tin octoate as a catalyst was added into the reactor while lactide is heated until it's melted with concentration of catalyst in the range of (0.05 – 0.6 w/w%). The mixture was carried out by temperature variation at 160 - 200°C for different duration time 0.5 - 20 h. Upon completely this stage, the product mixture was cooled to room temperature, and chloroform was added to dissolve crude PLA with 1:1.2 w/v for 30 min until well dissolved, and then allowed to the purification, which was precipitated into excess cold methanol with 1:1.5 v/v. White solid PLA was gradually formed and separated by vacuum filtration. The filtrate was dried in a vacuum oven with pressure 100 mbar at 40°C for 24 h. The diagram of PLA synthesis and purification is shown in Figure 3.6. After completely the process, the quantity of PLA produced was weighed, and its conversion yield is calculated by Eq. (3.2).

$$\text{PLA yield (\%w/w)} = \frac{\text{Mass of purified PLA (g)}}{\text{Mass of purified lactide input (g)}} \times 100 \tag{3.2}$$

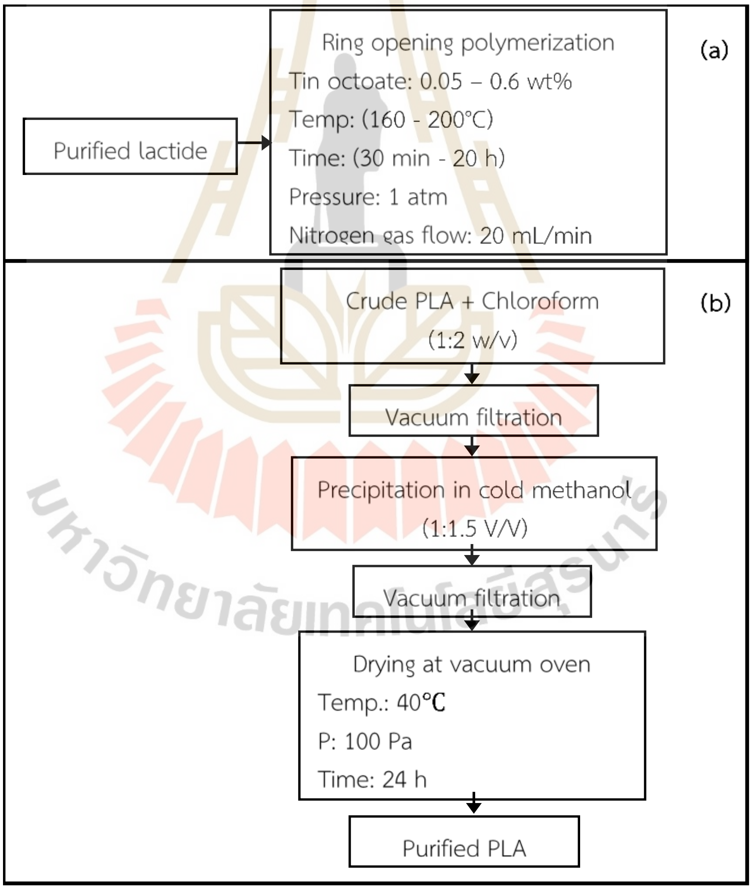


Figure 3.6 PLA synthesis: (a) Ring opening polymerization of lactide, (b) purification of PLA

For Independent variable and dependent variable of PLA synthesis from lactide product shown in Table 3.2.

Table 3.2 Independent variable and dependent variable for lactide synthesis

Independent variables	Dependent variables
1) Temperature (℃)	1) Yield (%)
2) Time (h)	2) Functional group
3) Amount of catalyst	3) Melting temperature (℃)
	4) Molecular weight (Da)

3.2.5 Experimental design of the thesis work

The synthesis of PLA from lactide, which is derived from raw materials butyl lactate, is the subject of this thesis. Therefore, there are two main steps of the works are lactide production and PLA synthesis, as previously mentioned. The effect initiator addition during PLA synthesis, the recrystallization of lactide and PLA is included to study in this thesis work. Thus, the work is divided into five experimental series as is summarized for overview diagram shown Figure 3.7, and detail of variation of conditions in Table 3.3. For each series of the experiment is described as following, Series 1 is for PLA synthesis from synthesized lactide based lactic acid. Series 2 is described of the PLA synthesis from commercial lactide to obtain the optimum condition of ring opening polymerization of lactide to form PLA. Series 3 is to develop the lactide production as lactide synthesis from butyl lactate, and the purification. Lactide products is compared to commercial lactide and then to select the optimum condition. Series 4 is for PLA synthesis from synthesized lactide based butyl lactate, and purification of PLA. Series 5 is PLA synthesis from synthesized lactide by using the optimum condition in series 3 and 4 with adding initiator.

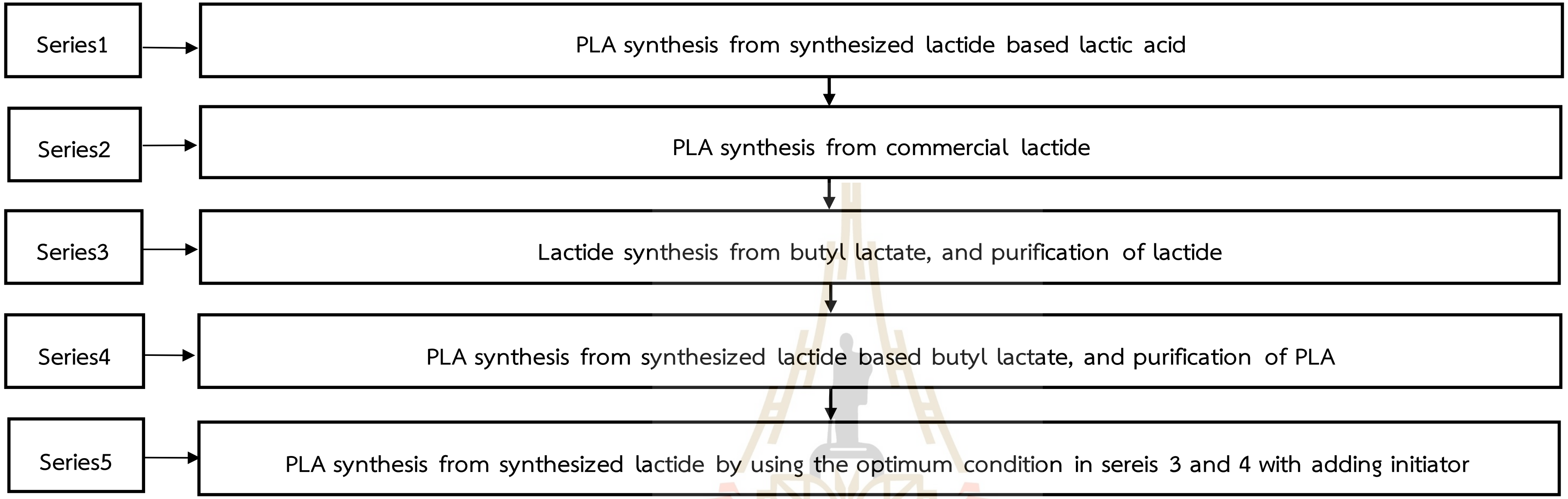


Figure 3.7 The design of experiment in each series

Table 3.3 Testing conditions of PLA synthesis though ring opening polymerization of lactide

Series1: PLA synthesis from synthesized lactide based lactic acid									
Lactide synthesis				PLA synthesis					
Raw material	Fixed variable		Result	Raw material	Independent variable		Parameter affect the reaction	Dependent variable	
	Symbol	Condition	Yield and property of LT		Symol	Condition		Yield and property of PLA	Optimum result
LA	T (℃)	80-150-170	(Functional group, Tm, Tg, Td, Mn, Molecular structure)	Synthesized LT	T (℃)	140, 160, 180	$T^{L11,...,L1n}$	$PLA^{L11...L1n}$ (Functional group, Tm, Tg, Td, Mn, Molecular structure)	Optimum PLA
	Cat (wt%)	0.6			Cat (wt%)	0.4			
	P (mbar)	600-30			P (mbar)	1013.25			
	t (h)	8			t (h)	5, 8, 10	$t^{L11,...,L1n}$		
Condition1: 1				Condition2: 9					
Total Conditions: 10									

Series 2: PLA synthesis from commercial lactide					
Raw material	Independent variable		Parameter affect the reaction	Dependent variable	
	Symbol	condition		Yield and Property of PLA	Optimum result
Commercial lactide	T (℃)	160, 180, 190, 200	$T^{L21...L2n}$ (T^{l2n} is optimum)	$PLA^{L21...L2n}$ (Functional group, Tm, Tg, Td, Mn, Molecular structure)	PLA^{L2n}
	Cat (wt%)	0.4			
	P (mbar)	1013.25			
	t (h)	0.5, 5	$t^{L21...L2n}$ (t^{l2n} is optimum)		
Total Conditions: 8					

Table 3.3 Testing conditions of PLA synthesis though ring opening polymerization of lactide (Continued)

Series 3: PLA synthesis from lactic acid and butyl lactate					
Lactide synthesis					
Raw material	Independent variable		Parameter affect the reaction	Dependent variable	
	Symbol	Condition		Yield and Property of LT	Optimum Result
BL	T (°C)	170, 180, 190, 210	$T^{B31...,B3n}$ (T^{B3n} is optimum)	$LT^{B31,...,B3n}$ (Functional Tm, Tg, Td, Mn, Molecular structure)	LT^{B3n}
	Cat (wt%)	0.03, 0.05, 0.06, 0.07, 0.1, 0.3	$Cat^{B31,...,B3n}$ (Cat^{B3n} is optimum)		
	P (mbar)	960=>30=>5			
	t (h)	8, 11, 13, 30	$t^{B31,...,B3n}$ (t^{B3n} is optimum)		
Condition1: BL=12					
Lactide purification					
Raw material	Independent variable		Dependent variable		
	Symbol	Condition	Yield and properties of LT	Result	
Crude LT	Ethyl acatate (w/v)	(1:1); (1:1.2); (1:1.3); (1.1.4)	Optimum LT	Optimum Parameter	
	T (°C)	4; Room temperature			
	t (h)	5; 12; 24			
Condition: 7					
Total condition: 19					

Table 3.3 Testing conditions of PLA synthesis though ring opening polymerization of lactide (Continued)

<table>
<tr><th colspan="6">Series 4: PLA synthesis from synthesized lactide based butyl lactate</th></tr>
<tr><th colspan="6">PLA synthesis</th></tr>
<tr><th rowspan="2">Raw material</th><th colspan="2">Independent variable</th><th rowspan="2">Parameter affect the reaction</th><th colspan="2">Dependent variable</th></tr>
<tr><th>Symbol</th><th>Condition</th><th>Yield and property of PLA</th><th>Optimum result</th></tr>
<tr><td rowspan="4">Synthesized LT</td><td>T (℃)</td><td>160; 170; 180; 190; 200</td><td>$T^{B41,\ldots,B4n}$
(T^{B4n} is optimum)</td><td rowspan="4">$PLA^{B41,\ldots,B4n}$
(Functional group,
Tm,
Tg,
Td,
Mn, Molecular structure)</td><td rowspan="4">PLA^{B4n}</td></tr>
<tr><td>Cat (wt%)</td><td>0.05; 0.1; 0.2; 0.4; 0.6</td><td>$Cat^{B41,\ldots,B4n}$
(Cat^{B4n} is optimum)</td></tr>
<tr><td>P (mbar)</td><td>1013.25</td><td></td></tr>
<tr><td>t (h)</td><td>0.5; 2; 5; 8; 10; 20</td><td>$t^{B41,\ldots,B4n}$
(t^{B4n} is optimum)</td></tr>
<tr><td colspan="6">Condition1: 12</td></tr>
<tr><th colspan="6">PLA purification</th></tr>
<tr><th colspan="2" rowspan="2">Raw material</th><th colspan="2">Independent variable</th><th colspan="2">Dependent variable</th></tr>
<tr><th>Symbol</th><th>Condition</th><th>Yield and Property of PLA</th><th>Result</th></tr>
<tr><td colspan="2" rowspan="6">Crude PLA</td><td>Chloroform (w/v)</td><td>(1:1); (1:1.2); (1:1.4); (1:1.6)</td><td rowspan="6">Optimum PLA</td><td rowspan="6">Optimum
Parameter</td></tr>
<tr><td>T(℃)</td><td>Room temperature</td></tr>
<tr><td>t(h)</td><td>15 min</td></tr>
<tr><td>Methanol (v/v)</td><td>(1:1.5)</td></tr>
<tr><td>T(℃)</td><td>4; Room temperature</td></tr>
<tr><td>t(min)</td><td>1-10</td></tr>
<tr><td colspan="6">Condition: 5</td></tr>
<tr><th colspan="6">Total conditions: 17</th></tr>
</table>

Table 3.3 Testing conditions of PLA synthesis though ring opening polymerization of lactide (Continued)

Series5: PLA synthesis from synthesized lactide by using the optimum condition in sereis 3 and 4 with adding initiator					
Lactide synthesis		PLA synthesis			
Raw material	Process	Raw material	Adding other initiators/chemicals	Process	Result Yield and
BL	Fixed optimum condition of series3	2) LT^{B4n}	1) polyglycerol-10 (0.02mole%) 2) 1,4-Butanediol (0.05mole%)	Fixed optimum condition of series4	PLA^{B4n}(Function Tg, Td, Mn,
Condition1: BL=1		Condition2: BL=1			
Total condition: 2					

3.3 Analysis instruments

The characterization of products were analyzed with the analytical instruments:

1) Fourier transform infrared spectrometer (FTIR), IR spectroscopy
2) Polarimeter characterization
3) X-ray diffraction (XRD)
4) Differential scanning calorimetry (DSC)
5) Thermogravimetric analysis (TGA)
6) Gel permeation chromatography (GPC)
7) Nuclear magnetic resonance (NMR)

3.3.1 Fourier transform infrared spectrometer (FTIR)

Fourier-transform infrared spectroscopy (FTIR) is a technique for obtaining an infrared spectrum of a solid, liquid, or gas's absorption or emission. It's a technique for analyzing the functional groups of organic compounds that works on the basis of absorption in the middle infrared range (4000-400 cm^{-1}). When a molecule receives energy from infrared waves with a frequency that corresponds to the molecule's covalent bond stretching or bending. This allows the molecules to absorb infrared light and modify their dipole moment. The equipment will then calculate the light intensity per frequency or wavelength (wave number) using a "Interferogram" spectrum, in which each bond of a function group has a different wavelength: C=O of ~ 1,800 cm-1, O-H stretching very broad at 3,300-2,500 cm-1, N-H stretching ~ 3500-3300 cm-1, -C=C- Stretching ~ 1667-1613 cm-1, C-H Stretching ~ 3,000-2,840 cm-1 etc. A light source, typically an infrared radiator, an interferometer, such as a Michaelson with both fixed and moving mirrors, a sample chamber, and a thermal or photonic detector are all essential components of FTIR. The broadband infrared energy from the source is focused onto a beam splitter, which divides it into two streams. One road's terminus is a fixed mirror, while the other path's end is a moving mirror. At the beam splitter, the infrared radiation from these two channels returns and recombines, resulting in a constructive and destructive interference pattern known as an interferogram. This modulated infrared beam is directed at the sample, where it is absorbed according to the material's molecular structure. A block diagram of a classic dispersive FTIR spectrometer and IR spectroscopy are shown in Figure 3.8 and 3.9, respectively.

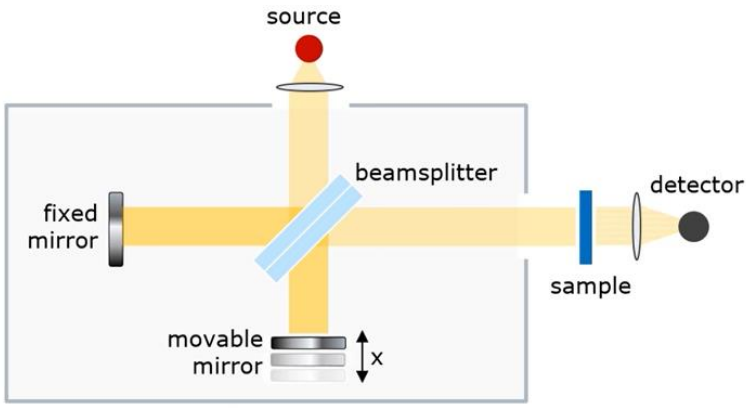


Figure 3.8 Simplified representation of a dispersive FTIR spectrometer

IR spectroscopy is a method for determining the existence of functional groups in a molecule as well as identifying pure chemicals and specific contaminants. Furthermore, IR spectroscopy absorbs monochromatic IR light and extracts its spectrum all at once. To form a spectrum, it absorbs multi-chromatic IR light and integrates scattering.

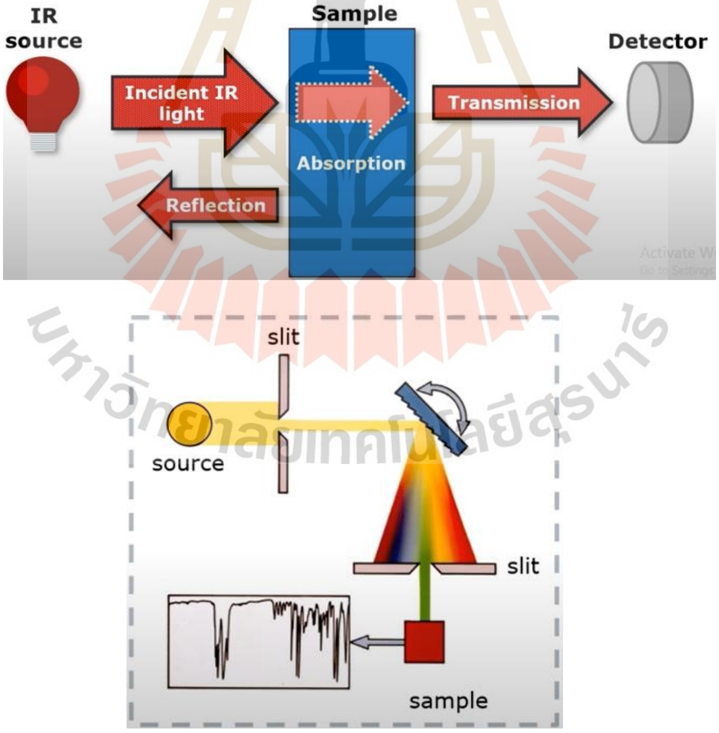


Figure 3.9 Simplified representation of a dispersive IR spectroscopy

PCA (Principal Component Analysis) is a statistical technique for reducing dimensionality. It converts a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables termed principle components via an orthogonal transformation. It is often used as a dimensionality reduction technique as shown in Figure 3.10 (a). PCA's mission is to identify a straight line, or hyperplane, that can be used to project data from one dimension to another. Let's look at a simple example, such as going from 3D to 2D see Figure 3.10 (b).

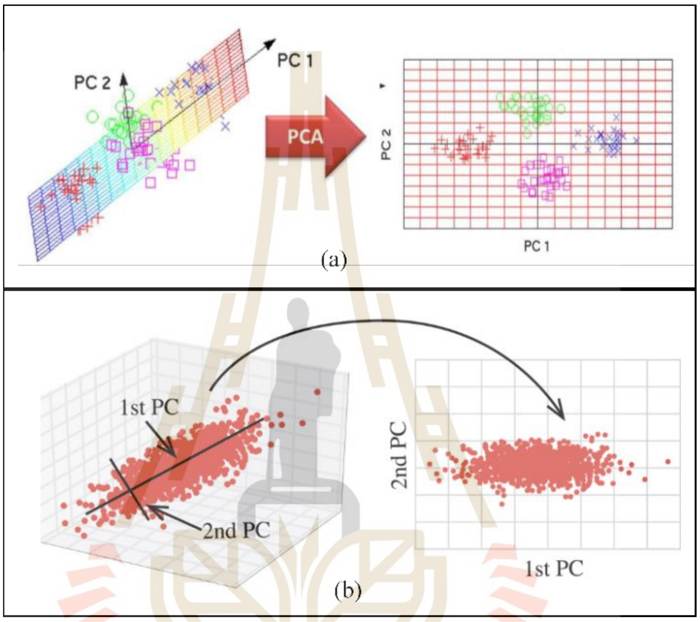


Figure 3.10 Principal Component Analysis (PCA): (a) reducing more complex data to make it easier to understand, or (b) converting a higher-dimensional hyperplane to a lower-dimensional hyperplane

3.3.2 Polarimeter characterization

The angle of rotation generated by passing polarized light through an optically active substance is measured by a polarimeter, which is a scientific device. Conducting of a polarimeter is based on the principle that when light passes through a sample, it has the ability to warp plane polarized light. A light source which unpolarized light waves vibrate in all directions. Monochromatic light from a sodium vapor lamp is the most frequent light source in polarimeters. A polarizer is a device that creates plane polarized light by vibrating light in a single plane. A block diagram of a polarimeter shown in Figure 3.11. The specific rotation, and enantiomer excess were calculated by Eq. (3.3) and (3.4), respectively.

$$[\alpha]_D^{20°C} = \frac{\alpha}{C \times L} \tag{3.3}$$

$$\%ee = \frac{\alpha}{(\alpha)_{pure}} \times 100 \tag{3.4}$$

Where,

$[\alpha]_D^{20°C}$: Specific rotation, (degree)
α : Observed rotation, (degree)
$(\alpha)_{pure}$: Pure rotation of sample, (degree)
C : Concentration of sample, (g/ml)
L : Cell length, (dm)
ee : Enantiomer excess, (%)

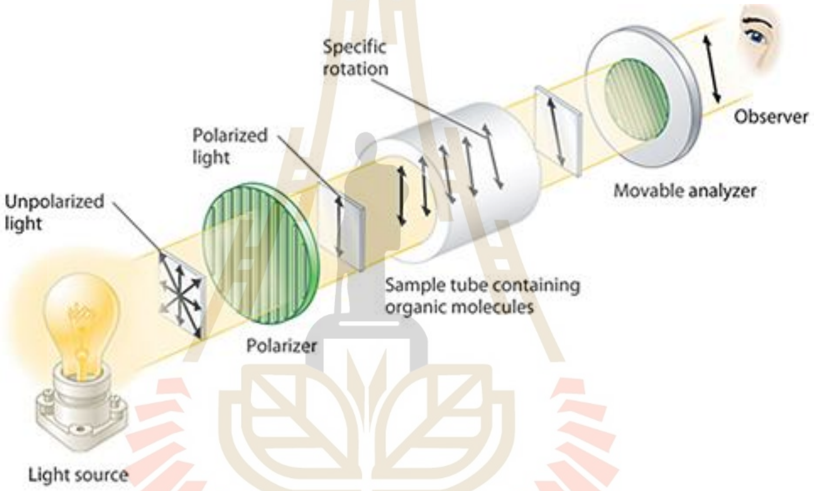


Figure 3.11 Components of polarimeter analysis for angle of rotation generated

3.3.3 X-ray diffraction (XRD)

X-ray diffraction, also known as X-ray diffraction analysis (XRD), is a technique for analyzing and identifying chemicals, as well as their crystal structure, in both qualitative and quantitative samples. The XRD analysis technique is based on the premise of firing X-rays at a target, which generate diffraction and are reflected at various angles by a signal probe (Detector), which is a data receiver. X-ray diffraction of a substance's composition and structure produces varied angles based on the composition, shape, and crystal properties. The result can be used to determine the type of compound contained in the sample and to investigate the crystal structure of that sample in greater detail. Single crystal and Powder XRD are the two most common configurations for XRD experiments. The x-ray spectrometer's component pieces, as shown in Figure 3.12, are in general common and consist of an x-ray source, a sample stage, and a detector. By comparing the area of crystalline zones to the overall area, the degree of crystallinity was identified. Crystalline and amorphous areas added up to the total area. The total area was sum of crystalline and amorphous area showing in Figure 3.13 and Eq. (3.5)

$$\%\text{Degree of crystallinity} = \frac{\text{Crystalline area (5-80°)}}{\text{Total area (5-80°)}} \tag{3.5}$$

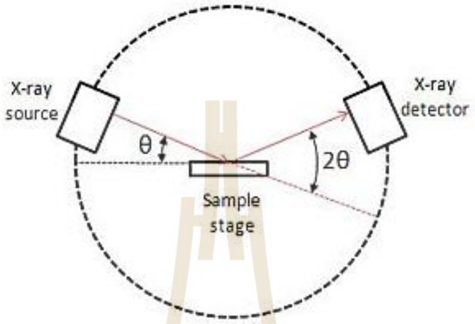


Figure 3.12 Arrangement of XRD Diffractometer components

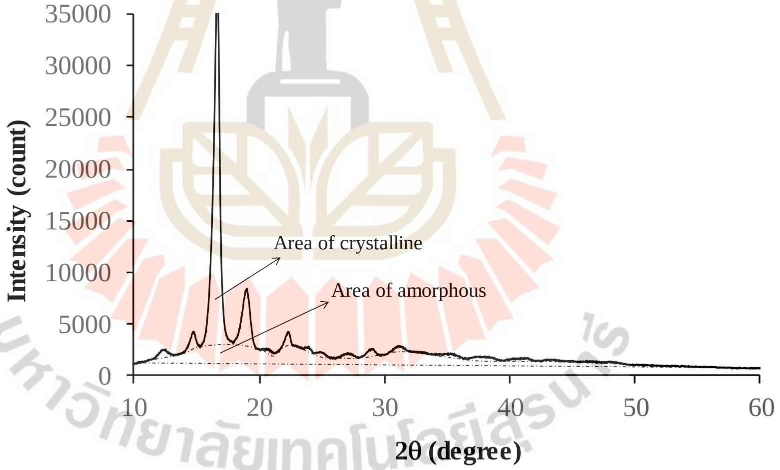


Figure 3.13 The XRD spectrum of PLA product

3.3.4 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a useful analytical tool for determining a polymer's physical properties. DSC can be used to determine the temperatures of melting, crystallization, and mesomorphic transitions, as well as the characterization of the glass transition and other phenomena that reveal changes in heat capacity or latent heat. It’s contains two sample positions: one for the sample under inquiry and one for a reference sample, which is usually an empty crucible or one filled with an inert substance (Schick, 2009). The sample and reference holder, the heat resistor, the heat sink, and the heater are all part of the DSC. Heat from the heater is transferred to the sample and reference via a heat sink and a heat resistor. The heat difference between the heat sink and the holders determines the heat flow. In comparison to the sample, the heat sink has sufficient heat capacity. When endothermic or exothermic phenomena, such as transition and reaction, occur in the sample, the endothermic or exothermic phenomena are compensated by the heat sink. As a result, the temperature differential between the sample and the reference is maintained at the same level. The temperature differential between both holders is proportional to the difference in the amount of heat given to the sample and the reference. The unknown sample quantitative measurement can be achieved by calibrating the standard material. The block diagram of DSC as an example shown in Figure 3.14.

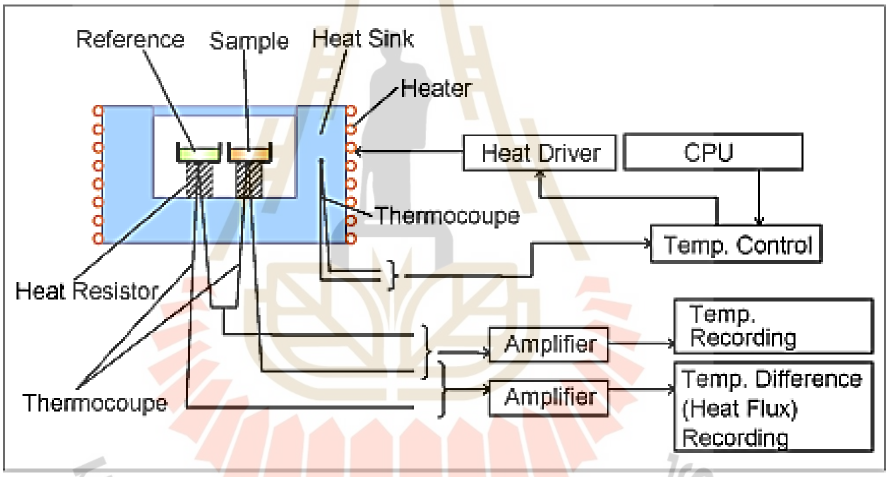


Figure 3.14 Block diagram of Heat Flux DSC

3.3.5 Thermogravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) is a type of thermal analysis in which the mass of a sample is assessed over time as the temperature varies. Physical processes like as phase transitions, absorption, including chemisorption, and thermal breakdown are all investigated using this method. While the temperature of a sample is altered over time, a thermogravimetric analyzer continually measures mass. In thermogravimetric analysis, mass, temperature, and time are considered base measurements, from which numerous additional measurements can be derived. A thermogravimetric analyzer typically comprises of a precision balance with a sample pan inside a furnace with programmable temperature control. To cause a thermal reaction, the temperature is normally increased at a consistent pace (or, in some cases, the temperature is controlled for a constant mass loss). TGA can be used to characterize materials by examining typical decomposition patterns. It's particularly useful for studying thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings, paints, and fuels, among other polymeric materials. It includes a high-precision balance as well as a sample pan. The pan holds the sample material and is heated or cooled during the experiment in a furnace or oven. The temperature in the oven is controlled and measured using a thermocouple. Throughout the study, the mass of the sample is constantly checked. To purify and manage the environment, an inert or reactive gas can be utilized. The weight of the substance shown against temperature as the temperature is gradually raised. The instrument is controlled by a computer, which also processes the output curves (temperature vs. weight). The Diagram of TGA as an example shown in Figure 3.15.

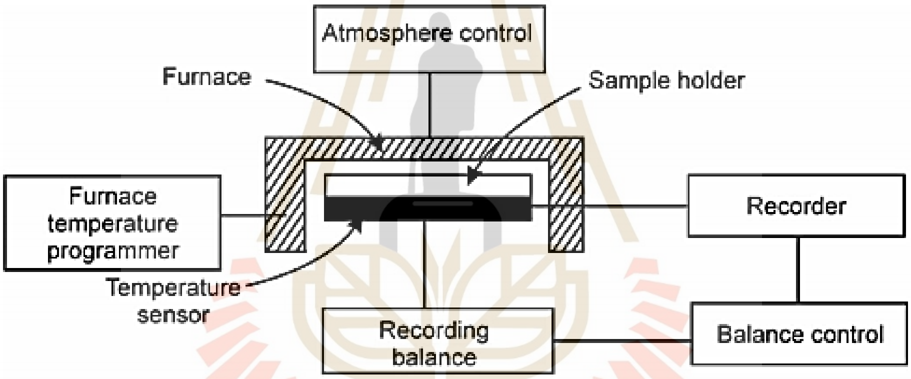


Figure 3.15 Block diagram of thermal gravimetric analysis (TGA)

3.3.6 Gel permeation chromatography (GPC)

Gel permeation chromatography (GPC) is a form of size exclusion chromatography (SEC) that uses organic solvents to separate analytes based on their size. This method is frequently used to examine polymers. When characterizing polymers, it is important to consider the dispersity as well molecular weight. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight (Mn), the weight average molecular weight (Mw), the size average molecular weight (Mz), or the viscosity molecular weight (Mv). Injectors were required by GPC Systems in order to introduce the polymer solution into the flowing system. Pumps transport the sample and solvent between the columns and throughout the apparatus. Separation is monitored and recorded by detectors. The test is automatically controlled, the results are recorded, and the molecular weight averages are calculated using data acquisition accessories. The gel permeation chromatography is made up of several separate parts that work together to deliver the best system performance with the least amount of effort. The Figure 3.16 shows a basic gel permeation chromatography.

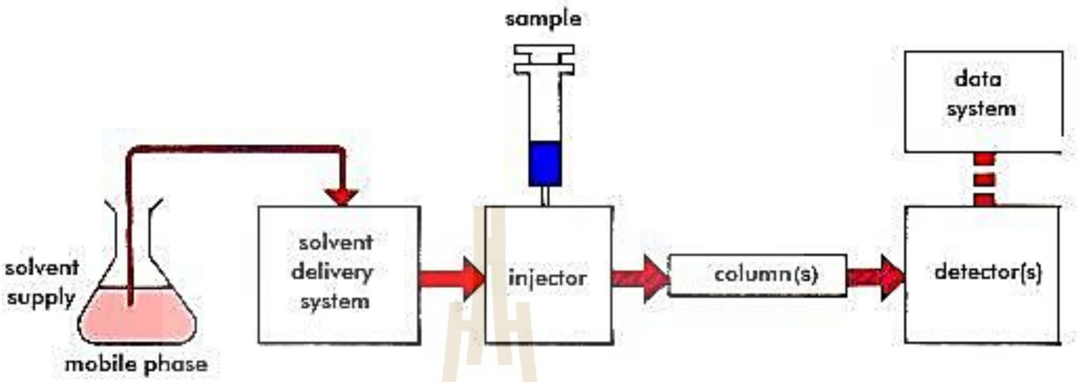


Figure 3.16 Schematic of a basic gel permeation chromatograph

In addition, the molar mass of PLA was measured based on viscosity in chloroform at 25°C and yielded a viscosity average molecular weight $[\eta]$ according to the Mark-Houwink equation (3.5) (Ma, Jiang, Ye, Dong, & Chen, 2014).

$$[\eta]=2.48\times10^{-4}\times M_v^{0.77} \qquad (3.5)$$

Where,

$[\eta]$: intrinsic viscosity, $(\mathrm{dL/g})$

$[M_v]$: viscosity average molecular weight, $(\mathrm{g/mole})$

3.3.7 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) Spectroscopy is a technique for determining the content and purity of a sample as well as its molecular structure. It can be utilized in a variety of sectors, including pharmaceutical production and structure enhancement, materials science, and polymers, among others. Spectroscopy with Nuclear Magnetic Resonance (NMR). The NMR signal is formed by converting the nuclear sample's radio frequency into a nuclear electromagnetic wave, which is detected by a sensitive radio receiver, by placing the sample in a magnetic field. The resonant frequency is changed by the magnetic field within the molecule surrounding the atom in the molecule. This gives you access to information about the molecule's electrical structure as well as its functional groups. This is due to the fact that each combination's fields are unique or extremely characteristic. NMR spectroscopy is the gold standard for identifying molecular organic molecules in modern organic chemistry. An NMR spectrometer is made up of a probe that revolves inside a powerful magnet. A radio frequency transmitter and receiver with a probe (antenna unit) that surrounds the sample in a magnet. Color-coded curves can also be utilized for propagation measures, and the electronic device to control the NMR spectroscopy system shown in Figure 3.17.

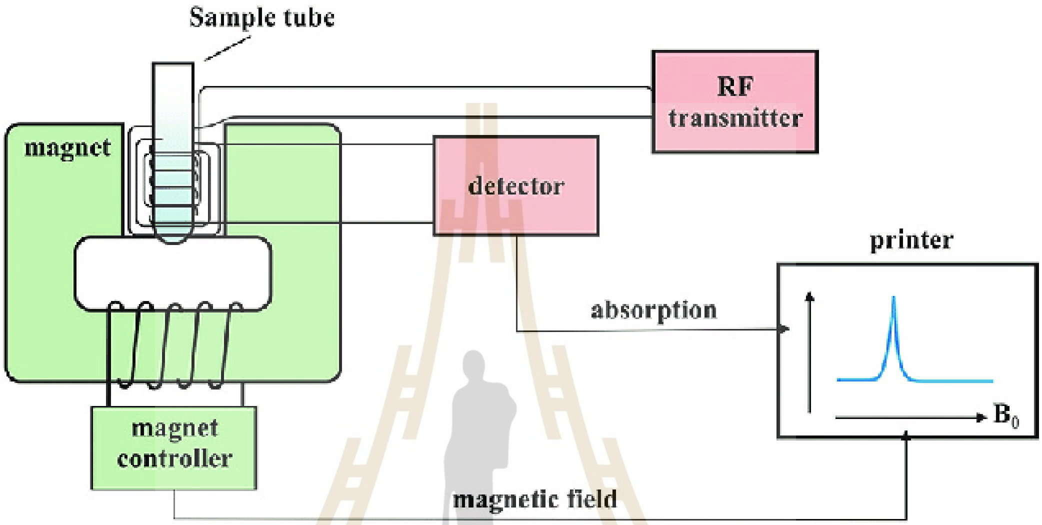


Figure 3.17 Component schematic of NMR spectroscopy

CHAPTER IV

RESULTS AND DISCUSSION

Lactide and PLA synthesis was provided the result from each experimental series. It described under the headings as follows: Series 1 is described in heading 4.1, PLA synthesis from synthesized lactide based lactic acid. Series 2 is reported in heading 4.2, for PLA synthesis from commercial lactide to obtain the optimum condition of ring opening polymerization of lactide to form PLA by various reaction temperature. Series 3 describes in heading 4.3.1 – 4.3.2, to synthesize lactide from butyl lactate, and purification of lactide. Series 4, 5 expresse in heading 4.3.3 for PLA synthesis from synthesized lactide based butyl lactate, and purification of PLA, and by adding initiator to the reaction. Energy index for cost analysis of PLA synthesis was reported in heading 4.4.

4.1 Preliminary results for PLA synthesis from lactic acid based lactide

4.1.1 Synthesis of lactide and PLA

Lactide yield obtained from the stage of lactide synthesis by using zinc oxide as catalyst was 31.25% determined by Eq. (3.1) and PLA yields at the various temperatures and reaction time were calculated by the Eq. (3.2) as shown in Figure 4.1. PLA products yield using stannous octoate 0.4 w/w% as a catalyst in the processes, which carry out for 5 h at temperatures of 140, 160, and 180°C were 49.62 %, 64.5%, and 50.39%, respectively. Increasing the reaction time of 8 h, PLA yield 53.1% and 62.06% of temperature 140 and 160°C, respectively. For increasing time of 10 h, yield of PLA are 58.73%, 55.7%, and 49.04% at temperatures of 140, 160, 180°C, respectively. The maximum yield was found at 160°C for 5 h. The result shown that the increasing temperature for a long time does not improve the product yield (Yarkova et al., 2015).

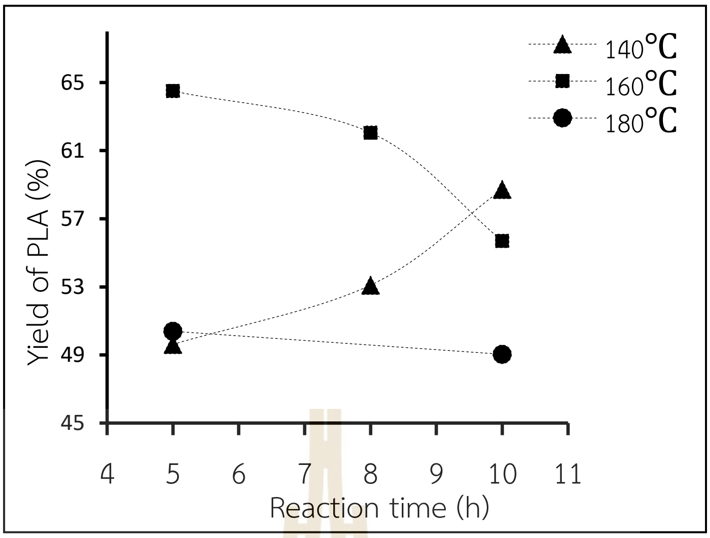


Figure 4.1 Effect of reaction temperature and time on PLA synthesis

4.1.2 Characterization of lactide and PLA

4.1.2.1 Functional group of lactide and PLA

The product of lactide and PLA were analyzed the functional group determine by FTIR and shown that the products for both lactide and PLA were the same compared to the commercial PLA, as shown in Figure 4.2. The bonds of carbonyl stretch and oxy carbonyl (ester) were observed at wave number 1748 cm-1 and 1181 cm-1, respectively. The -CH bond was observed at 2996 cm−1, and -OH bond stretching was observed at wavenumber 3530 cm−1, which is characteristic of a carboxylic acid. However, at the lower wavelength of bond are tended to show considerable overlap because it is difficult for the characterization. The infrared spectroscopy wavenumbers (cm−1) for the bonds and products functional groups were as follows: -OH stretch (free): 3100; -CH-stretch: 2996 (asymmetric), 2946 (symmetric), 2877; -C=O carbonyl stretch: 1748; -CH3 bend: 1452; -CH- symmetric and asymmetric: 1382 and 1360; -C-O- stretch: 1181, 1083; -OH bend: 1042 (Hans R. Kricheldorf & Weidner, 2019).

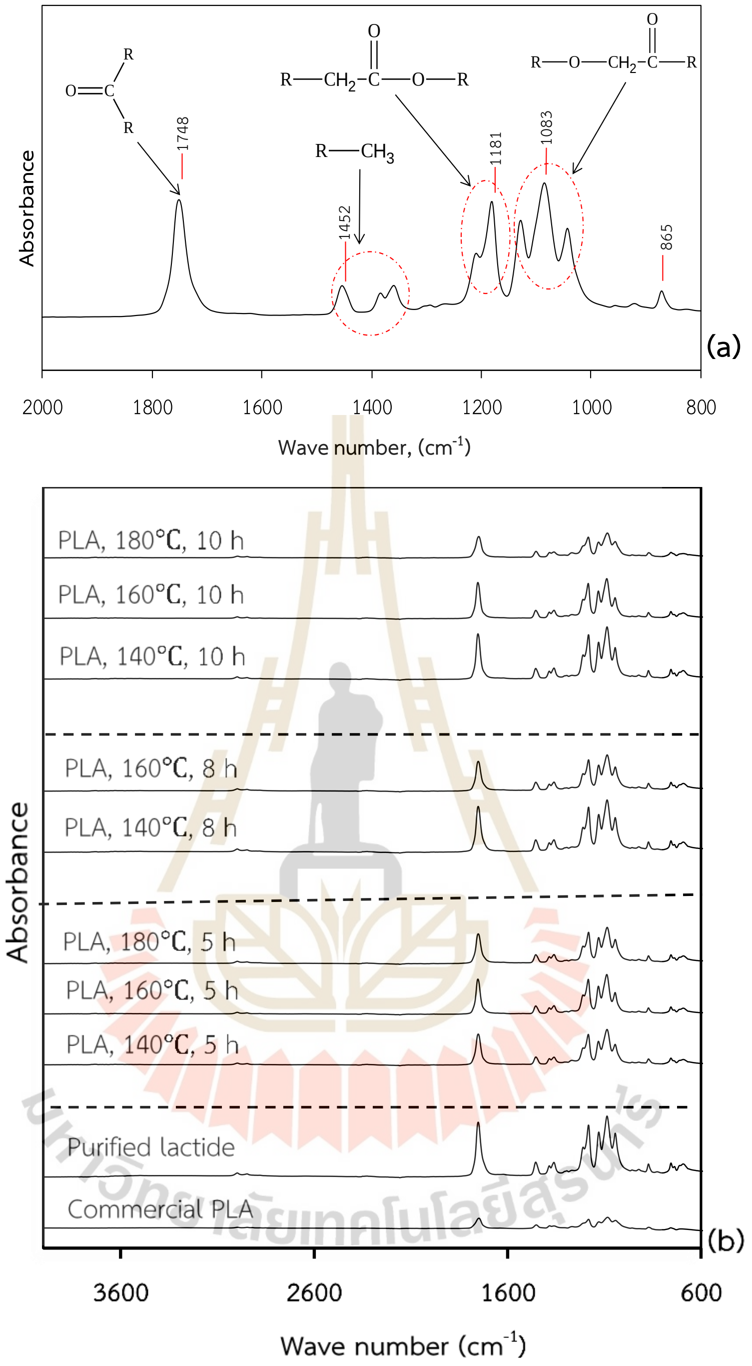


Figure 4.2 The functional group of lactide and PLA products: (a) commercial PLA and (b) comparing of each product to commercial lactide and PLA

4.1.2.2 Stereoisomer of lactide

In general stereoisomer of lactide provided in three stereoforms as L-lactide, D-lactide, and optically inactive meso-lactide form which is an equimolar (racemic) mixture of D and L isomers (Masutani & Kimura, 2014). The lactide product was detected, the resulting observed rotation **α** = -13.4° was used to calculate by Eq. (3.3) to obtain the specific rotation was $\left(\left[\alpha\right]_D^{20}\right)_{LLA} = -291°$. This result to confirm the stereoform of lactide synthesized was L-stereoisomer as L-lactide. Determination of enantiomer excess value of synthesized lactide was calculated by Eq. (3.4), to find its percentage stereopurity. While the neat optical rotation of L- and D-lactides were $\left(\left[\alpha\right]_D^{20}\right)_{LLA} = -298.8°$ and $\left(\left[\alpha\right]_D^{20}\right)_{DLA} = +298.8°$ at 20°C in a toluene solution, respectively (Feng et al., 2017). The value of enantiomer excess of synthesized lactide was obtained for 4.5%, and the stereopurity of synthesized lactide was 52.25% of L-stereoform.

4.1.2.3 Molecular structure of PLA

The molecular structure of PLA produced was evaluated by ^{1}H NMR and ^{13}C NMR as shown in Figure 4.3(a) and 4.3(b), respectively. The PLA powder was considered for the analyzation obtained from reaction temperature at 160°C by using stannous octoate 0.4 w/w% as a catalyst for 5 h in polymerization stage. Figure 4.3(a) shows the ^{1}H NMR as H-doublet signal for methyl proton resonance in the main chain at 1.57 ppm. The spectrum shows signal of methine proton resonances in the main chain of PLA at 5.19 ppm. The ^{1}H NMR spectrum of PLA at 2.6 and 4.37 ppm was assigned to the methine proton next to the terminal hydroxyl group and carboxyl group, respectively. The result from analyzed of ^{1}H NMR, the spectrum of PLA was similar to that reported by other works (Choubisa et al., 2012; Rahmayetty et al., 2018). Figure 4.3(b) shows the ^{13}C NMR spectrum of PLA product. The ^{13}C NMR spectrum of PLA signals visible for molecular structure of methyl carbon, carbon methane and carbon ester assigned at 16.75, 69.12 and 169.73 ppm, respectively. The result of synthesized PLA shown that PLA formed in the present study for ^{13}C NMR evaluated similar to that reported by other works (Ding et al., 2011).

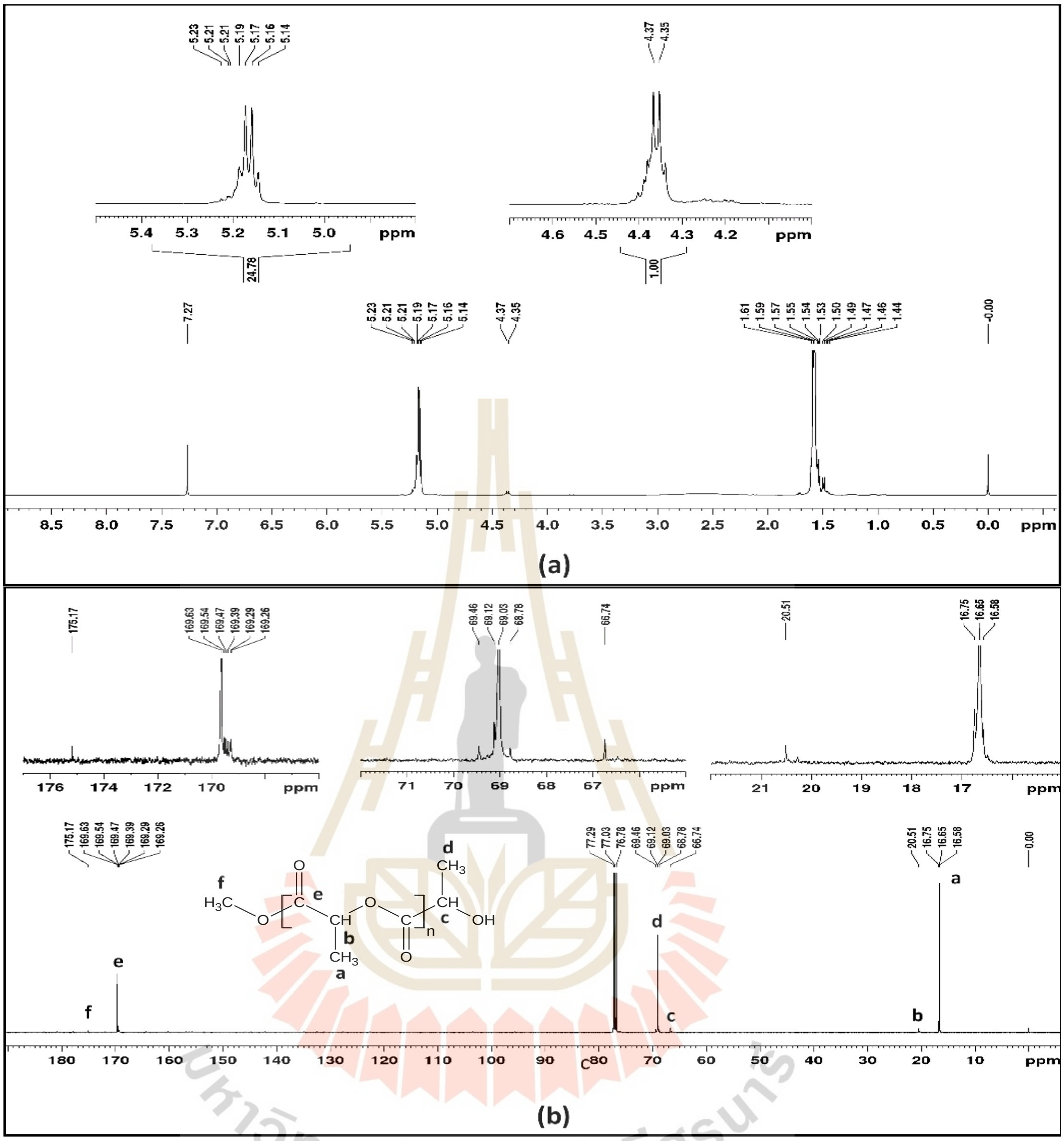
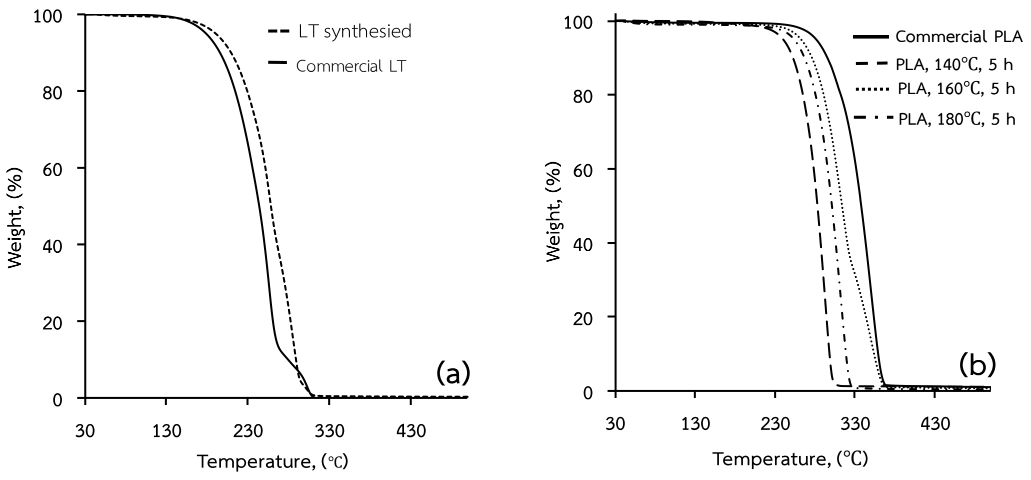


Figure 4.3 NMR analysis spectra of PLA products: (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum

4.1.2.4 Thermal stability of PLA

The thermal stability of the lactide and PLA were determined by TGA/DSC1. The profiles of decomposition temperature obtained from TGA are shown in Figure 4.4(a-d), whereas the melting temperature from DSC is displayed in Figure 4.4(e). These results of commercial lactide and PLA are also included in those Figures to compare with the synthesized samples. Synthesized lactide has decomposition, and melting point of 250°C and 96°C, respectively, which is related to commercial lactide, the decomposition, and melting point of 245°C and 93°C, respectively, shown in Figure 4.4(a) and 4.4(e). The temperature of decomposition and melting point of PLA samples are concluded and exhibited in Figure 4.5(a-b), respectively. Decomposition and melting temperature of commercial PLA were analyzed and found to be at 338°C and 153°C, respectively. It is found that the overall trend of decomposition and melting temperature of synthesized PLA tends to increase with an increasing of reaction temperature to reach a maximum point at 160°C, then decreasing in higher reaction temperature. The increasing of decomposition and melting temperature implies that the increasing of molecular weight of synthesized PLA. In general, during the reaction, there is a competition reaction between polymerization and depolymerization of lactide monomers to obtain PLA products. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The polymerization was proposed to describe by the insertion-coordination mechanism (Fang, Qi, Liu, Juan, & Huang, 2009). For the effect of reaction time, it shown that the decomposition and melting temperature mostly decreases with an increasing of reaction time for all reaction temperature except at the 140°C. This could be explained by the depolymerization play a major role of reaction. It is observed that at reaction temperature 140°C, the melting temperature increases with an increasing in reaction time. This result could be due to at this low reaction temperature the shorter chain molecules may occur in higher amount in bulk phase thus the melting temperature may be increased. The optimum condition for PLA synthesis in this work is found at reaction temperature 160°C with reaction time of 5h, which obtained the decomposition and melting temperature of 311°C and 152°C, respectively. The melting temperature of 152°C is comparable to commercial PLA of 153°C as shown in Figure 4.5 (b), which is nearly to the range of commercial PLA pellet supplied by NatureWorks, with Tm at 155 - 170°C (Yunzi Hu et al., 2017).



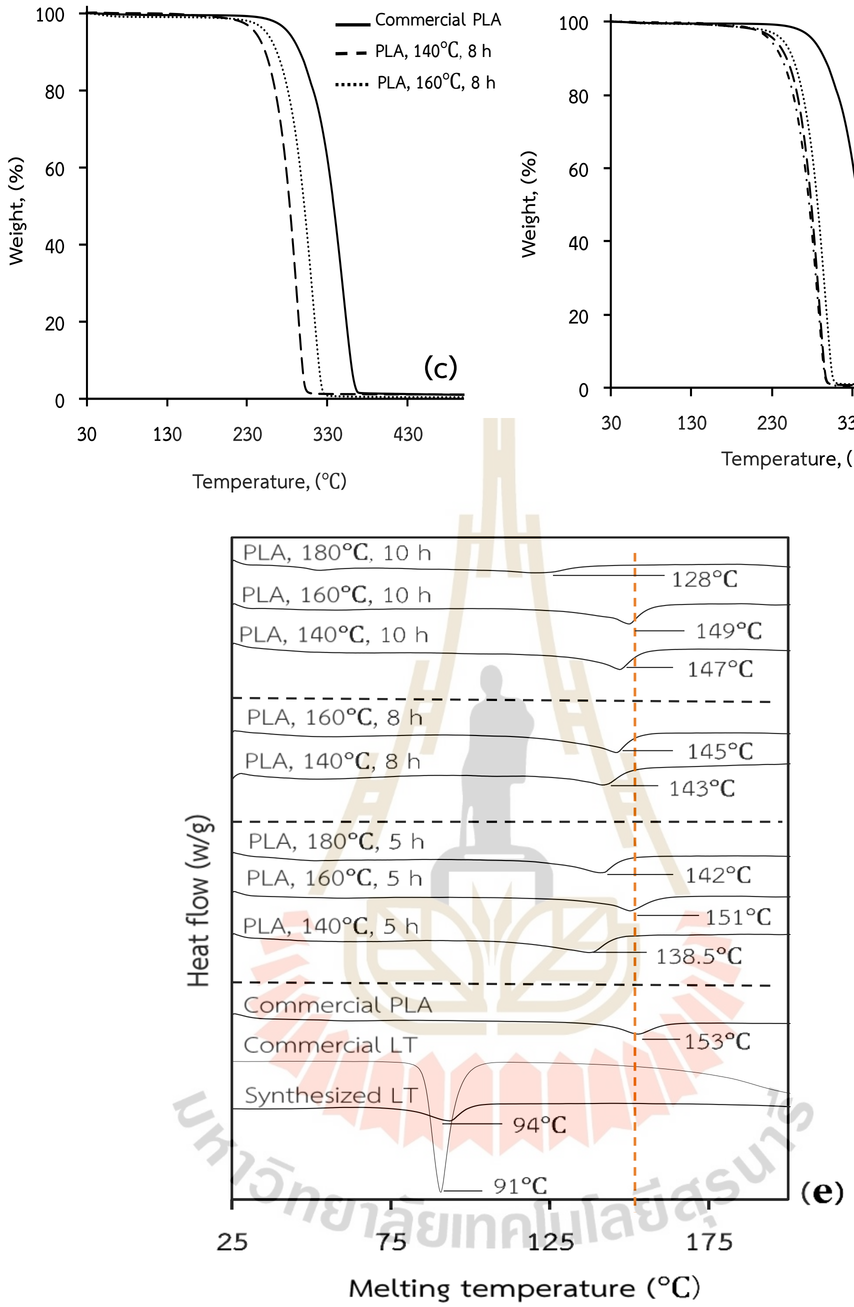


Figure 4.4 Analysis thermal stability results of (a-d) TGA and (e) DSC of synthesized lactide and PLA and commercial samples

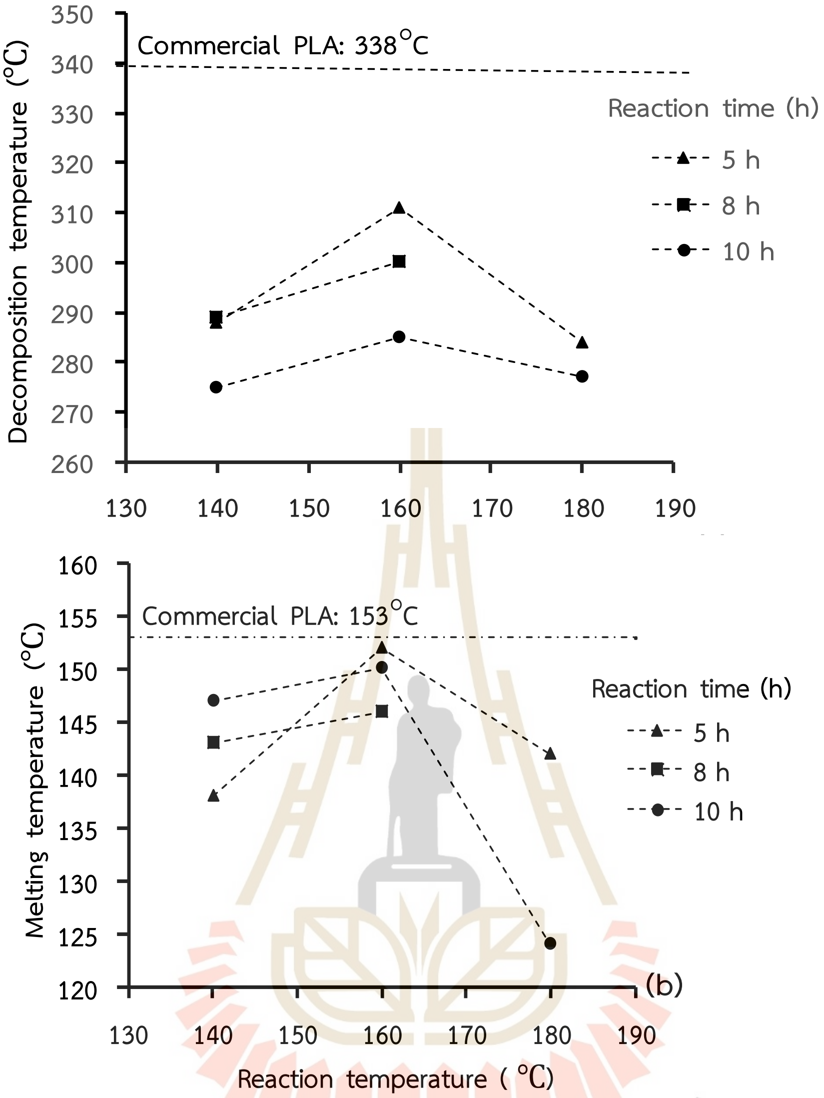


Figure 4.5 The decomposition and melting temperature of commercial PLA and synthesized PLA in different reaction temperature and time: (a) decomposition temperature and (b) melting temperature

4.2 PLA synthesis from commercial lactide

Commercial lactide was used as a raw material to produce PLA this series 2. In the ring opening polymerization stage, stannous octoate was used as a catalyst with fixed amount of 0.4 %w/w and was carried out in variation reaction temperature range of 160 - 200°C for various reaction time range at 0.5 h, and 5 h. It is found that for 0.5 h and at 200°C, none of PLA was produced. Thus, the reaction time should be longer for opening the chain of lactide to PLA with longer chain. Therefore, the fixed reaction time for 5 h is to be used, which linked from the series 1 as the reaction time to get highest thermal stability of PLA. As the result for various reaction temperature was shown that high temperatures, such as 190 and 200°C may damage PLA chain bonding by depolymerization leading in lower product yields than at 180°C because the process may occur polymerization and depolymerization of lactide and PLA simultaneously with the higher rate of depolymerization reaction of lactide. On the other hand, reaction temperature has an impact on the process because no other product yields were observed at low temperatures such as 160°C, owing to the higher energy required to break the lactide bond in the reaction system. The highest yield is found from experimental series 2 is the condition at reaction temperature at 180°C with reaction time at 5 h, which resulted in PLA yield of 40 % w/w as shown in Figure 4.6. For thermal stability and viscosity average molecular weight (Mv) of PLA of each condition was compared. The profiles of Tg, Tm from DSC is displayed in Figure 4.7 (A), whereas decomposition temperature obtained from TGA are shown in Figure 4.7 (B).

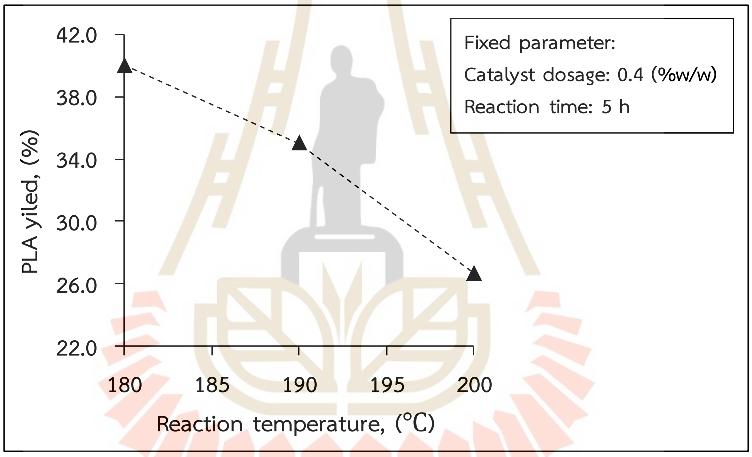
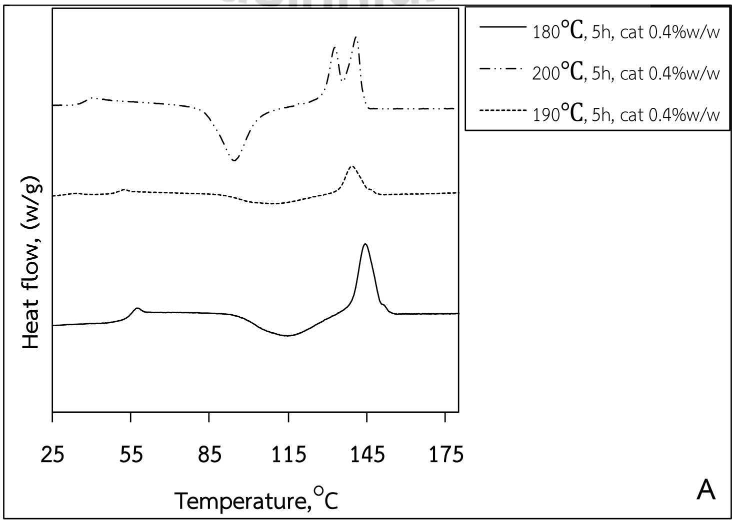


Figure 4.6 Yield of synthesized PLA from commercial lactide for various reaction temperature



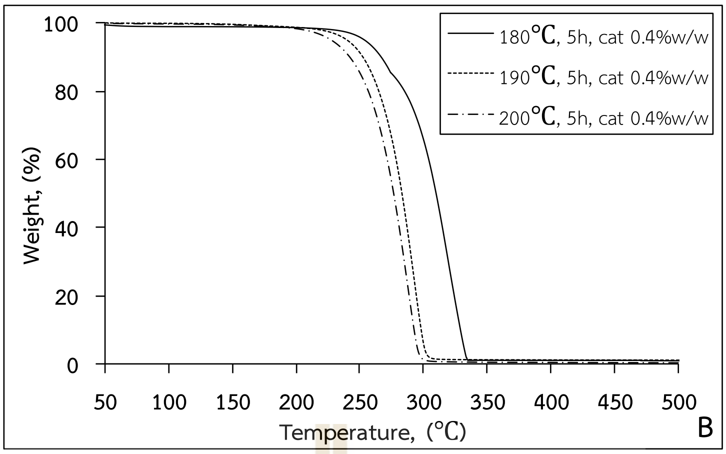
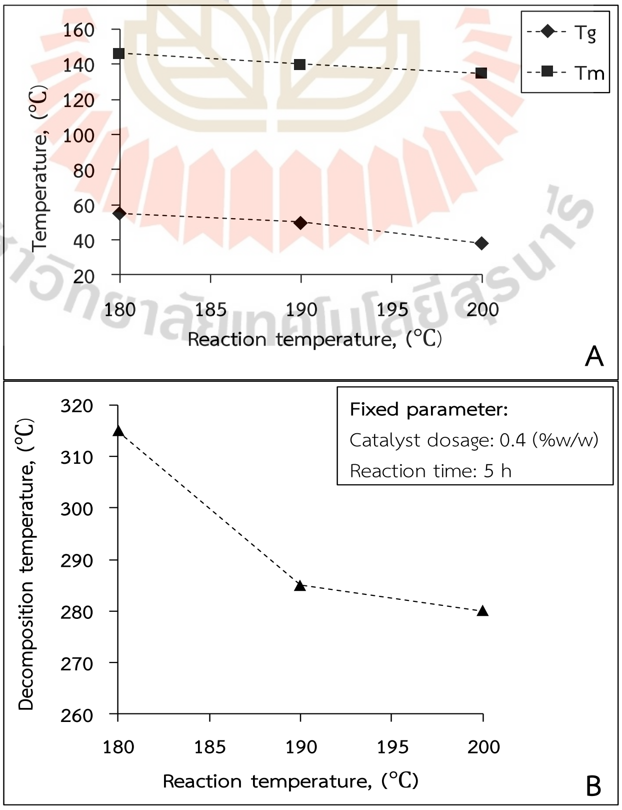


Figure 4.7 Analysis thermal stability results of (A) DSC, and (B) TGA analysis of synthesized PLA from commercial lactide

For Figure 4.8(A-C) show the result of thermal stability as Tg, Tm, and Td of PLA tended to increase with increasing in molecular weight (Mv). It was clearly shown that all these properties decreased with an increasing of reaction temperature. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The optimum condition is obtained Tg, Tm, Td, and Mv of values 55, 146, 315°C, and 23000 g/mole, respectively.



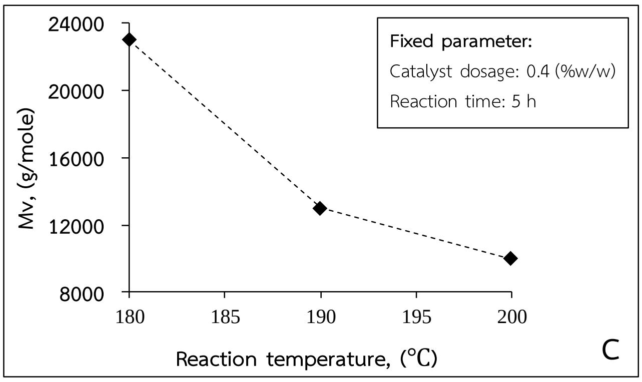


Figure 4.8 Various reaction temperature of PLA synthesis from commercial lactide for resulting: (A) glass transition temperature (Tg), melting temperature (Tm), (B) decomposition temperature (Td), and (C) viscosity average molecular weight (Mv)

4.3 PLA synthesis from butyl lactate

4.3.1 Purification and yield of synthesized lactide from butyl lactate

There was a preliminary study of an experiment for synthesis of lactide from butyl lactate without a catalyst in the oligomerization process, but it is found that the reaction did not occur. Therefore, the synthesis of lactide from butyl lactate is necessary to use catalysts. Synthesized lactide was produced by various reaction time, catalyst concentration and temperature in the process stage, which each parameter effected to the process leaded to get different crude lactide yield as the further describe below. Mechanism of oligomerization stage to obtain oligomer and depolymerization to obtain lactide was reported in (Ghadamyari et al., 2018; S. V. Khlopov Dmitry, Kozlovskiy Roman, Suchkov Yury, Otyuskaya Darya, 2012). Butyl lactate based lactide was obtained through oligomerization of butyl lactate and depolymerization of oligomer. The reaction time was investigated on oligomerization stage as the range of 5 – 27 h and stage of depolymerization was fixed reaction time as 3 h. The result of various reaction time shown in Figure 4.9, which the low yield was found at the shorter reaction time since the reaction time is not long enough to grow the chain of oligomer. For longer reaction time from 8 h up to 27 h gave the yield in relatively similar results indicating that when the reaction time is proper then the longer reaction time was not influenced to the reaction. It is implied that the reaction at a longer time may depend on the other parameters such as temperature and amount of catalyst. The proper condition is obtained when the reaction lasted for 8 h on the oligomerization stage.

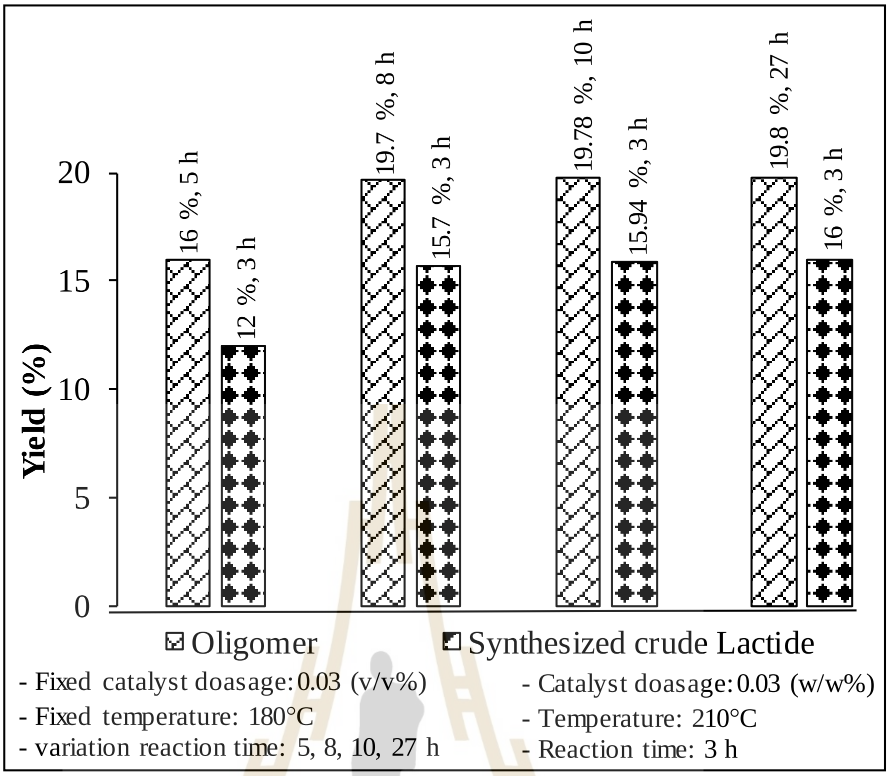


Figure 4.9 Product yield on various reaction time

The variation of catalyst in the process was investigated as 0.03 – 1 %v/v on the stage of oligomerization and 0.03 – 1%w/w on the stage of depolymerization as seen in Figure 4.10. It is observed that synthesized lactide yield increased with an increasing in catalyst concentrations up to 0.1 %v/v on oligomerization of butyl lactate and 0.1 %w/w on depolymerization of oligomer by using tin(IV) chloride as a catalyst in both stages. However, when the amount of catalyst above of 0.1 %w/w or at range of 0.3 – 1 %w/w caused lower production yield because of any excess amount of catalyst enhanced rate of racemization to increase amount of impurities lead to decreasing in lactide product.

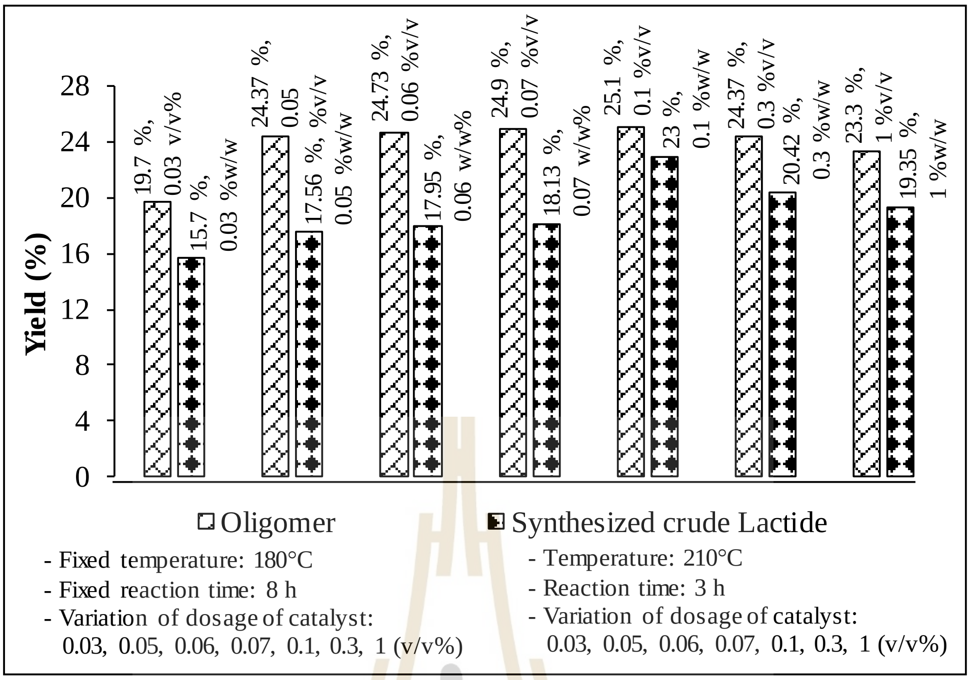


Figure 4.10 Product yield on various of amount of catalyst

The process for lactide synthesis on the oligomerization was carried out at temperatures range of 170 - 190°C and fixed condition on the depolymerization stage at 210°C as shown in Figure 4.11. As the result is clearly shown that increasing temperature gave the increasing in oligomer yield. However, lactide product yield decreased at reaction temperature of 190°C on the oligomerization. The reason may be due to at high temperature creating large synthesized molecules of oligomer lead to decreasing the rate of depolymerization. From these results, the optimum condition of reaction temperature of the process of oligomerization and depolymerization is found to be 180°C and 210°C, respectively.

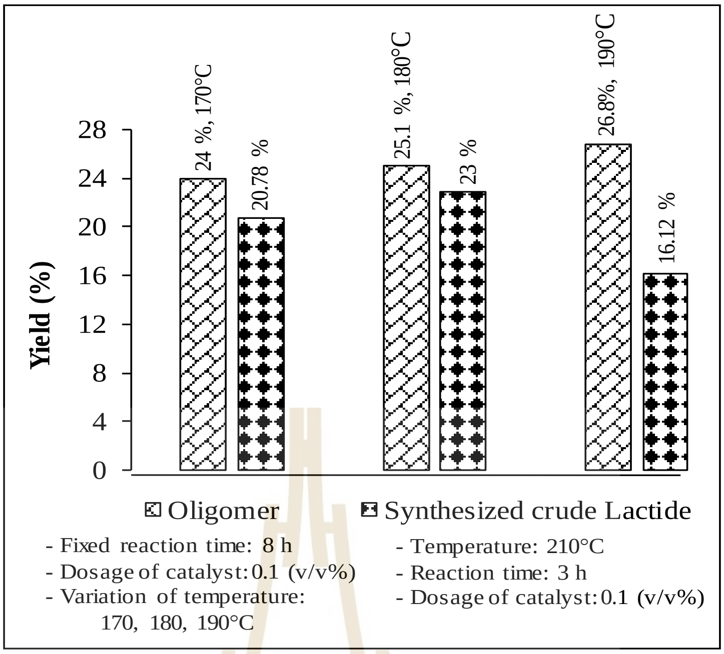
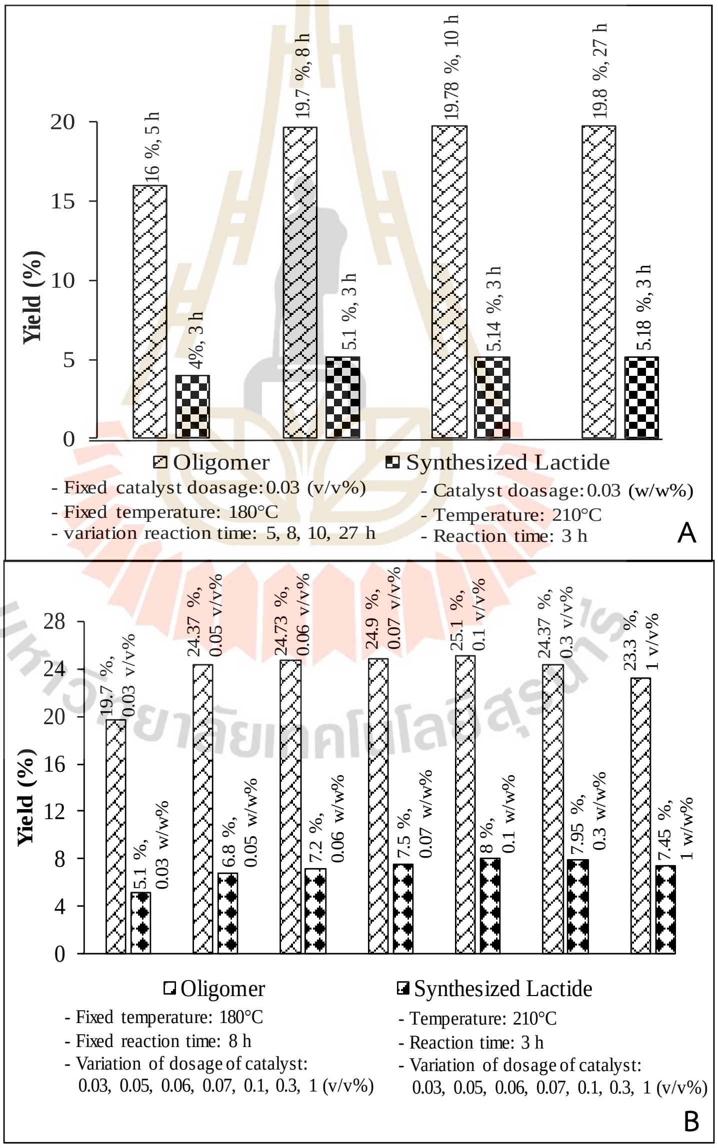


Figure 4.11 Product yield on various reaction temperature

During the process of lactide synthesis, synthesized crude lactide was further purified to remove some impurities like unreacted monomer, catalyst or other particles by using ethyl acetate as a solvent. It was conducted for various concentration of solution of ethyl acetate and synthesized crude lactide, various temperature and time for recrystallization. The result is displayed in Table 4.1. The experiments were performed for variation of crude lactide to ethyl acetate with the ratio of 1:1, 1:1.2, 1:1.3 and 1:1.5 (w/v) in the condition of fixed temperature and time of 4°C and 24 h, respectively. The results show that the ratio of 1:1 (w/v), crude lactide did not dissolve well in the solvent. Whereas, at higher solvent amount of 1:1.5 (w/v), there was low concentration of solution leading to no crystallization. Moreover, purified lactide can be occurred with ratio of 1:1.2 at room temperature for 12 h, or at 4°C in the shorter time as 5 h. The optimum condition of lactide purification is found with ratio of crude lactide versus solvent of 1:1.2 at room temperature for 12 h. The highest of 43 %yield of lactide product was obtained, and it was the condition that using the less amount of solvent, and short time for crystallization at room temperature. The purified lactide was revealed a high purity of around 95% determined by 1H-NMR. Purified lactide was analyzed for its percent yield of product to compare each condition of variation of reaction time, concentration of catalyst usage, and, and reaction temperature are shown in Figure 4.12 (A), (B), and (C), respectively. The optimum condition can be provided with yield of purified lactide of 8 %yield as displayed in Figure 4.12 (C).

Table 4.1 Variation of conditions of recrystallization of crude lactide

Solvent	Ratio of crude lactide vs Solvent (w/v)	Temperature (°C)	Time, (h)	Crude lactide (g)	Purified lactide (g)	Lactide product yield (%)
Ethyl acetate	1:1	4	24	25	-	-
Ethyl acetate	1:1.2	4	24	25	10.5	42
Ethyl acetate	1:1.3	4	24	20	8.5	42.5
Ethyl acetate	1:1.5	4	24	25	-	-
Ethyl acetate	1:1.2	Room temp	24	26	11.13	42.81
Ethyl acetate	1:1.2	Room temp	12	26	11.15	42.88
Ethyl acetate	1:1.2	Room temp	5	14	-	-
Ethyl acetate	1:1.2	4	5	14	6	42.86



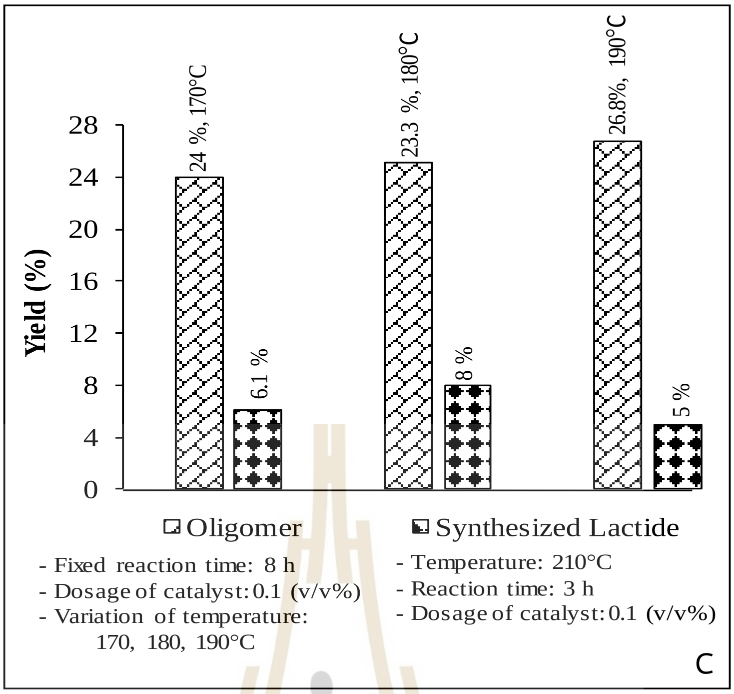


Figure 4.12 Production yield of purified lactide from butyl lactate: (A) Various reaction time, (B) Various amount of catalyst dosage, (C) Various reaction temperature

4.3.2 Characterization of synthesized lactide

Synthesized lactide was performed in two stages, the first stage is oligomerization in which was investigated for the catalyst loading in the range of 0.03 – 1 %v/v, reaction temperature range of 170 - 190°C, and the range of reaction time of 5 – 27 h. For the second stage, depolymerization was investigated for the catalyst loading in the range of 0.03 – 1%w/w, at fixed reaction temperature at 210°C and time for 3 h. The FTIR spectrums of synthesized lactide obtained from different conditions were compared to commercial lactide resulting in a similar functional group as shown in Figure 4.13. The FTIR spectrums display the presence of vibration stretching the -OH at wave number 3530 cm-1, -C-H stretching at wave number 2996 cm-1. The bonds of carbonyl stretch and oxy carbonyl (ester) are observed at wave number 1748 cm-1 and 1181 cm-1, respectively. In addition, there are more functional groups that present in less amounts such as -CH_3 bend: 1452; -CH- symmetric and asymmetric: 1382 and 1360; -C-O- stretch: 1181, 1083; -OH bend: 1042.

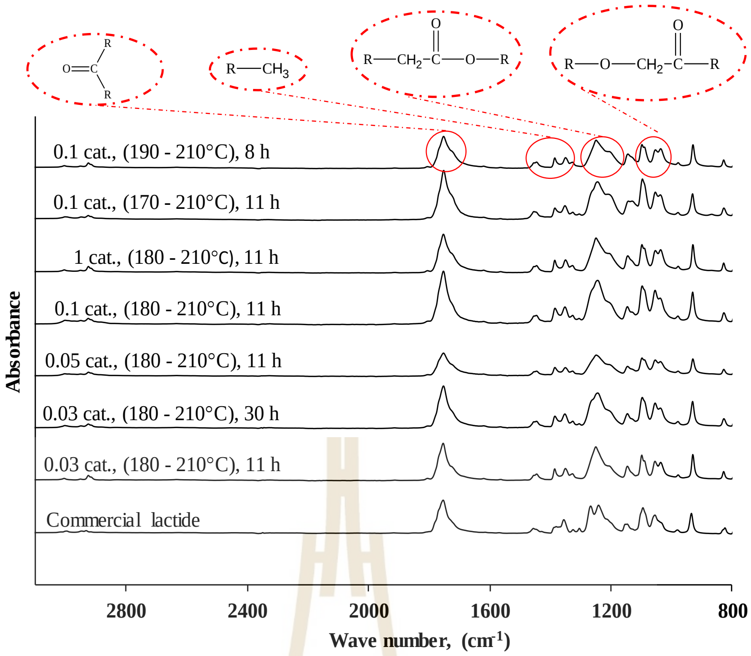


Figure 4.13 The functional group of synthesized lactide from butyl lactate

The synthesized lactide was analyzed for thermal stability determined by DSC and TGA as shown in Figure 4.14, 4.15, respectively. The DSC results indicate that the melting temperature of synthesized lactides obtained from different conditions is comparable to commercial lactide, which is close to the commercial sample at 120 - 128°C. The result from TGA gave the decomposition temperature of the synthesized lactide at 240°C which is nearly the commercial sample at 245°C. After these experiments, all the synthesized lactide samples were mixed together in order to use it as the raw material for further PLA synthesis.

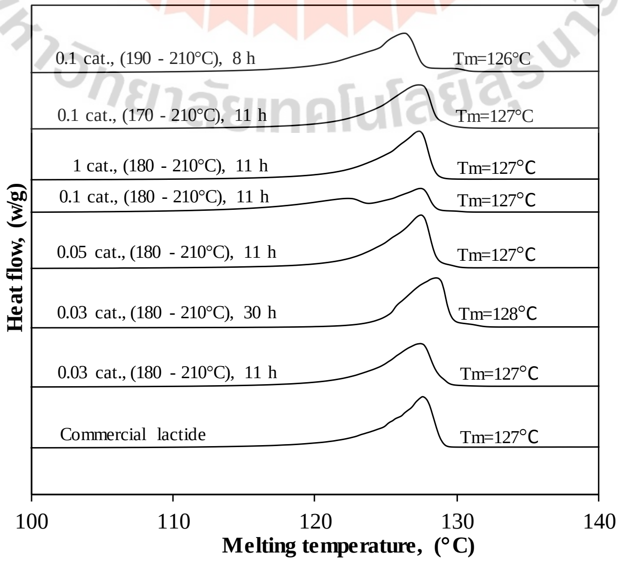


Figure 4.14 Analysis thermal stability results of DSC of synthesized lactide

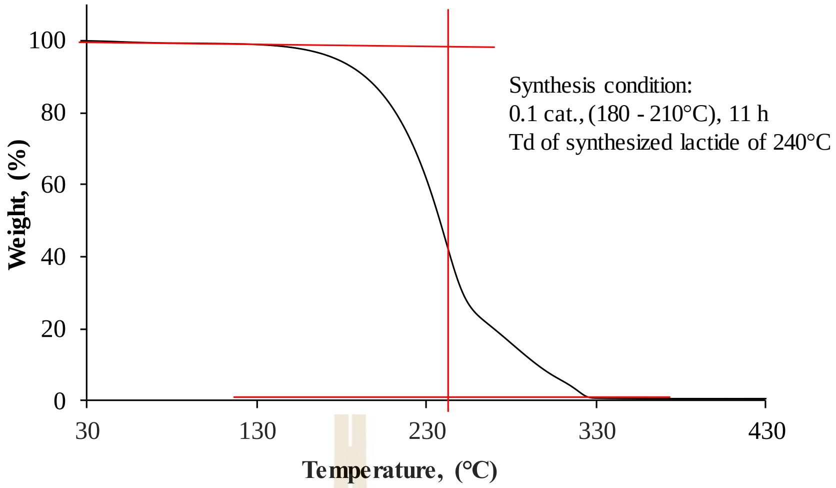


Figure 4.15 Thermal stability results of TGA of synthesized lactide

Through recrystallization of lactides in ethyl acetate as a solvent, some contaminants were eliminated. The purity of synthesized lactide were identified using 1H-NMR. The analytical spectra are displayed in Figure 4.16. Synthesized lactide was indicated by a peak of the methine group (-CH: 5.04–5.08 ppm) and the methyl group (-CH3: 1.48–1.8 ppm). The spectrum shows that basic purifying procedures improve lactide purity. It is interesting to note that for lactides synthesized from lactic acid under homogeneously tin-based catalyst conditions, such high purity lactide can only be formed after multiple recrystallizations (at least 4-5 times). However, lactide synthesized from butyl lactate were purified only two times with ethyl acetate, which revealed a high purity of around 95% determined by 1H-NMR. The weight average molecular weight (Mw) of lactide of 124 g/mole was measured by GPC.

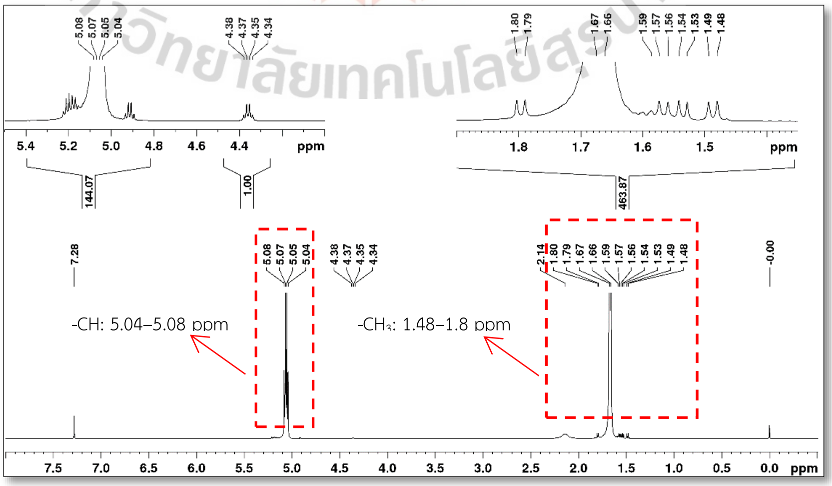


Figure 4.16 NMR analysis spectra of synthesized lactide 1H NMR spectrum

4.3.3 Purification and yield of PLA from synthesized lactide based butyl lactate

The production of PLA from butyl lactate based lactide in the process of ring-opening polymerization, which was carried out as previously described. Synthesized PLA used stannous octoate at range of 0.1 - 0.4 %w/w as a catalyst with variation of reaction time in the range of 0.5 - 20 h at reaction temperatures range of 160 - 200°C. After the process, crude PLA from each different experimental condition as PLA1, PLA2, PLA3 was purified using chloroform, and methanol was used precipitation PLA to eliminate impurities such as unreacted monomer, catalyst, and other particles of the product. The PLA1, PLA2, and PLA3 were done to vary concentration of chloroform as ratio of 1:1, 1:1.2, 1:1.4, and 1:1.6 (w/v) at room temperature, then using the excess in methanol with fixed value of ratio of 1.5 (w/v) by various the temperature at 4°C, and room temperature. The samples were precipitated then filtered and dried. These samples were analyzed for the % yield, and molecular weight. The result was listed in Table 4.2. It shown that each condition of purified PLA for variation ratio of crude PLA and chloroform of 1:1.2-1:1.6 (w/v) gave a good dissolution except 1:1 (w/v). For different temperatures for PLA3 are observed that the room temperature giving the same result as at 4°C. This temperature is selected for further experiments of PLA precipitation. The excess methanol may induce the PLA precipitation. From Table 4.2, it is also observed that the higher molecular weight samples give faster in PLA precipitation, such as if molecular weight higher than 20000 g/mole, it immediately precipitates. From these experiments, the optimum condition from purification of PLA is found at the condition of chloroform as ratio of 1:1.2 (w/v) to excess in methanol with fixed value of ratio of 1.5 (w/v) at room temperature. This optimum condition is selected based on the room temperature of precipitation, and the minimum of chloroform as a solvent with the highest percent yield of 52.5 PLA with over 95 % of purity.

Table 4.2 Various condition of PLA purification

Crude PLA	Chloroform	Ratio of crude PLA	Methanol	Ratio of solution1	Temp, (°C)	Time, (min)	Crude PLA (g)	Purified PLA	PLA Product	Mv (g/mole)
PLA1	Chloroform	1:1	Methanol	1:1.5	4	—	18	—	—	—
	Chloroform	1:1.2	Methanol	1:1.5	4	5	18	8	44.44	10000
PLA2	Chloroform	1:1.4	Methanol	1:1.5	4	2	10	5.25	52.50	13000
	Chloroform	1:1.6	Methanol	1:1.5	4	2	10	5.2	52.00	13000
PLA3	Chloroform	1:1.6	Methanol	1:1.5	4	30s	10	5.2	52.00	23000
	Chloroform	1:1.2	Methanol	1:1.5	Room temp	30s	10	5.25	52.50	23000

The results of synthesized PLA from different conditions of various reaction temperature, reaction time, and amount of catalyst were carried out to find out the optimum condition without initiator. It was preliminary tested that at low reaction temperature 160°C is too low, thus the PLA synthesis in this section was studied at higher reaction temperature as 170, 180, 190, and 200°C and these temperatures gave the PLA yield of 34, 40, 35 and 27%, respectively, as shown in Figure 4.17. The result was clearly determined that higher temperature as 190, and 200°C degraded bonding of PLA chain by depolymerization from the process resulted in lower yield of the products.

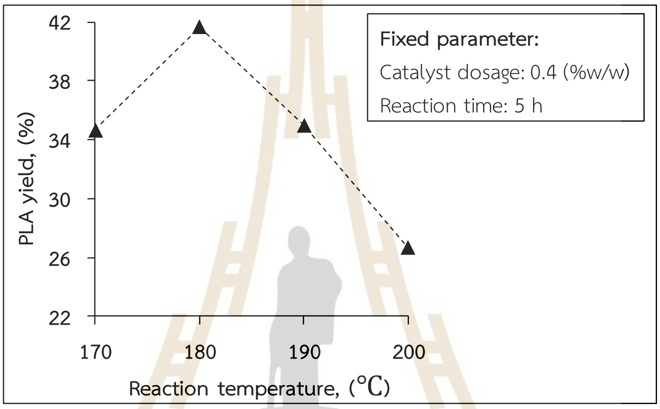


Figure 4.17 Various reaction temperature for yield in PLA synthesis

Further taking condition of temperature at 180°C, 0.4%w/w catalyst for doing variation of reaction time to pick out of the maximum condition which, starting from 0.5, 2, 5, 8, 10, and 20 h. The result shown that at 0.5 h was not occurred any product implying that each lactide monomer did not react or broken the acyl oxygen bond to insert to be chain growth in being PLA product so that the energy would be broke and making the lactide chain opened to insert into the tin oxygen bond of catalyst in longer reaction time. The variation of reaction time for 2 and 5 h were gotten yield as 33 and 40%, respectively. However, increasing reaction time for longer as 8, 10, and 20 h were found tended to be lower product yield as 38, 37, 35.5%, respectively as shown in Figure 4.18. The reason was that rate of reaction of depolymerization was faster than the polymerization rate to form the product due to the thermal degradation since long heating duration may cause degradation instead. After the variation of reaction time was picked maximum reaction time up to be 5 h at 180°C.

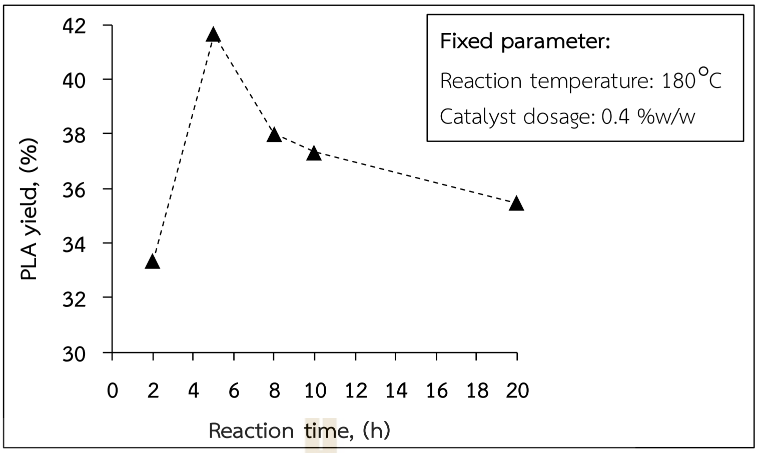


Figure 4.18 Various reaction time for yield in PLA synthesis

For the experimental result to study the effect of catalyst loading by variation in the range of 0.05 – 0.4 %w/w, at 180°C for 5 h, shown in Figure 4.19. It is exhibited that the synthesized PLA yield tends to increase with the increasing in catalyst loading up to 0.2 %w/w, providing 41.5 %yield. However, the PLA yield tends to be nearly constant when the amount of catalyst above of 0.2 %w/w. This behavior may be due to the excess amount of catalyst for longer reaction time leading to the high amount of water in the reaction system that affected the PLA degradation. From these runs, the optimum condition for PLA synthesis without any initiator is found to be at a condition of catalyst loading 0.2 %w/w at 180°C for 5h in which yield of 41.5 %.

In addition, increasing hydroxyl content in polymerization process by adding initiator as 1,4-butanediol and polyglycerol-10 for increasing molecular weight of PLA product were performed. The results of adding initiator are shown in Figure 4.19. It is found that the percentage of product yield by adding initiator polyglycerol-10, and 1,4-butanediol were 35, and 28, respectively. The reason to explain this may be due to the lower hydroxyl group lead to low product yield since the theoretical number of hydroxyl group initiating polymerization of 1,4-butanediol is 2 OH groups, and polyglyceryl-10 is 12 OH groups which can be better effect to polymer in longer chain. Furthermore, the low % yield of the product while adding catalysts of the reaction may appear unsuitable from the magnetic stirrer. It was jammed or stopped working while high viscosity for some part of reacted lactide monomer. It is made with different molecular weight PLA so that it leads to low yield after the precipitation because some high molecular weight PLA is first to precipitate. The initiator of polyglycerol-10 for enhancing in the process of ring opening polymerization was studied in different amounts and shown in Figure 4.20. The higher concentration of initiator affected the reaction for degradation rate of PLA leading to obtain lower product yield.

After purifying in cold methanol, ^{1}H-NMR was used to determine the purity of the PLA product, which revealed a high purity of around 95%.

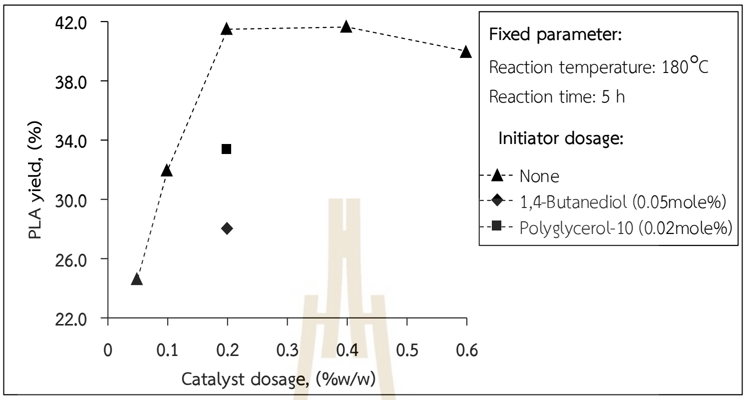


Figure 4.19 Various catalyst for yield in PLA synthesis with and without initiator

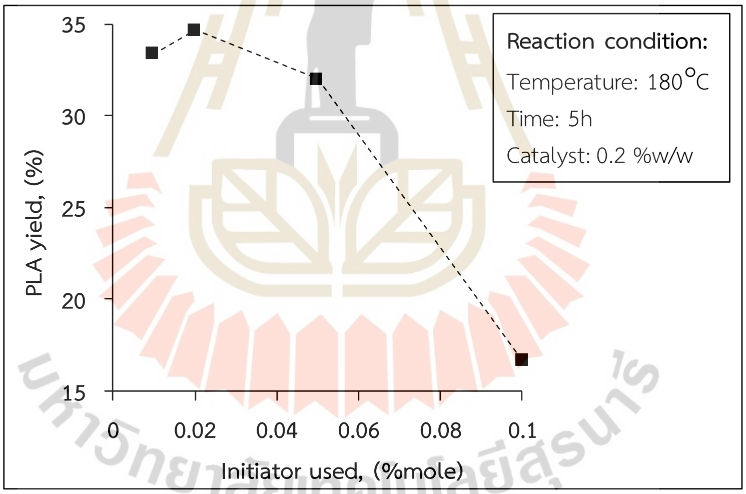


Figure 4.20 Various initiator dosage for yield in PLA synthesis

4.3.4 Characterization of PLA from synthesized lactide based butyl lactate, and commercial lactide

1) Molecular weight measurement by Cannon-Fenske: PLA was made from butyl lactate-based lactide by a ring-opening polymerization procedure, which was carried out as previously described. Each product of synthesized PLA was utilized as a catalyst in the process, with stannous octoate ranging from 0.1 - 0.4 %w/w, and reaction times ranging from 0.5 - 20h at temperatures ranging from 160 - 200°C. Each product was characterized viscosity based average molecular weight by Cannon-Fense

to compare with commercial PLA. It is found that the synthesized PLA at reaction temperatures of 170, 180, 190, and 200°C has viscosity based average molecular weight of 16000, 23000, 13000, and 10000 g/mole, respectively, as shown in Figure 4.21. It was clearly shown that higher temperatures, such as 190 and 200°C, the PLA bonding is damaged by depolymerization, resulting in lower molecular weight. From all these runs, the highest of viscosity based average molecular weight is 23000 g/mole of PLA product, in which obtaining from reaction temperature at 180°C with 5 h.

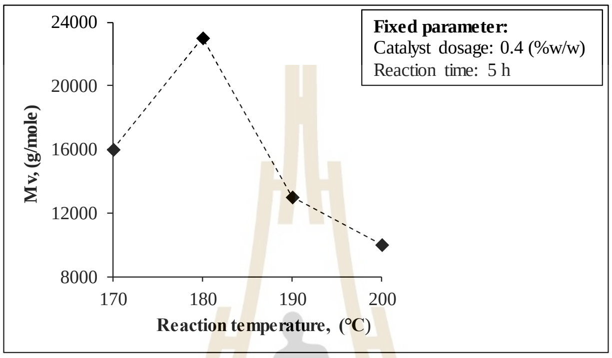


Figure 4.21 The variation of reaction temperature for PLA synthesis

Considering that the temperature at 180°C is the optimum condition for reaction temperature and catalyst loading of 0.4 %w/w was used to vary reaction time at 2, 5, 8, 10, and 20 h. The molecular weight for the variation in reaction time for 2 and 5 h was 12000 and 23000 g/mole, respectively. Furthermore, as shown in Figure 4.22, increasing the reaction time to 8, 10, and 20 h resulted in lower of molecular weight (Mv) of 16000, 14000, and 13000 g/mole, respectively. This trend can be explained at longer reaction time, the higher amount of PLA degradation in reaction. From this set of experiments, the optimum condition is reaction time of 5 h with temperature at 180°C and catalyst loading of 0.4 %w/w.

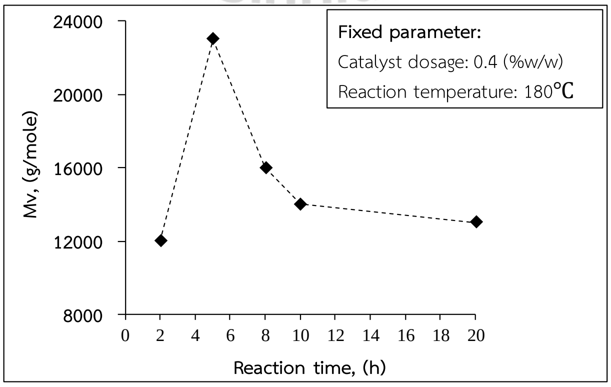


Figure 4.22 The variation of reaction time for PLA synthesis

As depicted in Figure 4.23, the variation of catalyst loading was examined for PLA synthesis at 0.05 – 0.4 %w/w, for 5 h at 180°C. According to the result of molecular weight (Mv) of synthetic PLA tended to rise as catalyst concentration was increased up to 0.2 %w/w, which resulted in the value of 24000 g/mole. For the catalyst concentration over 0.2 %w/w, the molecular weight (Mv) tended to be lower such as catalyst concentration increased to 0.4 and 0.6 %w/w, leading Mv decreased to 23000 and 22000 g/mole, respectively. The excess catalyst for a longer reaction period can be explained as previously mentioned due to the PLA degradation. As a consequence, the optimum condition for PLA synthesis without initiator is discovered to be 0.2 %w/w at 180°C for 5 hours, producing the PLA with molecular weight of 24000 g/mole. The polyglycerol-10 has the hydroxyl of 12 OH groups which is higher than in 1,4-butanediol. In order to increase the molecular weight of the PLA product, 1,4-butanediol and polyglycerol-10 were also added as initiators to the polymerization process to increase the hydroxyl content. Consequently, the addition of initiator such as polyglycerol-10 and 1,4-butanediol gave the PLA molecular weight of 29000 and 26000 g/mole, respectively.

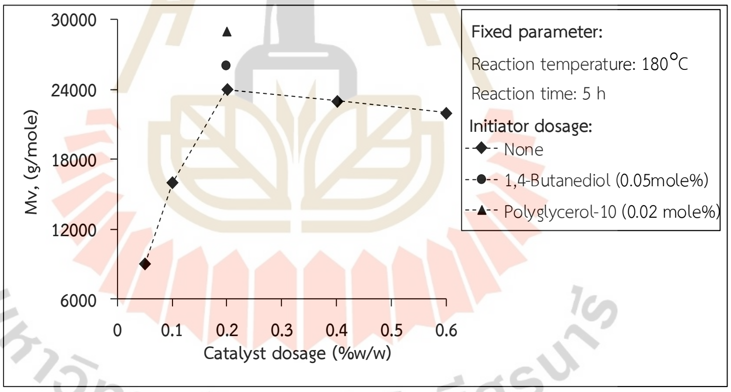


Figure 4.23 Viscosity average molecular weight of various catalyst for PLA synthesis with and without initiator

According in addition of initiator to the reaction with higher molecular weight of PLA, synthesized PLA was produced by various initiator examined for PLA synthesis at 0.02 – 0.3 %mole for previously obtained optimum condition of PLA of 0.2 %w/w catalyst, at 180°C, and for 5h. The result shown in Figure 4.24, which indicates that the amount of initiator polyglycerol-10 of 0.02 %mole was achieved with the highest molecular weight. The higher amount of initiator gave the lower molecular weight.

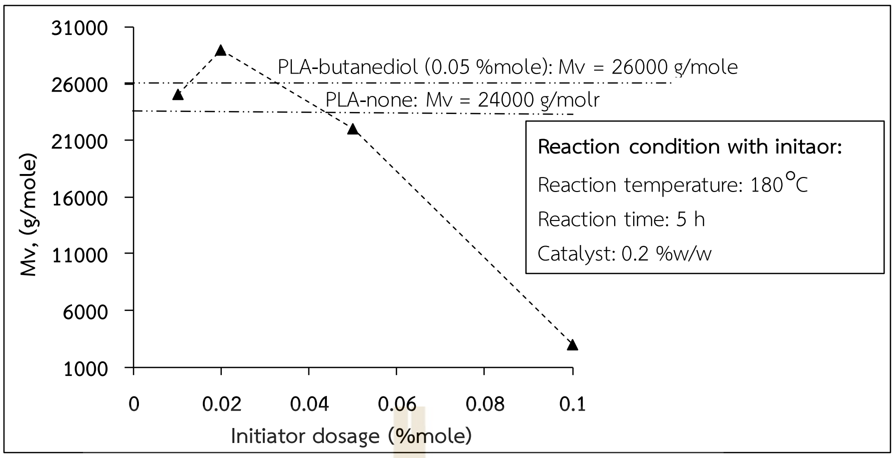


Figure 4.24 Viscosity average molecular weight of various amount of initiator for PLA synthesis

Furthermore, Synthesized PLA was analyzed for weight average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (PI) in order to measure of the broadness of a molecular weight distribution of PLA. Gel permeation chromatography (GPC) was used to analyze the molecular weight of PLA product. For synthesized lactide, the weight average molecular weight (Mw) was analyzed by GPC which obtained 124 g/mole. Instrumental GPC is connected with RI and UV detector. Refractive index (RI) signal is proportional to the mass concentration while Ultraviolet (UV) signal is proportional to the number concentration which responsibility to analyze the molecular weight for Mw, Mn, and polydispersity index (PI) of PLA. The synthesized PLA from optimum condition i.e. the condition of 0.2 %w/w catalyst, 0.02 %mole initiator at 180°C for 5 h was analyzed. The result was discovered to get weight average molecular weight (Mw) of 50000 g/mole, and number average molecular weight (Mn) of 6800 g/mole. Whereas, viscosity average molecular weight (Mv) of 29000 g/mol. This result is reasonable value of molecular weight, since all synthetic polymer was Mw > Mv > Mn. The value of polydispersity index (PI) is obtained of 7.3. In general, the best controlled synthetic polymer was obtained PI of 1.02 to 1.1. In this work, polydispersity index of synthesized PLA is larger, the broader molecular weight. It is described the monodisperse polymer where all the chain lengths are different, which may cause from the mixing system. This may due to the existing equipment, a hotplate was used as the heat source of reaction that was relatively hard to control, and the main reason is that the magnetic stirrer was jammed while the reaction started in the higher viscosity since the less power for dealing it. This matter could be improved by using the more effective equipment. In order to have well reaction control is that changing to use the motor stirrer instead which can conduct with high viscosity, and the heating is would be well temperature controller. Synthesized PLA were analyzed, the result is shown in Table 4.3.

Table 4.3 Molecular weight of synthesized PLA

Catalyst dosage	Initiator dosage	Polymerization condition	Mw (g/mol)	Mv (g/mol)	Mn (g/mol)	Polydispersity index (PI)
Stannous octoate (0.2%w/w)	GPL-10 (0.02%mole)	180°C, 5 h, N_2	50000	29000	6800	7.3

Synthesized PLA was compared to the commercial one for the viscosity average molecular weight (Mv). It was found that the viscosity average molecular weight (Mv) of commercial PLA was 120000 g/mole. The commercial PLA was obtained from NatureWorks, Ingeo biopolymer- general purpose grade. This commercial PLA can be used to make monofilament for 3D printers, Ingeo 4043D. The 3D printing monofilament produced by this multipurpose extrusion grade has high printability qualities such fine detail, strong adherence to build plates, reduced warping or curling, and no odor. These characteristics make this grade suitable for a wide range of printing applications, including 3D printing with numerous different printer types.

PLA with low molecular weight is desirable as s a shorter degradation rate. Mainil-Varlet et al., reported the degradation rate of molecular weight PLLA (60000 g/mol) usually required for bone fracture healing. Low molecular weight PLA are used for drug delivery which has weak retarding effect. They undergo hydrolysis rather quickly into lactic acid, minimizing the risk of material buildup in tissue. Savioli Lopes et al reported PLA with Mw between 2000 and 20000 g/mol was as an implantable antibiotic release system (Savioli Lopes, 2012). While compare to our synthesized PLA, molecular weight (Mw) of 50000 g/mole may suitable for drug delivery application.

2) FTIR and IR characterization: According to Figure 4.25, the functional group determined by FTIR analysis of the lactide and PLA products revealed that the synthesized PLA was identical with the commercial PLA. The bonds of carbonyl stretch and oxy carbonyl (ester) were observed at wave number 1748 cm^{-1} and 1181 cm^{-1}, respectively. The -CH bond was observed at 2996 cm^{-1} (asymmetric), 2946 (symmetric), and -OH bond stretching was observed at wavenumber 3700 cm^{-1}, which is characteristic of a carboxylic acid, for -C=O carbonyl stretch: 1748; $-CH_3$ bend: 1452; -CH- symmetric and asymmetric: 1382 and 1360; -C-O- stretch: 1181, 1083 cm^{-1}.

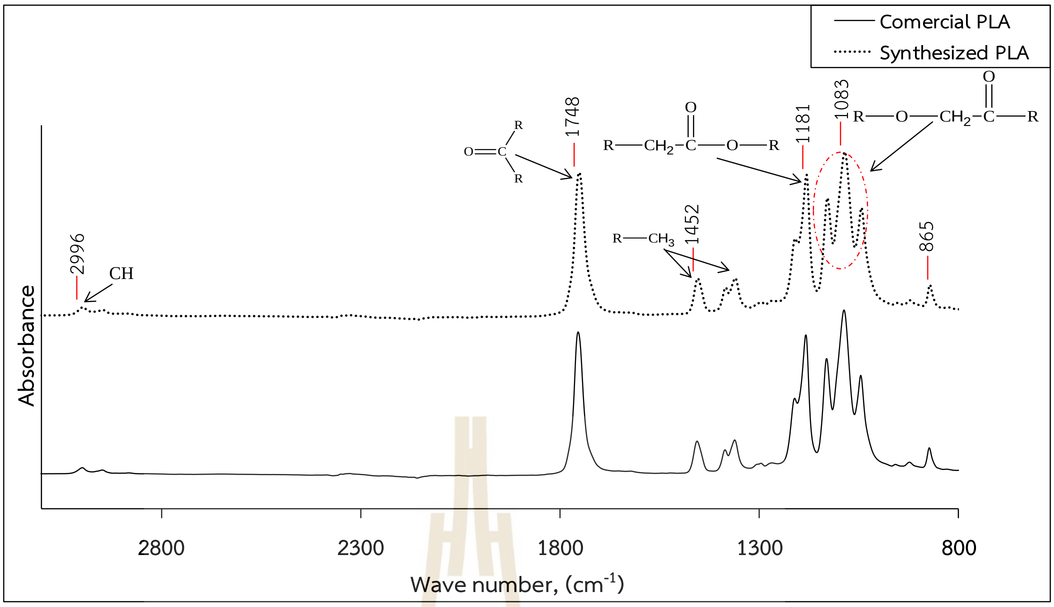


Figure 4.25 The functional group of synthesized PLA from butyl lactate compared to commercial PLA

PLA samples were further analyzed by IR for comparison of all samples to identify the existence of functional groups and reveal the bonding or interactions within the substance. The obtained data from IR spectroscopy were further analysed as cluster of each conditional sample. Synthesized lactide and PLA are compared to the commercial one. By cluster can be observed in two groups of separation as synthesized lactide and PLA comparing with specific commercial lactide and PLA, respectively, as shown in Figure 4.26. It is confirmed that synthesized lactide is similar to the commercial one separated in group A, and so do synthesized PLAs in group B. As the result of PLAs from cluster analysis are relatively different of each sample as observed from group B1, B1.1, B1.2, B1.3, B2, B2.1, B2.2, B2.3, B2.4, and B2.5 as shown in figure 4.26. The group PLA B1.1 obtained from condition T180t5C0.2-IP is mostly close to commercial PLA. The group PLA B2.5 obtained from the condition T180t5C0.05, and T200t5C0.4 are the most different from commercial PLA.

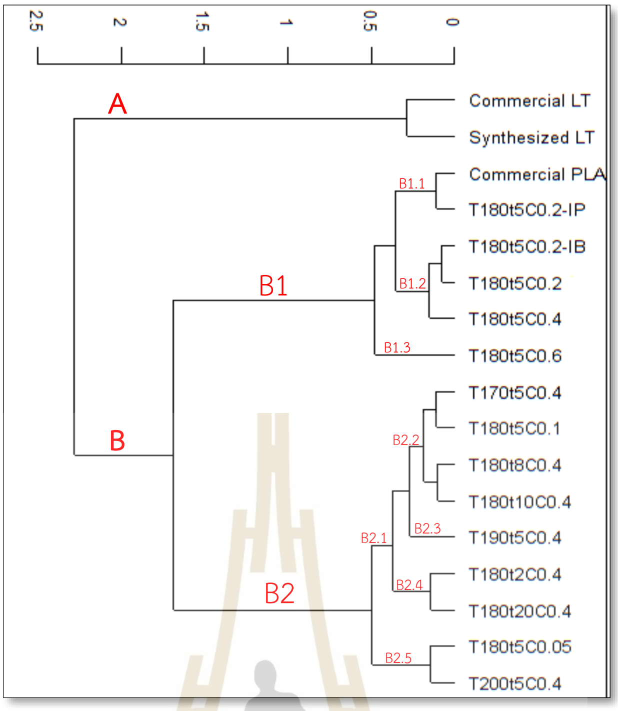


Figure 4.26 Cluster analysis of lactide and PLA

For synthesized PLA result was further analyzed for the differential sample by method of Principal Component Analysis (PCA). The Unscrambler X 10.5 (CAMO Software, Norway) was used to analyze the obtained multivariate data from differential conditions for various independent variables of the reaction process. To conduct all data is described as started pre-processing the transform data by Derivative Savitzky-Golay Transform which defined 2nd derivative. Furthermore, normalization is conducted through Extended Multiplicative Scatter Correction (EMSC). All samples are specified wave number range of 1900 – 800 cm^{-1}, then PCA score plot and loading plot are extracted to show the spectrum which can be described the comparable samples. Furthermore, conducted data as average spectrum of samples after the Extended Multiplicative Scatter Correction (EMSC) was carried out. Average spectrum of each sample was defined different peak with the same wave number to compare how the different of quantitative functional group of each sample by using Excel to plot the data in order to simplify for data analysis.

Figure 4.27 shows the result of principle component analysis (PCA) on various of reaction temperature compared to commercial PLA. PCA score plot and loading plot are shown the spectrum of comparable samples of various reaction temperatures 170, 180, 190, and 200°C. The result from each condition was relatively obviously separated by PC-1 (66%). The group data of conditions that close to commercial PLA is figured out at 180°C, then group data of conditions at 170 and 190°C are observed closely each other relatively different away from the commercial one. The condition at 200°C group data is quite different away from others. The total data of each mentioned group can be separated by peaks of 1776, 1762, 1747, 1731, 1216, 1185, 1087, and 1064 cm^{-1} as shown in Figure 4.27 (B). In order to analyze for how is it different from the peak of each sample from the various conditions was conducted through the reducing (average) by shown in Figure 4.27 (C). To define the quantitative functional group of each sample for more easier analysis was separated as shown in Figure 2.27 (D). Synthesized PLA at reaction temperatures of 170, 180, 190, and 200°C have different quantitatively functional groups as depicted in Figure 4.27 (E). It is clearly shown that higher temperatures, such as 190 and 200°C, the existence of CO carbonyl bend at 1218 cm^{-1} and stretch at 1757 cm^{-1} tend to lower quantity which caused to lower characteristic of -CH3 bend: 1413; -C-O- stretch: 1137 cm^{-1}; -OH bend:1045; and -C-C- stretch: 867 cm^{-1}. It may describe that PLA chain was damaged by depolymerization, resulting in lower molecular weight, and lower thermal stability. The highest quantitative amount of functional group of PLA is obtained from reaction temperature at 180°C with 5 h. The existence of CO carbonyl bend at 1218 cm^{-1} and stretch at 1757 cm^{-1} is the most important sign of PLA (Sin & Tueen, 2019). In general, during the reaction there is a competition reaction between polymerization and depolymerization of lactide monomers to obtain PLA products. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The polymerization is proposed by the insertion-coordination mechanism as shown in Figure 4.28 (B. Nyiavuevang, 2022). Kajsa et al. reported a hydroxyl compound (alcohol) or even water was added as an initiator in lactide polymerization catalyzed by Sn(Oct)$_2$. By ligand exchange, the alcohol initiator reacts with Sn(Oct)$_2$ to form a tin alkoxide bond. One of the lactide's exocyclic carbonyl oxygen atoms momentarily coordinates with the tin atom of the alkoxide catalyst in the next step. The nucleophilicity of the alkoxide component of the initiator as well as the electrophilicity of the lactide carbonyl group are both enhanced by the coordination. Next, acyl-oxygen bond in the lactide (between the carbonyl group and the endocyclic oxygen) is then broken, allowing the lactide chain to open and insert into the tin-oxygen bond in the catalyst (alkoxide). The transmission proceeds as more lactide molecules are introduced into the tin-oxygen bond, which is generated by the same mechanism (Kajsa M. Stridsberg, 2022; H. R. Kricheldorf & Damrau, 1998).

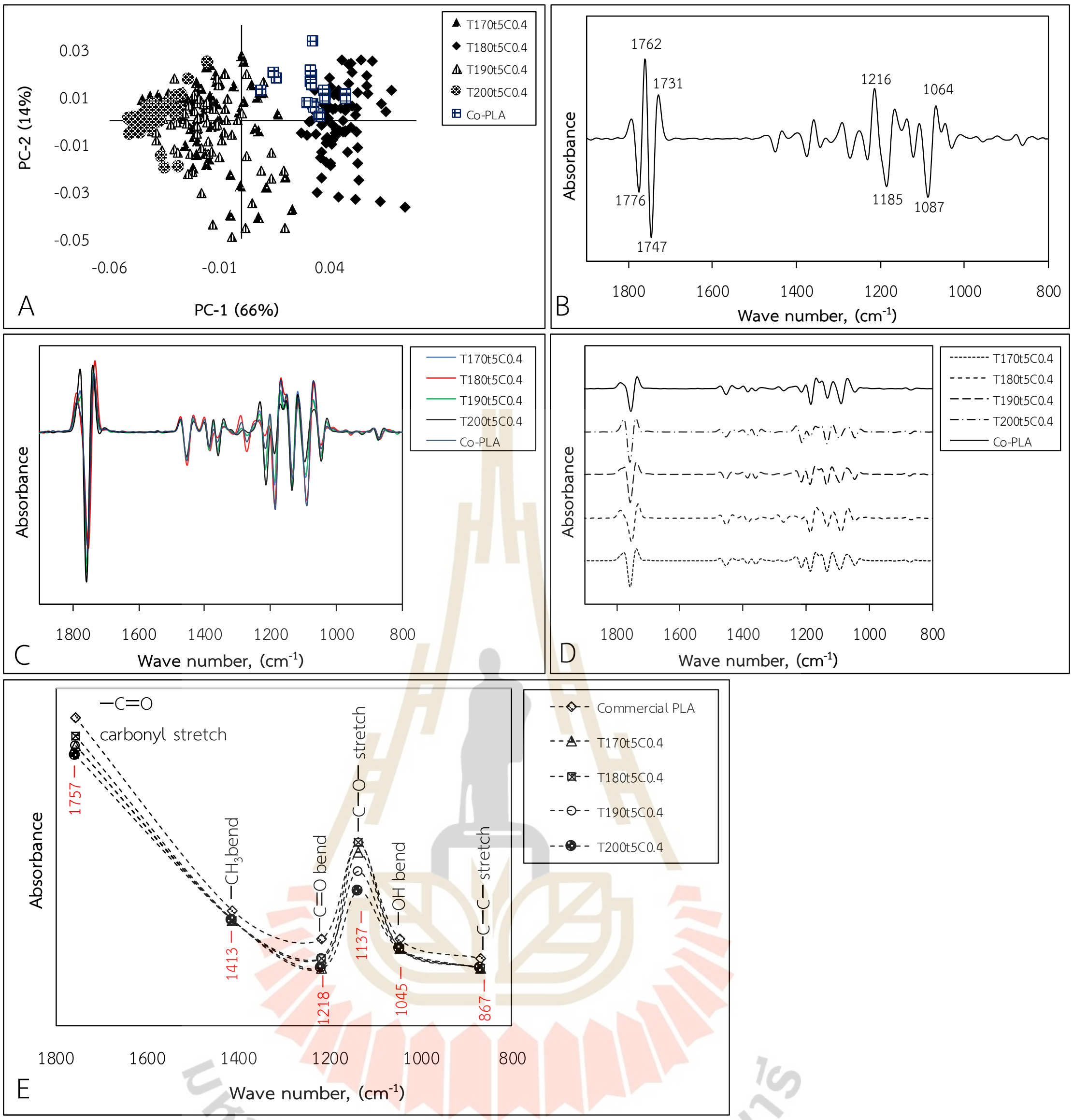


Figure 4.27 Principle component analysis (PCA) of synthesized PLA for various reaction temperature compared to commercial PLA: (A) Score plot, (B) Loading plot, (C) Reducing (average) of each PLA spectrum, (D) Reducing (average) separated of each PLA spectrum, and (E) Expressed quantity of functional group of each conditional sample

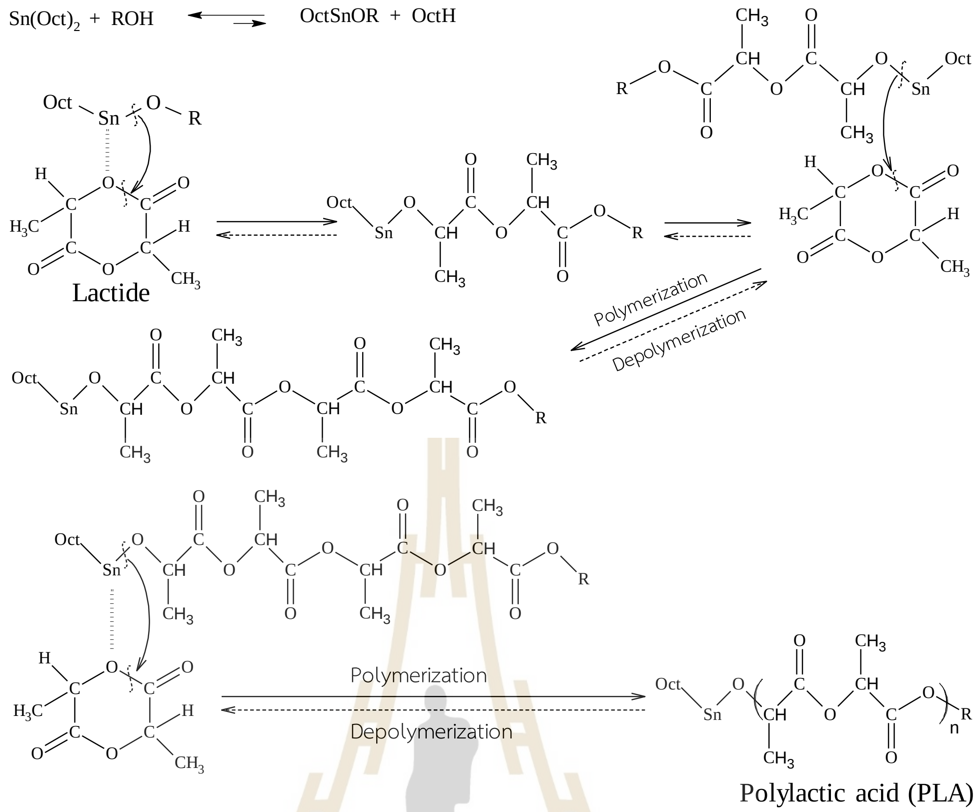


Figure 4.28 Synthesis of PLA through ROP of lactide with stannous octoate by coordination-insertion mechanism

For various reaction times compared to commercial PLA, the result of principle component analysis (PCA) is shown in Figure 4.29. For PCA score plot shown the result from each condition is relatively obviously separated by PC-1 (59%) as depicted in Figure 4.29 (A). The group data of conditions that are closed to commercial PLA is figured out at 5 h, then the other group data that is discovered to be differ from the commercial one such as 8 h, 20 h, and 2 h. The total data of each group can be separated on peak 1776, 1760, 1747, 1727, 1212, and 1216 cm^{-1} as shown in Figure 4.29 (B). To analyze for how is it different of each sample is conducted through reducing (average) of each group data as shown in Figure 4.29 (C). In order to simplify defining the quantitative functional group of each sample, it is separated from each spectrum of sample as shown in Figure 4.29 (D). Synthesized PLA at various reaction times for 2, 5, 8, and 20 h have quantitatively different functional groups as depicted in Figure 4.29 (E). It is shown that reaction time for 2 h and 5 h, the existence of CO carbonyl bend at 1218 cm^{-1} and stretch at 1757 cm^{-1} is figured out relatively different in quantity. The longer reaction time the lower the quantitative functional group of each sample which observed the increasing reaction time to 8, 20 h resulted in lower characteristic of -CH_3 bend: 1413; -C-O- stretch: 1137 cm^{-1}; -OH bend:1045; and -C-C-stretch: 867 cm^{-1}. This trend can be explained at longer reaction time, the higher amount of PLA degradation in reaction leads to lower the quantitative functional group which resulting in lower molecular weight, and low thermal stability. From all these runs, the highest functional group of PLA is obtained from reaction temperature for 5 h at 180°C.

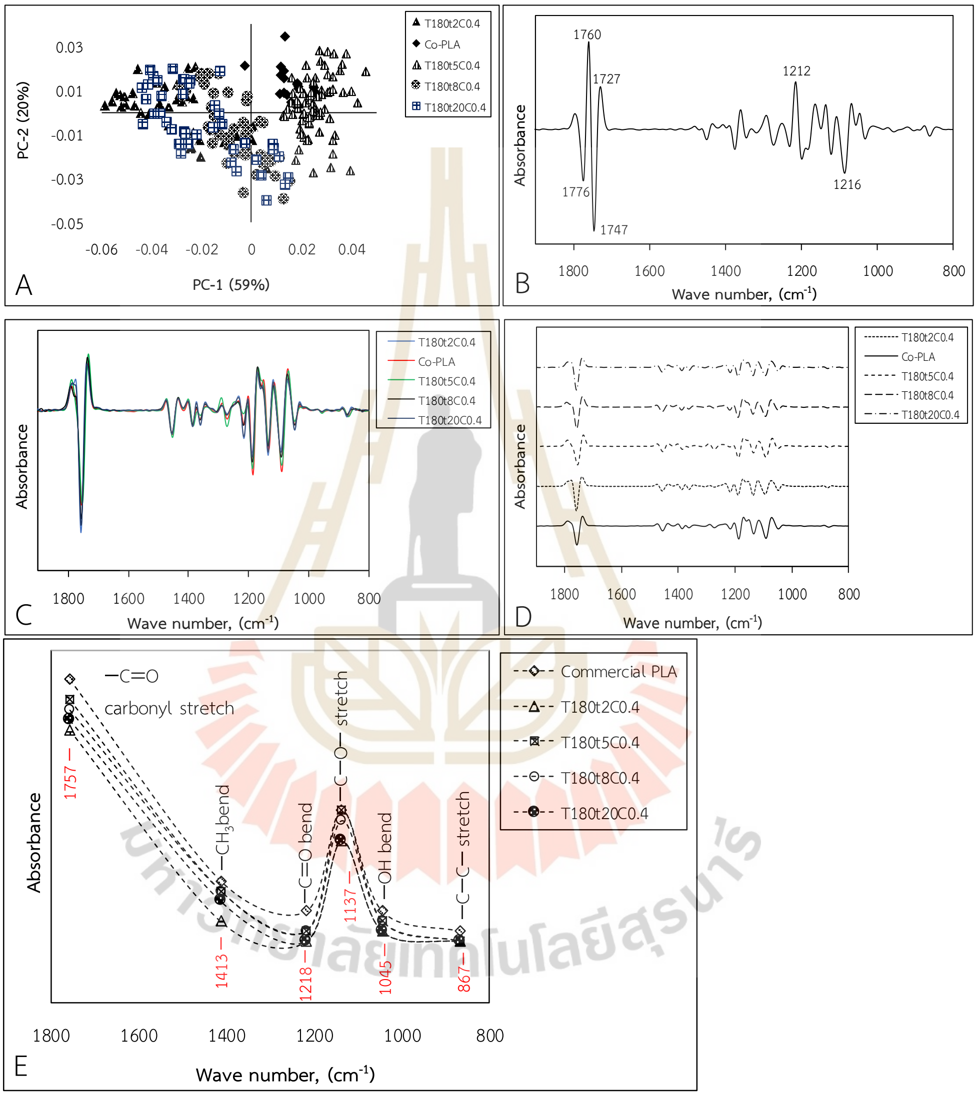


Figure 4.29 Principle component analysis (PCA) of synthesized PLA for various reaction time compared to commercial PLA: (A) Score plot, (B) Loading plot, (C) Reducing (average) of each PLA spectrum, (D) Reducing (average) separated of each PLA spectrum, and (E) Expressed quantity of functional group of each conditional sample

The results of principal component analysis (PCA) for varying catalyst amounts of 0.05, 0.1, 0.2, and 0.6 %w/w in comparison to commercial PLA are displayed in Figure 4.30. The data of each condition is separated by PC-1 (70%), according to the PCA score plot shown in Figure 4.30 (A). Group data of conditions that close to commercial PLA is determined of 0.2 %w/w catalyst, and the other group data of 0.6, 0.1, and 0.05 %w/w are not close to the commercial one. The total data of each mentioned group is separated on peak 1776, 1762, 1747, 1727, 1212, 1185, and 1085 cm^{-1} as shown in Figure 4.30 (B). Reducing (average) of each group data from the differential condition reaction as shown in Figure 4.30 (C) and (D) in order to define the quantitative functional group of each sample. Synthesized PLA with catalyst amounts of 0.05, 0.1, 0.2, 0.4, and 0.6 %w/w have quantitatively distinct functional groups, as illustrated in Figure 4.30 (E). According to the result of quantitative functional group of synthezised PLA tends to rise as catalyst concentration is increased up to 0.2 %w/w, which resulted in an increasing of the existence of CO carbonyl bend at 1218 cm^{-1} and stretch at 1757 cm^{-1} are figured out relatively different in quantity. For the catalyst concentration higher than 0.2 %w/w, the quantitative functional group tend to be lower such as catalyst concentration increased to 0.4 and 0.6 %w/w, leading the lower the quantitative functional group of characteristic of -CH_3 bend: 1413; -C-O- stretch: 1137 cm^{-1}; -OH bend:1045; and -C-C- stretch: 867 cm^{-1}. Excessive catalyst for a longer reaction time can be explained as previously mentioned due to the PLA degradation. As a consequence, the optimum condition for PLA synthesis without initiator is discovered to be 0.2 %w/w at 180°C for 5 h.

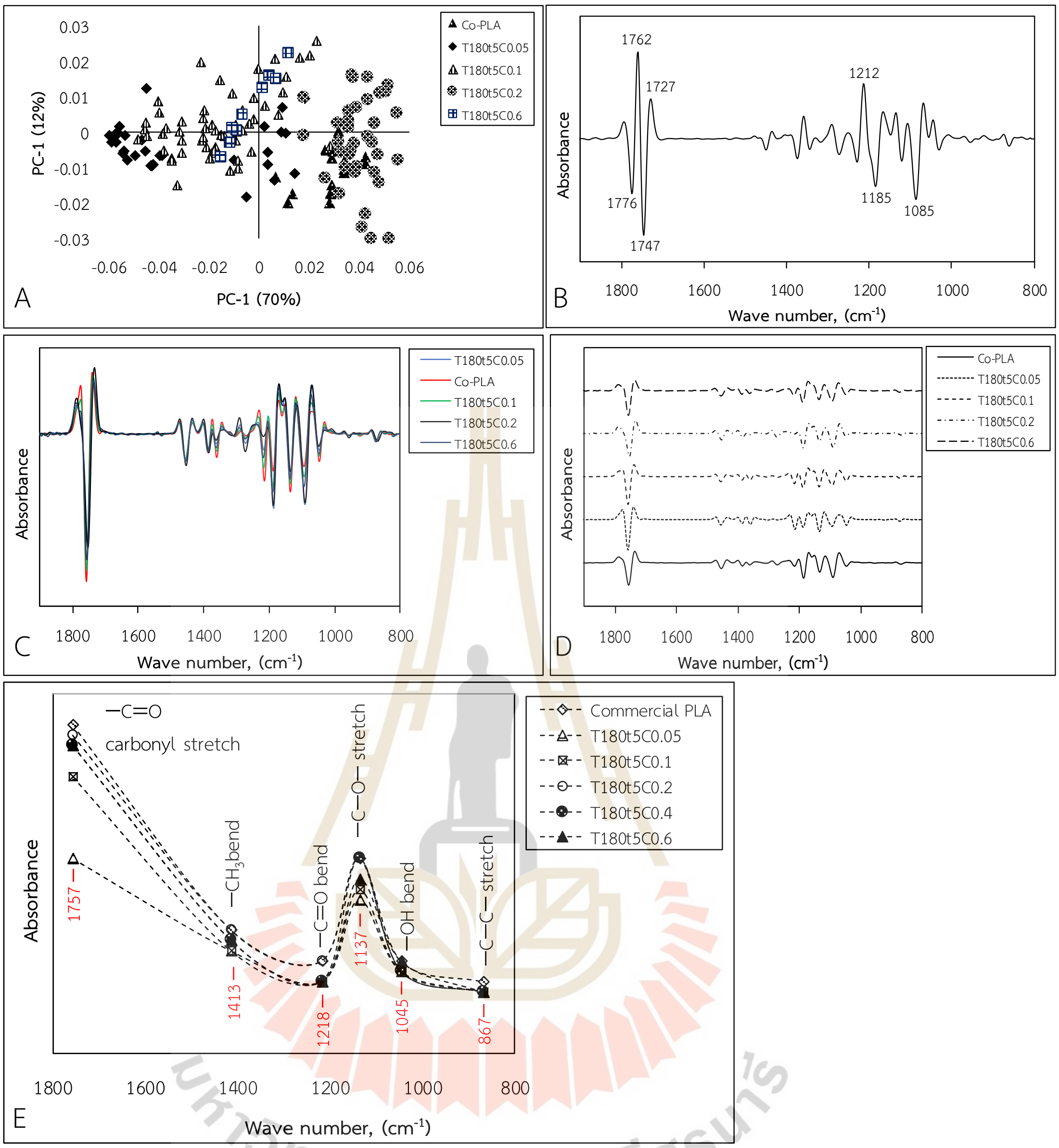


Figure 4.30 Principle component analysis (PCA) of synthesized PLA for various amount of catalyst compared to commercial PLA: (A) Score plot, (B) Loading plot, (C) Reducing (average) of each PLA spectrum, (D) Reducing (average) separated of each PLA spectrum, and (E) Expressed quantity of functional group of each conditional sample

Furthermore, the results of principal component analysis (PCA) on PLA synthesis in comparison of with and without initiator to commercial PLA are displayed in Figure 4.31. In comparison to 1,4-butanediol, the polyglycerol-10 hydroxyl has 12 OH groups, which is more than the other. 1,4-Butanediol and Polyglycerol-10 were introduced to the polymerization process as initiators to raise the hydroxyl content of the PLA product in order to improve its molecular weight. The result was that the molecular weights of the PLA were 29000 and 26000 g/mole, respectively, after the addition of initiators such as polyglycerol-10 and 1,4-butanediol. For PCA results from each condition were quite clearly close to each other to compare to commercial PLA. It is separated by PC-1 (28%) different, according to the PCA score plot shown in Figure 4.31 (A). The group data of the condition that close to the commercial PLA was relatively complex to be observed. The data of each condition reaction is separated by peak 1797, 1745, 1729, 1199, 1182, 1110, and 1079 cm^{-1} as shown in Figure 4.31 (B). To analyze how is it different of each sample from the different conditions was conducted through reducing (average) of each group data from the different condition reaction as shown in Figure 4.31 (C). In order to simplify defining the quantitative functional group of each sample, it is separated each spectrum of sample as shown in Figure 4.31 (D). They have quantitatively distinct functional groups, as illustrated in Figure 4.31 (E). According to the result of quantitative functional group of synthesized PLA tends to close each other with catalyst concentration of 0.2 %w/w. The existence of CO carbonyl bend at 1218 cm^{-1} for the condition of adding 0.02 polyglycerol-10 as initiator tends to be highest. This indicates that the amount of initiator polyglycerol-10 of 0.02 %mole is the most suitable actively initiator to the reaction. This sample is similar to the commercial PLA for the quantitative functional group leads to obtain the highest molecular weight, and higher thermal stability.

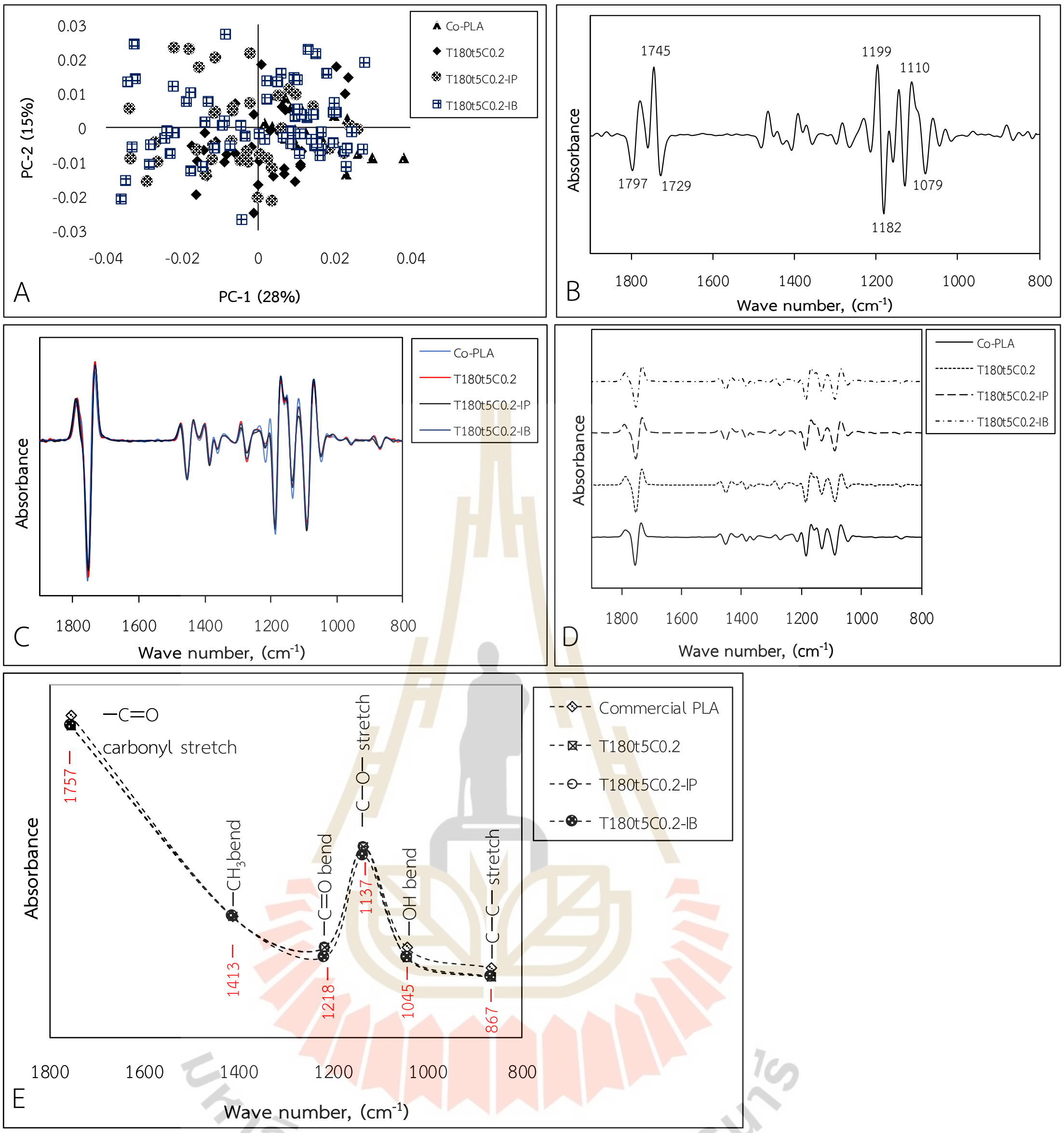


Figure 4.31 Principle component analysis (PCA) of synthesized PLA with and without initiator to commercial PLA: (A) Score plot, (B) Loading plot, (C) Reducing (average) of each PLA spectrum, (D) Reducing (average) separated of each PLA spectrum, and (E) Expressed quantity of functional group of each conditional sample

3) Thermal stability analysis: The PLA products were taken to measure the thermal stability as glass transition temperature (Tg), melting temperature (Tm), and decomposition temperature (Td). The profiles of Tg, Tm from DSC is displayed in Figure 4.32 (A), and Td was obtained from TGA are shown in Figure 4.32 (B). For commercial PLA was measured the stability as Tg, and Tm of 58°C, and 150°C, respectively. The results were shown that the overall trend of Tg and Tm of synthesized PLA increased with an increasing of reaction temperature to reach at maximum point at 180°C, then decrease in higher reaction temperature. Figure 4.33 (A-B) was shown that value of thermal stability as Tg, Tm, and Td of PLA tended to increase along with molecular weight (Mv). At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. Therefore, increasing reaction temperature decreased the properties of thermal stability leading to obtain lower Tg, Tm, and Td. The optimum condition was at reaction temperature 180°C which obtained Tg, Tm, Td, and Mv of values 55, 146, 315°C, and 23000 g/mole, respectively.

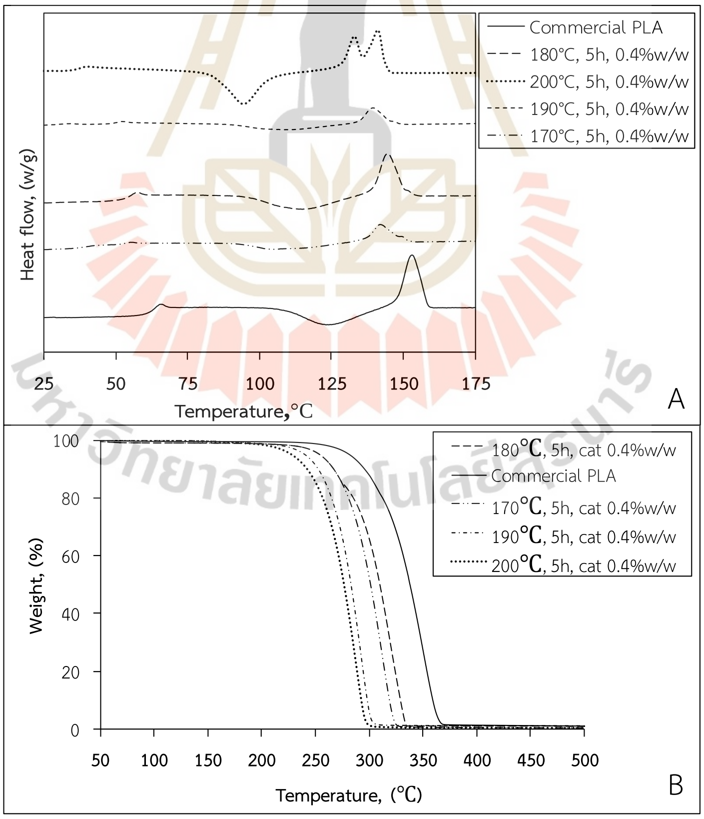


Figure 4.32 Analysis profile of thermal stability results of (A) DSC and (B) TGA for synthesized PLA in various reaction temperature, and commercial PLA

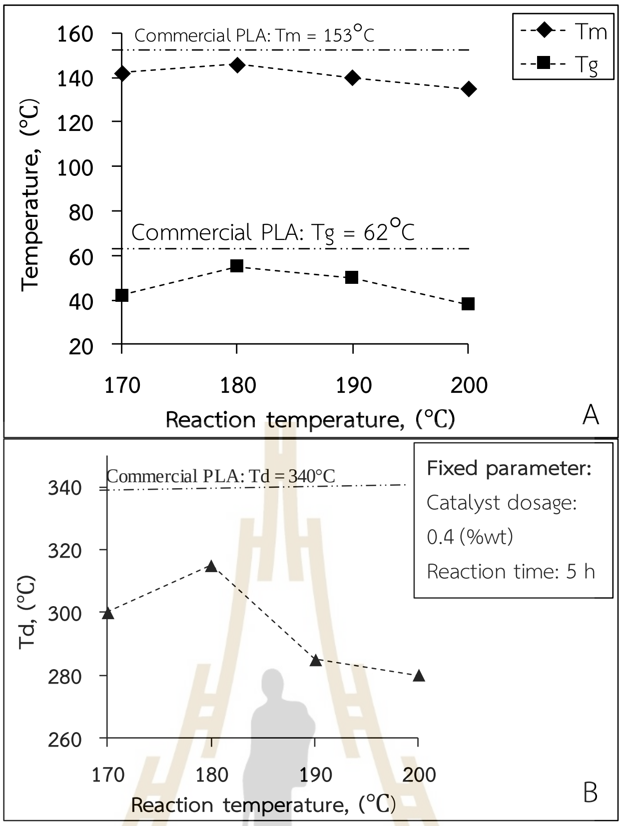


Figure 4.33 Glass transition temperature (Tg), melting temperature (Tm), and decomposition temperature (Td) of synthesized PLA in various reaction temperature: (A) Tg, Tm, and (B) Td

In general, during the reaction there are a competition reaction between polymerization and depolymerization of lactide monomers to obtain PLA products. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The polymerization is proposed to describe by the insertion-coordination mechanism (Masutani, Kazunari, Kimura, Yoshiharu, 2014). For the study of reaction time variation, the profiles of Tg, Tm from DSC is displayed in Figure 4.34 (A), and Td was obtained from TGA are shown in Figure 4.34 (B). It is found that that Tg, Tm, and Td increased with an increasing of reaction time up to 5h at reaction temperature at 180°C with amount of catalyst was 0.4 %w/w, then decreased in longer reaction time which could be explained by the depolymerization play a major role of reaction. The result shown in Figure 4.35 (A-B).

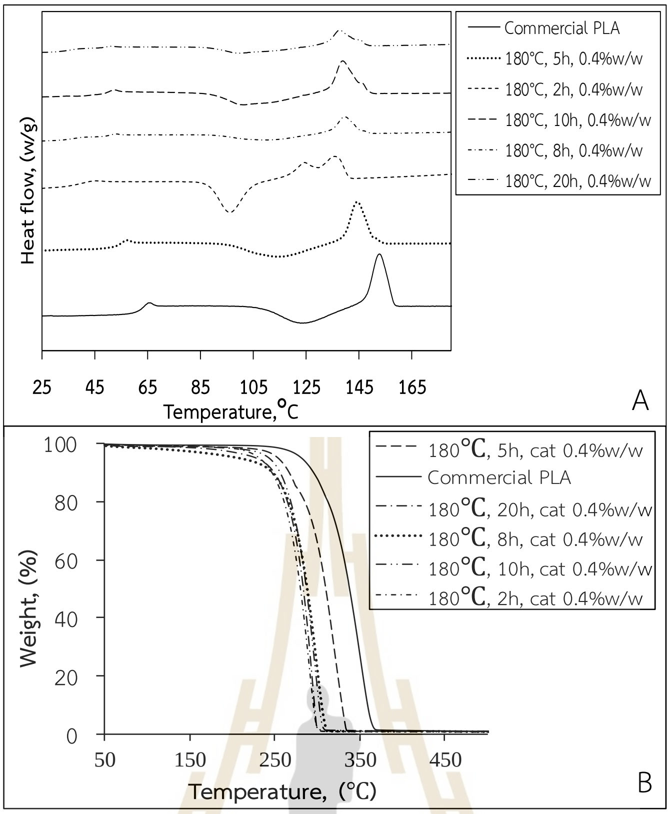
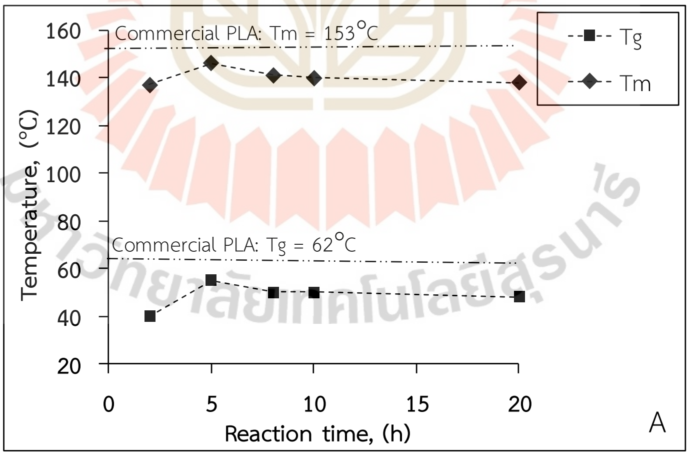


Figure 4.34 Analysis profile of thermal stability results of (A) DSC and (B) TGA for synthesized PLA in various reaction time, and commercial PLA



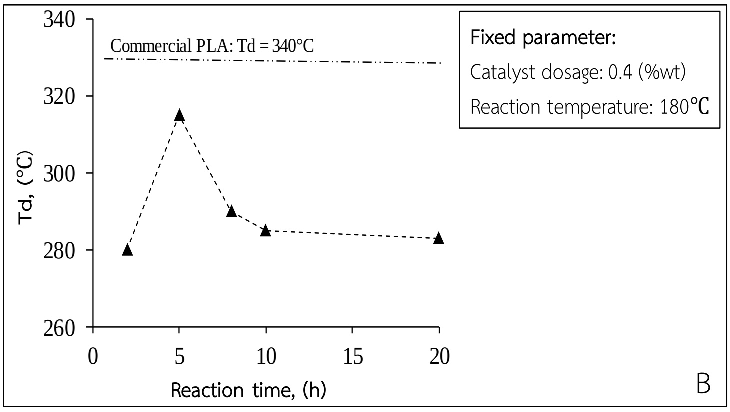
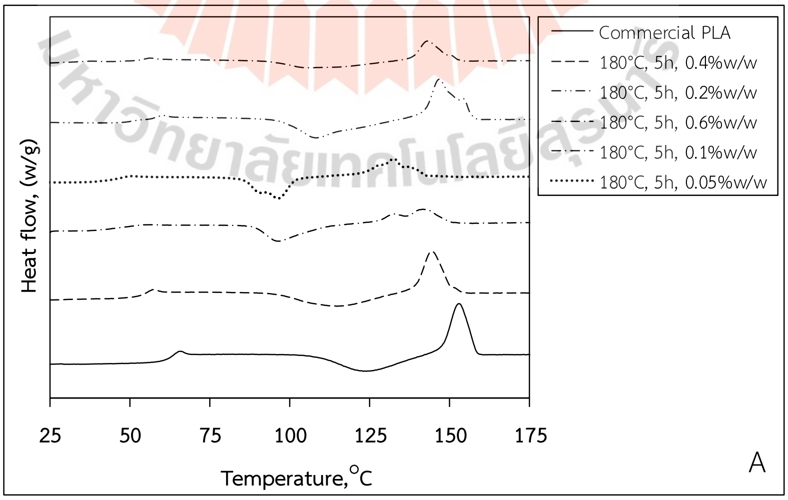


Figure 4.35 Glass transition temperature (Tg), melting temperature (Tm), and decomposition temperature (Td) of synthesized PLA in various reaction time: (A) Tg, Tm, and (B) Td

For various amount of catalyst, the profiles of Tg, Tm from DSC shown in Figure 4.36 (A), and Td was obtained from TGA are observed in Figure 4.36 (B). It shown that the value of Tg, Tm, and Td relatively tended to increase up to 0.2 %mole, then slightly decreased while increasing amount of catalyst over 0.2 %w/w, as shown in Figure 4.37 (A-B). The catalyst Sn(Oct)$_2$ could play a role as initiator since containing small amount of water. Therefore, if more amount of catalyst was added, polymer could be destroyed by degradation mechanism. The optimum condition in this part is found at reaction temperature 180°C for 5 h with amount of catalyst was 0.2 %w/w which obtaining the Tg, Tm, Td of 55°C, 147°C, and 315°C, respectively.



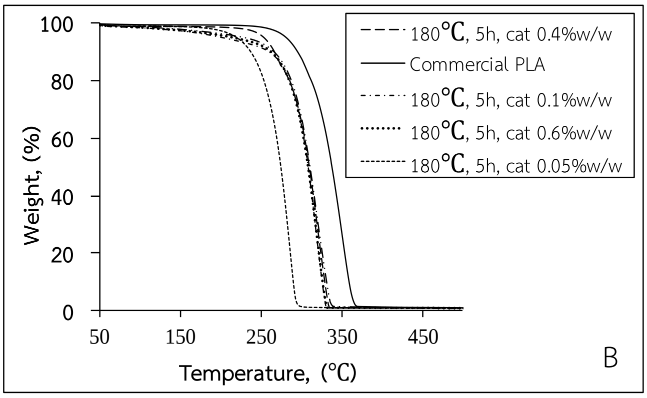


Figure 4.36 Analysis profile of thermal stability results of (A) DSC and (B) TGA for synthesized PLA in various amount of catalyst, and commercial PLA

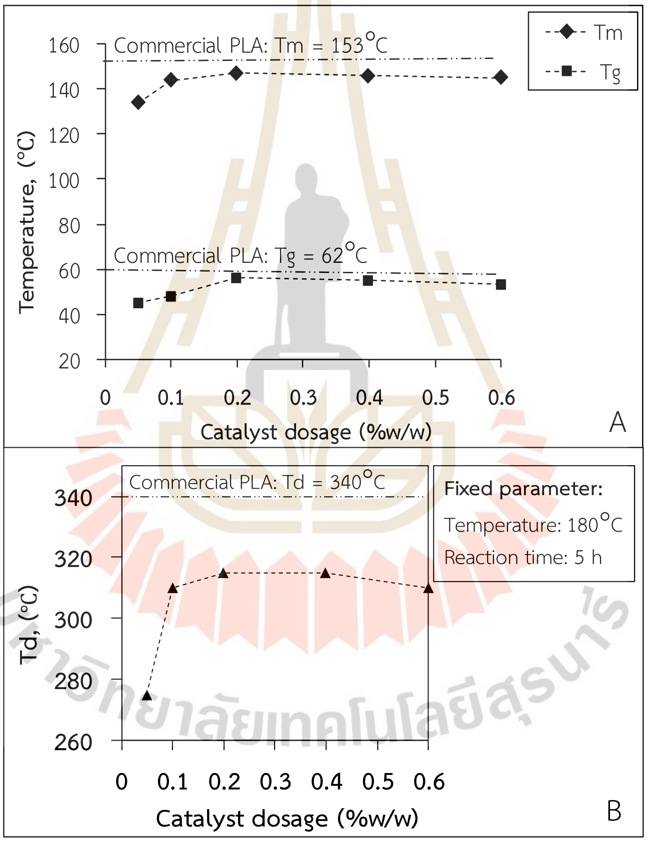


Figure 4.37 Glass transition temperature (Tg), melting temperature (Tm), and decomposition temperature (Td) of synthesized PLA in various amount of catalyst: (A) Tg, Tm, and (B) Td

In addition, increasing hydroxyl content in polymerization process by adding initiator as 1,4-butanediol and polyglycerol-10. The result shown in Figure 4.38 (A-B), which found that the properties as thermostability were better while applied the polyglycerol-10, and 1,4 - butanediol. After analysis the Tg, Tm, and Td of PLA product were found that polyglycerol-10 is the greater initiator for the reaction process of lactide. Variation of the initiator was carried out at 0.02 - 0.3 %mole from the optimal PLA synthesis conditions for 0.2 %w/w catalyst, at 180°C, for 5 h. The result is depicted in Figure 4.39 (A-C), which shows that the highest molecular weight was obtained at an initiator polyglycerol-10 level of 0.02 percent mole, and the lowest molecular weight was obtained at a greater initiator amount. Due to its role as a degradation rate, the initiator had an impact on the polymerization process lead to achieved lower value of Tg, Tm, and Td while conducting increase amount of initiator as polyglycerol-10. The optimum condition for various initiator was shown at 0.02 %mole, 180°C, 5h, and 0.2 %w/w as an amount of catalyst to achieved value of Tg, Tm, and Td of 60°C, 150°C, and 335°C, respectively. It is nearly to the commercial PLA that was analyzed of Tg, Tm, and Td of 62°C, 153°C, and 340°C, respectively. and the range of commercial PLA pellet supplied by Nature Works, with Tm at 155 – 170°C (B. Nyiavuevang, 2022; Yunzi Hu et al., 2017).

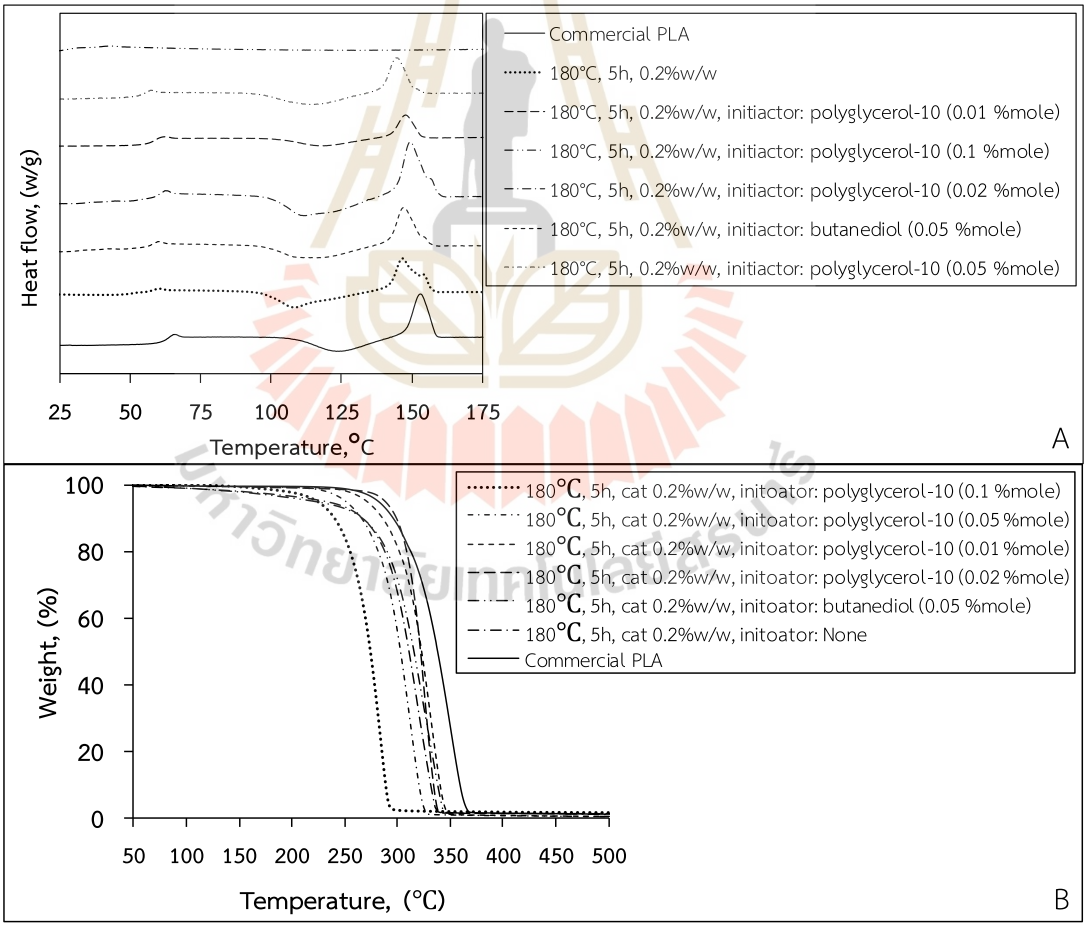


Figure 4.38 Analysis profile of thermal stability results of (A) DSC and (B) TGA for synthesized PLA in various amount of initiator, and commercial PLA

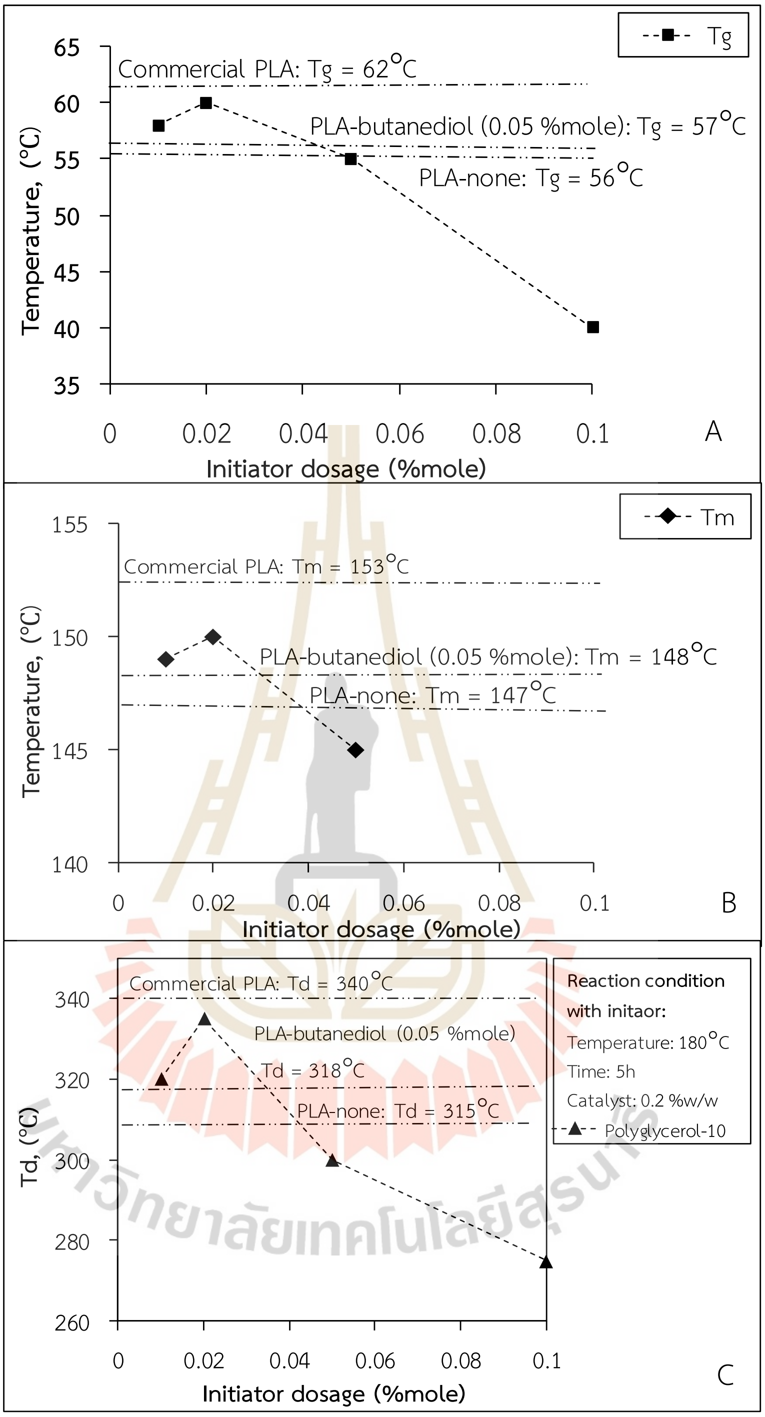
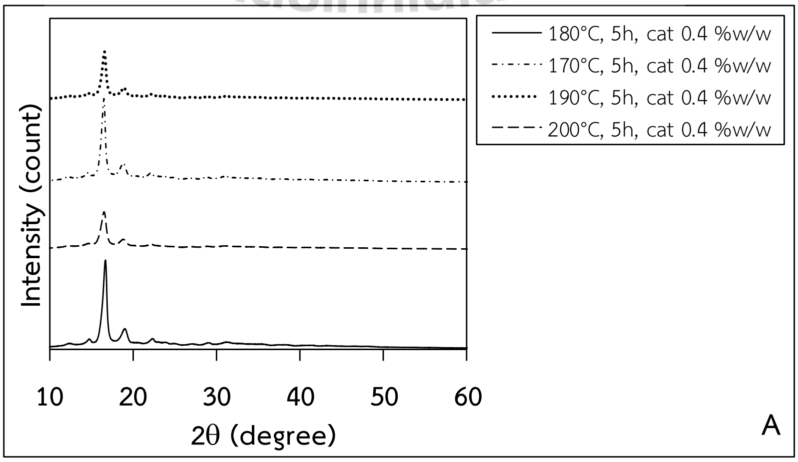


Figure 4.39 Glass transition temperature (Tg), melting temperature (Tm), and decomposition temperature (Td) of synthesized PLA in various amount of catalyst: (A) Tg, (B) Tm, and (C) Td

4) XRD characterization: X-ray diffraction was used to determine the crystallinity of the PLA product. Polymers typically contain amorphous and crystalline areas that are randomly mixed together. Diffractograms with high intensity are indicative of crystalline polymers. Structures for amorphous polymers frequently result in transverse and broad bands. The PLA diffractogram generated this study shown in Figure 4.40 (A-D). According to the XRD characteristic for PLA, two 2 diffraction peaks at approximately 16.6° and 19° were visible in the figure. The peaks are similar to those previous reports by (Carrasco, Pagès, Gámez-Pérez, Santana, & Maspoch, 2010; Müller, Ávila, Saenz, & Salazar, 2014). The peak amplitude provided information about the PLA crystal structure, with an increase in the peak indicating more PLA crystallizes. PLA synthesis with longer reaction times has reduced crystallization because flexible chain mobility is possible, which encourages rearrangement of crystallization. For all samples were provided the profiles are assigned to be the α form PLLA, which is orthorhombic shape parameters a = 10.7 Å, b = 6.45 Å, and c = 27.8 Å. By comparing the area of crystalline zones to the overall area, the degree of crystallinity was identified. Crystalline and amorphous areas added up to the total area based on Eq.(3.5) (Kurniawan, 2917). According to the result of Figure 4.41 (A-C), The results show that PLA's degree of crystallinity tended to decrease with increasing molecular weight, with a lower degree of crystallinity being produced. Due to the high molecular weight over than 24000 g/mole, its molecules are not well rearranged during the drying after the process of purification. The heist molecular weight PLA was measured degree of crystallinity for synthetic PLA of 24% under the condition that polyglycerol-10 was used as the initiator (0.02 %mole). The crystallinity value demonstrates that PLA was produced by the ring-penning polymerization of butyl lactate based lactide, which produced semi-crystalline polymers.



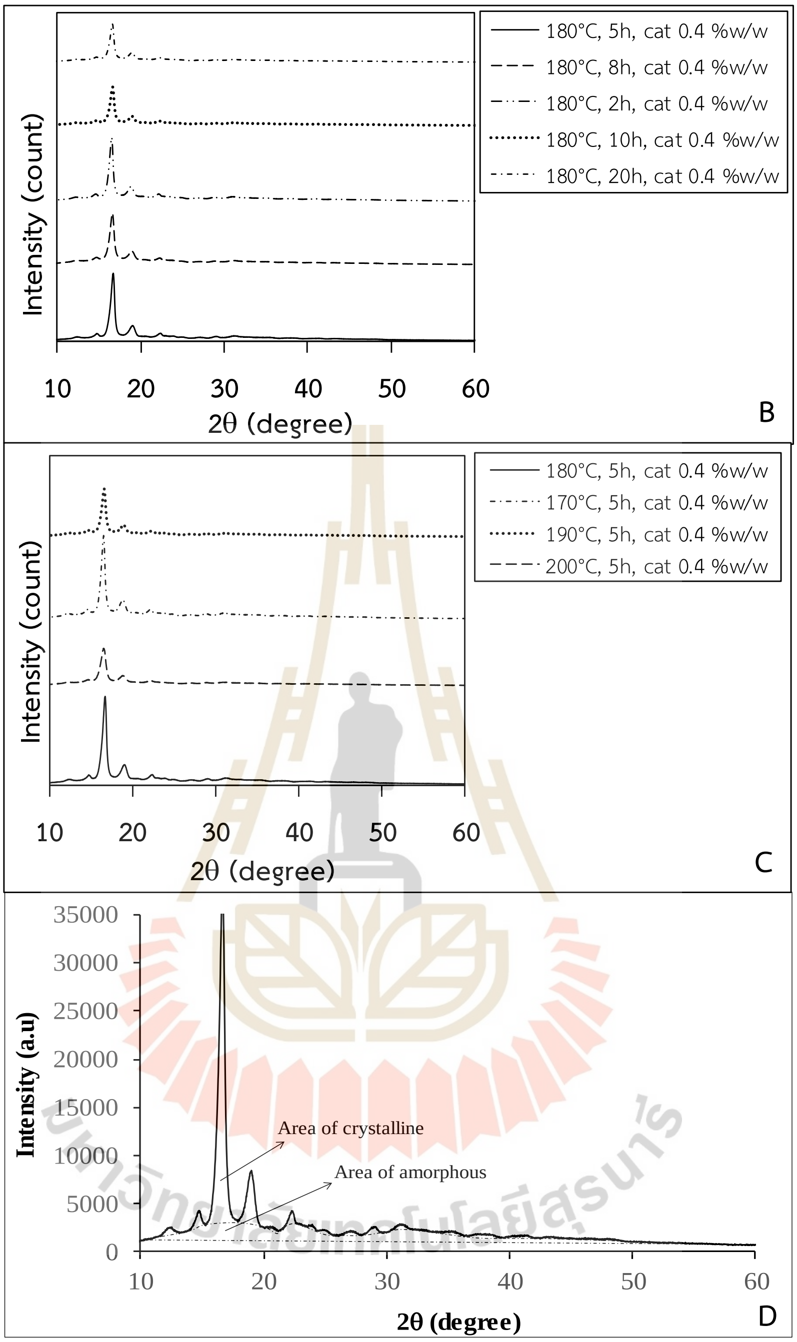


Figure 4.40 Analysis profile of XRD spectrum of synthesized PLA in (A), (B), (C) various reaction temperature, time, amount of catalyst, respectively, (D) condition reaction of 180°C, 5 h, cat 0.2 %w/w, initiator: Polyglycerol-10 (0.02 %mole)

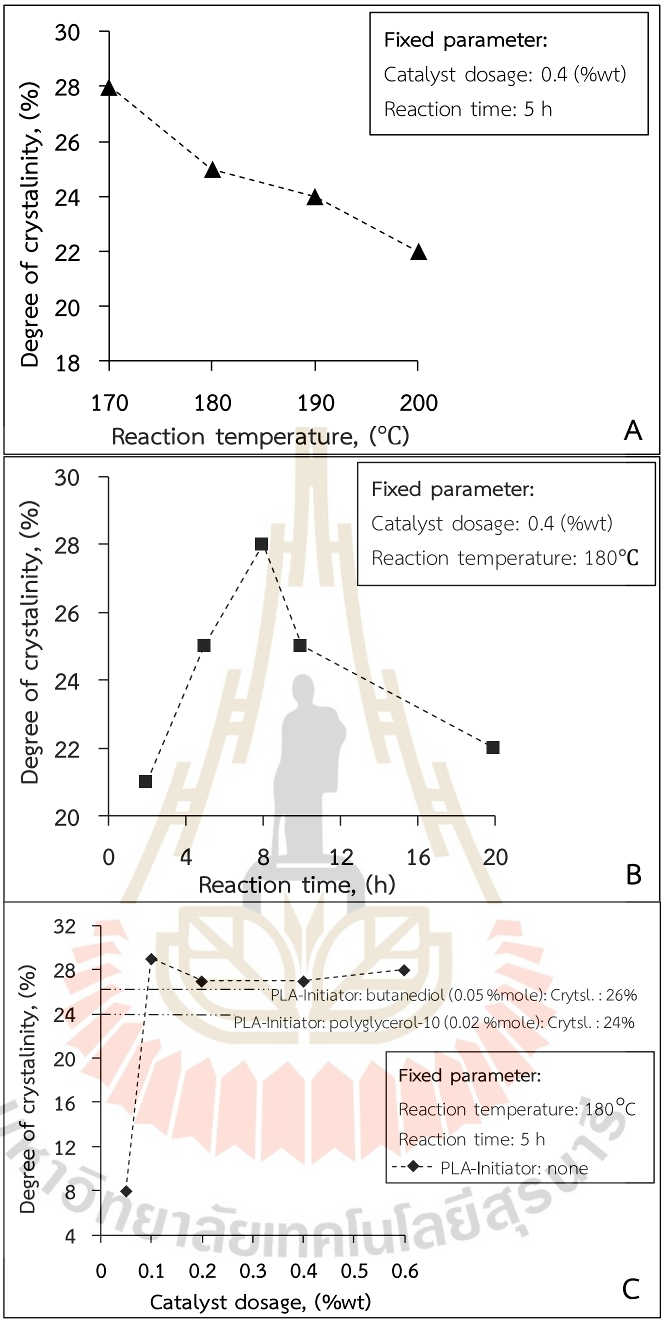


Figure 4.41 Crystalline of synthesized PLA by various independent variable: (A) various reaction temperature, (B) various reaction time, and (C) various amount of catalyst, and initiator dosage

5) NMR characterization: The molecular structure of PLA produced was evaluated by ^{1}H NMR and ^{13}C NMR as shown in Figure 4.42 and 4.43, respectively. The PLA powder was considered for the analyzation which taken from two condition with and without initiator. First sample was 180°C, stannous octoate 0.2 %w/w as a catalyst, polyglycerol-10 (0.02 %mole) as an initiator for 5 h. Second sample was at condition at 180°C, stannous octoate 0.2 %w/w for 5 h without initiator. Which, the results were analyzed to compare each other for the purity and molecular structure of PLA. The impurities from the product would be the residue of catalyst used, solvent, dirt or even moisture since the solvent as chloroform is well known as toxicity. So that, it would be sure that no residue in the product to verified how ability of purification and safety for further application. As the result was demonstrated for those structure of ^{1}H NMR and 13C NMR spectra were the same from two samples with and without initiator were shown in Figure 4.42 (A, B), and 4.43 (A, B), respectively. Whereas, Figure 4.42 (A, B) shows the ^{1}H NMR as H-doublet signal for methyl proton resonance in the main chain at 1.57 ppm. The spectrum shows signal of methine proton resonances in the main chain of PLA at 5.19 ppm. The ^{1}H NMR spectrum of PLA at 2.6 and 4.37 ppm was assigned to the methine proton next to the terminal hydroxyl group and carboxyl group, respectively. The result from analyzed of ^{1}H NMR, the spectrum of PLA was similar to that reported by other works. Figure 4.43 (A, B) shows the ^{13}C NMR spectrum of PLA product. The ^{13}C NMR spectrum of PLA signals visible for molecular structure of methyl carbon, carbon methane and carbon ester assigned at 16.75, 69.12 and 169.73 ppm, respectively. The resulting synthesized PLA was shown that PLA is formed in the present study for ^{13}C NMR evaluated similar to that reported by other works (Kricheldorf, Hans R., & Weidner, Steffen M., 2019). It could be verified that synthesized PLA from synthesized lactide base butyl lactate by using stannous octoate as catalyst and polyglycerol-10 as initiator. The products were high purity over 95% since the catalyst and initiator used can be well dissolved with the solvent.

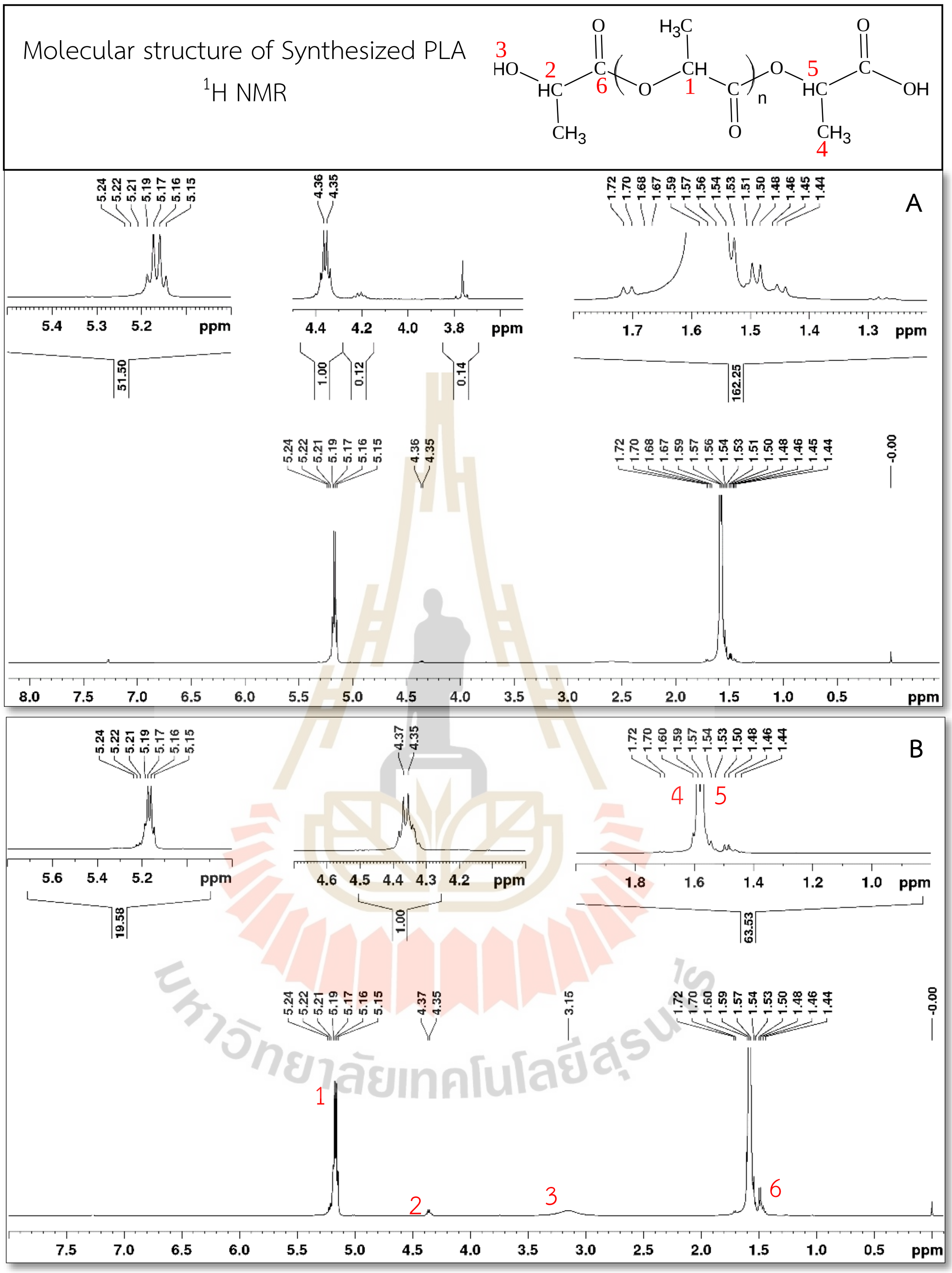


Figure 4.42 ^{1}H NMR spectra of synthesized PLA in the reaction condition of 180°C, 5 h, cat 0.2 %w/w for (A) without initiator, (B) with Polyglycerol-10 (0.02 %mole) as initiator

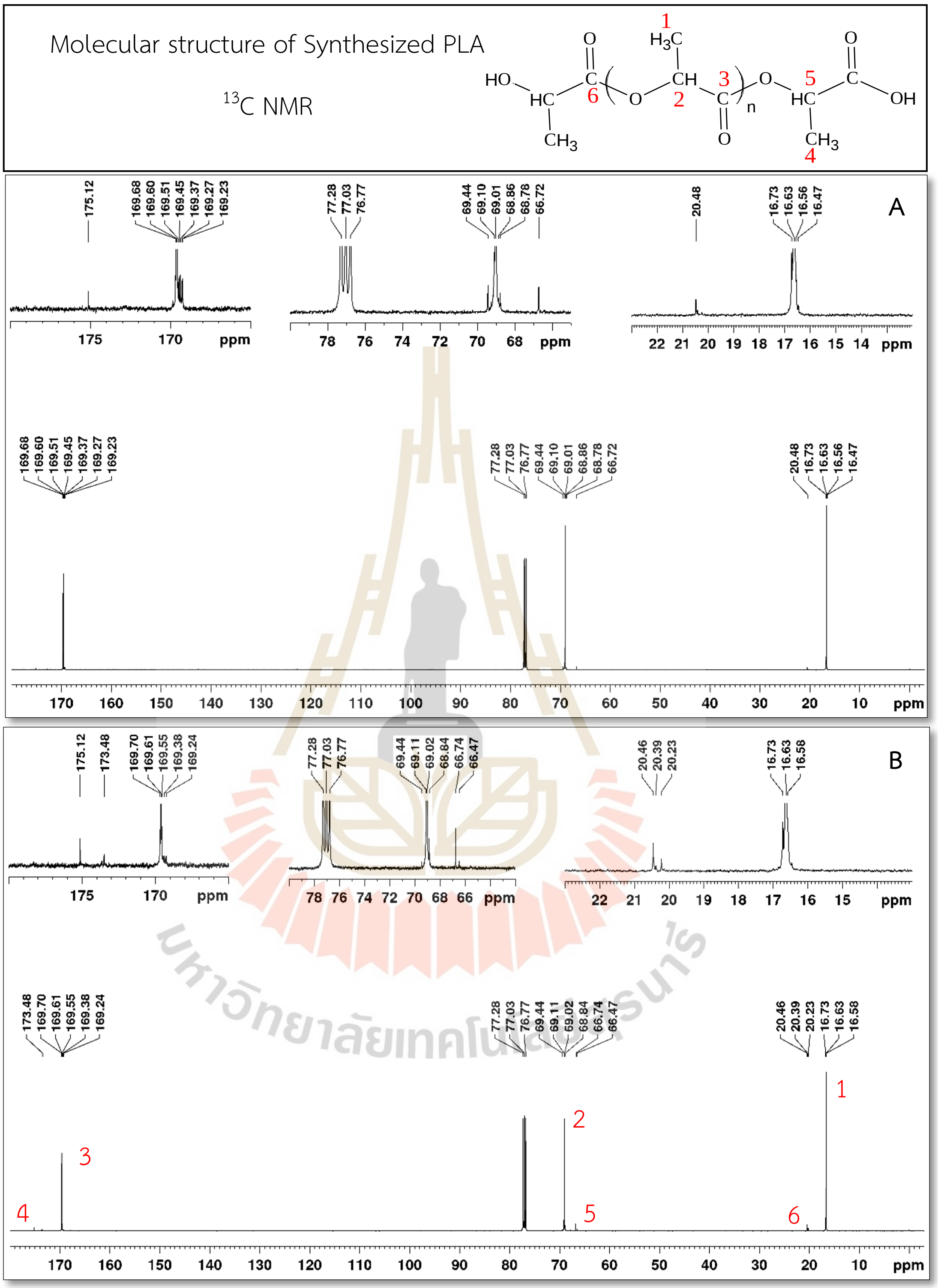


Figure 4.43 ^{13}C NMR spectra of synthesized PLA in the reaction condition of 180°C, 5 h, cat 0.2 %w/w for (A) without initiator, (B) with Polyglycerol-10 (0.02 %mole) as initiator

4.4 Energy index for cost analysis of PLA production

In general, cost analysis for a plant is coming up with three main costs such as capital cost, manufacturing cost, and general cost as shown in Table 4.4.

Table 4.4 Capital cost, manufacturing cost, and general cost

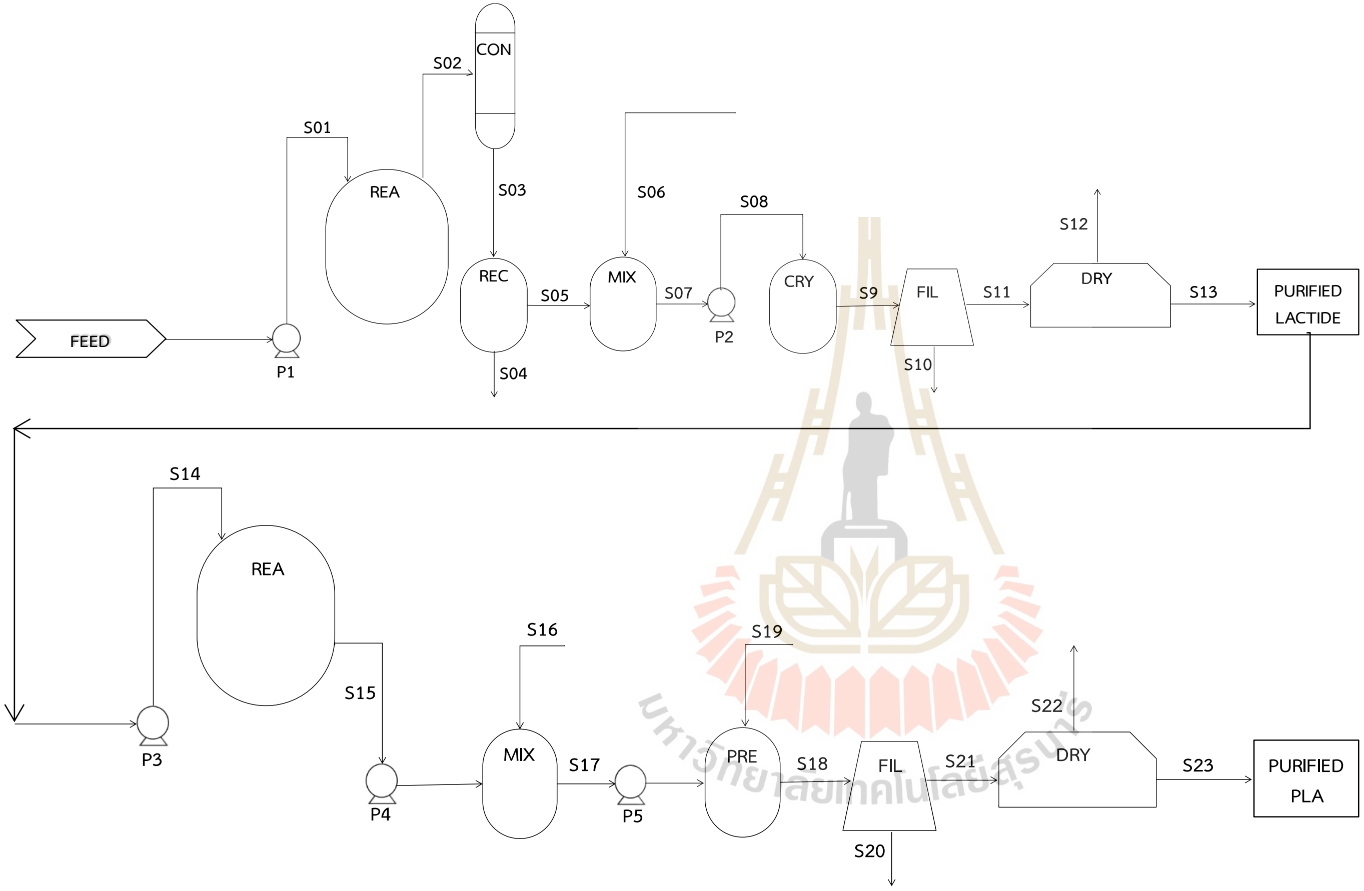
Main cost	Details
Capital cost	**# Fixed-capital investment** • Manufacturing fixed-capital investment: piping, instruments, insulation, foundations and site preparation. • Nonmanufacturing fixed-capital investment: - Plant components: land, processing buildings, administrative and other offices, warehouses, laboratories, shops, other permanent parts of the plant. - Construction overhead: field-office and supervision expenses, home-office expenses, engineering expenses, construction costs and contractor's fees. **# Working capital:** Raw materials and supplies carried in stock, accounts receivable, salaries, wages, and raw material purchases, taxes payable

Main cost	Details
Manufacturing cost	**# Direct production costs:** - raw materials (including freight or transportation, unloading, etc.), - direct operating labor, supervisory and clerical labor directly connect with manufacturing - plant maintenance and repairs - operating supplies such as power, utilities - laboratory charges - royalties and patents - catalysts and solvents **# Fixed charges:** Depreciation, insurance, rent, interest **# Plant overhead costs:** - Hospital and medical services - Safety and protection - Payroll overhead including pensions and vacation allowances - Packaging, warehouse and storage facilities - restaurant/canteen - Recreation - Salvage service - Control laboratories - Plant superintendence - Special employee benefits - General plant overhead and maintenance

Main cost	Details
General cost	**# Administrative expenses:** costs for executive and clerical wages, office supplies, engineering and legal expenses, upkeep on office buildings and general communications **# Distribution and marketing expenses:** costs incurred in the process of selling and distributing the various products, materials handling, containers, shipping, sales offices, salesmen, technical sales service and advertising. **# Research and development expenses:** Costs for salaries, wages, special equipment, research facilities, consultant fees related to developing new ideas or improved processes. To remain in a competitive industrial position. **# Financial expenses:** Extra costs involved in procuring the money necessary for the capital investment or interest on borrowed money. **# Gross earnings expenses:** Based on income-tax laws, special type of expenses.

The manufacturing cost can be distributed into cost of raw materials making up the majority (21-23%), followed by the cost of labor (12-13%), and the cost of utilities (11-12%) of total investment. For raw material and utilities are the majority cost, thus this work is interesting to use the estimating cost of raw material and energy consumption for simple cost analysis. Hence, the Energy Index (EI) is calculated in this work, this index is the ratio of total energy consumption to the total mass of desired product.

PLA synthesis from butyl lactate consists of two main stages such as lactide synthesis, and PLA synthesis. For lactide synthesis is produced from butyl lactate through oligomerization and depolymerization reaction. The crude lactide was purified from the process of purification by recrystallization, and further purified lactide was used to synthesize PLA through ring opening polymerization or polymerization reaction. After the process, crude PLA was further purified on the purification process by precipitation. The Energy Index was calculated based on the material balance and the energy consumption of the PLA synthesis in lab scale experiment. Figure 4.44 shows the process flow diagram of PLA production. Material balance for producing PLA from butyl lactate and the necessary chemical was calculated as shown in Table 4.5. The synthesis of lactide was started with raw material of 300 g butyl lactate and 0.66 g of tin(IV) chloride were added into the reactor as a catalyst. A total of 24 g of pure lactide was finally obtained from about 70 g of crude lactide after it had been dissolved in ethyl acetate for recrystallization and drying in vacuum oven. For the PLA synthesis, the purified lactide was utilized as a raw material using stannous octoate as the catalyst and polyglycerol as an initiator, yielding 15.84 g of crude PLA product. The crude PLA was further purified by dissolving in 28 g of chloroform, precipitating in 52.44 g of methanol, and then drying in vacuum oven. In overall, 300 g of butyl lactate yielded 24 g purified lactide and 8.16 g purified PLA. From these experimental processes are found that the total energy consumption is approximately 54 MJ, the details of energy consumption are listed in Table 4.6. The value of Energy Index from this work was estimated of 6600 MJ/kg. From the work of Kwan et al., 2018, they found that the Energy Index of PLA production is 958 MJ/kg (Kwan, Hu, & Lin, 2018). From these two works, it is found that the Energy Index of this work is higher than that found in Kwan's work because the energy consumption for lab scale is much higher than the industrial due to the lab synthesis was operated with a small amount of raw material leading to the higher loss of energy. However, it would be a valuable method for approximating the energy consumption in industrial production. The analysis of the change of Energy Index with respect to the percentage of equipment load by assumption of the full of equipment load (100%) is 2,000 g of butyl lactate as raw material, as shown in the Figure 4.45. It is observed that the Energy Index decreases as an increasing of percentage equipment load. At the 100% equipment load is found that the Energy Index is 1000 MJ/kg which is similar to that found by previously mentioned literature. It is indicated that in order to obtain the reasonable number of Energy Index from lab scale experiment, the calculation of material balance and energy consumption have to be done at the full equipment load. As the result, the value of Energy Index can be used for estimation of the cost of all energy used in the process by converting the unit of energy used per received product to be a unit for calculating the cost of electricity that how much is the price per 1 unit (1kWh = 1 unit). Then multiplying it to calculate cost per kilogram of product. The received product can be calculated to the amount and cost of raw material by calculating the amount of raw material from % yield of product and further estimation for raw material cost. Finally, the total cost of raw material and energy consumption per one kilogram of product can be estimated. In addition, Energy Index can be considered to improve the process whether the production loss or energy loss.



Abbreviation:

1. S: Stream
2. REA: Reactor
3. CON: Condenser
4. REC: Receiver
5. P: Pump
6. MIX: Mixing
7. CRY: Crystallization tank
8. FIL: Filtration
9. DRY: Drying

Figure 4.44 Process flow diagram for PLA production from butyl lactate

Table 4.5 Material balance estimation for PLA production from butyl lactate

Stream table for lactide production from butyl lactate

Stream flow	Substances											
	Total mass flow of each stream		Butyl lactate		Tin-4-Chloride		Lactide		Ethy acetate		Purified lactide	
	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w
S01	300.67	1.00	300.00	1.00	0.67	0.00	–	–	–	–	–	–
S02	297.40	1.00	272.73	0.92	0.67	0.00	24.00	0.08	–	–	–	–
S03	297.40	1.00	272.73	0.92	0.67	0.00	24.00	0.08	–	–	–	–
S04	228.40	1.00	228.00	1.00	0.40	0.00	–	–	–	–	–	–
S05	69.00	1.00	44.73	0.65	0.27	0.00	24.00	0.35	–	–	–	–
S06	74.69	1.00	–	–	–	–	–	–	74.69	1.00	–	–
S07	143.69	1.00	44.73	0.31	0.27	0.00	24.00	0.17	74.69	0.52	–	–
S08	143.69	1.00	44.73	0.31	0.27	0.00	24.00	0.17	74.69	0.52	–	–
S09	143.69	1.00	44.73	0.31	0.27	0.00	24.00	0.17	74.69	0.52	–	–
S10	107.69	1.00	44.73	0.42	0.27	0.00	-	-	62.69	0.58	–	–
S11	36.00	1.00	–	–	–	–	24.00	0.67	12.00	0.33	–	–
S12	12.00	1.00	–	–	–	–	–	–	12.00	1.00	–	–
S13	24.00	1.00	–	–	–	–	–	–	–	–	24.00	1.00

Stream table for PLA production from synthesized lactide

Stream flow	Substances																	
	Total mass flow of each stream		Synthesized lactide		Stannous octoate		Polyglycerol-10		Crude PLA		PLA		Chloroform		Methanol		Purified PLA	
	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w	g	%w/w
S14	24.07	1.00	24.00	1.00	0.05	0.00	0.02	0.00	–	–	–	–	–	–	–	–	–	–
S15	15.84	1.00	7.61	0.48	0.05	0.00	0.02	0.00	15.84	–	8.16	0.52	–	–	–	–	–	–
S16	28.30	1.00	–	–	–	–	–	–	–	–	–	–	28.30	1.00	–	–	–	–
S17	44.14	1.00	7.61	0.17	0.05	0.00	0.02	0.00	–	–	8.16	0.18	28.30	0.64	–	–	–	–
S18	52.44	1.00	–	–	–	–	–	–	–	–	–	–	–	–	52.44	1.00	–	–
S19	96.58	1.00	7.61	0.08	0.05	0.00	0.02	0.00	–	–	8.16	0.08	28.30	0.29	52.44	0.54	–	–
S20	46.78	1.00	7.61	0.16	0.05	0.00	0.02	0.00	–	–	8.16	0.17	28.30	0.60	2.64	0.06	–	–
S21	10.80	1.00	–	–	–	–	–	–	–	–	8.16	0.76	–	–	2.64	0.24	–	–
S22	2.64	1.00	–	–	–	–	–	–	–	–	–	–	–	–	2.64	1.00	–	–
S23	8.16	1.00	–	–	–	–	–	–	–	–	–	–	–	–	-	-	8.16	1.00

Table 4.6 The energy consumption of PLA production

Power consupmotion of equipment as standardization							
Information	Heater		Water bath		Vacuum pump	Vacuump oven	
	Heater	morter	Heating	Cooling		Heater	Vacuum pump
Power consumption (W)	1020	1.5	1000	200	360	60	360

Equipment used for PLA production from butyl lactate							
Information	Heater		Water bath		Vacuum pump	Vacuump oven	
	Heater	morter	Heating	Cooling		Heater	Vacuum pump
Assumption the maximization of mass (g)	2000	2000	2000	2000	2000	2000	2000
Power consumption (W)	102	0.15	50	10	18	2.25	13.5

Lactide synthesis						Lactide purification			PLA synthesis	PLA purification		
Unit and Information			Oligomerization		epolymerizatio	Mixing	Vacuum filtration	Drying	Polymerization	Mixing	Vacuum filtration	Drying
			Step1	Step2								
Temperature (°C)			240	270	330	120	-	40.00	240.00	-	-	40.00
Pressure (mbar)			atmospheric	30	5	-	600	100.00	atmospheric	-	600.00	100.00
Duration (h)			6	2	3	0.08	0.033	0.50	5.00	5	0.03	0.50
Power consumption (W)	Heating	Heater	102	102	102	102	—	—	102.00	—	—	—
		Motor	0.15	0.15	0.15	0.15	—	—	0.15	0.15	—	—
	Water bath	Heating	—	—	50	—	—	—	—	—	—	—
		Cooling	—	10	—	—	—	—	10.00	—	—	—
	Vacuump pump		—	18	18	—	18.00	—	—	—	18.00	—
	Vacuump oven	Heater	—	—	—	—	—	2.25	—	—	—	2.25
		Vacuum pump	—	—	—	—	—	13.50	—	—	—	13.50
Total power consumption (W)			102.15	130.15	170.15	102.15	18.00	15.75	112.15	0.15	18.00	15.75
Unit power consumption (kW*h)			0.61	0.26	0.51	0.01	0.00	0.01	0.56	0.00	0.00	0.01
Total energy consumption (MJ)			54.57									
Total of PLA product (kg)			0.01									
Energy index (MJ/kg)			6600									

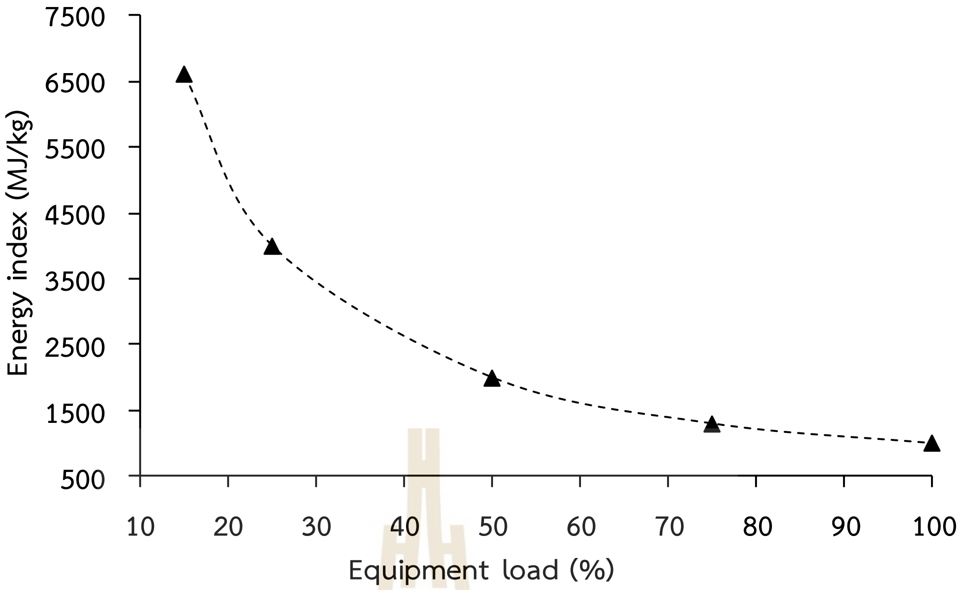


Figure 4.45 The energy index for various percentage of equipment load

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Lactide and PLA synthesis are summarized the result from each experimental series and estimation of mass and energy consumption on synthesis PLA was described under the headings as follows: Series 1 is summarized in heading 5.1.1, preliminary results for PLA synthesis from synthesized lactide based lactic acid. Series 2 is reported in heading 5.1.2, for PLA synthesis from commercial lactide to obtain the optimum condition of ring opening polymerization of lactide to form PLA by various reaction temperatures. Series 3 is described in heading 5.1.3, to synthesize lactide from butyl lactate. Series 4 and 5 are expressed in heading 5.1.4, is for PLA synthesis from butyl lactate based synthesized lactide, and purification of PLA, and the adding initiator to the reaction. Energy index for cost analysis of synthesis PLA is 5.1.5.

5.1.1 Preliminary results for PLA synthesis from synthesized lactide based lactic acid

PLA synthesis from lactic acid, which is produced through steps of dehydration, oligomerization, depolymerization, and ring opening polymerization. The stannous octoate was used as a catalyst in ring-opening polymerization of synthesized lactide with concentration of 0.4% (w/w) at a temperature of 160°C and reaction time for 5 h gave the highest yield PLA of 64.5% with its decomposition temperature of 311°C and melting point temperature at 152°C which is comparable to the commercial one. The reaction temperature and time are significant variables, there is a competition between polymerization and depolymerization mechanisms occurring in reaction and each mechanism plays a major role with respect to the conditions. At higher reaction temperature and longer time, the rate of depolymerization is higher than that of polymerization leading to the lower of decomposition and melting temperature of synthesized PLA.

5.1.2 PLA synthesis from commercial lactide

PLA synthesis from commercial PLA was conducted various reaction temperature on the ring opening polymerization stage, stannous octoate was used as a catalyst with fixed amount of 0.4 %w/w in the processes which was carried out in variation reaction temperature range of 160 - 200°C for various reaction time range at 0.5 h, and 5 h. The optimum condition was obtained Tg, Tm, Td, and Mv of values 55, 146, 315°C, and 23000 g/mole, respectively. higher temperatures, such as 190 and 200°C may damage PLA chain bonding by depolymerization from the process leading in poorer product yields than at 180°C because the process may occur polymerization and depolymerization of lactide and PLA simultaneously with the higher rate of depolymerization reaction of lactide. On the other hand, reaction temperature has an impact on the process because no other product yields were observed at low temperatures such as 160°C, owing to the higher energy required to break the lactide bond in the reaction system.

5.1.3 Purification and yield of synthesized lactide from butyl lactate

PLA synthesis from butyl lactate was obtained from step of oligomerization, depolymerization, and ring opening polymerization. Lactide synthesized from butyl lactate through step of oligomerization and depolymerization, the optimum condition for vitiating independent variable as reaction temperature, reaction time, and amount of catalyst was 180°C, 8 h, and 0.1 %v/v, respectively on the process of oligomerization then 210°C, for 3 h, 0.1 %w/w catalyst on depolymerization stage. This can be provided with yield of purified lactide of 8 %yield. Weight average molecular weight (Mw) of lactide of 124 g/mole, and melting temperature, and decomposition temperature was 127°C, and 240°C, respectively. The optimum condition of lactide purification was found with ratio of crude lactide versus solvent of 1:1.2 at room temperature for 12 h. Yielding 43 %yield of lactide product which is the highest yield, and it was the minimum condition for using of amount of solvent, time for crystallization at room temperature. The purified lactide was revealed a high purity of around 95% determined by ^{1}H-NMR.

5.1.4 Purification and yield of PLA from butyl lactate based synthesized lactide

PLA synthesized from purified lactide was obtained the optimum condition of 180°C, 5 h by the respectively use amount of catalyst, and initiator of 0.2 %w/w, and 0.02 % mole was observed 35 %yield. Viscosity average molecular weight (Mv) of synthesized PLA was value of 29000 g/mole measured by Cannon-Fenske, weight average molecular weight (Mw) was value of 50000 g/mole obtained from GPC measurement. Thermostability Tg, Tm, and Td was observed of 60, 150, and 335°C, respectively. Increasing molecular weight tended to increase properties thermostability. However, the molecular weight (Mv) above of 20000 g/mole, degree of crystallinity was decreased.

5.1.5 Energy index for cost analysis of PLA synthesis

This study determined the total mass of raw materials, including chemicals required, and the energy consumption for producing PLA from butyl lactate, respectively, were 0.008 kg and 54 MJ. In order to investigate the prices of raw materials utilized. The energy index of 6600 MJ/kg which it is required for further calculation of the used cost of raw material. Since, utilities and raw materials account for the majority of the manufacturing cost. It was discovered that factors like equipment load and product yield had an impact on the value of the energy index that would be used to calculate energy. Lowering the energy index results in lower energy use and production losses.

5.2 Recommendation

The following is a summary of some recommendations for the upcoming work:

1. PLA synthesis is provided in very complex and multi-step process that requires the design of high-performance devices in order to regulate the properties or attain large molecular weight of PLA. Due to the influences of different variables such as temperature, pressure, catalysts, reaction time and related equipment. So that, a thorough analysis on all impacts is necessary.

2. For synthesis lactide in order to improve the yield, the vacuum system is required to be work for long time at least 6 h at low pressure 1-5 mbar, heating system is required for controlling, and agitator system is needed to be strong power motor for responding to Newtonian and non-Newtonian fluid. Furthermore, the investigated catalyst would be considered for the others that could get the higher yield. Pravin et al. reported lactide was produced from butyl lactate of 24 % crude lactide yield.

3. The yield of synthesized PLA may improve by improved equipment for heating control system, the stirrer is needed to be a motor on suitability for non-Newtonian fluid. PLA was synthesized from lab scale by using a hotplate as a heating system, the stirrer was jammed while the process was on the higher viscosity which may leads to get low yield of product.

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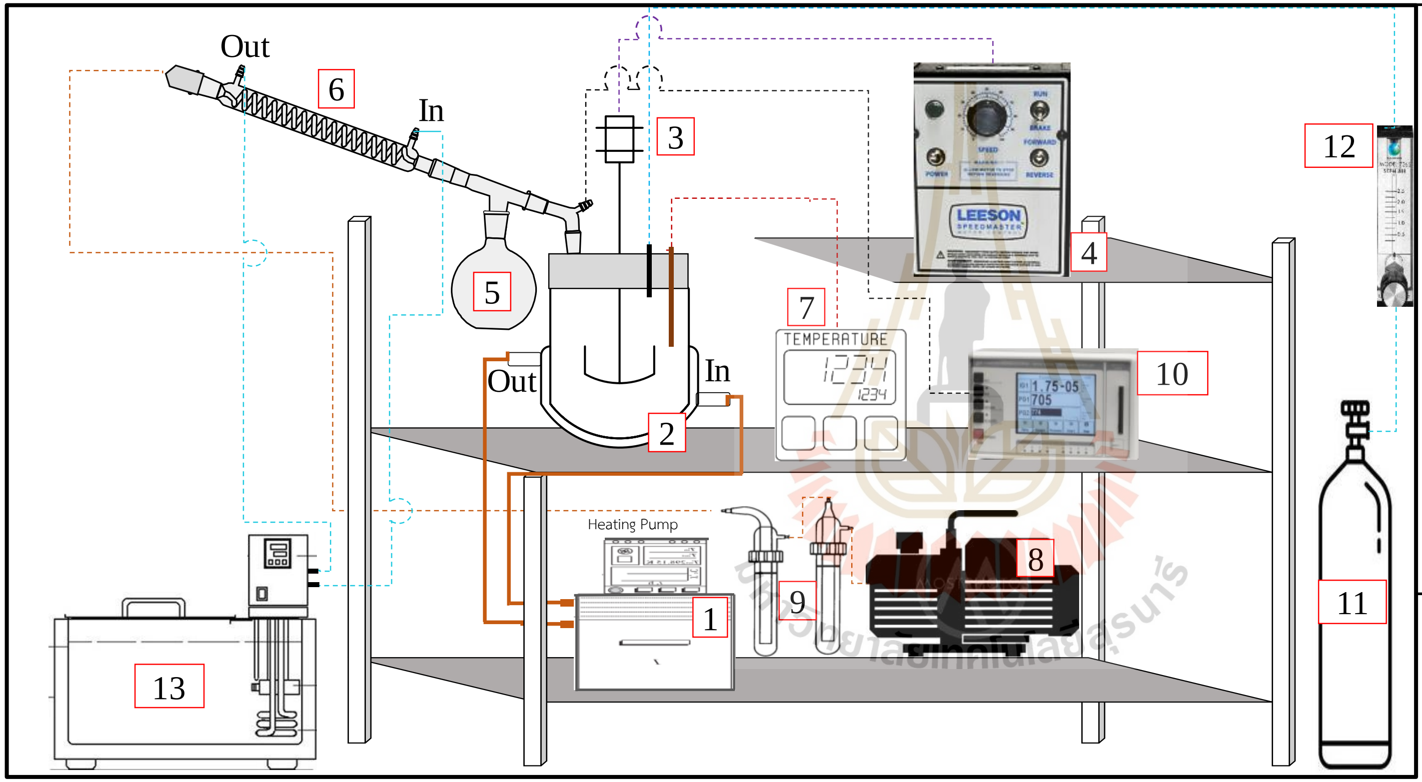
APPENDIX A

Preliminary study of 5 liter and 50 liter reactors

A.1 Preliminary study of 5 liter and 50 liter reactors

Main items of apparatus and instruments for 5 liter and 50 liter reactors are shown in Figure A.1, and A.2, respectively.



1) Oil bath
2) Reactor
3) Agitator motor
4) Agitator control
5) Receiver
6) Condenser
7) Thermocouple
8) Vacuum pump
9) Cold trap
10) Pressure control monitor
11) Nitrogen gas tank
12) Rotameter
13) Water bath

Figure A.1 Main items of apparatus and instruments for 5 liter for PLA production

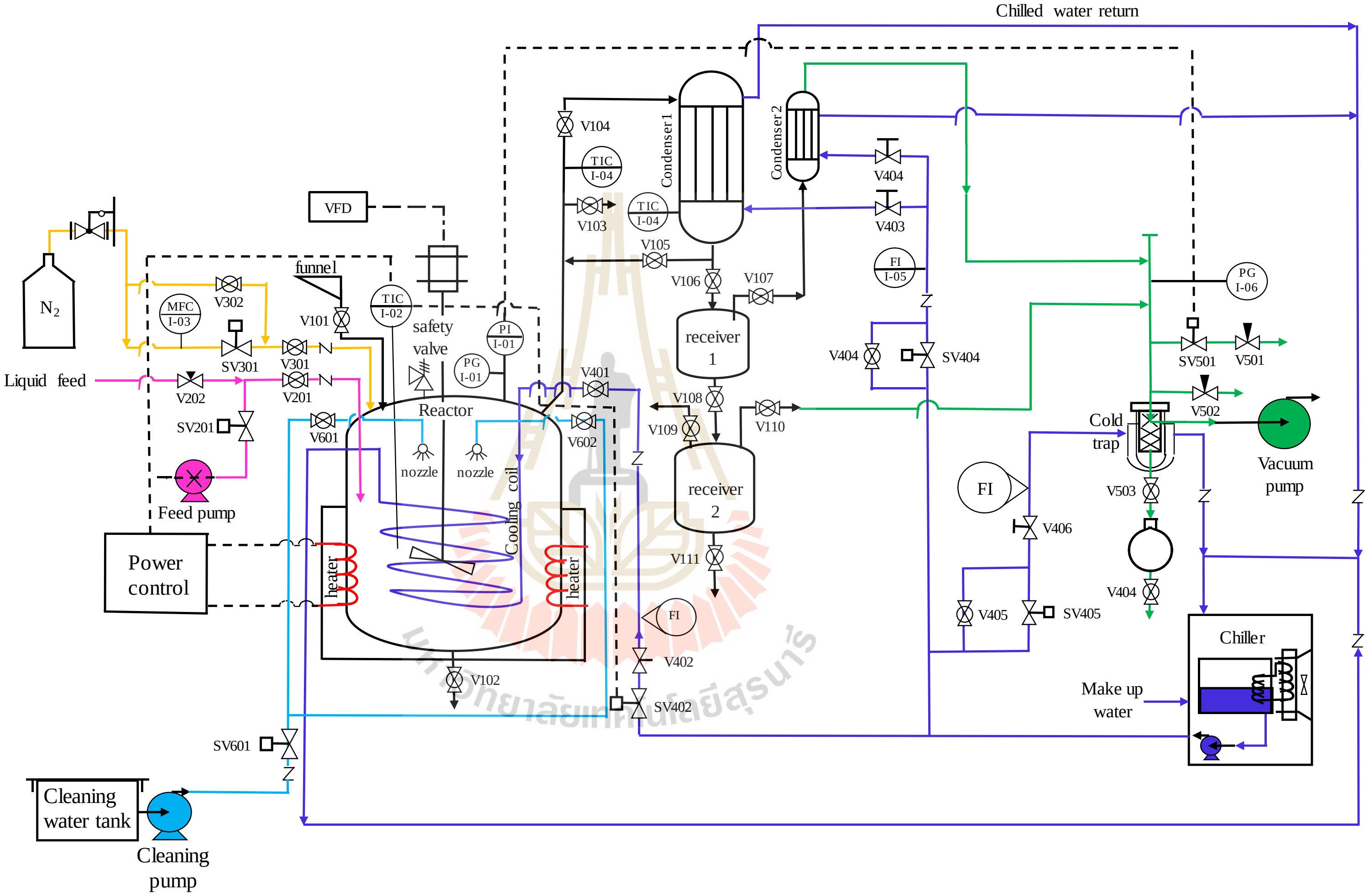


Figure A.2 Main items of apparatus and instruments for 50 liter for PLA production

The equipment of reactor for 5 liter is set up as shown in Figure A.3. It was first preliminary studied to use it to produce the lactide from lactic acid, as shown in Figure A.3. After the first run, some parts of equipment were encountered the problems that would not work properly.

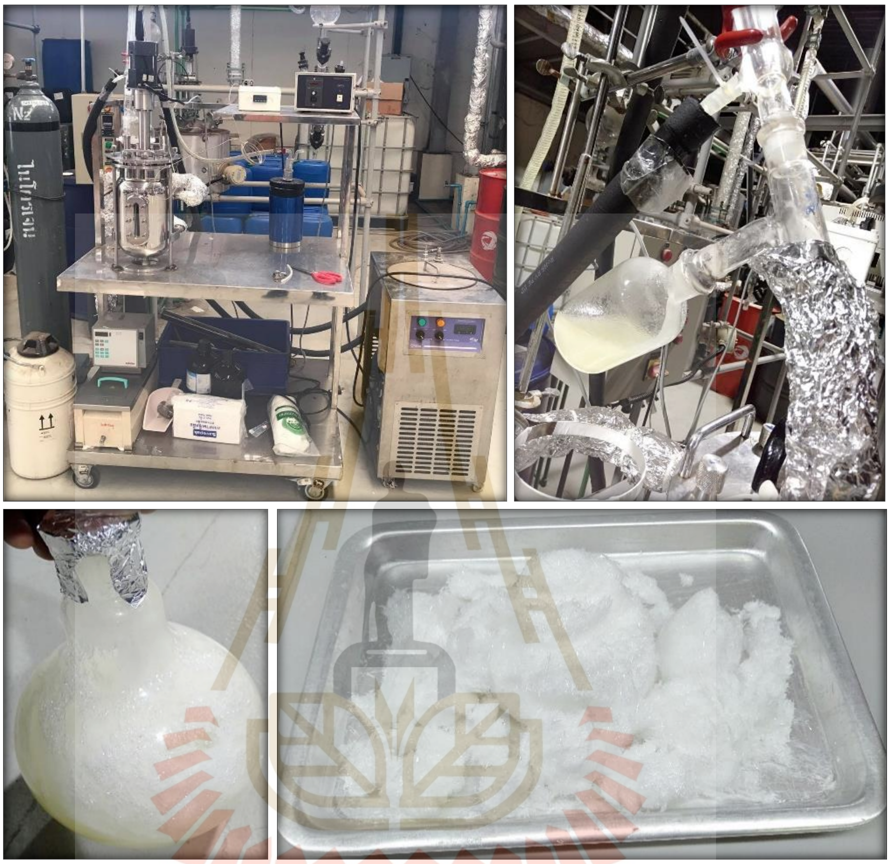


Figure A.3 Lactide was produced in reactor of 5 liter

Due to the ineffectiveness of the equipment at this time such as: heating and controlling system, agitator system, and vacuum system. The heating of the current reactor is used an oil bath with silicone oil as the heating fluid with heating pump to flow the hot silicone oil to the jacket reactor as shown in Figure A.1. Since the required temperature is too high for the heating pump to operate. The pumps were eventually burned as a result of overheating as seen in Figure A.4.

Figure A.4 Heating pump in oil bath section

Secondly issue was found on the agitator system, because the resulting reaction as a nonnewtonian fluid, the motor stirrer cannot operate for an extended period of time which it is be stopped working while the experiment is running, the reason is found that because of the power of the pump is not enough and it is not suitable to the process.

Third, vacuum system, in addition, the required high temperature and having a good controlled system, and an efficient stirring system, but the vacuum system is also one of the main factors that would be considered for improvement to be able for synthesize lactide due to the reaction of lactide was reacted at low pressure of 5 mbar. In this case, the synthesis in larger reactors 5 and 50 liter required to thorough leakage detection and improved since larger reactor was harder to control. For it is be described in following parts that are tended to vacuum leakage, such as the junction of the adapter from the reactor and condenser to the vacuum pump, the connected point between the reactor and cover, and feed funnel to insert or add a catalyst into the reactor or even the junction to measure the temperature inside reactor. The connected agitator system to the reactor could be caused leakage which effected to the process system as shown in Figure A.5. Another is to have a vacuum pump that can be operated for long reaction time at least 15 h.

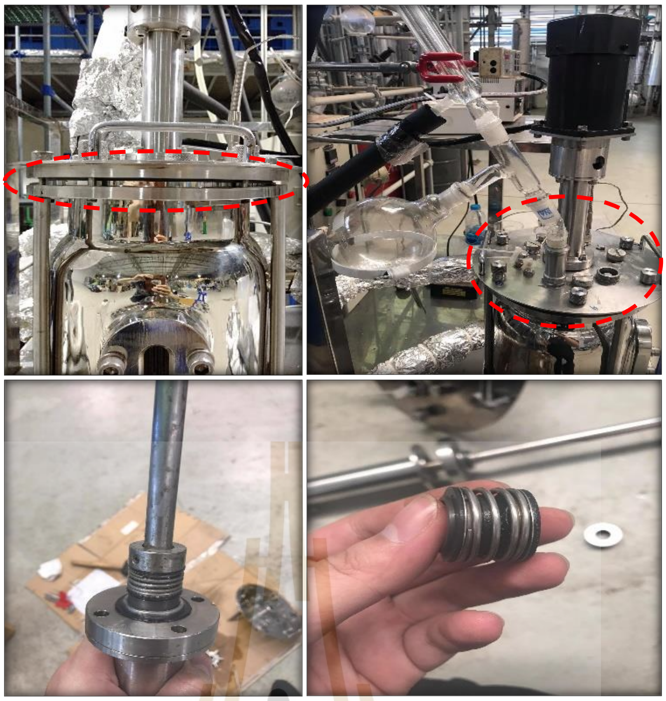


Figure A.5 Issue of apparatus to the vacuum system

The recent reason for 50 liter was encountered in 3 main parts of issue that are required for improvement. Firstly, it was the heating system and control to the reactor, which temperature did not reach the required temperature at around 330°C because the required reaction temperature for minimum, and maximum was at 180°C, and 210°C, respectively within low pressure to 1-3 mbar for at least 15 h, which this is including the step of lactide and PLA synthesis. The temperature control system did not work with along to the setpoint since the ceramic heater was broken with some parts, so that is needed repairing as the highlight as shown in Figure A.6.

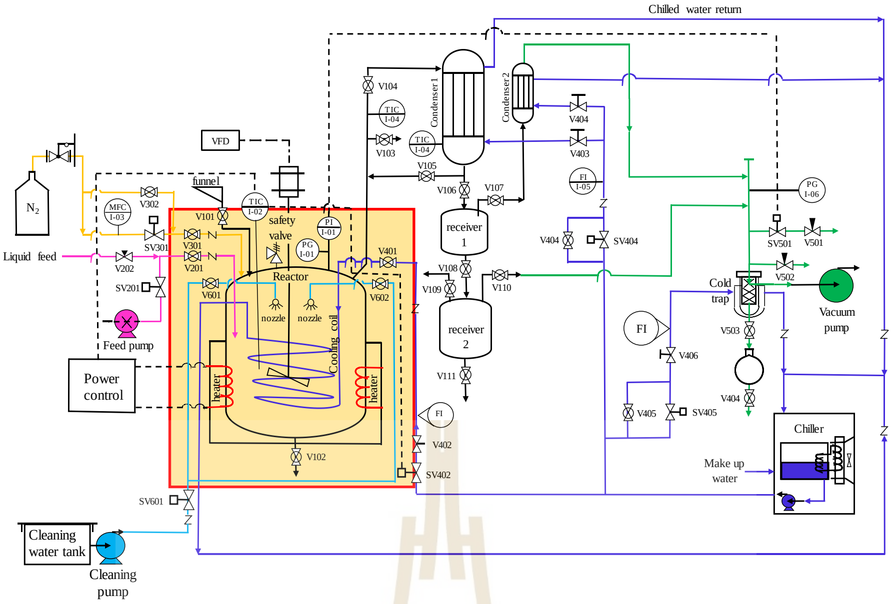


Figure A.6 Ceramic heater section for giving heat to the reactor

Secondly, is for the heating and cooling that was required to the condenser for condensation as shown in Figure A.7. The liquid that flows through the condenser is responding with 5°C, but it is also required higher above 95°C for depolymerization step in lactide synthesis so, this case is not supported yet. It was a reason that synthetic lactide attaches to the condenser while the process was run, and also vacuum system were required for improvement in order to respond to the process.

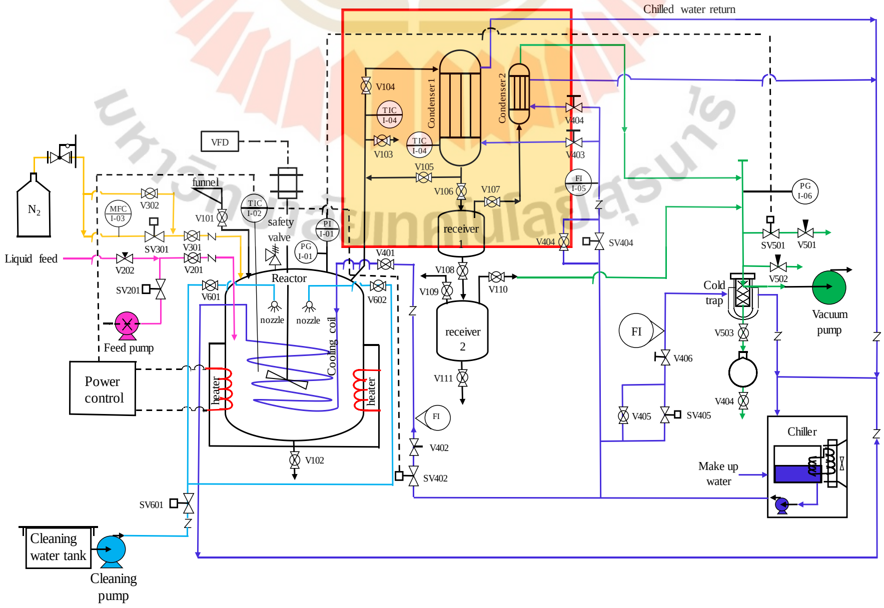


Figure A.7 Condenser section for condensation

Third, it was the vacuum system, which has pressure leakage from other junctions such as from the reactor and condenser to the vacuum pump, the connected between the reactor and cover whether the feed funnel to insert or add catalysts into the reactor on cover reactor. On top of that, we have connected and are suggested from Sumitomo Heavy Industries Process Equipment Company to improve the agitator system since, the reaction on PLA synthesis is including Newtonian and non-Newtonian fluid so that it would better considering the use of MAXBLEND impeller for the process since it can be conducted with the reaction involved high viscosity. Furthermore, motor of the agitator section would be considering along with the MAXBLEND impeller. The agitator section shown as the highlight in Figure A.8. For all experience and to the practical synthesis in the lab scale, 5 liter and 50 liter was found to be redesigning for specifically equipment for PLA synthesis as mentioned above. The summary of encountered issue which needed to improve specific for PLA synthesis including all involved stages are; heating and controlling for reactor section, heating and cooling for condenser section, vacuum section for pressure control, agitator section.

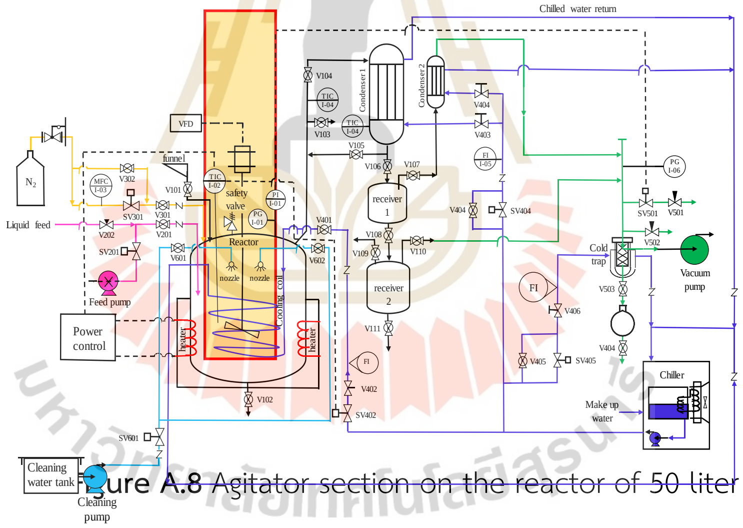


Figure A.8 Agitator section on the reactor of 50 liter

A.2 Preliminary study of 5 liter and 50 liter reactors (Conclusion)

PLA synthesis was conducted in 5 liter and 50 liter, the synthesis has encountered many problems for the supported equipment. Due to the ineffectiveness of the equipment at this time such as: heating and controlling system, agitator system, cooling and heating system of condensation from condenser, and vacuum system.

For reactor of 5 liter, three main issues are as follows: First, the heating system did not given heat to reach the required condition, which it is necessary to be redesigned specifically for synthesize PLA from the substrate. Due to the required temperature being too high for the heating pump to operate, the process was ineffective. The two pumps eventually burn out as a result of overheating. Second, because the resulting reaction is a nonnewtonian reaction, the disturbance system in the reactor cannot operate for an extended period of time. Third, vacuum system is one of the main factors that would be considered for improvement to be able for synthesize lactide due to the reaction of lactide was reacted at low pressure of 5 mbar. In this case, the synthesis in larger reactors 5 and 50 liter required to thorough leakage detection and improved since larger reactor was harder to control.

The recently reason for reactor of 50 liter was the heating system, which could not reach the required temperature at 330°C, and the temperature control system did not work with along to the setpoint. The liquid that flows through the condenser un be able higher above 95°C for depolymerization step in lactide synthesis. It was a reason that synthetic lactide attaches to the condenser while the process was run, and also vacuum system were required for improvement in order to respond to the process.

APPENDIX B
LIST OF PUBLICATION

List of Publication

B. Nyiavuevang, S. Sodkampang, S. Dokmaikun, K. Thumanu, A. Boontawan, S. Junpirom. (2022). Effect of temperature and time for the production of polylactic acid without initiator catalyst from lactide synthesized from ZnO powder catalyst. Journal of Physics: Conference Series, 2175, 2125-2131.

Journal of Physics: Conference Series

PAPER • OPEN ACCESS

Effect of temperature and time for the production of polylactic acid without initiator catalyst from lactide synthesized from ZnO powder catalyst

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Effect of temperature and time for the production of polylactic acid without initiator catalyst from lactide synthesized from ZnO powder catalyst

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Abstract. Polylactic acid (PLA) is a biodegradable polymer that most importance at the present due primarily to its properties as biological degradation and biocompatibility derived from renewable resources. This study investigated the role of zinc oxide powder and tin(II) 2-ethylhexanoate as the catalysts for lactide and PLA synthesis, respectively. Polylactic acid was obtained by four stages: dehydration, oligomerization, depolymerization and ring opening polymerization. The catalyst was added and water was removed at the first stage then the reactions are carried out at different temperatures and reaction time on the other stages. The ratio of lactic acid and zinc oxide powder was 1000:3 for lactide synthesis, the ratio of lactide product and tin(II) 2-ethylhexanoate was 1000:4 for PLA synthesis without any initiator. The PLA products were analysed for the yield, some chemical and physical properties such as functional group, decomposition temperature, melting temperature of synthesized PLA. It is found that at reaction temperature of 160°C and reaction time for 5 h gave the highest yield PLA of 64.5% with its decomposition temperature of 311°C and melting point temperature at 152°C. There are two main mechanisms, polymerization and depolymerisation occurring in reaction and each mechanism plays a major role with respect to the reaction condition. At higher reaction temperature and longer time, the rate of depolymerisation is higher than that of polymerization leading to the lower of decomposition and melting temperature of synthesized PLA.

1. Introduction

Polylactic acid (PLA) is one of the most well-known biodegradable and biocompatible polymer produced in small and large quantities [1]. It's interesting biopolymer in recently for the other applications because of its excellent mechanical properties and compatibility with the environment. PLA is one of the most appropriate polymers to replace non-biodegradable synthetic polymers based on fossil fuel [2]. Polylactic acid (PLA) is a highly versatile material, which can be obtained from the renewable resources such as garbage, potato, sugars in corn starch, cassava or sugar cane and glycerin waste of

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biodiesel and other agricultural products [3]. PLA is widely used for various applications, in the medical field using as tissue engineering, implants, drug delivery systems etc. It can be used for food packaging and textiles [4]. The low molecular weight PLA is appropriate used for drug delivery, which has a long history of safety in humans [5, 6]. PLA can be prepared by different ways from lactic acid such as direct condensation polymerization, ring opening polymerization and azeotropic condensation polymerization [5]. Ring-opening polymerization (ROP) of lactic acid is the most commonly route to achieve high molecular weight and consists of three steps: polycondensation, depolymerization and ring opening polymerization [1, 5]. PLA can be produced by using of different organometallic compounds as catalysts for aluminum, zinc, tin, etc. However, tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) is the most common catalyst for the synthesis of high molecular weight PLA [7]. Tin(II) 2-ethylhexanoate was approved for surgical and pharmacological applications and widely utilized initiator due to give the high molecular weight polymers in ring opening polymerization rout [8]. The catalyst aqueous dispersion of zinc oxide nanoparticles was used in lactide synthesis and could lead to highly efficient production of high molecular weight PLA by using PGL-10 as an initiator in the process [9]. Zinc oxide was an alternative catalyst for lactide synthesis to 72% yield after the process at 230 - 240°C [10]

In this work, we investigated the polymerization of lactide synthesized by using ZnO as a catalyst in the presence of tin(II) 2-ethylhexanoate without any initiator. The objective of this study was to determine the effect of reaction temperatures and time in the polymerization stage on the yield, and some of physical and chemical properties such as functional group, degradation temperature, melting point of produced PLA.

2. Material and methods

2.1. *Chemicals*

Commercially available L-lactic acid (liquid, 88%) was obtained from Purac Co., Rayong, Thailand. Catalysts zinc oxide, tin(II) 2-ethylhexanoate and organic solvents methanol, ethyl acetate, chloroform were purchased from Italmar Co., Bangkok, Thailand. Nitrogen gas was obtained from Linde Co., Rayong, Thailand.

2.2. *Methods of lactide and PLA synthesis*

2.2.1. Lactide synthesis. lactic acid (liquid, 88%) (400 ml) with zinc oxide as a catalyst were added into a 1000 mL three necked flask, which were equipped with a magnetic mixer, a thermocouple and a condenser connected to a vacuum system. The process performed under a pressure of 60 kPa at temperature 80°C for 2 h in order to remove water content. After the dehydration the product was further oligomerized, the temperature was slowly adjusted up to 150°C under pressure 20 kPa for 3 h without catalyst was added at this stage. After 3 h of oligomer stage, lactide was produced through depolymerization, which carried out at 170°C, pressure 2 kPa and maintaining for 3 h. After the completion of the depolymerization process the crude lactide was cooled to room temperature.

2.2.2. Lactide purification. The crude lactide was preheated at 70 - 80°C then dissolved in ethyl acetate with ratio of crude lactide and ethyl acetate (1:1.5 w/v) by stirring for 10 min. The undissolved impurities were then separated by vacuum filtration, the filtrate was cooled down to room temperature prior to the recrystallization at 4°C for 24 h. The recrystallized lactide was then isolated from ethyl acetate by vacuum filtration and the filtrate was further dried in a vacuum oven at 40°C, pressure 100 Pa for 24 h. The purified lactide was then collected in the sample container. After completing the process, the quantity of lactide was weighed and conversion yield of lactide was calculated by Eq. (1).

$$\text{Lactide yield (\%w/w)} = \frac{\text{Mass of lactide (g)}}{\text{Mass of lactic acid (g)}} \times 100 \qquad (1)$$

2.2.3. PLA synthesis by ring-opening polymerization of lactide. The purified lactide was weighed then placed in a three-neck flask, which was equipped with a magnetic stirrer, thermocouple with nitrogen gas flow at 1.5 mL min^{-1}. The tin(II) 2-ethylhexanoate as a catalyst was added into the reactor while lactide was heated until it melted with ratio of lactide produced and tin(II) 2-ethylhexanoate was 1000:4. The mixture was carried out by varying at 140, 160 and 180°C for different duration time 5, 8, and 10 h. Upon completely this stage, the product mixture was cooled to room temperature.

2.2.4. PLA purification. After the PLA synthesis process, crude PLA was cool to room temperature and collected to sample container then chloroform was added to dissolve crude PLA with 1:1 w/v for 30 min. After that, allow to the purification which precipitated into excess cold methanol, and then white solid PLA gradually formed and separated by vacuum filtration. The filtrate was dried in a vacuum oven with pressure 100 Pa at 45°C for 24 h. After completely the process, the quantity of PLA produced was weighed, and its conversion yield was calculated by Eq. (2).

$$\text{PLA yield }(\%\text{w/w}) = \frac{\text{Mass of PLA produced (g)}}{\text{Mass of lactide input (g)}} \times 100 \tag{2}$$

2.3. Methods of lactide and PLA characterization

2.3.1. FTIR Characterization. The functional groups of the products were characterized using a fourier transform infrared spectrometer (FT-IR, TENSOR 27, Germany). Before measurement, lactide and PLA were prepared to dry in vacuum oven at 45°C, and 100 Pa for 24 hours then made the sample to be powder. The measurement was performed at a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1} for a total of 64 scans.

2.3.2. Polarimeter characterization. Lactide synthesized from lactic acid was detected for its stereoforms and optical purity by polarimeter (BELLINGHAM & STANLEY P20 POLARIMETER, United Kingdom). Lactide was prepared and the optical rotation was measured in toluene solution at concentration of 1.0 % (w/v) at 20°C, and a 200 mm cell length. The specific rotation, and enantiomer excess were calculated by Eq. (3) and (4), respectively.

$$[\alpha]_D^{20°\text{C}} = \frac{\alpha}{c \times l} \tag{3}$$

$$\%ee = \frac{\alpha}{(\alpha)_{pure}} \times 100 \tag{4}$$

Where,

$[\alpha]_D^{20°\text{C}}$: specific rotation, (degree)
α : observed rotation, (degree)
$(\alpha)_{pure}$: pure rotation of sample, (degree)
c : concentration of sample, (g/ml)
l : cell length, (dm)
ee : enantiomer excess, (%)

2.3.3. NMR Characterization. Synthesized PLA was characterized its molecular structure using a nuclear magnetic resonance spectrometer (NMR 500 MHz Bruker AVANCE III HD, Germany). Proton NMR was obtained by using deuterated chloroform as a solvent, and tetramethylsilane was used as the internal standard.

2.3.4. TGA Characterization. The decomposition and the melting behaviour of samples were characterized by thermogravimetric analyser (Mettler Toledo TGA/DSC1, Switzerland) with the heating scan from 25 to 800°C. The heating rate was 10°C min^{-1} and the flow rate of nitrogen gas was 50 mL min^{-1}.

3. Results and discussion

The production of lactide from lactic acid involves a three-stage processes, namely dehydration, oligomerization and depolymerization, and PLA synthesis relates to the ring-opening polymerization of lactide product, which carried out as previously described.

3.1. Synthesis of lactide and PLA

Lactide yield obtained from the stage of lactide synthesis by using zinc oxide as catalyst was 31.25% determined by Eq. (1) and PLA yields at the various temperatures and durations were calculated by the Eq. (2) as shown in Figure 1. PLA products yield using tin(II) 2-ethylhexanoate 0.4 wt% as a catalyst in the processes, which carry out for 5 h at temperatures of 140, 160, and 180°C were 49.62 %, 64.5%, and 50.39%, respectively. Increasing the duration of 8 h, PLA yield 53.1% and 62.06% of temperature 140 and 160°C, respectively. For increasing time of 10 h, yield of PLA are 58.73%, 55.7%, and 49.04% at temperatures of 140, 160, 180°C, respectively. The maximum yield was found at 160°C for 5 h. The result is shown that the increasing temperature for a long time does not improve the product yield [5].

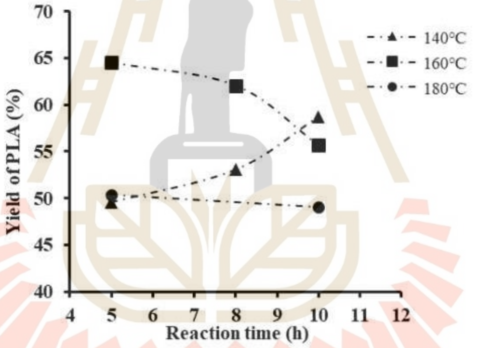


Figure 1. Effect of reaction temperature and time on PLA synthesis.

3.2. Characterization of lactide and PLA

3.2.1. Functional group of lactide and PLA. The product of lactide and PLA were analysed the functional group determine by FTIR and shown that the products for both lactide and PLA were the same compared to the commercial PLA, as shown in Figure 2. The bonds of carbonyl stretch and oxy carbonyl (ester) were observed at wave number 1748 cm^{-1} and 1181 cm^{-1}, respectively. The -CH bond was observed at 2996 $\text{cm}^{-}1$, and -OH bond stretching was observed at wavenumber 3530 cm^{-1}, which is characteristic of a carboxylic acid. Alcohol bond was higher than that of -OH stretching from the carboxylic acid due to very strong hydrogen bonds in carboxylic acids. However, at the lower wavelengths of bond are tended to show considerable overlap because it is difficult for the characterization. The infrared spectroscopy wavenumbers (cm^{-1}) for the bonds and products functional groups were as follows: -OH stretch (free): 3100; -CH-stretch: 2996 (asymmetric), 2946 (symmetric), 2877; -C=O carbonyl stretch: 1748; -CH_3 bend: 1452; -CH- symmetric and asymmetric: 1382 and 1360; -C-O- stretch: 1181, 1083; -OH bend: 1042 [3].

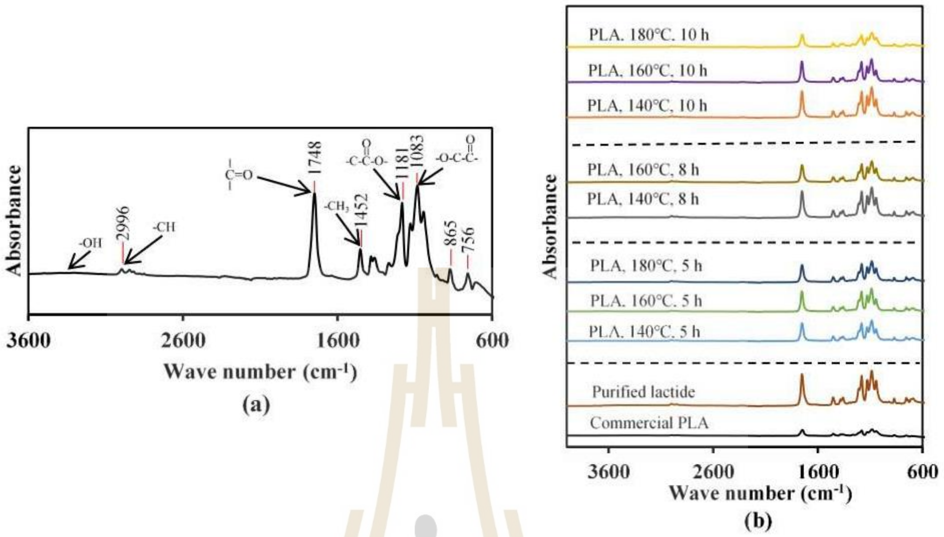


Figure 2. The functional group of lactide and PLA products: (a) commercial PLA and (b) comparing of each product to commercial lactide and PLA.

3.2.2. Stereoisomer of lactide. In general stereoisomer of lactide provided in three stereoforms as L-lactide, D-lactide, and optically inactive meso-lactide form which is an equimolar (racemic) mixture of D and L isomers [11]. The lactide product was detected, the resulting observed rotation α = -13.4° was used to calculate by Eq. (3) to obtain the specific rotation was $([\alpha]_D^{20})_{LLA}$ = -291°. This result to confirm the stereoform of lactide synthesized was L-stereoisomer as L-lactide. Determination of enantiomer excess value of synthesized lactide was calculated by eq. (4), to find its percentage stereopurity. While the neat optical rotation of L- and D-lactides were $([\alpha]_D^{20})_{LLA} = -298.8°$ and $([\alpha]_D^{20})_{DLA}$= +298.8° at 20 °C in a toluene solution, respectively [12]. The value of enantiomer excess of synthesized lactide was obtained for 4.5%, and the stereopurity of synthesized lactide was 52.25% of L-stereoform.

3.2.3. Molecular structure of PLA. The molecular structure of PLA produced was evaluated by ^{1}H NMR and ^{13}C NMR as shown in Figure 3(a) and 3(b), respectively. The PLA powder was considered for the analyzation obtained at 160°C by using tin(II) 2-ethylhexanoate 0.4 wt% as a catalyst for 5 h in polymerization stage. Figure 3(a) shows the ^{1}H NMR as H-doublet signal for methyl proton resonance in the main chain at 1.57 ppm. The spectrum shows signal of methine proton resonances in the main chain of PLA at 5.19 ppm. The ^{1}H NMR spectrum of PLA at 2.6 and 4.37 ppm was assigned to the methine proton next to the terminal hydroxyl group and carboxyl group, respectively. The result from analysed of ^{1}H NMR, the spectrum of PLA was similar to that reported by other works [3, 13]. Figure 3(b) shows the ^{13}C NMR spectrum of PLA product. The ^{13}C NMR spectrum of PLA signals visible for molecular structure of methyl carbon, carbon methane and carbon ester assigned at 16.75, 69.12 and 169.73 ppm, respectively. The resulting synthesized PLA was shown that PLA is formed in the present study for ^{13}C NMR evaluated similar to that reported by other works [3, 14].

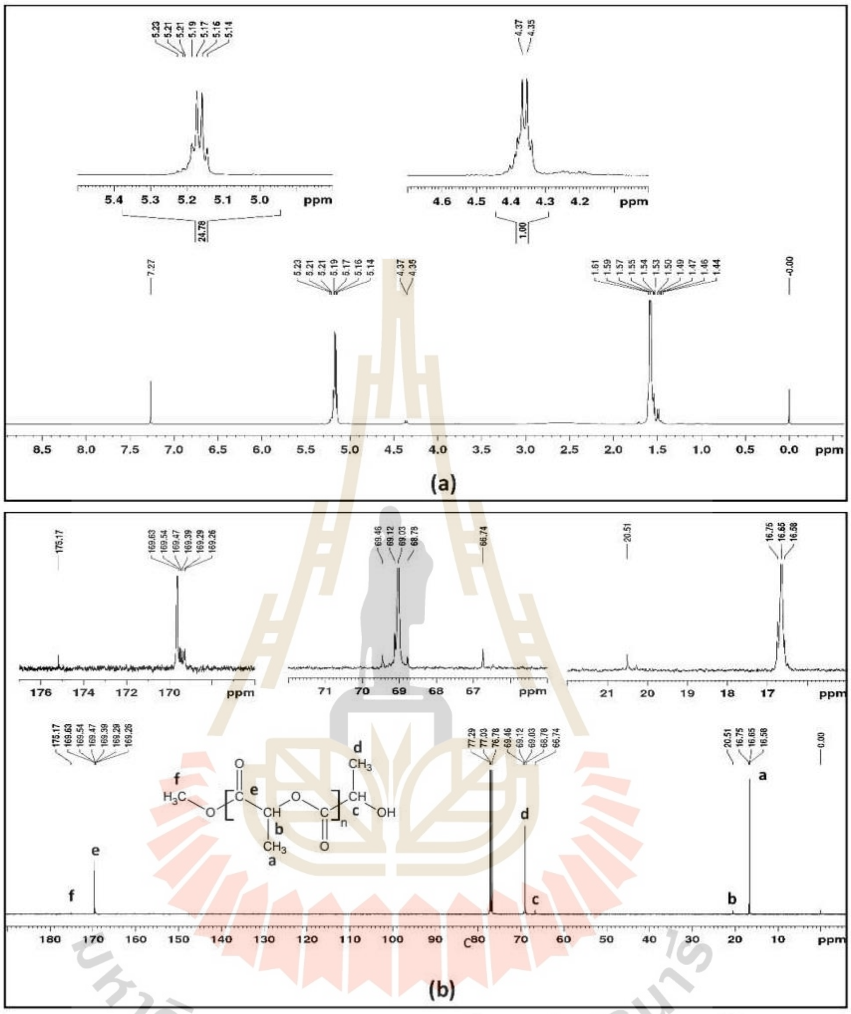
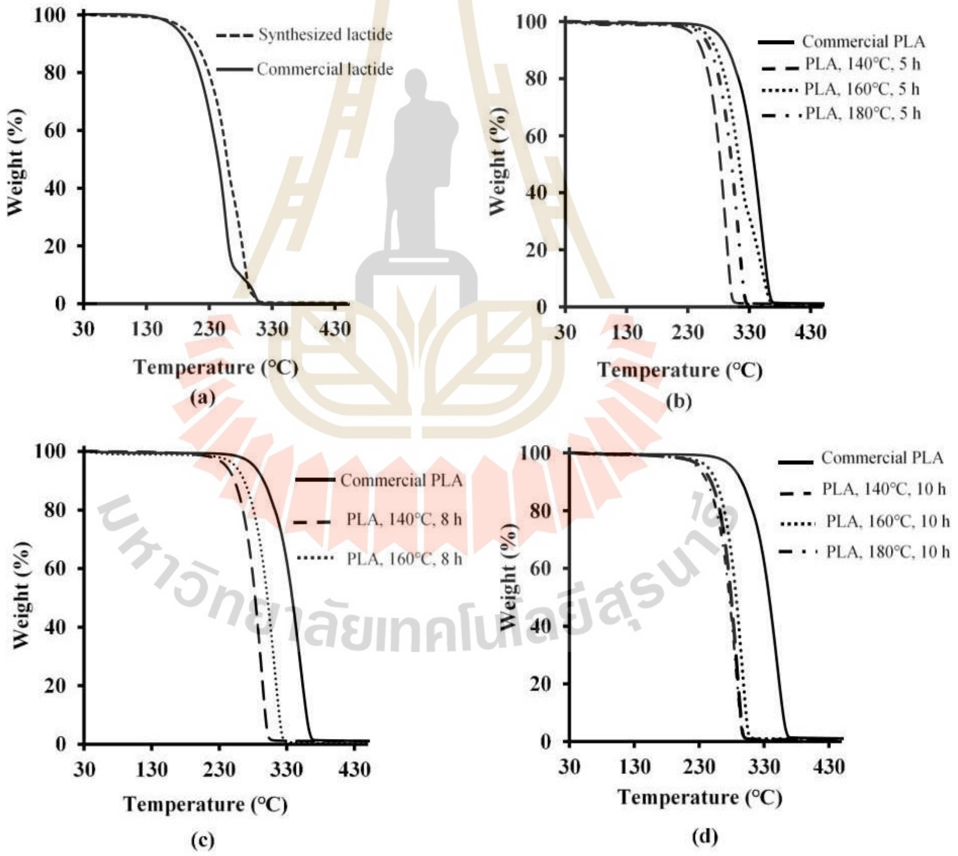


Figure 3. NMR analysis spectra of PLA products: (a) ^{1}H NMR spectrum and (b) ^{13}C NMR spectrum.

3.2.4. Thermal stability of PLA. The thermal stability of the lactide and PLA were determined by TGA/DSC1. The profiles of decomposition temperature obtained from TGA are shown in Figure 4(a-d), whereas the melting temperature from DSC is displayed in Figure 4(e). These results of commercial lactide and PLA are also included in those figures to compare with the synthesized samples. Synthesized lactide was obtained decomposition, and melting point of 240°C and 94°C, respectively is related to commercial lactide shown in Figure 4(a) and 4(e). The temperature of decomposition and melting point of PLA samples were concluded and exhibited in Figure 5(a-b), respectively. Decomposition and melting temperature of commercial PLA were analysed of 338°C and 153°C, respectively. It is found that the overall trend of decomposition and melting temperature of synthesized PLA tends to increase with an increasing of reaction temperature to reach a maximum point at 160°C, then decreasing in higher reaction temperature. The increasing of decomposition and melting temperature implies that the increasing of molecular weight of synthesized PLA. In general, during the reaction there is a competition reaction between polymerization and depolymerization of lactide monomers to obtain PLA products. At high reaction temperature, the polymerization rate to form the product is lower than the depolymerization due to the thermal degradation. The polymerization was proposed to describe by the insertion-coordination mechanism as shown in Figure 6 [11, 15]. For the effect of reaction time, it is shown that the decomposition and melting temperature mostly decreases with an increasing of reaction time for all reaction temperature except at the 140°C. This could be explained by the depolymerisation play a major role of reaction. It is observed at reaction temperature 140°C, the melting temperature increases with an increasing in reaction time. This result could be due to at this low reaction temperature the shorter chain molecules may occur in higher amount in bulk phase thus the melting temperature may be increased. The optimum condition in this work was found that at reaction temperature 160°C with 5 h, which obtained the decomposition and melting temperature of 311°C and 152°C, respectively. The melting temperature of 152°C is comparable to commercial PLA of 153°C as shown in Figure 5 (b), which is nearly to the range of commercial PLA pellet supplied by Nature Works, with T_m at 155 - 170°C [9].



(a) (b) (c) (d)

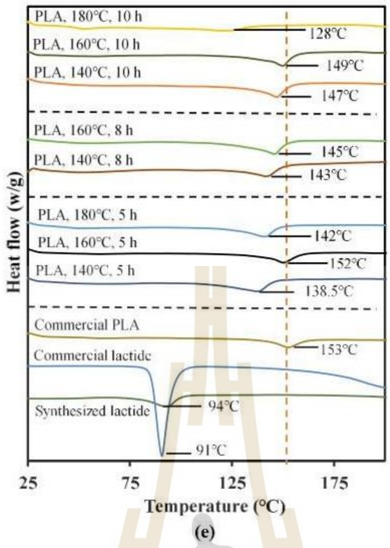


Figure 4. Analysis thermal stability results of (a-d) TGA and (e) DSC of synthesized lactide and PLA and commercial samples.

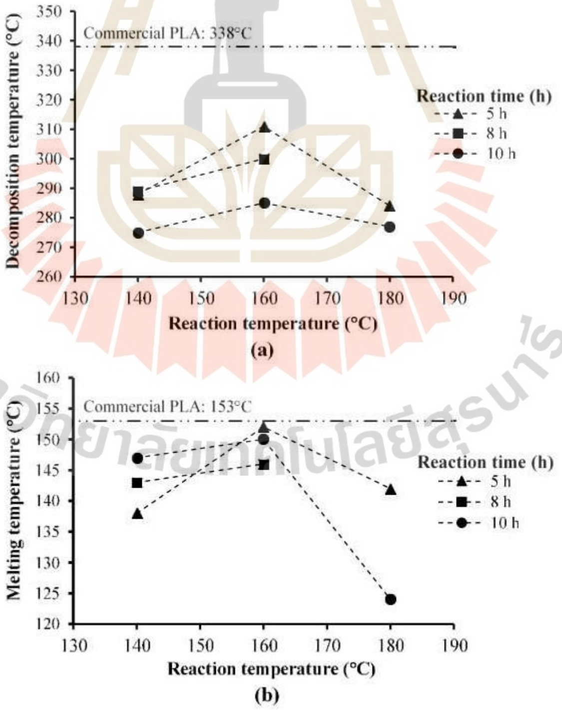


Figure 5. The decomposition and melting temperature of commercial PLA and synthesized PLA in different reaction temperature and time: (a) decomposition temperature and (b) melting temperature.

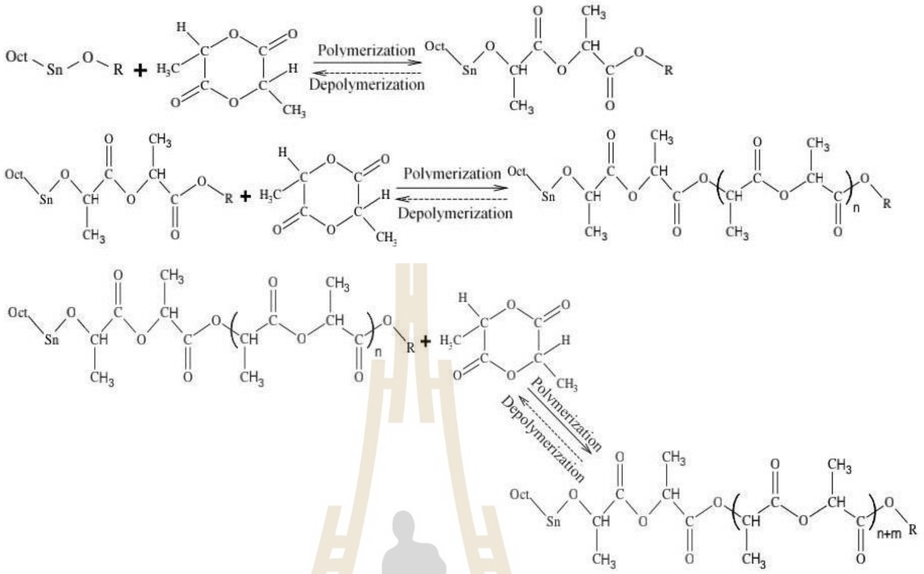


Figure 6. Synthesis of PLA through ROP of lactide with tin(II) 2-ethylhexanoate by coordination-insertion mechanism.

4. Conclusion

The tin(II) 2-ethylhexanoate was used as a catalyst in ring-opening polymerization of synthesized lactide with concentration of 0.4% (w/w) at a temperature of 160°C and reaction time for 5 h gave the highest yield PLA of 64.5% with its decomposition temperature of 311°C and melting point temperature at 152°C which is comparable to the commercial one. The reaction temperature and time are significant variables, there is a competition between polymerization and depolymerisation mechanisms occurring in reaction and each mechanism plays a major role with respect to the conditions. At higher reaction temperature and longer time, the rate of depolymerisation is higher than that of polymerization leading to the lower of decomposition and melting temperature of synthesized PLA.

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BIOGRAPHY

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