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THESIS

DIRECT MELT POLYCONDENSATION OF LACTIC ACID AND PLA MODIFICATION BY BLENDING

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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Synthesis of polylactic acid (PLA) by direct melt polycondensation (DMPC) using two cationic exchange resin catalysts (A and B) with 100 g, 1 kg and 10 kg of commercial lactic acid (LA) were studied. DMPC was carried out by varying the mole ratio, temperature and alternating between N_2 and reduced pressure for different time periods. It was found that PLA obtained from B has a higher $\overline{M}_W$ than A with 100 g of LA. The highest $\overline{M}_W$ of PLA obtained was from B = 113,000 with mole ratio of LA:B = 500:1 at 170^{o}C for 12 h. Thus catalyst B was chosen for carrying the PLA synthesis in 1 kg and 100 kg. $\overline{M}_W$ ~146,000 of PLA was obtained with mole ratio of LA:B = 500:1 at 180^{o}C for 24 h for 1 kg system when carrying the DMPC surrounding with dry ice atmosphere. Contrarily, only 13.0% of PLA with $\overline{M}_W$ = 87,000 was obtained with mole ratio of LA:B = 500:1 at 170^{o}C for 48 h for 10 kg system when carrying the DMPC surrounding with dry ice atmosphere.

Modification of PLA properties was carried out. It was found that % elongation was higher than pure PLA when blending PLA with polyethylene glycol (PEG) and polydioxolane (PDXL), thus PEG and PDXL can be used as plasticizers to toughen PLA. Using PEG and PDXL as compatibilizers in PLA/DF (duck feather fiber) blends shown although tensile strength (T.S.) and elongation at break (EB) of PLA/PEG/DF and PLA/PDXL/DF blends were higher than PLA/DF, they were still lower than pure PLA. Finally, the T.S. and EB of PLA blends with five impact modifiers; gloves latex (LT1), natural rubber latex (LT2), poly(*cis*-1,4-isoprene) (IR), poly(acrylonitrile-*co*-butadiene) (NBR) and poly (ethylene-*co*-vinyl acetate) (PEVA); confirmed that all impact modifiers had the capability to toughen PLA.

Student's signature Thesis Advisor's signature ___ / ___ / ___

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Nantharat Phruksaphithak

April, 2012

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LIST OF ABBREVIATIONS

ABS	=	poly(acrylonitrile-butadiene-styrene)
BuOH	=	butanol
BuLa	=	butyl lactate
CA	=	citric acid
CAGR	=	compound annual growth rate
DMPC	=	direct melt polycondensation
DSC	=	differential scanning calorimetry
Ea	=	activation energy
EB	=	elongation at break
FT-IR	=	fourier transforms infrared spectrometry
GPC	=	gel permeation chromatography
HDPE	=	high density polyethylene
LA	=	lactic acid
$\overline{M}_n$	=	number average molecular weight
$\overline{M}_w$	=	weight average molecular weight
NMP	=	1-methyl-2-pyrrolidone
NMR	=	nuclear magnetic resonance spectroscopy
MSA	=	methanesulfonic acid
PC	=	polycarbonate
PD	=	polydispersity index
PDXL	=	polydioxolane
PE	=	polyethylene
PEG	=	poly(ethylene glycol)
PET	=	polyethylene terephthalate
PHA	=	polyhydroxyalkanoate
PHB	=	poly(3-hydroxybutyrate)
PP	=	polypropylene
PLA	=	polylactic acid
PS	=	polystyrene

LIST OF ABBREVIATIONS (Continued)

PS-Sc	=	polymer supported scandium trifluoromethanesulfonate
PVC	=	poly(vinyl chloride)
ROP	=	ring opening polymerization
SP	=	solution polycondensation
SPLA	=	star-shaped polylactic acid
SSP	=	solid state polycondesation
T_c	=	crystalline temperature
T_g	=	glass transition temperature
TGA	=	thermogravimetric analysis
THF	=	tetrahydrofuran
T*max*	=	decomposition tempearature
T_m*max*	=	melting temperature
T_p	=	polymerization temperatures
T.S.	=	tensile strength

DIRECT MELT POLYCONDENSATION OF LACTIC ACID AND PLA MODIFICATION BY BLENDING

INTRODUCTION

Polymer in the form of plastic is a versatile material around us in everywhere, from simple items such as water bottle from polyethylene (PE), or from polyethylene terephthalate (PET); to more complex items in automobile parts such as fiber-reinforced thermoplastic composites from polypropylene (PP), polyamide-12 (PA-12 or nylon-12) or from poly(acrylonitrile-butadiene-styrene) (ABS)-reinforced with glass fiber. The reason such polymers have remained in popular uses is because they are strong and durable suitable for most applications. However, these everyday uses polymers, such as poly(propylene) (PP), poly(ethylene terephthalate) (PET), high density polyethylene (HDPE), poly(vinyl chloride) (PVC), polycarbonate (PC), are mainly based on petroleum, derived from oil, a nonrenewable resource. In 2009, around 230 million tones of plastics were produced, and consumed approximately 8 percent of world oil production: 4 percent as raw material and 3-4 per cent as energy for manufacture (Hopewell *et al*., 2009).

Because of the high cost of crude oil and problems of oil crisis at present, it is very costly due to large amount of energy is required to manufacture these plastics. In addition, these plastics are very difficult to decompose in natural environment and produce environmental impact such as landfill problems, water pollution, recycling problem, trash fields and flooding etc. In an effort to help preserve the environment and conserve energy, development of plastics based on renewable resources, a much more environmentally friendly and sustainable economy, as alternatives to replace the nonrenewable petroleum based polymers and to reduce the environmental and economic impact are growing rapidly and continuing to be an area of interest today. The demand for biodegradable plastics is reported to be growing by at least 30% each year (Leaversuch, 2002).

Generally, bio-based polymers can be classified into three main categories: 1) natural polymers from renewable resources, such as cellulose, starch and plant-based proteins; 2) polymers synthesized from natural monomers derived from renewable resources, for example, PLA (polylactic acid) from the fermentation of starch, corn or sugar; and 3) polymers produced by microorganisms, for example, PHA (polyhydroxyalkanoate) from bacteria through fermentation of sugar or lipids.

Many aliphatic polyesters such as poly(glycolic acid) (PGA); poly(lactic acid) (PLA); poly(3-hydroxybutyrate) (PHB); polyhydroxyalkanoate (PHA) and poly(ethylene glycol) (PEG) derived from renewable plant resources have been developed and are known to completely biodegrade by microorganisms such as bacteria, fungi and algae (Tokiwa and Noomhorm, 2006) as shown in Figure 1. After it was disposed into waste collection, these aliphatic polyesters are further composted easily to produce humus-like material, along with water, carbon dioxide and/or methane as shown from the closed life cycle of these aliphatic polyesters in Figure 2. These aliphatic polymers not only are biodegraded but also have good physical, chemical, mechanical, thermal and processing properties comparable with many commodity packaging thermoplastics from petroleum-based polymers. Biodegradable polymers end-use market growth is the strongest in the North America, Japan, and Europe, setting the pace of growth with a robust CAGR (Compound Annual Growth Rate) in excess of 6% over the period 2011 through 2015, for example, consumption in the biodegradable polymers end-use industry in Europe is projected to reach 6.7 thousand metric tons by the year 2015.

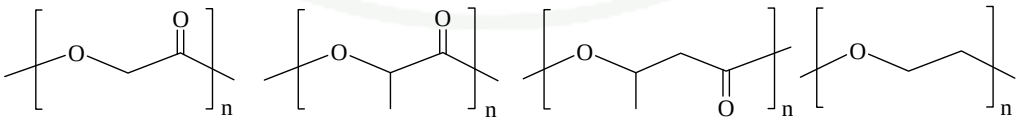


Figure 1 The structures of some examples of bio-based biodegradable polymers.

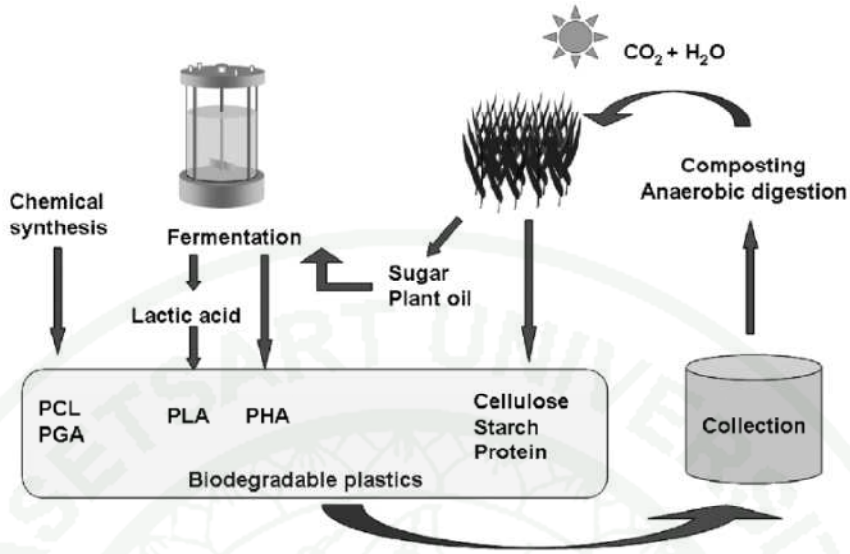


Figure 2 Production and degradation cycles for biodegradable plastics.

Source: Wang and Nomura (2010)

Among biodegradable polymers, polylactic acid (PLA) is at present one of the most promising biodegradable polymers has been developed so far to replace petroleum based polymers. It can be produced from renewable sources such as cassava, corn and sugarcane and has reasonable shelf life for most applications. The total degradation time of PLA is in few years. Figure 3 schematically showed the advantages of PLA among other plastics from renewable plants resources from the perspectives of material supply and industrial merits. It has good physical, mechanical and barrier properties comparable to those of commercial petroleum based polymers (Figure 4 and Figure 5). Tensile strength and flexural moduli of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS), but the izod impact strength and elongation at break are lower than those polymers. As the result, PLA is a stiff and brittle material. Moreover, it can be easily processed on standard plastics equipments to yield molded parts, film or fibers. PLA thus has found its numerous uses in packaging applications such as rigid packaging, loose-fill packaging, food packaging, compost bags, and others; in food and beverages such as disposable tableware and cups; in fibers and non-woven textiles, such as upholstery,

disposable garments, awnings, feminine hygiene products, and diapers; in medical devices such as sutures, stents, dialysis media and drug delivery devices etc.

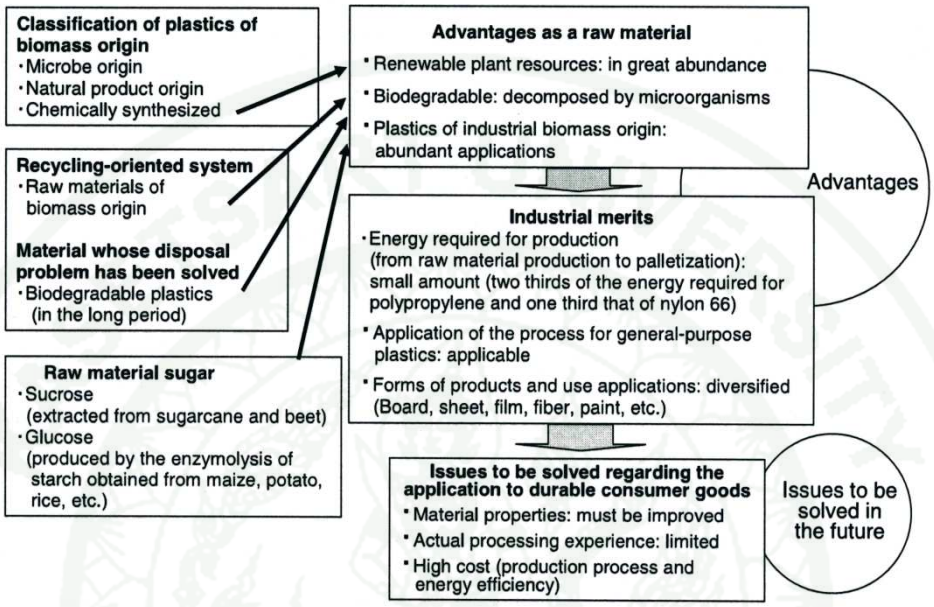


Figure 3 Advantages of PLA as an industrial material and issues to be solved.

Source: Kawamoto (2007)

The basic building block for production of PLA is lactic acid which was first isolated in 1780 from sour milk by the Swedish chemist Scheele and first produced commercially in 1881 (Hartmann, 1998). Lactic acid or 2-hydroxy propionic acid structure was established by Wislicenus in 1873. It is the simplest hydroxyl acid with an asymmetric carbon atom and exists in two optically active configurations: L-(+)- or (S)-lactic acid and D-(-)- or (R)-lactic acid (Figure 6). Lactic acid in the L(+)-isomer is produced in humans and other mammals whereas both the L-(+)- and D-(-)-enantiomers are produced in bacterial systems.

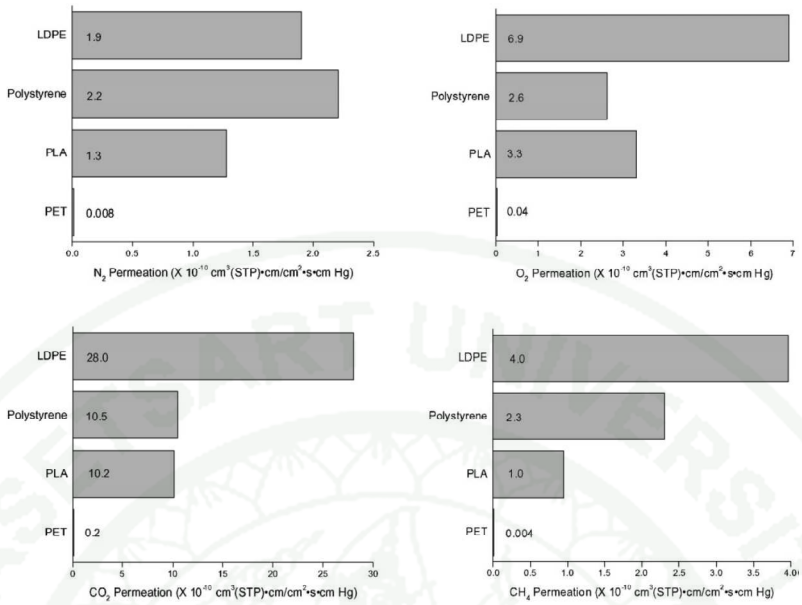


Figure 4 Permeation properties of 100% linear PLA having an L:D ratio of 96:4 compared to other common plastics at 30°C.

Source: Lehermeier *et al*. (2001)

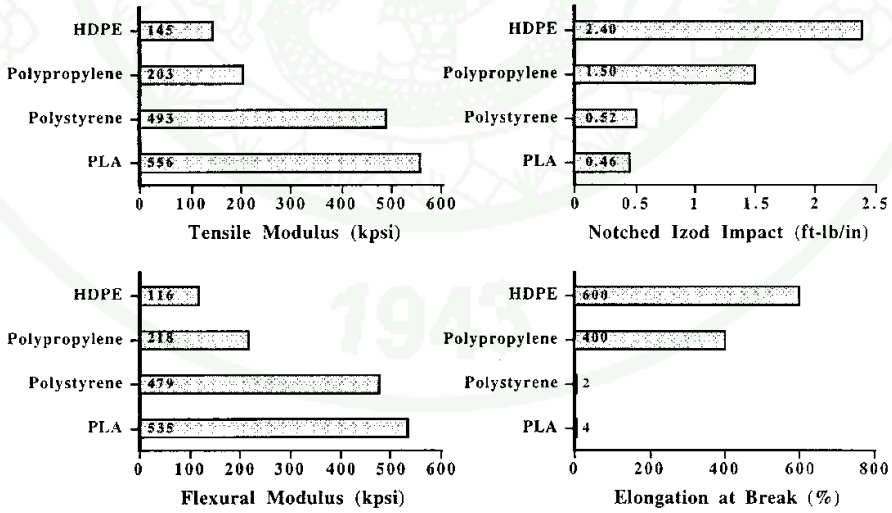
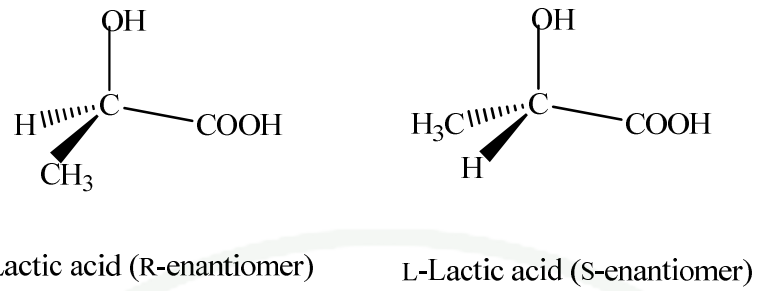


Figure 5 Comparison of mechanical properties of PLA with petroleum based thermoplastics.

Source: Dorgan *et al*. (2001)



D-Lactic acid (R-enantiomer) L-Lactic acid (S-enantiomer)

Figure 6 Stereoisomer of lactic acid.

In 1856, Louis Pasteur discovered *Lactobacillus* and its role in making of lactic acid. Lactic acid started to produce commercially by the German pharmacy Boehringer Ingelheim in 1895. Since then, the majority of the world's commercially production of L-form lactic acid is made by fermentation of carbohydrates from renewable resources using homolactic organisms such as various optimized or modified strains of the genus *Lactobacilli* which form greater than 90% of lactic acid. Thailand is the world's top producer and exporter of tapioca, derived from cassava, and its second biggest sugar exporter, two renewable resources in demand for the production of lactic acid, the precursor for production of polylactic acid. Annual production of cassava and sugarcane reached 30 million tons with around 8.3 million rais (1 rai = 0.16 hectares) of harvested area and 66.8 million tons with around 6.0 million rais of harvested area respectively in 2009 (Table 1). Recently, lactic acid production has been expanding rapidly due to the advancement of lactic acid fermentation which will dramatically reduce the production costs of highly purity lactic acid. The world market for lactic acid is projected to reach 259,000 tons by the year 2012 with an average 10% annual growth.

Table 1 Annual harvested area (1,000 rais) (1 rai = 0.16 hectare) and production (1,000 tones) of agricultural products in Thailand.

Year	Rice		Cassava		Sugarcane		Palm Oil	
	Harvested area	Product-ion	Harvested area	Product-ion	Harvested area	Product-ion	Harvested area	Product-ion
2001	63,284	28,034	6,558	18,396	5,481	49,563	1,518	4,097
2002	60,335	27,992	6,176	16,868	6,320	60,013	1,644	4,001
2003	63,524	29,474	6,386	19,718	7,121	74,259	1,799	4,903
2004	62,455	28,538	6,608	21,440	7,012	64,996	1,932	5,182
2005	63,906	30,292	6,162	16,938	6,670	49,586	2,026	5,003
2006	63,532	29,642	6,693	22,584	6,033	47,658	2,375	6,715
2007	66,681	32,099	7,339	26,916	6,314	64,365	2,664	6,390
2008	66,772	31,651	7,397	25,156	6,588	73,502	2,885	9,271
2009	68,519	31,508	8,292	30,088	6,023	66,816	3,189	8,162

Source: Office of Agricultural Economics (2010)

The manufacture of PLA from lactic acid was pioneered by Carothers in 1932 (Holten, 1971). PLA formed was of low molecular weight and thus possessed poor mechanical properties. Further work was investigated by DuPont and higher molecular weight PLA was obtained which was patented in 1954 (Lowe, 1954). Investigation and manufacture of PLA was discontinued due to the susceptibility to hydrolytic degradation of PLA at that time. The technology to produce PLA economically on a commercial scale has been intensively developed in the last two decades. There are two currently available pathways for synthesis of PLA (Figure 7). One step pathway by direct polycondensation of lactic acid and two steps pathway by a single catalytically esterified cyclization of two lactic acid molecules to form the cyclic lactide ester, and then ring-opening polymerization of dilactate ester to form polylactic acid, PLA.

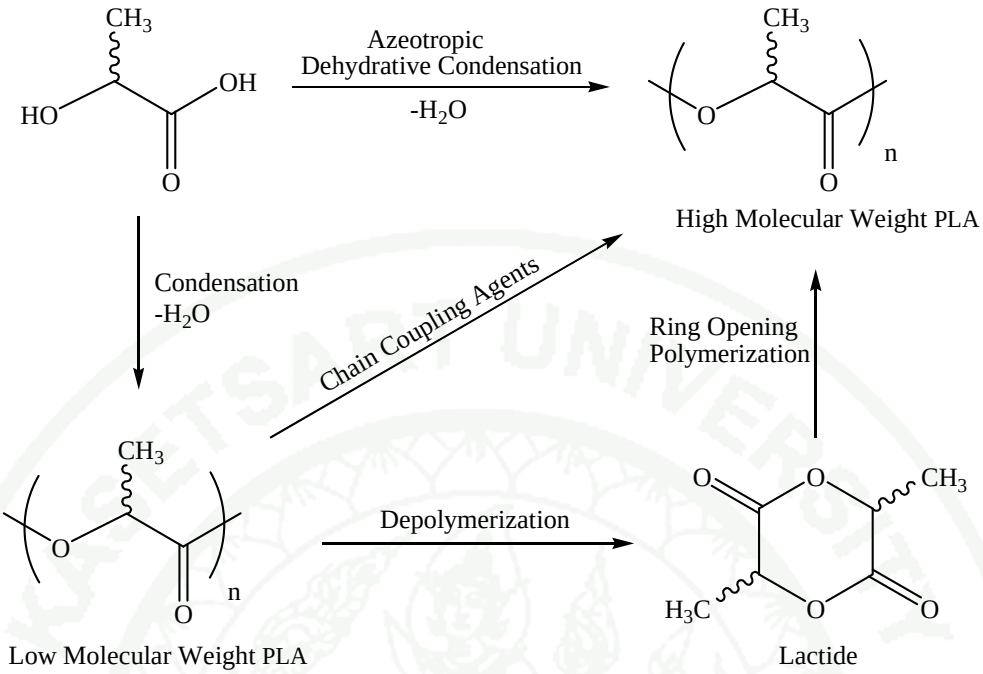


Figure 7 Pathways for synthesis of polylactic acid from lactic acid.

Most of the PLA synthesis has thus been developed extensively from the two step pathways processes since high molecular weight PLA can be easily produced. Although the first cyclization step in two step pathways generates water, but it can be separated prior to polymerization due to a significant drop in polarity. The cyclization into the dehydrated cyclic lactide ester dimer is conventionally done by increasing the temperature and lowering the pressure, and distilling off the produced lactide. Solution polymerization, bulk polymerization, melt polymerization and suspension polymerization are the various methods of ring opening polymerization (Nieuwenhuis, 1992). The polymerization mechanism can be cationic, anionic, coordination or free radical polymerization. It is catalyzed by compounds of transition metals such as tin, aluminum, lead, zinc, bismuth, iron and yttrium (Nijenhuis *et al*., 1992). The advantage of ring opening polymerization is that the chemistry of the reaction can be accurately controlled, thus varying the properties of the resultant polymer in a more controlled manner, but the addition step to from cyclic lactide ester has the disadvantage of increasing the production cost.

Instead, little attention has been directed toward the PLA synthesis via the one step direct polycondensation pathway process since only very low molecular weight, brittle and unusable PLA is obtained. Because of each polymerization reaction generates one molecule of water, the presence of which degrades the forming PLA chain to the point only very low molecular weight PLA is obtained. However, it has been reported that high molecular weight of PLA can be synthesized by one step polycondensation if appropriate azeotropic solvents are employed by means of the so-called azeotropic distillation technique. A large volume of high boiling point solvent compatible with PLA, multiple reactors, complex facilities together with high energy cost are needed for the removal of the dissociated water and the added solvent by this technique, make this technique less attractive. In addition, catalyst concentration, polymerization time and temperature cause profound effects on the polymer yield, molecular weight and optical rotation. The synthesis of PLA through directly polycondensation of the lactic acid monomer gave weight average molecular weights lower than 1.6×10^4, whereas ring opening polymerization of lactides gave average molecular weights ranging from 2×10^4 to 6.8×10^5 (Hyon *et al.*, 1997). Hence, PLA synthesis by one step direct polycondensation to form PLA with molecular weight comparable to the two steps ring opening polymerization must be overcome to be able for PLA to compete with the petroleum based polymers since it has the potential to drive the cost of PLA synthesis down from the addition step required in ring opening polymerization.

Total Thailand area is approximately 514,000 square kilometers (51.4 million hectares). Forty-one percent of the total land area is used for agricultural purposes, thirty-one percent is forest land and twenty-eight percent is unclassified land. Thailand is primarily an agricultural country. Although the country is in the process of industrialization, the agricultural sector still remains the important role in developing the Thai economy since more than one-third of population still earns their livings from agricultural sector. In addition, the two agricultural crops, cassava and sugarcane, used for the lactic acid production are the two major economic crops in Thailand. Technological knowledge advancements for PLA synthesis by one step

pathway and modification of PLA properties must be understood thoroughly to be able for Thailand to benefit from the available lactic acid as a whole.

The objectives of this thesis are focused mainly on the biodegradable polylactic acid, PLA, and are divided into two parts. The objective of the first part is to study the effects of factors such as catalyst, temperature and conditions in scaling up from a 100 g laboratory scale to a 10 kg scale for PLA synthesis by one step direct melt polycondensation. Although PLA exhibits a broad range of physico-chemical properties, its thermal and mechanical properties are not sufficient for use as ordinary structural materials. For improving these inferior properties, modification of PLA properties by blending with the goal to improve the properties while maintain the biodegradable properties is the objective of the second part. The effects of the natural polymers such as duck feather, natural rubber, impact modifiers and compatibilzer on the PLA blends are evaluated.

OBJECTIVES

This study is divided into two parts:

Part I: Direct melt polycondensation of lactic acid

The objectives of this part are:

1. To study factors and conditions for synthesis of PLA with 100 g of LA.
2. To study factors and conditions for synthesis of PLA with 1 kg of LA.
3. To design the reactor and study factors and conditions for synthesis of PLA with 10 kg of LA.

Part II: Modification of polylactic acid (PLA) properties by blending

The objectives of this part are:

1. To study the effect of polyethylene glycol (PEG) and polydioxolane (PDXL) as plasticizer on PLA/PEG and PLA/PDXL blends.
2. To study the effect of duck feather fiber (DF) on PLA/DF blends and the effect of PEG and PDXL as compatibilizer on PLA/PEG/DF and PLA/PDXL/DF blends.
3. To study the effect of four rubbery impact modifiers: household gloves latex (LT1), concentrated natural rubber latex (LT2), poly(*cis*-1,4-isoprene) (IR), poly(acrylonitrile-*co*-butadiene) (NBR) and one eco-friendly, non toxic and biodegradability polymer impact modifier: poly(ethylene-*co*-vinyl acetate (PEVA) on the PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA blends.

LITERATURE REVIEW

Part I: Direct melt polycondensation of lactic acid

Biodegradable polymers from renewable bio-based resources are being investigated as alternatives to replace non-degradable petroleum based synthetic polymers to reduce the impact on the environments. Polylactic acid (PLA) has the greatest potential to meet this purpose since the raw material, lactic acid for production of PLA, can be produced directly by microbial fermentation of renewable bio-based resources. Thus, extensive researches in synthesis, properties and applications of PLA have received wide attention both in academic and industrial sectors around the world.

1. Synthesis of polylactic acid (PLA)

Polylactic acid (PLA) is commonly made from α-hydroxy acids, lactic acid. The structural formula of PLA is show in Figure 6. It is one of the few polymers in which the stereochemical structure can easily be modified by polymerizing a controlled mixture of L- or D- isomers to yield high molecular weight amorphous or crystalline polymers. The L- form differs from the D- form by its effect on polarized light (Jahno *et al*., 2007).

At present there are two possibly pathways currently available for synthesis PLA from lactic acid monomer either from one step pathway by direct polycondensation (PC) or azeotropic dehydration condensation of lactic acid, or two steps pathway by cyclization of lactic acid to form the cyclic dimer, lactide, and then ring opening polymerization (ROP) of lactide (Figure 8). Table 2 lists the advantages and disadvantages of these pathways (Maharana *et al*., 2009). Many other alternative synthesis pathways have been suggested to avoid the drawbacks of these pathways, such as melt polycondensation and sequential melt-solid polycondensation and post polycondensation.

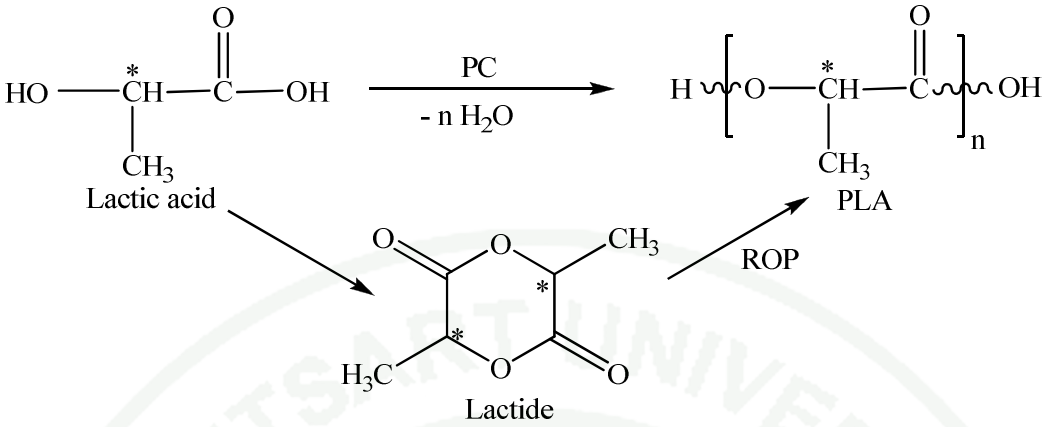


Figure 8 Synthesis pathways of PLA by direct polycondensation (PC) or ring opening polymerization (ROP).

1.1 Ring-opening polymerization (ROP) of lactide

Ring-opening polymerization of lactide obtained from lactic acid is a commonly pathway to produce polylactic acid commercially. ROP has been carried out by solution polymerization, bulk polymerization, melt polymerization and suspension polymerization. High molecular weight PLA is produced by ring-opening of lactide obtained by decomposition of low molecular weight PLA. The ring-opening polymerization route includes polycondensation of lactic acid followed by depolymerization to the dehydrated cyclic dimer of lactide (3, 6-dimethyl-1-4 dioxane-2,5-dione), which then undergo ring-opening polymerization to produce high molecular weight PLA with good properties and is widely used (Figure 9) (Maharana *et al.*, 2009). The depolymerization step is conventionally done by maintaining the temperature between 150^{o}C and 220^{o}C, lowering the pressure to ≤266.6 Pa, and then distilling off the produced lactide. Due to the stereo-forms of lactic acid the corresponding optically active lactide can be found in three different version, i.e. D,D-lactide, L,L lactide and D,L-lactide (meso-lactide) (one D- and L-lactic acid molecule).

Table 2 Advantages and disadvantages of different pathways for PLA synthesis.

Pathways	Methods	Advantages	Disadvantages
ROP	Solution Polymerization Bulk polymerization Suspension polymerization	(i) Chemistry of the reaction can be accurately controlled thus the properties of the resultant PLA can be varied in a more controlled manner (ii) $\overline{M}_W$ varies from $2x10^4$ to $6.8x10^6$ Da	(i) Higher cost of production due to the complicated purification process of the lactide (ii) Azeotropic distillation of solvent used (iii) High cost prevents commodity applications
PC	Solution PC Bulk PC Melt PC	(i) High $\overline{M}_W$ can be achieved (ii) Provides low production cost	(i) Hard to remove solvent completely from the end product (ii) Substandard mechanical properties (iii) Competitive reaction of lactide formation and simultaneous degradation process at high temperature (iv) Difficulty in driving the dehydration equilibrium to the direction of esterification (iv) Use of solvents results in complex process control, leading expensive PLA

Table 2 (Continued)

Pathways	Methods	Advantages	Disadvantages
			(vi) Inability of formation of PLA with a sufficient high molecular weight
			(vii) Severe increase in melt viscosity
			(viii) By products are formed
Post PC	Melt modification Solid state PC Radiation	(i) High $\overline{M}_W$ can be achieved (ii) Simple process (iii) Low investment (iv) Low cost of the operation (v) Easy handing (vi) Suppression of undesirable side reactions and hence produces higher purity PLA (vii) Cross linking increases heat resistance (viii) Less energy requirement	(i) May require external agent (example water tolerant catalyst and molecular sieve) (ii) Purification of lactide (iii) Low reaction rate (iv) Solid particle processability problems arising from sintering

Source: Maharana *et al*. (2009)

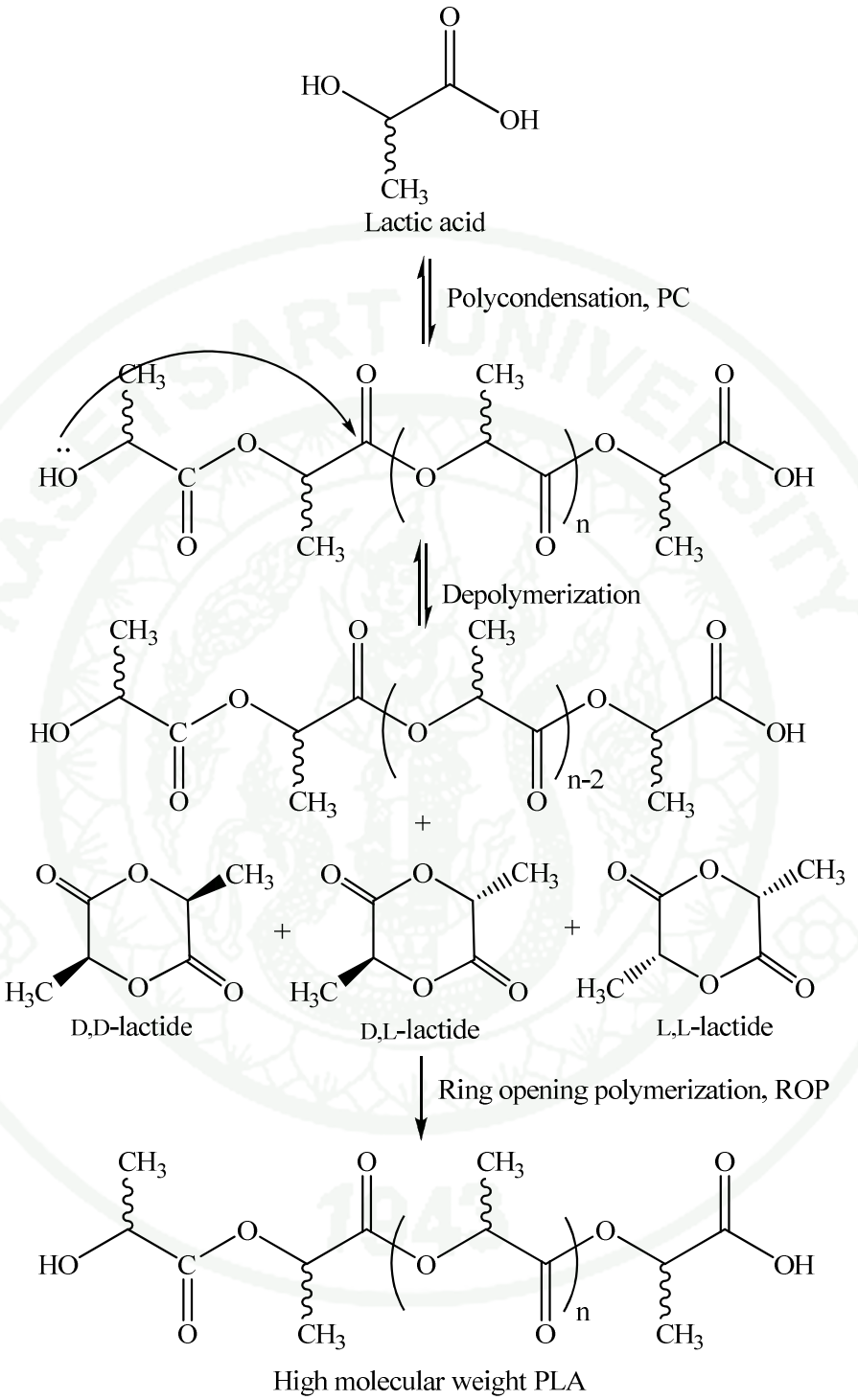


Figure 9 Polycondensation of lactic acid followed by depolymerization to the dehydrated cyclic dimer of lactide and then undergo ring-opening polymerization to produce high molecular weight PLA.

The ring-opening polymerization can be catalyzed by transition metal compound of tin, aluminum, lead, zinc, bismuth, iron and yttrium. Of these, tin(II) compounds are frequently used and considered to be most efficient. For example, ROP of lactide with tin (II)-2- ethylhexanoate ($Sn(CH_3)_2CH(C_2H_5)CO_2$) or $Sn(Oct)_2$) catalyst with catalyst concentration 100-1000 ppm gives PLA having molecular weight up to 10^6 Da at 140-180^oC in 2-5 h. Ring opening occurs under milder reaction conditions, and it sometime proceeds as a "living" manner, that is without side reaction to give polyester of controlled molecular weight. Although ROP produces high molecular weight PLA with high yield, it has also some disadvantages as shown in Table 2.

The mechanism of ring-opening polymerization (ROP) can be through cationic, anionic, coordination of free radical polymerization depending on the catalysts as followed (Kricheldorf, 2001).

1.1.1 Cationic mechanism

The cationic mechanism consists of a protonation or alkylation of the carbonyl O-atom, (exocyclic oxygen) with the consequence of an electrophilic activation of the O-CH bond. This bond is then cleaved by the nucleophilic attack of another monomer, a process which is repeated in every propagation step until a monofunctional nucleophile (e.g., water) causes a termination step (Figure 10). This mechanism involves a nucleophilic substitution at the chiral carbon, and it was found that optically pure poly(L-lactide) can be prepared only at temperatures ≤50°C. At higher temperatures the cationic polymerization causes more or less racemization, which dramatically changes the physical and mechanical properties of the resulting polylactide. Unfortunately, the cationic polymerization is rather slow below 50°C and only yields low to moderate molecular weights, and thus, this polymerization method is not attractive from the preparative point of view.

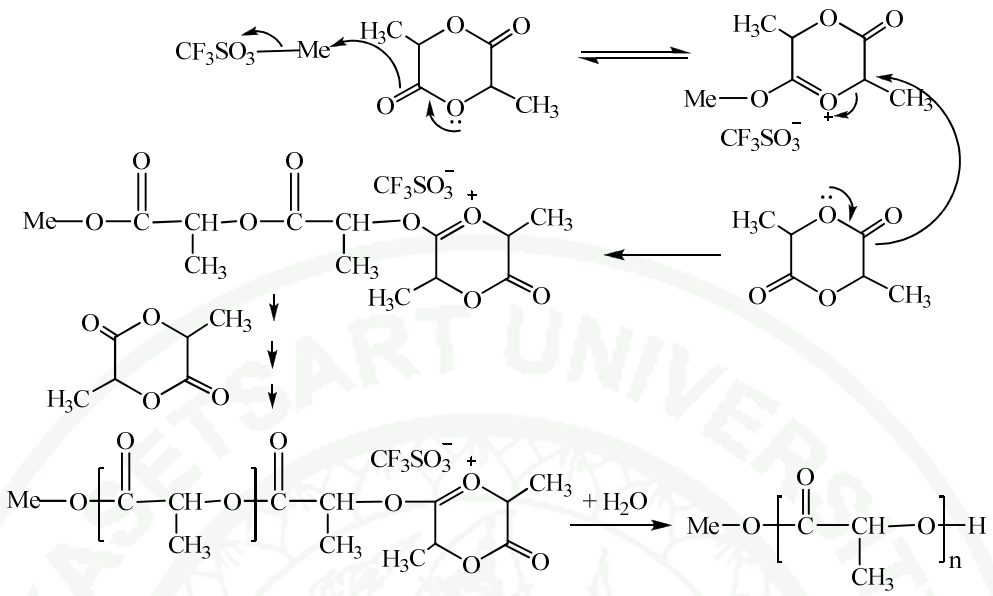


Figure 10 ROP via cationic mechanism for PLA synthesis.

1.1.2 Anionic mechanism

The anionic polymerization of lactides is best initiated by alkali metal alkoxides, but at higher temperatures phenoxides and carboxylates are also active. Both the initiation and the propagation step consist of a nucleophilic attack of an anion onto the CO-group of the lactide, followed by the cleavage of the CO-O bond. Therefore, the chain growth proceeds via an alkoxide, which is so basic that is, can also deprotonate the monomer in α-position (Figure 11). Due to the planarity of the delocalized anion this deprotonation/reprotonation reaction involves racemization. Hence, racemization is an unavoidable side reaction of anionic polymerization. Racemization, is, of course, no problem, when rac-, D,L-lactide is used as monomer. However, the lactide anion is also capable of initiating a new chain, and thus, the deprotonation of the monomer may involve a chain transfer process. The consequence is low to moderate molecular weight PLA is produced.

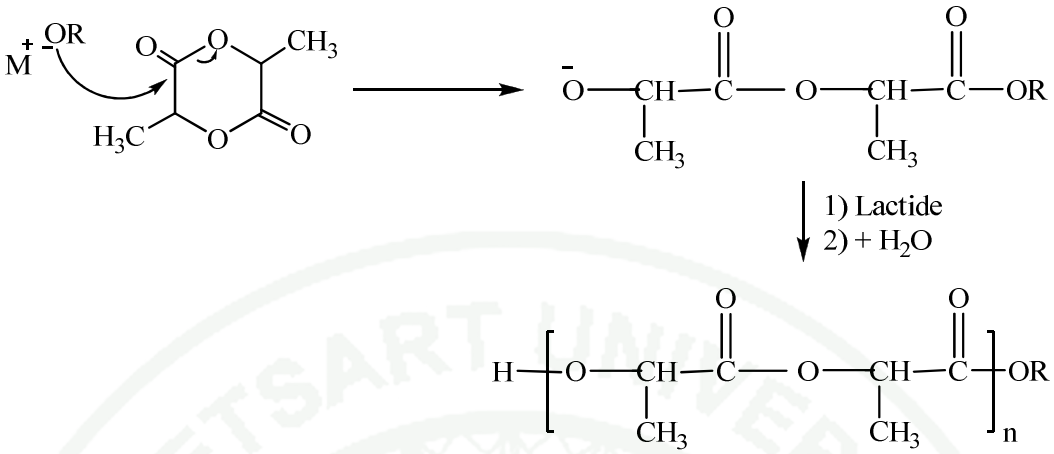


Figure 11 ROP via anionic mechanism for PLA synthesis.

1.1.3 Coordination mechanism

The third polymerization method, called coordination-insertion mechanism, is based on metal alkoxides having a covalent metal-oxygen bond and the character of weak Lewis acids. The lactide plays temporarily the role of a ligand coordinated with the metal atom via the carbonyl O-atom. This coordination enhances the electrophilicity of the CO-group and the nucleophilicity of OR-groups, so that an insertion of the lactone into the metal O-bond may occur. Typical initiators of this mechanism are the alkoxides of magnesium, aluminum, tin, zirconium, titanium and zinc. These initiators are usually prepared and applied as neat and pure compounds. However, in the case of diethyl zinc or triethyl aluminum it is a convenient and useful method to prepare the initiators in situ by reaction with alcohols or phenols (Figure 12).

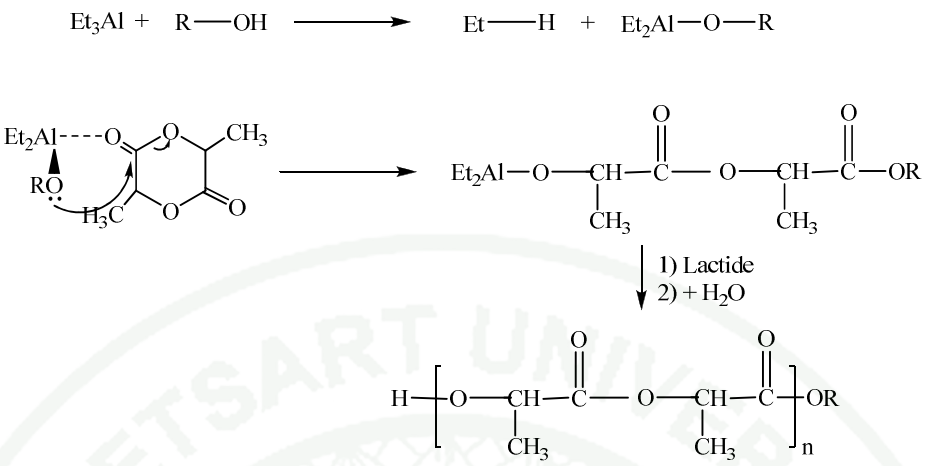


Figure 12 ROP via coordination mechanism for PLA synthesis in the reaction of triethyl aluminum with alcohol.

In summary, the coordination-insertion initiators are for preparative purposes and far more useful than ionic initiators. The most widely used initiator for the technical production of polylactides is Sn(II)-2-ethylhexanoate (usually abbreviated as $Sn(Oct)_2$). In the neat and pure state this tin compound does not contain a reactive alkoxide group. Recent mechanistic studies of several research groups have now demonstrated that the alcohol usually added as coinitiator substitutes at least one octanoate group in a rapid equilibration, and the resulting Sn-alkoxide is then the true initiator of the polymerization process (Figure 13). However, at temperatures above 150°C the initiation process is somewhat different.

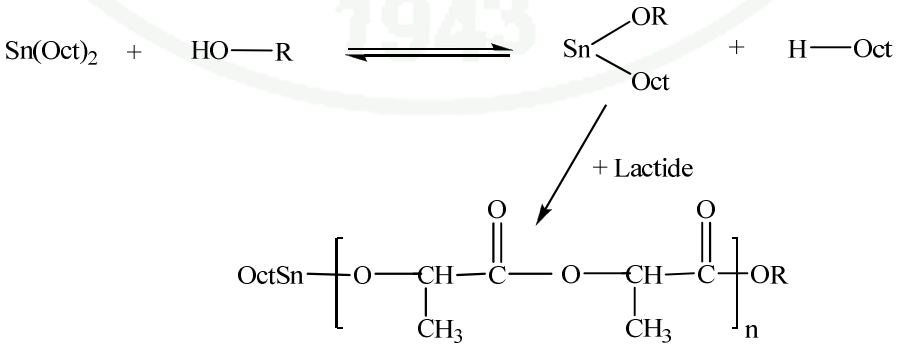


Figure 13 ROP via coordination mechanism in the reaction in the reaction of $Sn(Oct)_2$.

1.2 Polycondensation of lactic acid

1.2.1 Direct polycondensation

In comparison with the well-established method for the catalytic ring-opening polymerization of L-lactide, the direct dehydropolycondensation of L-lactic acid has received much less attention. Direct condensation polymerization or polycondensation of lactic acid yields PLA and condensate water as a byproduct. Thus, two reaction equilibria: (1) dehydratation equilibrium of esterification and (2) ring-chain equilibrium involving the depolymerization of PLA to lactide as shown in Figure 14 (Zhang and Wang, 2008). It was believed that high molecular weight PLA could not be achieved by the direct polycondensation of LA because of the difficulty in driving the dehydration equilibrium in the direction of esterification, which is the requirement for the formation of sufficient high molecular weight PLA. However, direct polycondensation of lactic acid (LA) performed in bulk polycondensation by distillation of condensate water with or without a catalyst while vacuum and progressively increasing the temperature has been known to produce polylactic acid with low molecular weight (in the order of only ~10^4 g/mol) due to the unfavorable reaction equilibrium constant. As the result, the key disadvantage for the direct polycondensation, is that PLA obtained has too low molecular weight to be used as a useful material because it hard to remove water completely from the severe increase of melt viscosity and higher operating temperature is required (Chen *et al*., 2006). To overcome this advantage, direct polycondensation of LA with high molecular weight is obtained by manipulating the equilibrium using either an organic solvent in azeotropic dehydration condensation or a multifunctional branching agent. Direct polycondensation with multifunctional monomers was done, for example, with dipentaerythritol to form a star shape polymer, and with diols or diacids to form telechelic prepolymers and further produced high molecular weight polymer with diisocyanate or bis(amino-ether). These polymers show similar behavior to PLA homopolymers prepared by ROP.

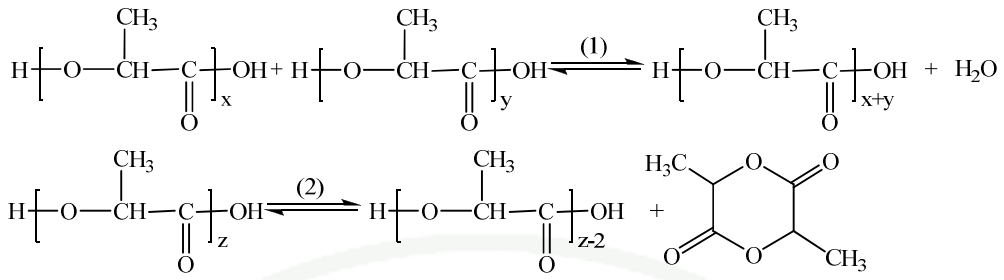


Figure 14 Two reaction equilibria involving in direct polycondensation.

Different strategies have also been investigated to provide the high molecular weight PLA by direct polycondensation. The low molecular weight PLA obtained by PC can be processed further by various post-polycondensation e.g. melt modification, radiation induced cross-linking and solid-state PC to obtain high molecular weight PLA. The PLA obtained after polycondensation, forms a homogeneous supercooled state with a monomer ratio more than 5 wt%. During post polymerization process, crystallization of PLA occurs. In addition, the monomer consumption reaches 100% as the monomer and catalyst are concentrated in the amorphous part.

1.2.1.1 Melt modification

Low molecular weight PLA can be modified by radical reactions using peroxides. Peroxide melt modification of PLA causes drastic changes in a number of properties. Branching has been suggested to be the dominating structural change in PLA at peroxide contents in the range of 0.1-0.25 wt% and also cross-linking at peroxide additions above 0.25 wt% (Sodergard, 1998). The peroxide reaction increases the melt strength. Further, the tensile modulus is reduced and a more flexible material is obtained.

1.2.1.2 Radiation induced cross-linking PLA

Low molecular weight PLA can be irradiated using electron beam in the presence of polyfunctional monomer such as triallyl isocyanurate

(TAIC), trimethallyl isocyanurate, trimethylol propane trimethacrylate, 1,6-hexanediol diacrylate, ethylene glycol, etc. as cross-linking agents. Cross-linking of PLA by high energy radiation, increases the degree of cross-linking as function of radiation dose, and manipulates the mechanical properties of PLA. Cross-linked PLA is transparent and has heat resistance above 200^{o}C. Thus, cross-linking is beneficial in expanding the applications of PLA.

1.2.1.3 Solid-state polycondensation (SSP)

Solid-state polycondensation (SSP) appears to be an effective route for PLA synthesis when compared with ROP and direct polycondensation. SSP increases the degree of polymerization considerably, and thus can increase the molecular weight of polycondensate up to 20 times. It is simple, easy to handle, and because of the lower reaction temperature compared with melt polycondensation, does not promote side reactions. SSP involves both chemical and physical steps. In SSP, a semicrystalline solid PLA prepolymer, of relatively low molecular weight is heated to a temperature below T_m but above T_g (to improve mobility and subsequent reaction of the end groups) in the presence of a suitable catalyst. SSP takes place in the amorphous region of the polymer, where all the reactive end groups reside. Since SSP starts at much lower temperature, compared to polymerization in the molten state or in the solution, the reaction temperature can range from sufficiently below T_m to just 5-15^{o}C above T_g. The T_m of PLA is ~175^{o}C. Although SSP takes a considerably longer time, very high molecular weight PLA can be obtained, which cannot be accomplished in melt or solution polymerization due to the viscosity restrictions and hydrolytic, thermal and oxidative degradation.

1.2.2 Azeotropic dehydration condensation

The azeotropic dehydration condensation is one method that can be used to obtain high molecular weight PLA. The azeotropic dehydration condensation developed by Mitsui Toatsu Chemicals in 1994 (Enomoto *et al.*, 1994). This method can afford PLA with molecular weight greater than 300,000 after long reaction time.

Solvents with high boiling point are used for the removal of water. The efficiency removal of water using solvents with boiling point above 130°C displayed in Figure 15. It showed that the polymerization rate increase related with the increasing of the solvent boiling point due to the more efficient removal of water. (Ajioka *et al.*, 1995)

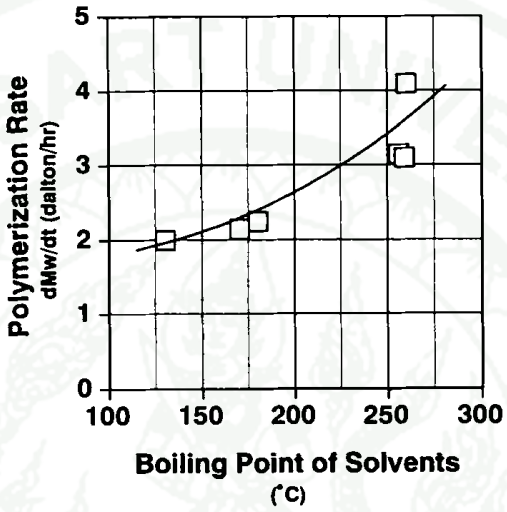


Figure 15 Polymerization rate of various high boiling point solvents in solution polycondensation of lactic acid.

Takasu *et al*. (2003) reported that scandium trifluoromethane-sulfonate [$Sc(OTf)_3$ and trifluoromethanesulfonimide [$Sc(NTf_2)_3$], and polymer-supported scandium trifluoromethanesulfonate (PS-Sc) as Lewis acid catalysts are effective for one step dehydration polycondensation of lactic acid. Bulk polymerization of lactic acid was carried out at 130°C-170°C to give PLA with molecular weight of 51,000-73,000. However, solution polycondensation was performed at 135°C for 48 hour with molecular weight of 10,000. The catalysts can be recovered after the reactions and reused. In addition, scandium is not categorized as heavy metal.

In 2005, Shyamroy *et al*. investigated the synthesis of low molecular weight of 45,000 of lactic acid polymers obtained through the dehydropolycondensation of L-lactic acid. Polymerizations were carried out in

solution with solvents (xylene, mesitylene, and decalin), without a solvent using different Lewis acid catalysts (tetraphenyl tin and tetra-*n*-butyldichlorodistannoxane), and at three different polymerization temperatures (143, 165, and 190°C). Dehydropolycondensation is performed in the absence of a solvent, some linear polymer is also obtained and oligomer crystallinity varied depending on the nature of the catalyst and solvent.

In 2010, Marques *et al.* studied the polymerization of L-lactic acid in solution using two high boiling point organic solvents, anisole and *m*-xylene. Tin (II) chloride dihydrate, $SnCl_2.2H_2O$ was the best catalysts tested as it allowed achieving PLA with molecular weight close to 80,000 g mol^{-1}. However, the stereoregularity control is a severe problem due to the transesterification reactions, which lead to an inversion of the conformation and a decrease of the optical purity of the polymer.

1.2.3 Melt-solid polycondensation

Another approach to synthesize PLA by polycondenation is melt-solid polycondensation. This approach can increase the molecular weight of PLA by first carrying polycondensation by melt to obtain a prepolymer and following by solid state polycondensation (SSP) (Figure 16). Xu *et al*. (2006) first prepared PLA prepolymer with a molecular weight of 18,000 by the ordinary melt polycondensation, crystallized at 105^{o}C for different time periods, and then heated at 135^{o}C for 15-50 h for further solid-state polycondensation. The results showed that the molecular weight reached at a maximum value for a crystallization period of 30 min and SSP of 35 h.

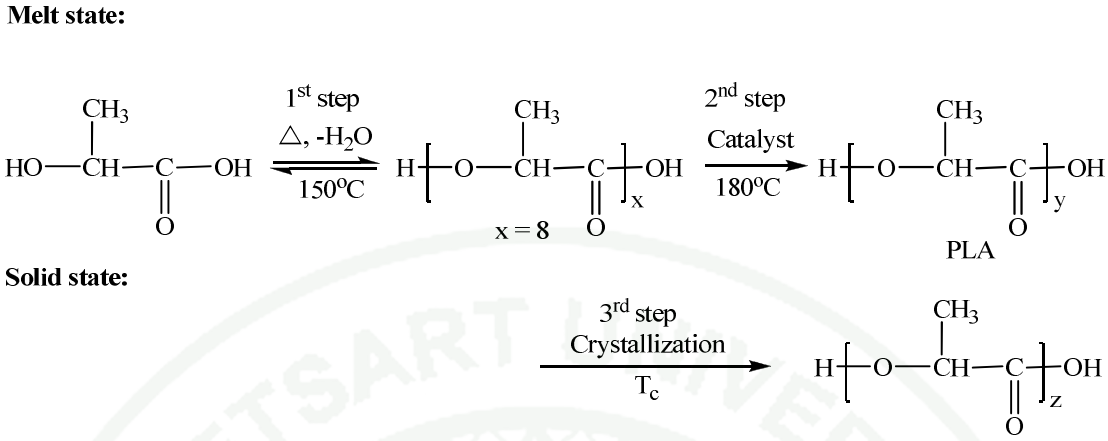


Figure 16 The overall process of melt/solid polycondensation of lactic acid.

Moon *et al*. (2001) have succeeded in preparing high polymer of poly(L-lactic acid) (PLLA) by the melt/solid polycondensation of L-lactic acid (LA) catalyzed by a tin chloride dihydrate/*p*-toluenesulfonic acid binary system. In this process, a polycondensate with a molecular weight of 20,000 Da is first prepared by ordinary melt-polycondensation, crystallized by heat-treatment around 105°C, and heated at 140 or 150°C for 10–30 h for further polycondensation. A high-quality polymer of PLLA can be obtained in high molecular weight exceeds 500,000 Da in a relatively short reaction time.

The keys basic steps leading to synthesize high molecular weight PLA by melt-solid polycondensation are as followed:

1.2.3.1 Dehydration

Commercial grade LA, used for PLA synthesis by polycondensation reaction, contains about 80–95 wt% L-LA (LLA) along with 10–15% water, D-LA (DLA) and other impurities. During polycondensation water is also produced and thus, for the forward reaction to proceed, the water molecules must be removed from the reaction product mixture as quickly as possible. This necessitates the removal of water from the raw material, LA, before the commencement of the reaction and is carried out during the dehydration step. This includes heating LA

under nitrogen at a temperature from 100 to 150°C under a pressure of 1000–2000 Pa to reduce the residual water content to 1–2%. The dehydration step is carried out under continuous flow of N_2 gas, removal of water vapor will be comparatively more rapid by helping to drive out water molecules. The complete dehydration process is carried out in a series of steps involving different temperatures, pressures and dehydration time periods. For example, LLA is first heated at constant temperature of 150°C at atmospheric pressure for 2 h; then the pressure is reduced to 100 mmHg and heating is continued for another 2 h at the same temperature; and finally the pressure is reduced to 30 mmHg (abs) and the sample is heated again for another 4 h without changing the temperature. (Moon *et al*., 2000; Moon *et al*., 2001; Lee *et al*., 2005; Chen *et al*., 2006). Dehydration is done in stepwise manner to expel water in a controlled way. However, single-step dehydration is not uncommon, Chen *et al*. (2006) carried out one-step dehydration at 100^{o}C for 1 h at 760 mmHg (abs). During dehydration, oligo(L-lactic acid) was obtained with a degree of polymerization varying from 8 to several hundred.

1.2.3.2 Esterification

In this step, LA is converted into PLLA along with the formation of water molecules as a byproduct. As the reaction product contains water it is imperative that the catalyst should be water–tolerant to get a better yield and high molecular weight. Some investigators have employed water tolerant catalysts so that the degree of polymerization is not affected. Appropriately substituted distannoxane catalysts are found to be hydrophobic due to the presence of bulky alkyl groups around the tin atoms and, therefore, can act as water-tolerant catalysts. The esterification reaction is generally carried out at 180^{o}C under a pressure of 30 mmHg (abs). Higher temperature increases the vapor pressure of water and helps water molecules to escape from the polymer melt and thereby enhances the rate of the forward reaction. The reduction of pressure also helps the water removal process. (Maharana *et al*., 2009)

1.2.3.3 Decompression

This step appears to be trivial but experimentation shows that it helps in achieving high molecular weight PLLA. Little information is available on the suitability of this step. The decompression time may range from 3 to 7 h in which pressure decreases from 30 to 1 mmHg. It appears that the decompression step also removes water formed during polycondensation and thereby enhances the rate of reaction. In fact, decompression can increase the molecular weight from 30,000-130,000 Da in the case of a titanium(IV) butoxide (TNBT) catalyzed polycondensation reaction (Chen *et al*. 2006).

1.2.3.4 Melt polycondensation

The polycondensation of lactic acid depends on two thermodynamic equilibriums: the dehydration/hydration equilibrium for ester formation and ring/chain equilibrium for depolymerization to lactide formation. Melt polycondensation is carried out above T_m of PLLA, as at this temperature the lactide formed is evaporated to produce a high yield of polymer.

1.2.3.5 Heat treatment

Heat treatment is done around the crystallization temperature (T_c) of PLLA. In this step the PLLA, which is in the form of white solid polycondensate, is crushed into granules and is put into a test tube which is then heated in vacuum at approximately 105°C for 1-2 h. Since the crystallization exotherm is known to extend from 100 to 107°C, the melt polycondensate is heated at 105°C to crystallize the PLLA. It has been reported that the extent of crystallinity is 29 and 30% after 1 and 2 h, respectively. The product, after heat treatment, becomes resistant to fusion, even when heated at a higher temperature. Further, it did not reveal a crystallization exotherm in the DSC curve, which showed only a melting endotherm at 158°C. In the process of crystallization, both monomer and catalyst are segregated in the amorphous region of PLLA. This helps the polymerization reaction to take

place, even in the solid state, to allow the yield to reach 100%. Moon *et al*. (2001) reported that during heat treatment, the molecular weight of polylactic acid increased from 13,000 Da to 15,000 Da.

1.2.3.6 Solid state polycondensation

Although the reaction rate is usually slow in solid state reactions, increase in crystallinity does not hinder the dehydration reaction significantly. Solis state polycondensation (SSP) is generally carried out above T_g to enhance the molecular translational mobility within the amorphous regions of semicrystalline polymers, while the crystalline regions retain the geometrical shape of the polymer during polymerization. It is reported that in moving from the melt polycondensation step to the heat treatment step molecular weight increases by 1.5 times and again increases by 44.7 times in proceeding from the heat treatment step to SSP step.

1.2.3.7 Catalyst

The catalysts selected for the PLA synthesis should be compatible with its applications. The effect of such catalysts such as transition metal compounds or a combination consisting of transition metal compound along with protonic acid for the synthesis of PLA in melt-solid polycondensation were reported (Table 3). Tin compounds are found to be effective for high molecular weight PLA. Inorganic tin compounds are less toxic than organotins and tin(IV) compounds are less toxic than tin(II) compounds. Thus, inorganic tin will be a better choice as a catalyst in comparison to organotins. Toxicity increases with increasing tin concentration. Tetraphenyltin is a catalyst approved by FDA and therefore, can be used safely for synthesis PLA for biomedical applications. On the other hand, although tin(II) octanoate is the most effective catalyst for the production of high molecular weight PLA with high yield, it is difficult to remove from the PLA, which can lead to cytotoxicity and thus limits its applications.

Table 3 Effects of catalysts on the molecular weight of PLA.

Catalyst	Molecular weight of PLA				
	10^4	10^5		10^6	
Protonic acid	H_3PO_4	H_2SO_4			
	Nafion-H	MSA		*p*-TSA	
Metal compounds					
Metals	Mg Ti Al	Zn			Sn
Oxides	Sn^{IV} Ti^{IV}	Zn^{II}		Sb^{II}	Sn^{II}
Halides	Ge^{IV} Zr^{IV}	Zn^{II}		Sn^{IV}	Sn^{II}
Organic acid salts	Cu^{II} Al^{III}	Mn^{II} Zn^{II}	Y^{II}	Co^{II} Fe^{II}	Sn^{II} Ni^{II}
Others	$Al(iPrO)_3$	Ti(acac)			
		$Ti(BuO)_4$			
Binary catalyst		Sn^{II}- *p*-TSA			

Catalyst conc: 0.5 wt% on polymer, acac: acetylacetonate anion, MSA: methane sulfonic acid, Nafion-H: perfluorinated resin sulfonic acid, *p*-TSA: *p*-toluene sulfonic acid.

Source: Ajioka *et al.* (1995)

1.2.3.8 Kinetics and reaction mechanism of melt-solid polycondensation

Polycondensation of lactic acid is a reversible process, and in order to prepare a high molecular weight polymer the equilibrium constant of condensation (K_c) has to be high enough. The polycondensation rate depends on both chemical (chemical reaction) and physical processes (heat treatment, crystallization). The possible rate-determining steps are (i) chemical reaction control (a reversible chemical reaction), (ii) interior diffusion control (diffusion of the volatile reaction

products in the solid polymer and (iii) surface diffusion control (diffusion of the volatile reaction product from the surface of the polymer to the surrounding inert gas). Depending on the process and operating variables, the rate of SSP is controlled by one or more of these steps as shown in Figure 16. Vouylouka *et al*. (2005) concluded that there was no universal agreement on the relevant chemical kinetic expressions for SSP. The kinetic analysis showed that the rate of monomer consumption is inversely proportional to the square of the amorphous ratio of PLA, defined as the reciprocal of the crystal ratio, or the fraction of the polymer which is crystalline.

1.3 Selection of catalyst for PLA synthesis

The effect of catalysts for the synthesis of PLA had been investigated. For example, Marques *et al.* (2010) used $SnCl_2 \cdot 2H_2O$ as catalyst for solution polymerization of lactic acid as it provided PLA with molecular weight close to 80,000. Sedlarik *et al.* (2010) showed that methanesulfonic acid produced low molecular of PLA in direct melt polycondensation. Very few investigators have studied the effect of binary catalysts. Zhang and Wang, (2008) studied by using $SnCl_2 \cdot 2H_2O$/TSA, $SnCl_2 \cdot 2H_2O$/succinic anhydride, and $SnCl_2 \cdot 2H_2O$/maleic anhydride as binary catalysts and found that the catalysts had high effect on producing high molecular weight PLA of more than 120,000. However, catalysts for the production of high molecular weight PLA with high yield are homogenous catalyst which are miscible with reaction medium, therefore, it is difficult to remove these catalysts from the polymer in addition strong acid catalyst also cause corrosion to the equipments (Lilja *et al*., 2002). Hence the use of a heterogeneous catalyst has the following inherent advantages over homogeneous catalyst: (a) they eliminate the corrosive environment; (b) the catalyst can be easily removed from the reaction mixture by decantation or filtration; (c) the purity of the products is higher because the side reactions can be completely eliminated or are less significant (Babu *et al*., 2011). Ion-exchange resin catalysts had been used for years in esterification processes. Typical resin catalysts are sulfonic acids fixed on polymer carriers, such as polystyrene cross-linked with divinylbenzene (DVB). Solid ion-exchange resins as catalysts have several advantages: the catalyst can be removed from the reaction

product, continuous operation in column reactors is enabled, and the product purity is high, since side reactions can be suppressed or completely eliminated, reaction intermediates can be isolated and furthermore, ion-exchange resins can discriminate between small and large molecules**.** The most popular solid acid catalysts used to produce esters have been ion exchange organic resins, such as amberlyst 15 (Toor *et al.* 2011) amberlyst 36 (Yadav and Thathagar, 2002), indion 130 and indion 190 (Babu *et al*., 2011).

1.4 Structure and properties of polylactic acid

An important feature of lactic acid is that it exists in two optically active forms. Fermentation derived lactic acid consists of 99.5% of the L-isomer. Production of the cyclic lactide dimer intermediate results in three potential forms. The D- and L-forms are optically active, the D,L- or meso-form is optically inactive. The ratio of these three forms is readily controlled in the process. Ring opening polymerization of the lactide results polymers containing different isomer ratios and a range of molecular weights. Polymers with high L-levels can be used to produce crystalline products whereas the higher D-levels (>15%) result in an amorphous product.

1.4.1 Physical properties

Physical properties of polymeric materials depend on their molecular arrangement as well as ordered structures such as crystalline thickness, crystallinity, spherulite size, morphology and degree of chain orientation. For many products, crystallinity is a desirable property. For PLLA or PDLA single polymer, molecular weight increases rapidly in comparison with block copolymer of PLLA and PDLA. Physical properties are very important as they reflect the highly ordered structure of the polymer and influence mechanical properties and their change during hydrolysis. Some significant properties of PLA are given in Table 4.

Table 4 Physical and mechanical properties of PLA.

Property	**L-PLA**	**D,L-PLA**
Glass transition temperature (T_g)	60-65°C	50-60°C
Melting point (T_m)	184 °C	amorphous
Specific gravity	1.24	1.25
Tensile strength (MPa)	55.2-82.7	27.6-41.4
Elongation (%)	5-10	3-10
Modulus (MPa)	2758-4137	1329-2758
Inherent viscosity (dl/g)	0.90-1.2	0.55-0.75

Source: Maharana *et al*. 2009

1.4.2 Thermal properties

Thermal properties of PLA have been studied by various thermal analyzers such as thermogravimetic analysis (TGA), differential thermal analysis (DTA), differential scanning calorimeter (DSC). The thermal properties of polylactic acid are largely dependent on the ratio and distribution of the two stereoisomers of LA within the polymer chains. Value of T_m and T_g are dependent mainly on the structure of PLA and molecular weight as shown in Table 5. Thermal properties of PLA can be changed by copolymerization of PLA with other monomers such as glycolic acid, some lactone derivatives, trimethyl carbonated, etc. and by addition of cross-linker and plasticizer. (Maharana *et al*., 2009). Moreover, PLA has relatively low glass transition (T_g) and melting temperature (T_m) as compared to other thermoplastics as shown in Figure 17.

Table 5 Thermal properties of PLA

Polymer	Glass transition (T_g) (°C)	Melting point (T_m) (°C)
L-PLA		
$\overline{M}_W$ = 50,000	54	170
$\overline{M}_W$ = 100,000	58	159
$\overline{M}_W$ = 300,000	59	179
D,L-PLA		
$\overline{M}_W$ = 20,000	50	-*
$\overline{M}_W$ = 107,000	51	-
$\overline{M}_W$ = 550,000	53	-

* Not applicable

Source: Mehta *et al*. (2005)

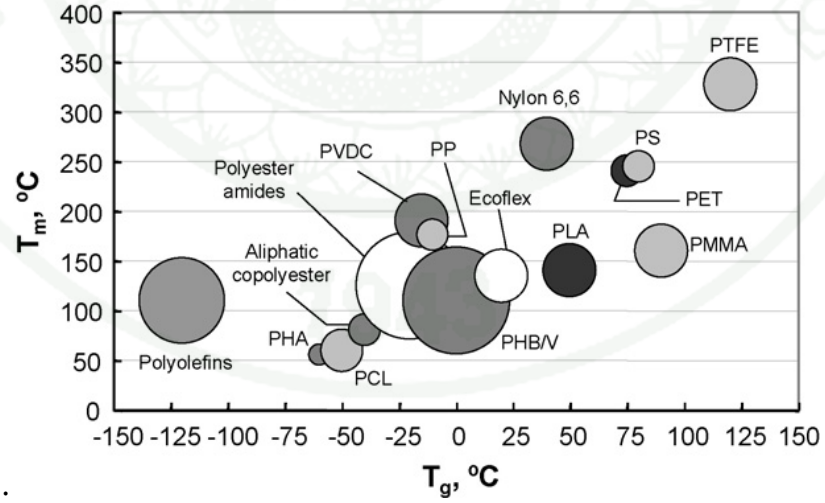


Figure 17 Comparison of glass transition and melting temperature of PLA with petroleum based thermoplastics.

Source: Lim *et al.* (2008)

1.4.3 Mechanical properties

The mechanical properties of L- and D,L- PLA are summarized in Table 6. The mechanical properties of PLA can be varied to a large extent, ranging from soft and elastic plastics to stiff and high-strength materials. Semicrystalline PLA is preferred to amorphous polymer when better mechanical properties are desired. The molar mass of the polymer as well as the degree of crystallinity has a significant influence on the mechanical properties. Table 7 showed values of common mechanical properties and compared with other commodity plastics.

Table 6 Mechanical properties of PLA

Polymer	**Tensile strength (MPa)**	**Flexural modulus (MPa)**	**Elongation**	
			Yield (%)	**Break (%)**
L-PLA				
$\overline{M}_W$ = 50,000	28	1400	3.7	6.0
$\overline{M}_W$ = 100,000	50	3000	2.6	3.3
$\overline{M}_W$ = 300,000	48	3250	1.8	2.0
D,L-PLA				
$\overline{M}_W$ = 20,000	n/a*	n/a	n/a	n/a
$\overline{M}_W$ = 107,000	1950	1950	4.0	6.0
$\overline{M}_W$ = 550,000	2350	2350	3.5	5.0

* Not available

Source: Mehta *et al*. (2005)

Table 7 Comparison properties of typical PLA with several petroleum-based commodity thermoplastic resins.

	PLA	**PET**	**PS**	**PP**	**HIPS**
T_g (^oC)	55	75	105	-10	-
Tensile strength at Break (MPa)	53	54	45	31	23
Tensile modulus (GPa)	3.5	2.8	2.9	0.9	2.1
Elongation at break (%)	6	130	7	120	45
Notched Izod IS (J/m)	13	59	27	27	123
Gardner impact (J)	0.06	0.32	0.51	0.79	11.30

PET: poly(ethylene terephthalate); PS: polystyrene; HIPS: high-impact polystyrene; PP: polypropylene; IS: impact strength.

Source: Liu and Zhang (2011)

2. Direct polycondensation

At present, a number of industries for production of PLA are already commercialized as shown in Table 8. Until 1995, it was believed that high molecular weight PLA could not be achieved by the direct polycondensation of LA because of the difficulty in driving the dehydration equilibrium in the direction of esterification, which is the requirement for the formation of sufficient high molecular weight PLA. Since then, research and development on the synthesis, properties and applications of polylactic acid has been investigated and reviewed extensively (Foltynowicz and Jakubiak, 2002; Kim and Woo, 2002; Sodergard and Stolt, 2002; Duda and Penczek, 2003; Mehta *et al*., 2005; Dorgan *et al*., 2006; Bo, 2008; Cheng *et al*., 2009; Nampoothiri *et al*., 2010; Pang *et al*., 2010; Fomin *et al*., 2011; Seyednejad *et al*., 2011 and Thomas and Lutz, 2011).

Table 8 Industrial PLA operations in 1999-2009.

Company	Location	Tradename
Boeringer-Ingelheim	Germany	Resomer
Fortum (Neste Chem.)	Finland	Pollait
Cargill (Cargill-Dow)	Nebraska, US	NutureWorks
Purac	The Netherlands	Purasorb
Mitsui Chemicals	Japan	Lacea
Hycail b.v.	The Netherlands	Hycail*
Toyota (Shimadzu)	Japan	Lacty
Hisun Biomaterials	China	Revode
Birmingham Polymers	Alabama, US	Lactel
Pyramid	Germany	-**
Synbra	The Netherlands	-**

* Technology sold out, ** Under construction.

Source: Sodergard (2010)

Fukushima *et al*. (2000) developed an innovative two-steps polycondensation process so as to produce economically PLLA with high molecular weight. The process is composed of both melt polycondensation under the lactide-reflux and solid-phase polycondensation. First, a direct polycondensation of L-lactic acid with a small amount of solvent, using a mixture of L-lactic acid as raw material, diphenyl ether as solvent, Tin (II) chloride dihydrate as catalyst, and *p*-toluene sulfonic acid as a discoloration prevention agent was investigated. After the dehydrative oligomerization of L-lactic acid, the polycondensation of the oligocondensates and solid-phase postpolycondensation, PLLA of $\overline{M}_W$ = 266,000 could be obtained. Then, direct bulk polycondensation from L-lactic acid without any solvents was tested. After

optimization of the reaction conditions, PLLA with $\overline{M}_W$ = 134,000 was successfully produced by the melt polycondensation of L-lactic acid accompanied by solid-phase post polycondensation. In both systems, the lactide-reflux was indispensable for promoting dehydration/water removal. The refluent lactide was taken into the polymer chain by trans-esterification reaction during the melt polycondensation. Furthermore, the catalyst was allowed to deactivate and stabilize during the solid-phase polymerization to cause the $\overline{M}_W$ growth.

In 2002, Kim and Woo synthesized high-molecular-weight poly(L-lactic acid) (PLLA) with improved mechanical properties by the direct polycondensation of lactic acid in solution phase. During polymerization, the molecular weight of PLA was influenced by the water content present in the solution; thus, the experimental apparatus was designed to remove the water efficiently and this study was focused on the optimization of the polymerization conditions such as polymerization time, solvent, and kinds of catalyst, etc. Additionally, to search for a good catalyst in the polymerization, the mixed oxide catalysts were synthesized by sol-gel method and it was characterized by XRD and BET. The results showed that the $\overline{M}_V$ of PLA obtained was about 33,000, when 0.2 wt% of $SnCl_2 \cdot 2H_2O$ was used as a catalyst in the polymerization. The DSC study showed that the thermal properties of PLA such as Tg and Tm were influenced by the kind of solvent as well as the molecular weight of PLA.

In 2003, polylactic acid as bio-based polymers from the perspective of its life cycle contributing to the saving of fossil resources and the reduction of greenhouse gas emissions was described by Kawashima. This paper also describes a polylactic acid manufacturing process which is typified by ring opening polymerization and direct polycondensation and discussed the issues to be addressed for the growth of the market for the material.

In 2003, melt polycondensation of L-lactic acid (LA) was examined in the presence of binary catalyst systems consisting of $SnCl_2 \cdot 2H_2O$ and metal alkoxides as

co-catalysts by Moon and Kimura. Among the co-catalysts examined, $Al(OiPr)_3$, $Ti(OiPr)_4$, $Y(OiPr)_3$, $Si(OEt)_4$ and $Ge(OEt)_4$) and $Ge(OEt)_4$, were found effective in enhancing the catalytic activity of Sn(II). With an optimized composition of $SnCl_2 \cdot 2H_2O$-$Ge(OEt)_4$, the molecular weight ($\overline{M}_W$) of PLLA reached 40,000 Da in a short reaction time (15 h) at the optimum reaction conditions of 180°C and 10 torr. This catalyst system was also superior to the conventional single metal ion catalysts such as Sn(II) in terms of racemization and discolouration of the resultant polymer. The metal alkoxides, added as co-catalysts, should work as oxo acids that can effectively control the catalytic activity of Sn(II) ion in the direct polycondensation of LA, in a manner similar to that of proton acids.

Chen *et al*. (2006) attempted to produce high-molecular-weight poly(L-lactic acid) (PLLA) through the direct polycondensation of L-lactic acid in bulk state. Polymerizations were carried out with titanium (IV) butoxide (TNBT) as a catalyst employing different duration of decompression, esterification and polycondensation. They reported the first time; PLLA was synthesized by the direct bulk condensation polymerization using titanium (IV) butoxide as a catalyst at different polymerization time. The duration of the decompression of the reaction pressure to 1 torr was important to produce high-molecular-weight PLLA. When the polymerization reactor was decompressed extremely slowly step by step for 7 h, the molecular weight of PLLA reached as high as 130,000. Increase of the time for the esterification reaction from 3 to 7 h also raised the molecular weight of PLLA from 30,000 to 120,000.

The process of the new research of the PLA synthesis was reviewed by Bo in 2008. Besides, the PLA synthesis methods of reactive extrusion and direct melting polycondensation were introduced, which are two high efficiency methods. Finally, the foreground of PLA synthesis was prospected.

Polylactic acid (PLA) was synthesized from L-lactic acid by direct polycondensation under vacuum without the use of catalysts (NC-DP) by Achmad *et al.* in 2009a. Experiments were conducted at polymerization temperatures (T_p) between 150 and 250°C and under reduced pressure. The maximum weight average

molecular weight of PLA obtained was 90 kDa after 89 h at 200°C. Above 200°C, PLA was thermally degraded, and racemization occurred as PLA became atactic. Indeed, PLA only exhibited a glass transition temperature (T_g) and exhibited neither a crystallization temperature nor a melting point. The relations between T_g and the molecular weight were in agreement with the Flory-Fox equation.

Polylactic acid (PLA) is synthesized by direct polycondensation without catalyst (NC-DP) method using a lactic acid (HLa) solution which had been refined by concentration, esterification and hydrolysis of fermented broth from fresh cassava roots (FCR) (Achmad *et al*., 2009b). Higher polymerization rates and earlier thermal degradation had been observed, compared with those from a pure lactic acid solution. It is due to residual impurities in refining process, such as butanol (BuOH) and butyl lactate (BuLa), which act as an external catalyst. Additionally, it was found that thermal degradation of PLA containing these impurities occurs via random scission with vinyl end groups, in regard to specific scission for PLA from a pure HLa solution.

Polylactic acid (PLA), L-lactic acid was polymerized by direct polycondensation (DP) under vacuum without catalysts, solvents and initiators in order to reduce the production cost (Achmad *et al*., 2009c). Experiments were conducted at polymerization temperatures (T_p) of 150-250°C. The maximum PLA molecular weight obtained was 90 kDa at 200 °C after 89 h under vacuum. Above 200°C, PLA is thermally degraded by specific scission. The DP activation energy (Ea) was also investigated and was found to be larger than that required by catalyzed ring opening polymerization (ROP). Furthermore, the Ea was higher than the deactivation energy (Ed) for both DP and ROP. PLA yields were higher at lower T_p, while the yield of lactide increased with T_p. The total yield of PLA and lactide was approximately 52-75 wt%. The uncatalyzed DP method may have applications in on-site cell plant production, where compactness is required, as well as safe and simple operating procedures.

Sedlarik *et al*. (2010) investigated the synthesis of poly(lactic acid) (PLA) catalyzed by a non-metal-based compound. Low-molecular-weight PLA by direct melt polycondensation of L-lactic acid catalyzed by methanesulfonic acid (MSA). This study was focused on the investigation into optimal MSA concentration determination and into the temperature (130, 145, 160, 175, and 190°C) and time (6, 12, 18, and 24 h) influence on the structure of the samples. The results showed an optimal MSA content of 0.5 wt% and the highest molecular weight of PLA prepared by this method was reached after 18 h of reaction at 175°C (weight-average molar mass = 17.2×10^3 g/mol).

The biodegradable material poly(lactic acid-*co*-glycerol) [P(LA-*co*-GL)] was synthesized using L-lactic acid (LLA) and glycerol (GL) as the starting materials (Luo *et al*., 2011). For the molar feed ratio n(LA)/n(GL) of 60/1, the optimal synthetic conditions were discussed. Using 0.3 wt% stannous oxide (SnO) as the catalyst, after the prepolymerization was carried out at 140 °C for 8 h, the melt copolymerization for 8 h at 160 °C gave the polymer with the biggest intrinsic viscosity ([η]) 0.76 dL g^{-1}. Increasing the molar feed ratio n(LA)/n(GL), the weight-average molecular weight ($\overline{M}_W$) didn't increase all the time, but a peak of $\overline{M}_W$ was formed, which indeed validated the above special phenomenon during the direct melt copolycondensation of LA with the monomers containing multifunctional groups. However, the forming mechanism of multi-core copolymer was different when multihydroxyl alcohol (e.g. GL) was used as the monomer containing multifunctional groups. Because the multi-core structure was linked by the ether bonds with less reversibility in the reaction, the biggest $\overline{M}_W$ of copolymers was relatively lower. For GL with three terminal hydroxyls as the core, only when n(LA)/n(GL) was more than 100/1, the star-shaped polylactic acid (SPLA) containing one core could be obtained.

Kucharczyk *et al*. (2011) described the preparation of carboxyl-functionalized polylactic acid (PLA) through the method of direct melt copolycondensation of lactic and citric acid (CA). The effect of tricarboxylic CA on the resulting properties of the functionalized lactic acid (LA) polycondensates was studied in a wide range of LA/CA molar ratios. The influence of CA on molecular weight, thermal and

physicochemical properties, and chemical structure of the products was investigated. The results showed the significant effect of CA on the structure and physicochemical properties as well as high efficiency of functionalization. Furthermore, a branched structure was detected at low CA concentrations, while higher CA content leads to termination of the polycondensates chains by citryl units and a reduction in the molecular weight.

A modified polylactic acid (PLA) with terminal carboxyl, novel biodegradable material poly(lactic acid-trimesic acid) (PLT), directly from lactic acid (LA) and trimesic acid (TMA) was synthesized via melt copolycondensation by Wang *et al*. in 2011. When L-lactic acid (L-LA) and TMA as molar feed ratio n(L-LA)/n(TMA) = 120/1 was prepolymerized for 8 h at 140°C, the copolycondensation catalyzed by 0.9 wt% $SnCl_2$ at 190°C for 8 h gave PLT with the biggest intrinsic viscosity ([η]) 1.91 dL g^{-1}, and the corresponding weight-average molecular weight ($\overline{M}_W$) was 14,100 Da. Increasing n(L-LA), $\overline{M}_W$ increased first, and the biggest $\overline{M}_W$ was 17,500 Da at n(L-LA)/ n(TMA) 240/1, then decreased. Using D,L-lactic acid (D,L-LA) instead of L-LA, the influences of LA stereochemical configuration were investigated. The peak phenomenon of $\overline{M}_W$ was similar, but the biggest $\overline{M}_W$ was 23,100 Da at n(D,L-LA)/n(TMA) 320/1. The serial L-PLTs had a certain crystallinity (10.2%~23.0%), while all D,L-PLTs were amorphous. These differences may be in touch with the reaction mechanism of direct melt copolycondensation. The method was simple and practical for the synthesis of PLA biomedical materials applied in drug delivery, carrier, and vessel substitution material.

The direct polycondensation of lactic acid at 200°C under vacuum was investigated by Riaz *et al.* in 2011. Five samples of lactic acid were heated under vacuum. In three samples stannous chloride, glycerin and polyacrylamide gel were used as catalyst. Two samples were without the catalyst and heated at pressure 100 mm Hg with different time duration. The effects of catalysts and reaction time on the molecular weight and yield were studied. The results showed that polymer which was

heated under vacuum at 200°C without the use of catalyst, had highest yield, highest viscosity and highest molecular weight.

In 2012, a novel approach to prepare poly(D,L-lactic acid) (PLA) as a biodegradable polymer was reported by Harrane *et al*. PLA was prepared by direct polycondensation of D,L-lactic acid using Maghnite-H^+, a non-toxic proton exchanged montmorillonite clay, as catalyst. The reaction conditions for the simple direct polycondensation of D,L-lactic acid, including the reaction times, temperatures, and catalyst amount were investigated. The molecular weight of synthesized PLA was dependent on both the reaction temperature, amount of catalyst and time. Kinetics indicated that the polycondensation of lactic acid behaved as second-order reaction mechanism. The method for PLA synthesis established here will facilitate production of PLA of various molecular weights, which may have a potential utility as biomaterials.

Part II: PLA modification by blending

1. Modification of polylactic acid

Biodegradable polymer such as polylactic acid, PLA, has become significantly important at present. PLA can be a well behaved thermoplastic with reasonable shelf life for most single-use packaging applications. It can be easily process on standard plastic equipments to yield parts, film or fiber. PLA has become an alternative to traditional general-purpose plastics for such applications because the polymer exhibits comparable or better mechanical properties than these petroleum-based plastics (PP, PE, PVC, PS). PLA too can be melt-processed with the standard thermoplastic processing methods such as extrusion or injection molding. However, with a glass transition temperature ranging from 55 to 65°C, PLA is too stiff and brittle for room temperature applications, and this brittleness limits its applications in some areas particularly as packaging materials (Tao and Jie, 2009; Taib *et al*., 2012).

The brittleness of PLA has been modified in two approaches. It can be either by copolymerization of lactic acid with other monomers such as ε-caprolactone, or by blending PLA with a second polymer or a plasticizer. Although, the first approach has been extensively studied to modify the brittleness of PLA, nevertheless, none of these copolymers are commercially available in the market (Taib *et al*., 2012). Blending two homopolymers to get the desired change in mechanical properties is one of the most inexpensive and widely used methods in the plastics industry. Thus, blending PLA with other flexible biodegradable or non-biodegradable polymers is more practical and more economical way to modify the brittleness of PLA. The largest amount of research on the toughening of PLA has occurred in the blending field, for example, blending PLA with polycaprolactone (PCL), poly(hydroxyalkanoate) (PHA), and polyethylene (PE). Different from polymeric plasticizers, in this case the two homopolymers are immiscible. Frequently, the binary blends give poor properties and a block copolymer compatibilizer is necessary to increase the compatibility and improve the properties of the blends. This will improve the dispersion of the minority phase, the adhesion between the blend components and stabilize the blend morphology, resulting in better mechanical properties. In addition, the flexibility and ductility of PLA can also be improved by blending PLA with a plasticizer (Pillin *et al*., 2006). Several low molecular weight compounds have been employed such as glycerol, poly(ethylene glycol) (PEG) (Hu *et al*., 2003a; Hu *et al*., 2003b), and poly(propylene glycol (PPG) (Piorkowska *et al*., 2006).

1.1 Polylactic acid blends

Despite PLA numerous advantages such as high strength and high modulus, the inherent brittleness significantly impedes its wide applications in many fields. PLA not only has comparable tensile strength and modulus but also exhibits very similar inherent brittleness as general purpose polystyrene (PS). In recent year, PLA toughening has become the focus of numerous investigations.

PLA blends are comprised of two or more polymers, and are of commercial interest for a variety of reasons and are widely used for toughening PLA.

Thermodynamically there are two classes of blends: immiscible and miscible blends. In immiscible blends, the constituent polymers do not mix, but remain in separate phase, leading to the formation of a dispersion of one of the polymer in a continuous matrix of the other. Experimental evidence indicates that most polymer pairs are completely immiscible. Blends can be exhibit complete immiscibility and partial immiscibility, just as in small molecule systems. In miscible blends, the constituent polymers mix on a molecular level, to form a homogeneous material equivalent to a polymer-polymer solution. The physical, chemical and mechanical properties are generally a weight average of the mixture components. PLA blends can be prepared by different techniques such as solution blending, mechanical blending and mechano-chemical blending etc.

1.1.1 Solution blending

In this process, polymers are dissolved in a common solvent such as chloroform. Blends are produced by evaporating the solvent and precipitating the resulting polymer mixture. If pure solvent and clear glass wares are used, contamination can be precluded. In solution blending, selected diluents are used to dissolve the component polymers. There are several reported in literature on the solution blending of different PLA blend pairs. In solution blending, very small quantities of PLA can be handled easily and degradation is not a problem. There are certain limitations to this method. PLA and the other component may not soluble in the same common solvent. Residual solvents can influence the properties of the PLA blends. It is difficult to make thick film. Moreover, in solution casting, the removal of the diluents may lead to uncertain changes in the phase morphology, thus weakening the blends. As a result of evaporation of solvent, the concentration of polymer increases and thereby, phase separation occurs. The rate of evaporation play a dominant role on the morphology and miscibility of the solution cast blends.

Chen *et al*. (2003) prepared blends of biodegradable poly-L-lactic acid (PLLA) and poly-DL-lactic acid (PDLLA) or polycaprolactone (PCL), in addition to a third component, the surfactant-a copolymer of ethylene oxide and propylene

oxide, by blending these three polymers at various ratios using dichloromethane as a solvent. The weight percentages of PLLA/PDLLA (or PCL) blends were 100%/0%, 80%/20%, 60%/40%, 50%/50%, 40%/60%, 20%/80% and 0%/100%, respectively. DSC data indicate that PLLA/PDLLA blends without the surfactant had two T_g with the addition of the surfactant, there was a linear shift of the single T_g as a function of composition, with lower percentages of PLLA producing lower glass transition temperatures indicating that better miscibility had been achieved. DMA data show that the 40/60 PLLA/PDLLA blend without the surfactant had high elastic modulus and elongation, and similar results were observed after adding 2% surfactant into the blends. The 50/50 PLLA/PDLLA/2% surfactant blend had the highest elastic modulus, yield strength, and break strength compared with other ratios of PLLA/PDLLA/2% surfactant blends. The elongation at break of 50/50 PLLA/PDLLA was similar to that of PLLA. Again, the elongation at break of 50/50 PLLA/PDLLA/2% surfactant was almost 1.2-1.9 times higher than that of 50/50 PLLA/PDLLA and PLLA. Elongation of PLLA increased with the addition of PCL, but the strength decreased at the same time. In conclusions, adding PDLLA and surfactant to PLLA via solution-blending may be an effective way to make PLLA tougher and more suitable to use in orthopedic or dental applications.

Poly (lactic acid) (PLA) was blended with poly(vinyl butyral) (PVB) through solution casting method using chloroform as the common solvent (Khurma *et al.*, 2005). The films obtained were characterized for miscibility using differential scanning calorimetry (DSC), tensile testing and FT-IR spectroscopy. The DSC results showed that the glass-transition temperature (T_g) of the PLA and PVB remained more or less constant with the composition of the blend. The existence of two T_g's in the blends indicated that PLA and PVB were immiscible over the composition range investigated. Percentage crystallinity (χ_c), of PLA phase remained constant with increasing PVB content in the blend. FTIR measurements showed that there was no appreciable change in the spectra with respect to blend composition, implying the immiscibility of the two polymers. Mechanical analysis showed that the tensile strength and elongation decreased on blending.

Martino *et al*. 2005 prepared PLA film with four different platicizers: di-2-ethylhexyl adipate (DOA), and three commercial polymeric adipates (polyesters of adipic acid) with different viscosities, named as G206/3, G 206/5 and G 206/7 by easily dissolving in cold chloroform. Films obtained from chloroform solutions with different plasticizer concentrations (5%, 10%, 15% and 20 wt %) showed good transparency, but some residual solvent was detected in them. Therefore, all samples were exposed to a heat treatment at 90ºC for five minutes in order to extract the residual chloroform to limit its plasticizing effect and to assure that all plasticization is due to the additives used.

Chen *et al*. (2009) studied binary blends of poly(ethylene terephthalate) with poly(lactic acid), PET/PLA by differential scanning calorimetry and X-ray scattering. The PET/PLA blends, prepared by solution casting, were found to be miscible in the melt over the entire composition range. Both quenched amorphous and semicrystalline blends exhibit a single, composition dependent glass transition temperature. We report the non-isothermal crystallization of (a) PET, with and without the presence of PLA crystals and (b) PLA, with and without the presence of PET crystals. PET can crystallize in all blends, regardless of whether PLA is amorphous or crystalline, and degree of crystallinity of PET decreases as PLA content increases. In contrast, PLA crystallization is strongly affected by the mobility of the PET fraction. When PET is wholly amorphous, PLA can crystallize even in 70/30 blends, albeit weakly. But when PET is crystalline, PLA cannot crystallize when its own content drops below 0.90. These different behaviors may possibly be related to the tendency of each polymer to form constrained chains, *i.e*., to form the rigid amorphous fraction, or RAF. PET is capable of forming a large amount of RAF, whereas relatively smaller amount of RAF forms in PLA. Like the crystals, the rigid amorphous fraction of one polymer component may inhibit the growth of crystals of the other blend partner.

1.1.2 Mechanical blending

Mechanical blending or melt blending of constituent polymers plus any derived fillers, reinforcement and additives in PLA blend results in mechanical polyblends. The preparation of mechanical polyblends by mill mixing or melting is problem free compared to blending by other methods. Comparable polymer viscosities at the mixing temperature (i.e. above the melting points of the polymer constituents) are desirable for the ease of dispersion in open roll mill. Mechanical blending can be carried out with any standard processing such as two roll mill, extrusion, injection molding etc.

Sheth *et al*. (1997) studied the melt-blended of poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) and extruded into films in the PLA/PEG ratios of 100/0, 90/10, 70/30, 50/50, and 30/70. It was concluded from the differential scanning calorimetry and dynamic mechanical analysis results that PLA/PEG blends range from miscible to partially miscible, depending on the concentration. Below 50% PEG content the PEG plasticized the PLA, yielding higher elongations and lower modulus values. Above 50% PEG content the blend morphology was driven by the increasing crystallinity of PEG, resulting in an increase in modulus and a corresponding decrease in elongation at break. The tensile strength was found to decrease in a linear fashion with increasing PEG content. Results obtained from enzymatic degradation show that the weight loss for all of the blends was significantly greater than that for the pure PLA. When the PEG content was 30% or lower, weight loss was found to be primarily due to enzymatic degradation of the PLA. Above 30% PEG content, the weight loss was found to be mainly due to the dissolution of PEG. During hydrolytic degradation, for PLA/PEG blends up to 30% PEG, weight loss occurs as a combination of degradation of PLA and dissolution of PEG.

Zhao *et al*. (2010) prepared blends of poly(lactic acid) (PLA) and biodegradable polyester using a twin screw extruder. PBAT, PBS, or PBA can be homogenously dispersed in PLA matrix at a low content (5–20 wt%), yielding the blends with much higher elongation at break than homo-PLA. DSC analysis shows

that the isothermal and nonisothermal crystallizabilities of PLA component are promoted in the presence of a small amount of PBAT.

Ke and Sun (2003) studied starch, poly(lactic acid) (PLA) and poly(vinyl alcohol) (PVOH) blending using a lab-scale conical twin-screw extruder. Bitinis *et al.* (2011) improved the brittleness of PLA by melt blending with NR. Ge *et al.* (2011) produced PLA blends with acrylic impact modifier (BPM) by the melt blending method. In 2012, polylactic acid (PLA) was melt-blended with ethylene acrylate copolymer impact modifier by Taib *et al*. 2012.

1.1.3 Latex or dispersion mixing

Latex or dispersion mixing is using coagulation to give an intimate blend mixture. Films can also be cast. Mixing requires no extensive equipment, no high temperatures are required. Dispersion mixing is followed with melt mixing (or compounding) to produce polymer stands for pelletizing. Carvalhoa *et al.* (2003) presented preparing thermoplastic starch/natural rubber polymer blends using directly natural latex and cornstarch. The blends were prepared in an intensive batch mixer at 150°C, with natural rubber content varying from 2.5 to 20%. The results revealed a reduction in the modulus and in tensile strength, becoming the blends less brittle than thermoplastic starch alone. Phase separation was observed in some compositions and was dependent on rubber and on plasticizer content (glycerol). Increasing plasticizer content made possible the addition of higher amounts of rubber. However, the addition of rubber was limited by phase separation the appearance of which depended on the glycerol content. Scanning electron microscopy showed a good dispersion of the natural rubber in the continuous phase of thermoplastic starch matrix.

Blending PLA with other flexible biodegradable or non degradable polymers presents a more practical and economic way of toughening the material. PLA has been blended with a number of polymers such as polycaprolactone (PCL), poly(hydroxyalkaonate) (PHA), and polyethylene (PE). The flexibility and ductility of PLA can also be improved by blending PLA with a plasticizer. The choice of

plasticizers to be used as modifier for PLA is limited by the requirement of the application. Only non toxic substance approved for environmental contact which can be considered as plasticizing agent in bioplastic. Several low molecular weights have been employed as plasticizers an important demand is good miscibility with PLA to keep transparency while low mobility in PLA is also essential to avoid migration of plasticizer to the surface. For the miscibility, the plasticizers with low molecular weight are better than that with high molecular weight because of their large entropy of mixing. Especially, monomer unit of PLA example lactide is the best plasticizer for PLA. Other than the lactide, many kind of ester-like plasticizer for PLA were studied such as poly(ethylene glycol) (PEG) (Sheth *et al*., 1997 and Hu *et al*., 2003b).

1.1.4 Mechano-chemical blending

In this method of blending, two polymers are mixed by melt mixing and then cross-linked using a co-crosslinker. This intercrosslinking between the two polymers improves the phase morphology by the proper control of domain size and distribution thereby providing resistance to phase separation. Introduction of an appropriate level of crosslinking to PLA could also impart the simultaneous enhancements in tensile and impact strengths. Crosslinked PLA materials have been synthesized by either (1) copolymerization of lactic acid with a multifunctional monomer or (2) by introducing a crosslinkable moiety into the polymer backbone and then performing postpolymerization crosslinking modification, for example, Helminen *et al*. (2002) studied the crosslinking of PLA with functionlizing telechelic star-shaped poly(CL/D,L-LA) oligomers with methacrylate anhydride followed by chemical crosslinking of the double bonds using dibenzoyl peroxide as crosslinking agent.

1.2 Properties relationship of PLA blends

1.2.1 Thermal properties

Thermal properties are relevant to the potential use of polymeric materials in many consumer oriented applications. Fabrication of a variety of articles and their end usages need a detailed understanding of the thermal degradation of polymers. Blending of polymers has been reported to have much influence on the thermal stability of individual polymers. The thermal stability of the blends depends strongly on the compatibility of the polymers. The assessment of thermal stability is one of the most important applications of thermogravimetric (TGA) analysis in the study of polymers. Thermogravimetric curves provide information about the decomposition mechanisms for various materials. Both TGA and derivative thermogravimetry (DTG) can provide information about the nature and extent of degradation of the material. A comparison of the thermal properties of miscible and immiscible blends can also be predicted using differential scanning calorimetric method. This will measure the glass transition temperature (T_g) and melting temperature of the polymeric material. Miscible blends will show single, sharp transition peak (T_g) intermediate between those of the blend components. Separate transitions are obtained for immiscible blends (Rao and Johns 2008). Partial miscibility of PLA blends was also observed where two glass transitions temperatures were detected at temperatures differing from the corresponding T_g of the components. The T_g of the polymer with the lower glass transition temperature increases and, conversely, the T_g of the polymer with the higher glass transition temperature decreases, thus shortening the temperature interval between the two glass transitions (Somdee, 2009). Many researchers have studied behavior of glass transition temperature on both PLA/nonbiodegradable and PLA/biodegradable polymer blends. Okamoto *et al*. (2009) observed miscible of poly(lactic acid) and polyester-diol (PED) blending which nominal molecular weight = 2000, such as poly(ethylene adipate), poly(diethyl adipate), poly(butylenes adipate) and poly(hexamethylene adipate) by differential scanning calorimetry (DSC). DSC thermograms of PLA/poly(ethylene adipate) and PLA/poly(diethyl adipate) blends indicate that these blends are miscible

with PLA at ratio of PED less than or equal to 20%. In theses blend, T_g is significantly lower than that of PLA. On the other hand, PLA/poly(butylenes adipate) and PLA/poly(hexamethylene adipate) are partially miscible with PLA at weight ratio of 20% .

1.2.2 Mechanical properties

The mechanical properties of PLA blends were investigated by tensile testing, impact testing, dynamic mechanical testing and rheological measurement. Many researches have been studied for the improvement of the mechanical properties of PLA. For example, Sheth *et al.* (1997) blends polylactic acid (PLA) and poly(ethylene glycol) (PEG) in the PLA/PEG ratios of 100/0, 90/10, 70/30, 50/50, and 30/70. It was concluded from the differential scanning calorimetry and dynamic mechanical analysis results that PLA/PEG blends range from miscible to partially miscible, depending on the concentration. Below 50% PEG content the PEG plasticized the PLA, yielding higher elongations and lower modulus values. Above 50% PEG content the blend morphology was driven by the increasing crystallinity of PEG, resulting in an increase in modulus and a corresponding decrease in elongation at break. The tensile strength was found to decrease in a linear fashion with increasing PEG content.

Ge *et al*. (2011) produced PLA blends with acrylic impact modifier (BPM). The test results show that the composites with BPM possess better flexibility when compared with neat PLA. However, the notched izod impact strength showed improvement only when the BPM content was higher than 15 wt%.

Taib *et al*. (2012) found that PLA with 30 wt % impact modifier showed comparable yield stress and tensile modulus and better elongation at break and impact strength (90%) than those of polypropylene. The blends showed some improvement in the elongation at break and notched impact strength indicating the toughening effects of the impact modifier. In contrast, the yield stress and tensile modulus decreased with the increase in the impact modifier content.

Three component blending of PLA, starch and poly(vinyl alcohol) (PVOH) were studied by Ke and Sun (2003). Blending starch with poly(lactic acid) (PLA) is one of the most promising efforts because starch is an abundant and cheap biopolymer and PLA is biodegradable with good mechanical properties. PVOH contains unhydrolytic residual groups of poly(vinyl acetate) and also has good compatibility with starch. It was added to a starch and PLA blend (50:50, w/w) to enhance compatibility and improve mechanical properties. PVOH (MW 6,000) at 10%, 20%, 30%, 40%, 50% (by weight) based on the total weight of starch and PLA, and 30% PVOH at various molecular weights (MW 6,000, 25,000, 78,000, and 125,000 Da) were added to starch/PLA blends. PVOH interacted with starch. At proportions greater than 30%, PVOH form a continuous phase with starch. Tensile strength of the starch/PLA blends increased as PVOH concentration increased up to 40% and decreased as PVOH molecular weight increased. The increasing molecular weight of PVOH slightly affected water absorption, but increasing PVOH concentration to 40% or 50% increased water absorption. Effects of moisture content on the starch/PLA/PVOH blend also were explored. The blend containing gelatinized starch had higher tensile strength. However, gelatinized starch also resulted in increased water absorption.

1.3 Polylactic acid composites

For many applications, the mechanical properties of PLA such as tensile strength and stiffness can be much improved by natural fibers like flax, hemp, sisal and jute. Natural fiber has good intrinsic mechanical properties, a low density compare to glass fiber as well as lower price as shown in Table 9. Natural fibers are recyclable and biodegradable. They are also renewable and have relatively high strength and stiffness and cause no skin irritations. On the other hand there are also some disadvantages: moisture uptake, quality variations and low thermal stability.

Table 9 Material and mechanical properties of E-glass and other plants-based fibers.

Properties /fiber	**E-glass**	**Hemp**	**Jute**	**Ramie**	**Coir**	**Sisal**	**Flax**	**Cotton**
Density (g/m^2)	2.55	1.48	1.46	1.5	1.25	1.33	1.4	1.51
Tensile Strength (MPa)	2400	550-900	400-800	500	220	600-700	800-1,500	400
Tensile Modulus (GPa)	73	70	10-30	44	6	38	60-80	12
Elongation at break (%)	3	1.6	1.8	2	15-25	2-3	1.2-1.6	3-10
Moisture absorption (%)	-	8	12	12-17	10	11	7	8-25

Source: Cheung *et al*. (2009)

1.3.1 Plant-based fiber

Many investigations have been reported on the potential of the natural fibers as reinforcements for composites and in several cases the results have shown that the natural fiber composites own good stiffness but the composites do not reach the same level of strength as glass fiber composites (Oksman *et al*. 2003). Okubo *et al*. (2005) improved PLA composite mechanical properties using bamboo fiber. They reported that composite mechanical properties increased such as bending strength and fracture toughness. Tao and Jie (2009) investigated the mechanical and thermal properties of the composites which were prepared with ramie and jute short fiber as reinforcement and PLA as matrix. The results show that the properties of the

composites are better than those of plain PLA. When the content of the fiber is 30%, the composites can get the best mechanical properties. The dynamic mechanical analysis results show the storage modulus of the PLA/ramie and PLA/jute composites increase with respect to the plain PLA. The softening temperature of the composites is greatly higher than that of PLA. The results of thermogravimetric analysis show that adding fiber to the PLA matrix can improve the degradation temperature of PLA.

Islam *et al.* (2010) developed polylactic acid composites reinforced with biodegradable hemp fibers that showed improved mechanical properties. They also observed that alkali-treated hemp fibers produced composites of increased tensile and flexural strengths. In the same year, Nyamboo *et al*. (2010) developed green composite from PLA using agriculture residues reinforcement such as wheat straw, corn stover, soy stalk as reinforcement phase. They showed that adding of fiber improved the tensile modulus and led to a decrease in tensile strength and suggested that agricultural residues can be substituted or be combined with each other for commercial application without sacrificing mechanical performance.

Prompunjai and Sridach (2010) prepared composite from sawdust, cassava starch and natural rubber latex on various proportions. The composite materials which contained the gelatinized cassava starch and PVOH in the ratio of 2:1, natural rubber latex 20% by weight of the dry starch and treated sawdust with 5% NaOH or 1% BPO were the best. The experimental results showed that it contributed the maximal compression strength (341.10 + 26.11 N), puncture resistance (8.79 + 0.98 N/mm^2) and flexural strength (3.99 + 0.72 N/mm^2). It is also found that the physicochemical and mechanical properties of composites are strongly depends on the interface quality of sawdust, cassava starch and NR latex.

1.3.2 Animal-based fiber

Moreover, many researchers investigated animal-based fiber as natural fiber to alternative for producing biodegradable composites. The animal-based

fibers are used like silk fiber (wool, spider and silkworm silk) and poultry feather (chicken feather) (Rao *et al.* 2007).

Poultry feathers are abundant, inexpensive, and renewable byproducts that have been studied as potential raw materials for various applications. Among various poultry feathers, chicken feathers are approximately half feather fiber (barbs) and half quill (rachis) by weight, the quill being the stiff central core with hollow tube structure. Both feather fiber and quill are made of keratin (about 90% by weight), an insoluble and highly durable protein found in hair, hoofs, and horns of animals. Keratin consists of a number of amino acids but largely made up of cystine, lysine, proline, and serine. These amino acids tend to cross-link with one another by forming disulfide or hydrogen bonds resulting in fibers that are tough, strong, lightweight, and with good thermal and acoustic insulating properties (Figure 18). The unique characteristic of keratin has generated interest in investigating the use of waste chicken feathers for a number of potential applications such as reinforcement in plastics (Acda, 2010).

Rao *et al*. (2007) studied mechanical properties of the randomly oriented short poultry feather fiber reinforced into epoxy resin to prepare composite slabs. It had been showed that tensile strength of the composite is measured to be 70.45 MPa where as that of neat epoxy is about 70 MPa. The incorporation of feathers has not caused any significant improvement in the flexural strength. However, the reinforcement caused a reduction of about 13% in the composite density which leads to improvement in the strength to weight ratio. The density of the composite was measured to be 0.97 gm/cc which is less than the density of neat epoxy (1.12 gm/cc).

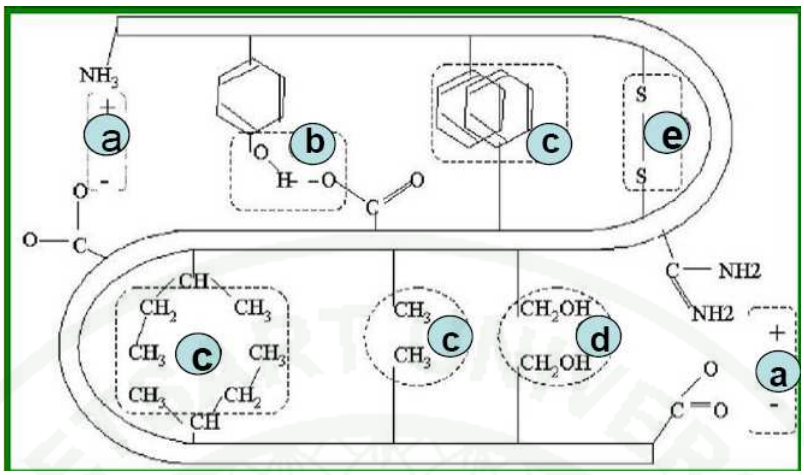


Figure 18 Schematic representation of feather fiber (keratin protein fiber) showing the multiple functionalities: (a) electrostatic interaction, (b) hydrogen bonding, (c) hydrophobic force, (d) hydrogen bonding, and (e) disulfide linkage (Misra *et al*. 2001).

Winandy *et al*. (2007) investigated the use of chicken feather fibers as a substitute for wood fibers in medium density fiberboard. The results showed that the fiberboards had a slight reduction in strength but improved dimensional stability and decay resistance compared with boards made from wood fiber.

Other investigators used feather fibers to develop new bio-composites, for example, Acda 2010 showed that waste chicken feather can be used as reinforcement in cement bonded composites but only up to about 10% feather content. Boards containing 5% to 10% fiber and/or ground feather were comparable in stiffness and strength properties to commercial wood fibercement board of similar thickness and density. Increasing the proportion of chicken feather above 10% resulted in significant reduction of Modulus of elasticity and modulus of rupture, and decreased dimensional stability. Potential use of waste chicken feather as reinforcement in cement bonded composites could benefit the poultry industry by reducing waste disposal costs and gain profit from the sale of chicken feathers to the building and construction industry.

Barone (2005) prepared short-fiber reinforced composites made from keratin fibers obtained from poultry feathers and polyethylenes Uzun *et al*. (2011) used chicken feather fiber as reinforcement in vinyl ester or polyester. It was found that the impact properties of the CFF reinforced composites are significantly better than the control composites however both the tensile and the flexural properties of the CFF reinforced composites had poor values compared to the control composites. For 10% CFF, reinforced vinylester composite, Charpy impact value was 4.42 kJ/mm^2 which was 25% higher than the control vinylester composites (3.31 kJ/mm^2) and also for the 10% CFF reinforced polyester (4.56 kJ/mm^2) composite had three times better impact resistance than the control composite (1.85 kJ/mm^2). It was concluded that the tensile and flexural properties can be enhanced with the increasing percentage of chicken feather fiber and also with the different resin. Another way to enhance the composite was to determine an effective treatment to eliminate lack of adhesion between matrix and chicken feather fiber.

Martinez-Hernandez *et al*. (2005) prepared poly(methyl methacrylate) composites reinforced with natural protein biofibers from chicken feathers. Result showed that the hydrophobic nature of keratin fibers produces an excellent compatibility between fibers and PMMA matrix. This fact was reflected in the good dispersion of protein fibers achieved without use of coupling agents. The normally rigid behavior of PMMA may be modified using keratin fibers as were demonstrated by tensile test; while at the same time, Young's modulus of composite material is also increased. The microscopic studies realized at the corresponding fracture surface level showed good adherence between fibers and matrix. These results demonstrated that feather fibers could be a new source of natural high structure fibers useful to create new materials provided with satisfactory properties.

MATERIALS AND METHODS

Part I: Direct melt polycondensation of lactic acid

Materials

1. Chemicals

The following chemicals were obtained from commercial sources and used directly without further purification unless noted:

1.1 Catalyst A was dried at 103^{o}C for 24 h before used.

1.2 Catalyst B was dried at 103^{o}C for 24 h before used.

1.3 Chloroform (Analytical reagent grade, Lab Scan)

1.4 Toluene (Analytical reagent grade, Fisher)

1.5 1-Methyl-2-pyrrolidone (NMP) (Analytical reagent grade, Fluka)

1.6 L-Lactic acid (LA1) (85+% solution in water, Aldrich) was dried over molecular sieves 4A (Angstrom) overnight and filtered. The LA was further dehydrated by distillation off the excess water at 105^{o}C for 1 h under purging with dry N_2 and under reduced pressure (15 mmHg) for 3 h before used. The dehydrated L-lactic acid was a colorless transparent viscous gel.

1.7 L-Lactic acid **(**LA2) (Hipure 90, Purac) was dried over molecular sieves 4A overnight and filtered. The LA was further dehydrated by distillation off the excess water at 105^{o}C for 1 to 3 h under purging with dry N_2 and under reduced pressure (15 mmHg) for 3 to 6 h before used. The dehydrated L-lactic acid was a colorless transparent viscous gel.

1.8 Methanol (Analytical reagent grade, Merck)

1.9 Molecular sieves (4A beads, Aldrich)

1.10 Tetrahydrofuran (HPLC grade, BDS polabo)

2. Instruments

2.1 Polymer molecular weight determination

The weight average molecular weight ($\overline{M}_W$), the number average molecular weight ($\overline{M}_n$) and polydispersity index ($\overline{M}_W / \overline{M}_n$) were determined with respect to polystyrene standards by gel permeation chromatography (GPC) (Polymer laboratories, UK) through a series of two combined Phenogel™ GPC/SEC columns; OOH-04444-KO (Molecular weight range from 1,000 to 75,000) and OOH-0445-KO (Molecular weight range from 5,000 to 500,000) (Phenomenex, USA) with refractive index detector at Department of Chemistry, Faculty of Science, Kasetsart University. HPLC grade tetrahydrofuran (THF) was used as the eluent and delivered at a flow rate of 1 mL min^{-1}. The polymer samples were dissolved in HPLC grade THF at a concentration of 1.0% (w/v) and filtered through a 0.2 μm filter membrane after keeping the sample solution for approximately 24 h. All samples were analyzed at 30^{o}C and the injection volume was 60 μL.

2.2 Nuclear magnetic resonance (NMR)

All nuclear magnetic resonance (NMR) spectra were recorded on Varian Unity Model Innova 400 MHz spectrometer with deuterated $CDCl_3$ as solvent at the Department of Chemistry, Kasetsart University. Chemical shifts for protons are reported in parts per million scale (scale) downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvents ($CDCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million (δ scale) downfield from TMS and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and integration.

2.3 Fourier transform infrared spectroscopy (FTIR)

The structure of the PLA was performed using a Fourier Transforms Infrared Spectrophotometer (Perkin Elmer Series 7) by mixing PLA with potassium bromide (KBr) at 1:1 ratio to form a KBr pellet. All spectra were collected with a resolution of 4 cm^{-1} and 32 scan in the spectral range of 4000-400 cm^{-1} at room temperature at the Department of Chemistry, Kasetsart University.

2.4 Differential scanning calorimeter (DSC)

The glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) of PLA were measured with a differential scanning calorimeter Perkin-Elmer DSC7 Series (USA) from 0-200^oC using heating rate of 10^oC/min and cooling rate of 5^oC/min at the Department of Chemistry, Kasetsart University. Indium was used as standard for temperature calibration and the measurements were made under constant flow of nitrogen.

The degree of crystallization of PLA blend was calculated using the following equation (Spinu, 1993):

$$\chi_C = \frac{\Delta H_{PLAsample}}{\Delta H_{PLA100}} \times 100$$

where: χ_c = the degree of crystallinity.

$\Delta H_{PLAsample}$ = the heat of fusion or crystallization of the PLA sample.

ΔH_{PLA100} = the heat of fusion or crystallization for 100% crystalline PLA = 93.7 J/g.

2.5 Thermogravimetric analysis (TGA)

The thermal decomposition (decomposition temperature, T_{max}) of PLA was carried out by thermogravimetric analysis with a Perkin-Elmer TGA7 Series (USA) with approximately 10-20 mg sample from 25-500°C with heating rate of 10^{o}C/min at nitrogen atmosphere at the Department of Chemistry, Kasetsart University.

Part II: PLA modification by blending

Materials

1. Duck feather

Duck feather was purchased from Ban Huay Jakan Royal Farm Projects, Chiang Mai, Thailand. Duck feather was cleaned to remove stains with household detergent 2 times, tap water 3-4 times, distilled water 2 times and dried in conventional oven at 60°C for 48 h (Figure 19(a)). Dried and cleaned duck feather was cut to separate the barb from the rachis (Figure 19) manually. The barb of duck feathers was then chopped using a two speed laboratory blender (Waring 8010s, USA) at least 3 times at 18,000 rpm for 1 minute, so that the final length of the barbs was in between 2-4 cm. The chopped duck feather was further soaked in acetone for 24 h and in chloroform for 24 h to remove fat attached on the surface of duck feather. After decanting out the chloroform, duck feather was laid at room temperature for 5-6 h to evaporate off the chloroform, dried in conventional oven at 60°C for 24 h and kept in a desiccator for further use as shown in the Figure 19(b). The chopped barb obtained is called as duck feather fiber (DF) in this study. Prior to blending, DF was dried in a conventional oven at 60^{o}C for at least 10 h.

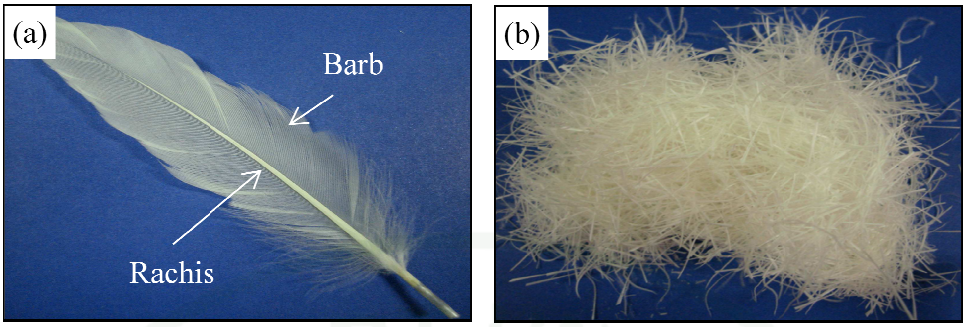
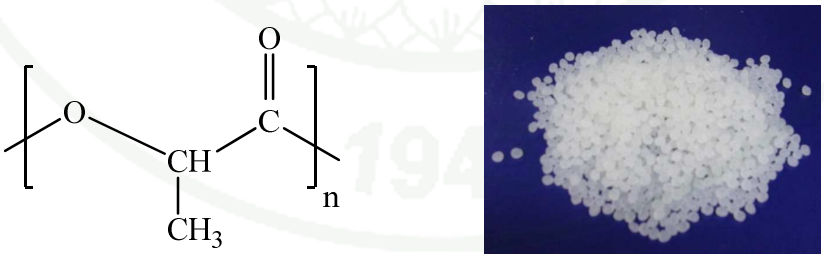


Figure 19 (a) Duck feather after cleaning, washing and drying showing the barb and rachis (b) duck feather fiber obtained from the barb.

2. Chemicals

The following chemicals and polymers were obtained from the commercial sources and used directly without any further purification unless noted:

2.1 Polylactic acid, PLA, (NatureWork PLA Polymer 2002D) was purchased from Fresh Bag Co. Ltd., Bangkok, Thailand. It has a density of 1.24 g/cm^3 and the melt flow index (MFI) of 5-7g /10 min at 210°C/2.16 kg (Figure 20). Prior to blending, PLA was dried in a vacuum oven for overnight.



(a) (b)

Figure 20 (a) Structure of polylactic acid, PLA and (b) PLA pellets.

2.2 Polyethylene glycol, PEG, ($\overline{M}_n$ = 4,600 (PEG1) and 10,000 (PEG2)) was purchased from, Sigma-Aldrich, USA (Figure 21). Prior to blending, PEG was dried in a vacuum oven for overnight.

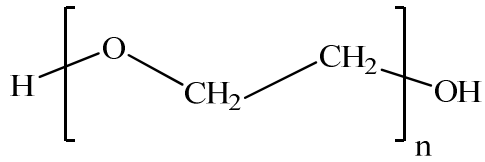


Figure 21 Structure of polyethylene glycol, PEG.

2.3 Polydioxolane, PDXL, ($\overline{M}_n$ = 10,000 (PDXL1) and 200,000 (PDXL2)) was supplied by Nippon Shokubai, Japan (Figure 22). Prior to blending, PDXL was dried in a vacuum oven for overnight.

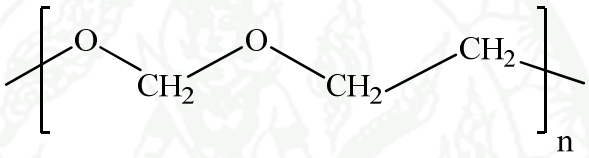


Figure 22 Structure of polydioxolane, PDXL.

2.4 Household gloves latex, LT1, was purchased from Rubber-Based Industry Club, Federation of Thai Industries, Thailand. The formulation of the household gloves latex was shown in Table 10.

Table 10 Formulation of the household gloves latex.

Ingredient	Composition (g)
60% Natural rubber latex	167.0
10% Potassium hydroxide	2.5
20% Potassium laurate	1.0
50% Sulfur	2.5
50% Zinc diethyldithiocarbamate (ZDEC)	0.8
50% Zinc 2- mercaptobenzothiazole (ZMBT)	2.0
50% Wingstay L	2.0
33% Diphenylguanidine (DPG)	4.5
50% Calcium carbonate	45.0
50% Zinc oxide	2.0
Water	70.0

2.5 Concentrated natural rubber latex, LT2, was purchased from Thai Rubber Latex Corporation (Thailand) Public Company Limited. It was stabilized with 0.70 by mass of ammonia having total solid content (TSC) and dry rubber content (DRC) of 62% and 60% by mass, respectively.

2.6 Poly(*cis*-1,4-isoprene), IR, having 97% *cis*-1,4 content and $\overline{M}_W$ ~ 38,000 (by GPC), was purchased from Sigma-Aldrich, USA (Figure 23).

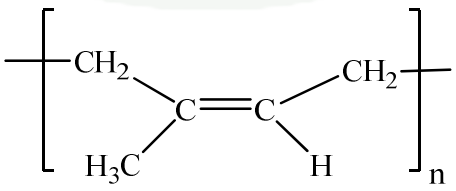


Figure 23 Structure of poly(*cis*-1,4-isoprene), IR.

2.7 Poly(acrylonitrile-*co*-butadiene) dicarboxy terminated, NBR, having $\overline{M}_n$ ~3,800, 8-12 wt% acrylonitrile content and T_g of -66°C (by DSC), was purchased from Sigma-Aldrich, USA (Figure 24).

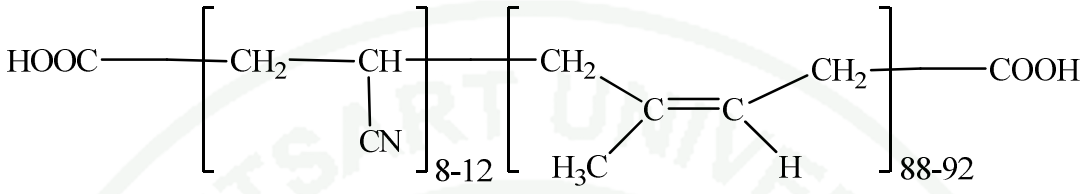


Figure 24 Structure of poly(acrylonitrile-*co*-butadiene) dicarboxy terminated, NBR.

2.8 Poly(ethylene-*co*-vinyl acetate), PEVA, having 40 wt% of vinyl acetate content, melt flow index of 57g/10 min at 190°C/2.16 kg, T_g of -40 - -30°C and T_m of 110-120°C, was purchased from Sigma-Aldrich, USA (Figure 25).

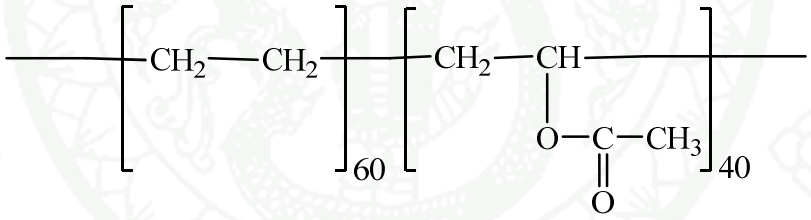


Figure 25 Structure of poly(ethylene-*co*-vinyl acetate), PEVA.

2.9 Chloroform (Analytical reagent grade, Lab Scan).

2.10 Acetone (Analytical reagent grade, Lab Scan).

3. Equipments

3.1 Polylactic acid (PLA) blends

3.1.1 Blending

PLA blends partly were mixed to assure well dispersion using a one liter two speed laboratory stainless steel container blender (Waring 8010s, USA) at 18,000 rpm for 10 min at room temperature prior to casting or milling (Figure 26).

Figure 26 Two speed laboratory stainless steel container blender (Waring 8010s, USA).

3.1.2 Casting

PLA blends partly were cast using a glass plate (30 cm x 70 cm) at room temperature (25^{o}C) and about 72% relative humidity with the help of a glass rod to form sheet with the required thickness of approximately <2 mm (Figure 27).

Figure 27 Casting of PLA blends on a glass plate.

3.1.3 Milling

Polylactic acid blends partly were prepared using a two-roll-mill, model YFCR6, Chor. Sri-Anan Co., LTD, Thailand at the Chemistry Department, Kasetsart University at 120^{o}C by varying the roll gap from 1.6-0.2 mm with controlling the roll gap to decrease 0.2 mm in every 4 rounds (Figure 28).

Figure 28 Two roll mill (Model YFCR 6, Chor. Sri-Anan Co. Ltd., Thailand).

3.2 Mechanical properties

3.2.1 Compression molding

PLA blends were compression molded into a 1.00 mm thickness sheet (Compression molding, G30H-15-CX, Wabash, USA) from a 120 x 120 mm window frame by pre-heating at 190^{o}C for 15 min, compressing at 10 MPa for 10 min and then cooling down to room temperature for 30 min at the Department of Chemistry, Kasetsart University. The sheets were then cut into dumbbell-shaped pieces for tensile testing.

3.2.2 Tensile testing

Tensile properties of PLA blends were measured using a Tensile Universal Testing Machine, INSTRON 5566, according to ASTM D638 at Research and Development Centre for Thai Rubber Industry, Faculty of Science, Mahidol University, Salaya, Nakorn Pathom Campus. The specimens with 6.0 mm width, 60 mm length and 0.6 mm thickness were tested with 1 kN load cell at a rate of 50 mm/min. An average of at least five specimens for each blend was taken and the mean values and the standard deviation were calculated. Young's modulus was calculated from the initial part of the slope of the stress-strain curves. The ductility or the ability of PLA blends to undergo plastic deformation without fracture was calculates using the following relation:

Ductility = failure strain / yielding strain

3.3 Morphology analysis

The morphology of PLA blends was observed by scanning electron microscope (SEM), JEOL JSM-6400 and JEOL JSM 5800 LV, at Scientific and Technological Research Equipment Center, Chulalongkorn University. SEM with field emission gun and accelerating voltage of 15 kV was used to collect SEM images

from the compression moldeded sheets. The compression molded sheets were broken in liquid N_2 to avoid deformation of phase. Micrograph of each blend was recorded after the broken surfaces were coated with of 2-3 nanometer gold (Balzers, Union SCD 040).

3.4 Thermal properties

Differential scanning calorimetry (DSC)

The glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) of PLA blends were measured with a Perkin-Elmer DSC7 Series (USA) from the compression molded sheet from 0-200^{o}C using heating rate of 10^{o}C/min and cooling rate of 5^{o}C/min at the Department of Chemistry, Kasetsart University. Indium was used as standard for temperature calibration and the measurements were made under constant flow of nitrogen.

The degree of crystallization of PLA blend was calculated using the following equation (Spinu, 1993):

$$\chi_C = \frac{\Delta H_{PLAsample}}{\Delta H_{PLA100}} \times 100$$

where: χ_c = the degree of crystallinity.

$\Delta H_{PLAsample}$ = the heat of fusion or crystallization of the PLA sample.

ΔH_{PLA100} = the heat of fusion or crystallization for 100% crystalline PLA = 93.7 J/g.

Part I: Direct melt polycondensation of lactic acid

Methods

1. Synthesis of polylactic acid (PLA) with 100 g of lactic acid (LA)

1.1 Synthesis of PLA by direct melt polycondensation (DMPC)

Dehydrated LA1 (from Aldrich) and catalyst A or B with the mole ratio of LA1:catalyst = 100:1, 500:1 or 1000:1 were transferred into 100 ml two necks round bottom flask having a magnetic stirring bar inside. The first neck connected to a nitrogen inlet and the second neck connected to a three way adapter holding a nitrogen outlet in one end and a condenser at another end. The condenser then connected to the vacuum-distilling adapter for applying vacuum to the system and led to a collection flask. The heating is done by immersing the round bottom flask in a control temperature bath containing silicon oil on a hotplate stirrer as shown in Figure 29. The system was heated by alternating between purging with dry nitrogen for 15 min and evacuating under reduced pressure (15 mmHg) for 15 min (approximately 3 times) until the temperature of the reaction mixture reached to the required temperature.

1.1.1 Synthesis of PLA by DMPC for 12 h

After heating the reaction mixture to 160^{o}C, 170^{o}C or 180°C, it was kept at either one of these temperatures for 12 h by alternating between under nitrogen atmosphere for 3 h and under reduced pressure (15 mmHg) for 1 h to remove the condensate water byproduct from the DMPC (Figure 30). The reaction conditions were concluded in Table 11.

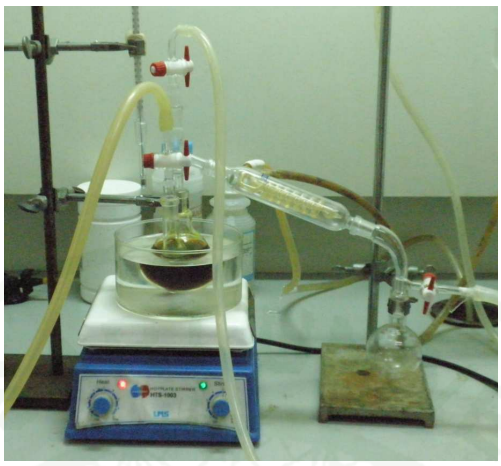


Figure 29 System setup for carrying the DMPC with 100 g of LA.

1.1.2 Synthesis of PLA by DMPC for 6, 6 h

The DMPC was carried out by heating in two steps. After heating the reaction mixture to 135^{o}C, it was kept at this temperature for 6 h by alternating between under N_2 atmosphere for 2 h and under reduced pressure (15 mmHg) for 1 h. Then the temperatures was increased to 160^{o}C, 170^{o}C or 180°C and was kept at either one of these temperatures for 6 h by alternating between under nitrogen atmosphere for 2 h and under reduced pressure (15 mmHg) for 1 h to remove the condensate water byproduct from the DMPC (Figure 30). The reaction conditions were concluded in Table 12.

At the end of the reaction in 1.1.1 and 1.1.2, the reaction mixture was cooled down to room temperature; 30 ml of chloroform was added to dissolve the crude PLA, filtered and subsequently precipitated into methanol. The resulting PLA powder were filtered and dried under vacuum for 24 h.

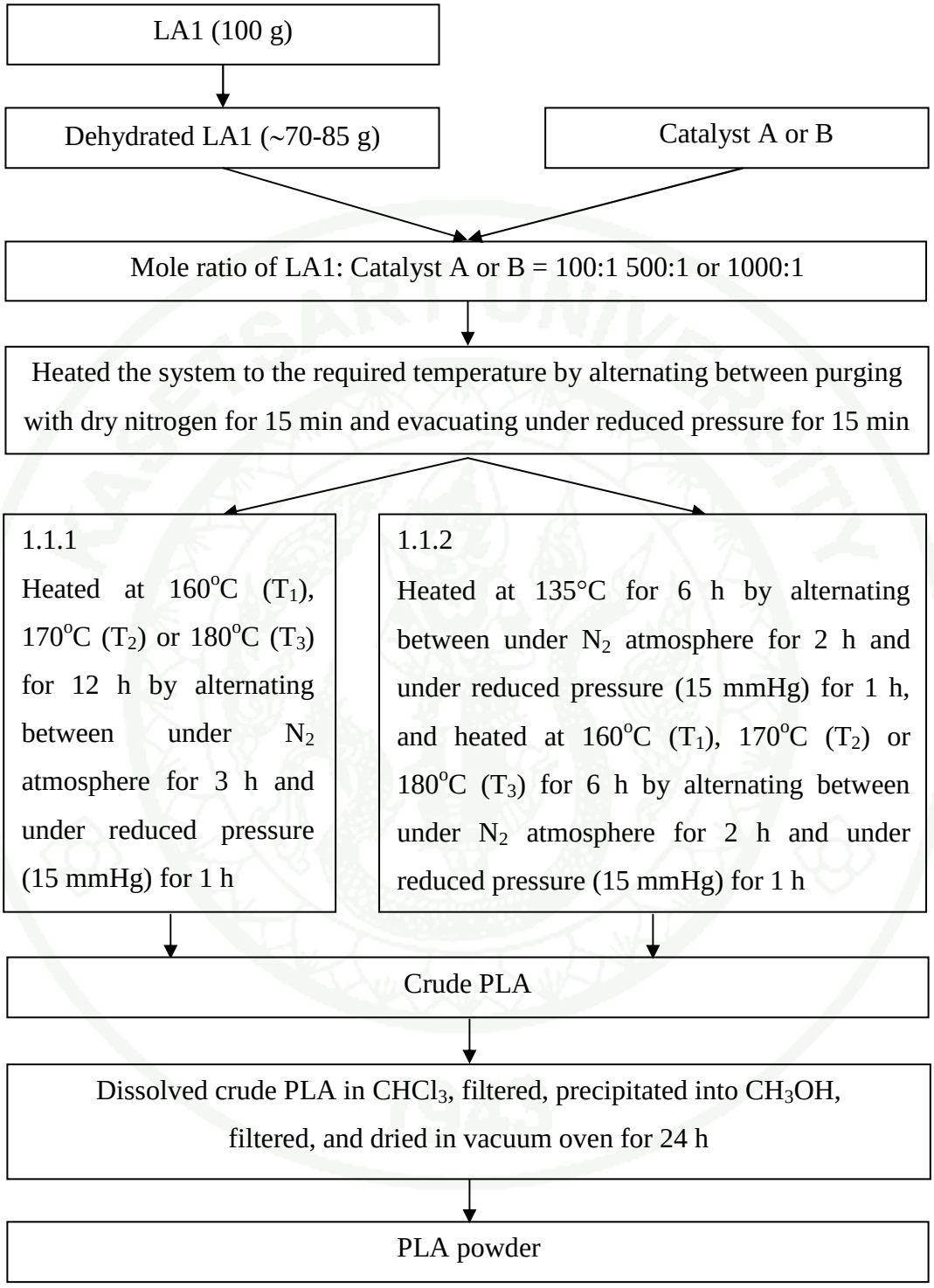


Figure 30 Flow chart for synthesis of PLA by DMPC with100 g of LA.

Table 11 Synthesis of PLA by DMPC with 100 g of LA using catalyst A or B for 12 h.

Temperature	LA1: catalyst A			LA1: catalyst B		
(^{o}C)	100:1	500:1	1000:1	100:1	500:1	1000:1
160	A_1T_1	A_2T_1	A_3T_1	B_1T_1	B_2T_1	B_3T_1
170	A_1T_2	A_2T_2	A_3T_2	B_1T_2	B_2T_2	B_3T_2
180	A_1T_3	A_2T_3	A_3T_3	B_1T_3	B_2T_3	B_3T_3

Table 12 Synthesis of PLA by DMPC with 100 g of LA using catalyst A or B for 6, 6 h.

Temperature	LA1: catalyst A			LA1: catalyst B		
(^{o}C)	100:1	500:1	1000:1	100:1	500:1	1000:1
160	A_1T_1M	A_2T_1M	A_3T_1M	B_1T_1M	B_2T_1M	B_3T_1M
170	A_1T_2M	A_2T_2M	A_3T_2M	B_1T_2M	B_2T_2M	B_3T_2M
180	A_1T_3M	A_2T_3M	A_3T_3M	B_1T_3M	B_2T_3M	B_3T_3M

1.1.3 Synthesis of PLA by solution polycondensation (SP) for 6 h

Dehydrated LA1 (from Aldrich) and catalyst A or B with the mole ratio of LA1:catalyst = 100:1, 500:1 or 1000:1, 25 ml toluene and 25 ml of 1-methyl-2-pyrrolidone (NMP) were transferred into a 100 ml two necks round bottom flask having a magnetic stirring bar inside. The first neck connected to a nitrogen inlet and the second neck connected to a Dean-Stark trap fitted with a condenser holding a nitrogen outlet which led to the vacuum valve for applying vacuum to the system. The heating is done by immersing the round bottom flask in a control temperature bath containing silicon oil on a hotplate stirrer as shown in Figure 31. The nitrogen sparkled reaction mixture was heated for 6 h under reflux (at approximately 135-140°C) until the condensate water byproduct from the polycondensation was removed completely from the system by toluene-water azeotropic distillation. When it

appeared that no addition water was being collected, toluene and NMP were quantitatively removed from the reaction system by distillation respectively. The polycondensation was continued by heating the reaction mixture to 160^{o}C, 170^{o}C or 180^{o}C and was kept at either one of these temperatures for 6 h by alternating between under nitrogen atmosphere for 2 h and under reduced pressure (15 mm Hg) for 1 h (Figure 32). The reaction condition was concluded in Table 13.

At the end of the reaction, the reaction mixture was cooled down to room temperature; 30 ml of chloroform was added to dissolve the crude PLA, filtered and subsequently precipitated into methanol. The resulting PLA powder were filtered and dried under vacuum for 24 h.

Figure 31 System setup showing the Dean-Stark trap for carrying the SP with 100 g of LA.

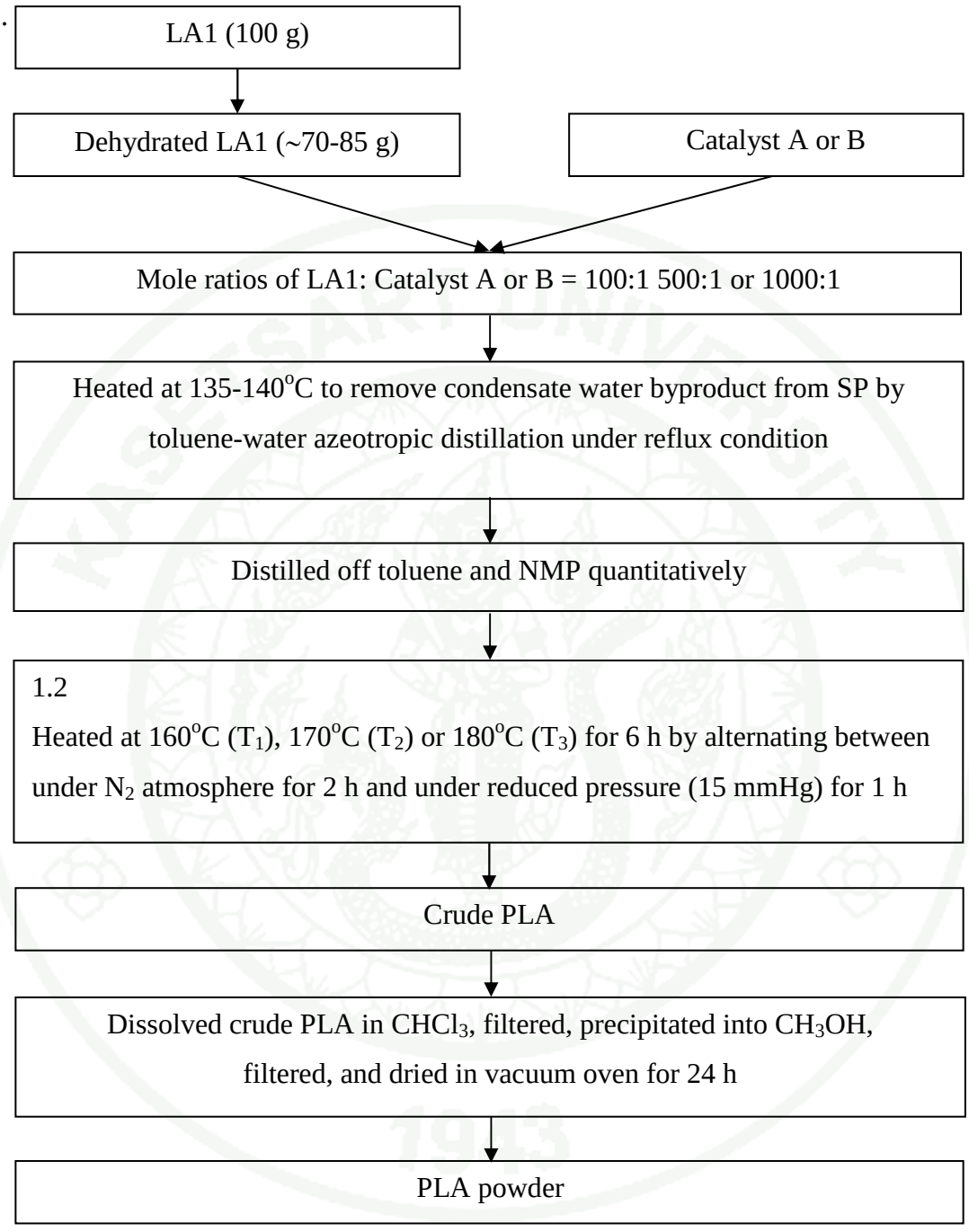


Figure 32 Flow chart for synthesis of PLA by SP with 100 g of LA.

Table 13 Solution polycondensation with 100 g of LA using catalyst A or B for 6 h.

Temperature	LA1: catalyst A			LA2: catalyst B		
(^{o}C)	100:1	500:1	1000:1	100:1	500:1	1000:1
160	A_1T_1S	A_2T_1S	A_3T_1S	B_1T_1S	B_2T_1S	B_3T_1S
170	A_1T_2S	A_2T_2S	A_3T_2S	B_1T_2S	B_2T_2S	B_3T_2S
180	A_1T_3S	A_2T_3S	A_3T_3S	B_1T_3S	B_2T_3S	B_3T_3S

2. Synthesis of PLA by DMPC with 1 kg of LA

Lactic acid (LA1 from Aldrich or LA2 from Purac) 1 kg was transferred into a 1000 ml two necks round bottom flask having a magnetic stirring bar inside. The first neck connected to a nitrogen inlet and the second neck connected to a three way adapter holding a nitrogen outlet in one end and a condenser at another end. The condenser then connected to the vacuum-distilling adapter for applying vacuum to the system and led to a collection flask. The heating is done by immersing the round bottom flask in a control temperature bath containing silicon oil on a hotplate stirrer as shown in Figure 33. The LA was dehydrated for a different time period at 105°C by alternating between under purging with dry nitrogen for 3 h and under reduced pressure (15 mmHg) for 1 h as stated in Table 14 to remove the excess water before used. The system was cooled down to room temperature and catalyst B was added into the round bottom flask with mole ratios of distilled LA: catalyst B = 500:1 and 1000:1. The system was heated by alternating between purging with dry nitrogen for 15 min and evacuating under reduced pressure (15 mmHg) for 15 min (approximately 3 times) until the temperature of the reaction mixture reached to 160^{o}C, 170^{o}C or 180°C and was kept at either one of these temperatures for different time period by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg) to remove the condensate water byproduct from the DMPC (Figure 34). The reaction conditions were concluded in Table 14.

At the end of the reaction, the reaction mixture was cooled down to room temperature, 300 ml of chloroform was added to dissolve the crude PLA, filtered and subsequently precipitated into methanol. The resulting PLA powder were filtered and dried under vacuum for 24 h. In case there was no precipitation after adding the crude PLA/$CHCl_3$ solution into methanol, the solvent in the mixture was evaporated off by rotary evaporator and brown viscous gel like PLA was obtained.

Figure 33 System setup for carrying the DMPC with 1 kg of LA.

Table 14 Synthesis of PLA by DMPC with 1 kg of LA using catalyst B.

Codes	**LA/B**	**Temp. (^oC)**	**LA/dehydrated (h)***	**N_2/pressure** h:h (total h)**	**Reaction Time (h)**
$C_1B_2T_2$-1	500:1	170	LA1/8	3:1 (12)	12
$C_1B_2T_2$-2	500:1	170	LA1/8, $C_1B_2T_2$-1	3:1 (12), 3:1 (12)	24
$C_1B_2T_2$-3	500:1	170	LA1/8, $C_1B_2T_2$-1 $C_1B_2T_2$-2	3:1 (12), 3:1 (12), 3:1 (12)	36
$C_2B_2T_2$-1	500:1	170	LA1/8	3:1 (16)	16
$C_2B_2T_2$-2	500:1	170	LA1/8, $C_2B_2T_2$-1	3:1 (16), 3:1 (16)	32
$C_3B_2T_2$-1	500:1	170	LA1/8	3:2 (10), 12:2 (14)	24
$C_3B_2T_2$-2	500:1	170	LA1/8; $C_3B_2T_2$-1	3:2 (10), 12:2 (14); 3:1 (10)	34
$C_3B_2T_2$-3	500:1	170	LA1/8; $C_3B_2T_2$-1; $C_3B_2T_2$-2	3:2 (10), 12:2 (14); 3:1 (10); 3:1 (10)	44
$C_3B_2T_2$-4	500:1	170	LA1/8; $C_3B_2T_2$-1; $C_3B_2T_2$-2; $C_3B_2T_2$-3	3:2 (10), 12:2 (14); 3:1 (10); 3:1 (10); 3:1 (10)	54
$C_3B_2T_2$-5	500:1	170	LA1/8; $C_3B_2T_2$-1; $C_3B_2T_2$-2; $C_3B_2T_2$-3; $C_3B_2T_2$-4	3:2 (10), 12:2 (14); 3:1 (10); 3:1 (10); 3:1 (10); 3:1 (10)	64
$C_4B_2T_1$-1	500:1	160	LA1/8	3:2 (10), 14:0 (14), 10:2 (48)	72
$C_4B_2T_1$-2	500:1	160	LA1/8; $C_4B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$C_5B_2T_2$-1	500:1	160	LA1/8	3:2 (10), 14:0 (14), 10:2 (48)	72
$C_5B_2T_2$-2	500:1	160	LA1/8; $C_5B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$C_6B_3T_2$-1	1000:1	170	LA1/8	3:2 (10), 14:0 (14), 10:2 (48)	72

Table 14 (Continued)

Codes	LA/B	Temp. (^oC)	LA/dehydrated (h)*	N_2/pressure** h:h (total h)	Reaction Time (h)
$C_6B_3T_2$-2	1000:1	170	LA1/8; $C_6B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$C_7B_2T_0$-1	500:1	135	LA1/8	3:2 (10), 14:0 (14), 10:2 (48)	72
$C_7B_2T_2$-2	500:1	170	LA1/8; $C_7B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$C_8B_3T_0$-1	1000:1	135	LA1/8	3:2 (10), 14:0 (14), 10:2 (48)	72
$C_8B_3T_2$-2	1000:1	170	LA1/8; $C_8B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$C_9B_2T_1$	500:1	160	LA1/4	3:1 (24)	24
$C_{10}B_2T_1$	500:1	170	LA1/4	3:1 (24)	24
$C_{11}B_2T_2$-1	500:1	170	LA1/4	3:1 (24)	24
$C_{11}B_2T_2$-2	500:1	170	LA1/4, $C_{11}B_2T_2$-1	3:1 (24), 3:1 (24)	48
$C_{12}B_2T_2$-1	500:1	170	LA1/8	3:1 (24)	24
$C_{12}B_2T_2$-2	500:1	170	LA1/8; $C_{12}B_2T_2$-1	3:1 (24), 3:1 (24)	48
$C_{13}B_2T_3$	500:1	180	La1/8	3:1 (24)	24
$C_{14}B_2T_3$***	500:1	180	LA2/8	3:1 (24)	24
$C_{15}B_2T_3$***	500:1	180	LA1/8	3:1 (24)	24
$C_{16}B_2T_3$	500:1	180	LA2/24	3:1 (24)	24

*LA1 (Lactic acid from Aldrich), LA2 (Lactic acid from Purac)/dehydrated at 105^{o}C under purging with dry N_2 and under reduced pressure for different time period

**Alternating between under N_2 atmosphere and under reduced pressure (15 mmHg) for different time period

*** Surrounding with dry ice

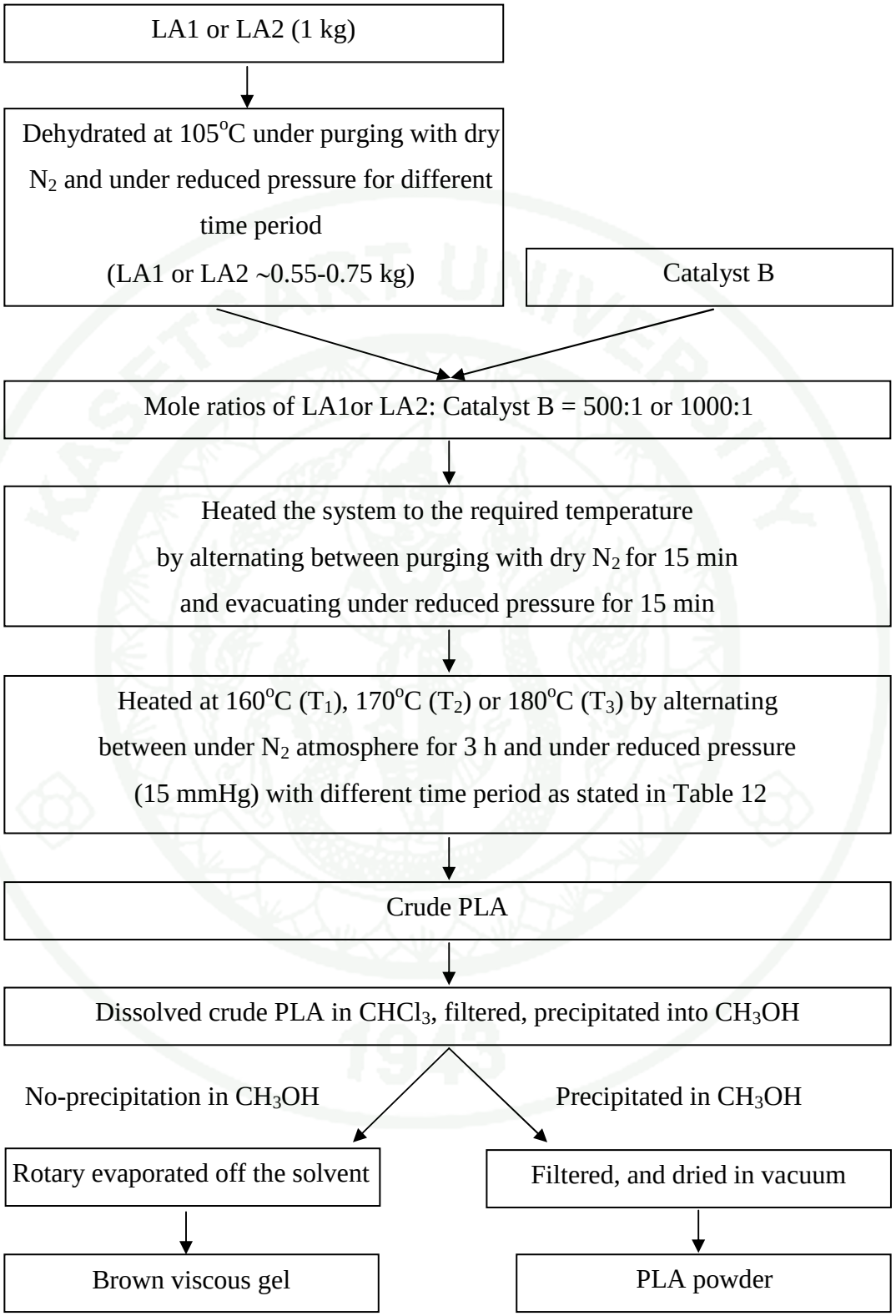


Figure 34 Flow chart for synthesis of PLA by DMPC with 1 kg of LA.

3. Synthesis of PLA by DMPC with 10 kg of LA using catalyst B

LA2 (Lactic acid from Purac) 10 kg were transferred into a 10 L stainless steel jacketed cylindrical reaction kettle with open cover. The open cover has one neck in the center and two equally spaced necks on both sides. The center neck was equipped with a variable speed motor movable stainless steel 4-blades propeller stirrer shaft having a side arm connected to a stainless steel condenser. The delivery end of the condenser connected to the vacuum valve for applying vacuum to the system and the condenser is positioned so that the delivery end directed the distillate into the collection vessel. The two side necks were equipped with nitrogen inlet and a thermocouple for controlling the reaction temperature via a temperature controlled panel respectively. The LA2 was dehydrated at 105°C by alternating between under purging with dry nitrogen and under reduced pressure (15 mmHg) for 12 or 24 h as stated in Table 15 to remove the excess water before used. The system was cooled down to room temperature and catalyst B was added into the round bottom flask with mole ratio of dehydrated LA2: catalyst B = 500:1 and 1000:1. The system was heated by alternating between purging with dry nitrogen for 15 min and evacuating under reduced pressure (15 mmHg) for 15 min (approximately 3 times) until the temperature of the reaction mixture reached to 160^{o}C or 170^{o}C and was kept at either one of these temperatures for different time period by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg) to remove the condensate water byproduct from the DMPC (Figure 36). The reaction conditions were concluded in Table 15.

At the end of the reaction, the movable shaft was lifted above the reaction mixture to prevent the shaft from hardening in the reaction mixture after it was cooled down to room temperature, 2,000 ml of chloroform was added to dissolve the crude PLA, filtered and subsequently precipitated into methanol. The resulting PLA powder were filtered and dried under vacuum for 24 h. In case there was no precipitation after adding the crude PLA/$CHCl_3$ solution into methanol, the solvent in the mixture was evaporated off by rotary evaporator and brown viscous gel like PLA was obtained.

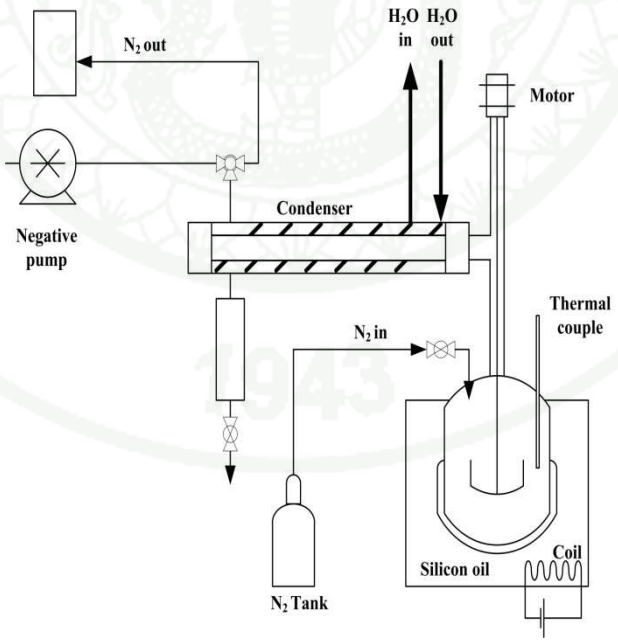


Figure 35 System setup for carrying the DMPC with 10 kg of LA.

Table 15 Synthesis of PLA by DMPC with 10 kg of LA using catalyst B.

Codes	**LA/B**	**Temp. (^oC)**	**LA/dehydrated (h)***	**N_2/pressure** h:h (total h)**	**Reaction Time (h)**
$D_1B_2T_0$-1	500:1	135	LA2/12	3:2 (10), 14:0 (14), 10:2 (48)	72
$D_1B_2T_2$-2	500:1	170	LA2/12; $D_1B_2T_0$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$D_2B_3T_0$-1	1000:1	135	LA2/12	3:2 (10), 14:0 (14), 10:2 (48)	72
$D_2B_3T_2$-2	1000:1		LA2/12; $D_2B_3T_0$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$D_3B_2T_2$	500:1	170	LA2/12	3:1 (12)	12
$D_4B_2T_2$	500:1	170	LA2/12	3:1 (16)	16
$D_5B_2T_1$-1	500:1	160	LA2/12	3:2 (10), 14:0 (14), 10:2 (48)	72
$D_5B_2T_1$-2	500:1	160	LA2/12; $D_5B_2T_1$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$D_6B_2T_2$-1	500:1	170	LA2/12	3:2 (10), 12:0 (12), 0:2 (2)	24
$D_6B_2T_2$-2	500:1	170	LA2/12; $D_6B_2T_2$-1	3:2 (10), 12:0 (12), 0:2 (2); 3:2 (10)	34
$D_6B_2T_2$-3	500:1	170	LA2/12; $D_6B_2T_2$-1; $D_6B_2T_2$-2	3:2 (10), 12:0 (12), 0:2 (2); 3:2 (10); 3:2 (10)	44
$D_6B_2T_2$ -4	500:1	170	LA2/12; $D_6B_2T_2$-1; $D_6B_2T_2$-2, $D_6B_2T_2$-3	3:2 (10), 12:0 (12), 0:2 (2); 3:2 (10); 3:2 (10); 3:2 (10)	54

Table 15 (Continued)

Codes	LA/B	Temp. (^oC)	LA/dehydrated (h)*	N_2/pressure** h:h (total h)	Reaction Time (h)
$D_6B_2T_2$-5	500:1	170	LA2/12; $D_6B_2T_2$-1; $D_6B_2T_2$-2, $D_6B_2T_2$-3; $D_6B_2T_2$-4	3:2 (10), 12:0 (12), 0:2 (2); 3:2 (10); 3:2 (10); 3:2 (10); 3:2 (10)	64
$D_7B_2T_2$-1	500:1	170	LA2/12	3:2 (10), 14:0 (14), 10:2 (48)	72
$D_7B_2T_2$-2	500:1	170	LA2/12, $D_7B_2T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$D_8B_3T_2$-1	1000:1	170	LA2/12	3:2 (10), 14:0 (14), 10:2 (48)	72
$D_8B_3T_2$-2	1000:1	170	LA2/12, $D_8B_3T_2$-1	3:2 (10), 14:0 (14), 10:2 (48); 3:2 (25)	97
$D_9B_2T_2$	500:1	170	LA2/12	4:2 (48)	48
$D_{10}B_2T_2$***	500:1	170	LA2/24	4:2 (48)	48
$D_{11}B_2T_2$	500:1	170	LA2/24	4:2 (48)	48

*LA2 (Lactic acid from Purac)/dehydrated at 105^{o}C under purging with dry N_2 and under reduced pressure for different time period

**Alternating between under N_2 atmosphere and under reduced pressure (15 mmHg) for different time period

*** Surrounding with dry ice

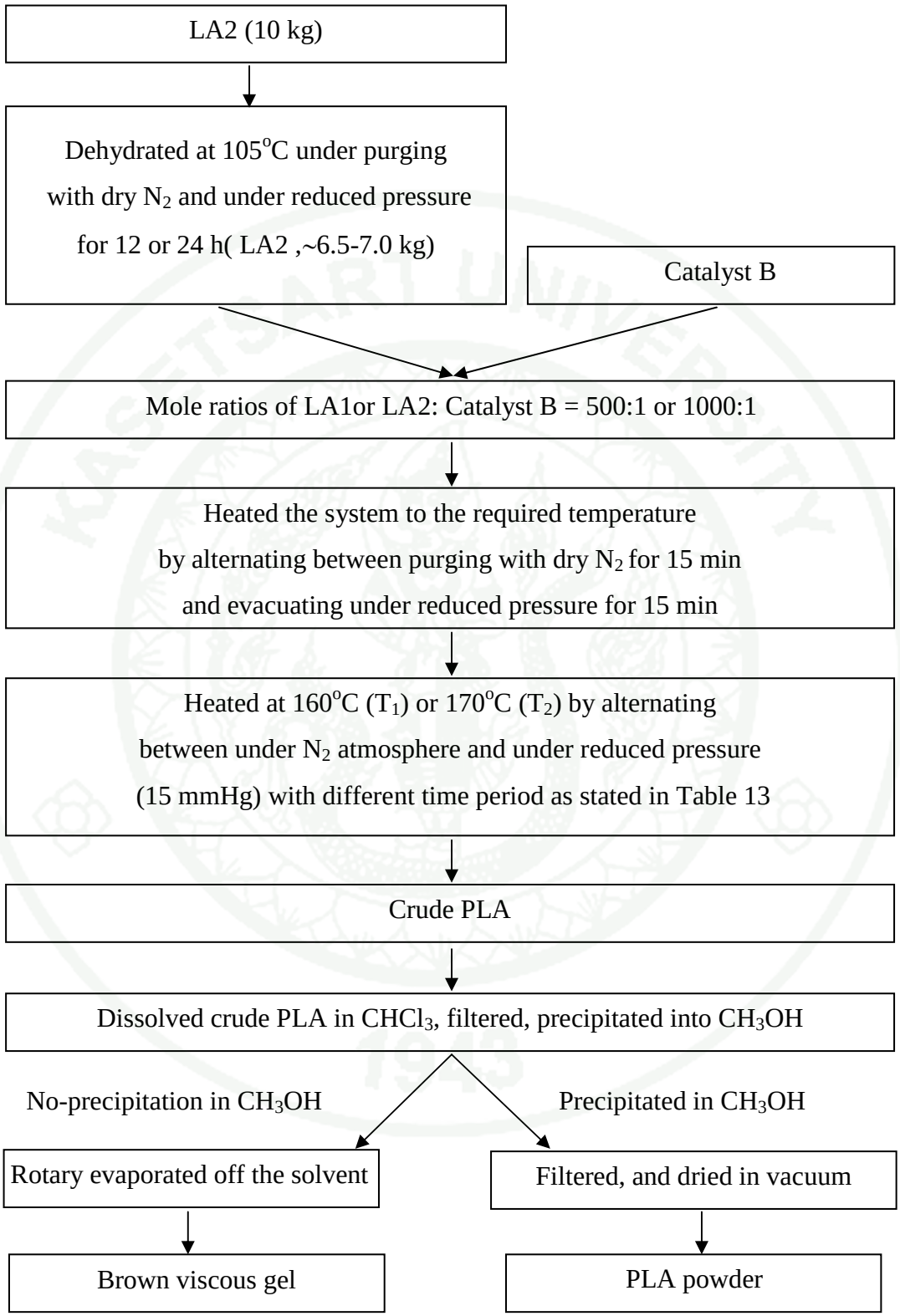


Figure 36 Flow chart for synthesis of PLA by DMPC with 10 kg of LA using catalyst B.

Part: PLA modification by blending

Methods

1. Polylactic acid (PLA)/duck feather fiber (DF) blends

1.1 PLA/PEG and PLA/PDXL blends

PLA/PEG and PLA/PDXL blends vary from 95/5, 90/10, 85/15 and 80/20 weight ratio (wt. ratio) were prepared as shown in Table 16 and Figure 37. The desired weight of dried PLA (95, 90, 85 and 80 wt. ratio) was first dissolved in 500 ml of chloroform and stirred on magnetic stirrer at room temperature for 24 h. Then desired weight (5, 10, 15 and 20 wt. ratio) of dried PEG ($\overline{M}_n$ = 4,600 (PEG1) and 10,000 (PEG2)) or dried PDXL ($\overline{M}_n$ = 10,000 (PDXL1) and 200,000 (PDXL2)) was added and the mixture was further stirred at room temperature for 3-4 h. The mixture was laid undisturbed for approximately 1-1½ h before casting to assure no more bubbles in the mixture. After casting uniformly, the PLA/PEG or PLA/PDXL sheet was laid undisturbed again at room temperature to evaporate off the chloroform for 24 h and the sheet was further dried in vacuum oven at room temperature for 24 h. PLA/PEG or PLA/PDXL sheet obtained from casting was then cut into small pieces, compression molded and then cut into dumbbell-shaped pieces for further characterization.

Table 16 PLA/PEG and PLA/PDXL blends.

Samples: weight ratio	PLA (g)	PEG (g)/ $\overline{M}_n$		PDXL (g)/ $\overline{M}_n$	
		4,600	10,000	10,000	200,000
PLA/PEG1:95/5	95	5	-	-	-
PLA/PEG1:90/10	90	10	-	-	-
PLA/PEG1:85/15	85	15	-	-	-
PLA/PEG1:80/20	80	20	-	-	-
PLA/PEG2:95/5	95	-	5	-	-
PLA/PEG2:90/10	90	-	10	-	-
PLA/PEG2:85/15	85	-	15	-	-
PLA/PEG2:80/20	80	-	20	-	-
PLA/PDXL1:95/5	95	-	-	5	-
PLA/PDXL1:90/10	90	-	-	10	-
PLA/PDXL1:85/15	85	-	-	15	-
PLA/PDXL1:80/20	80	-	-	20	-
PLA/PDXL2:95/5	95	-	-	-	5
PLA/PDXL2:90/10	90	-	-	-	10
PLA/PDXL2:85/15	85	-	-	-	15
PLA/PDXL2:80/20	80	-	-	-	20

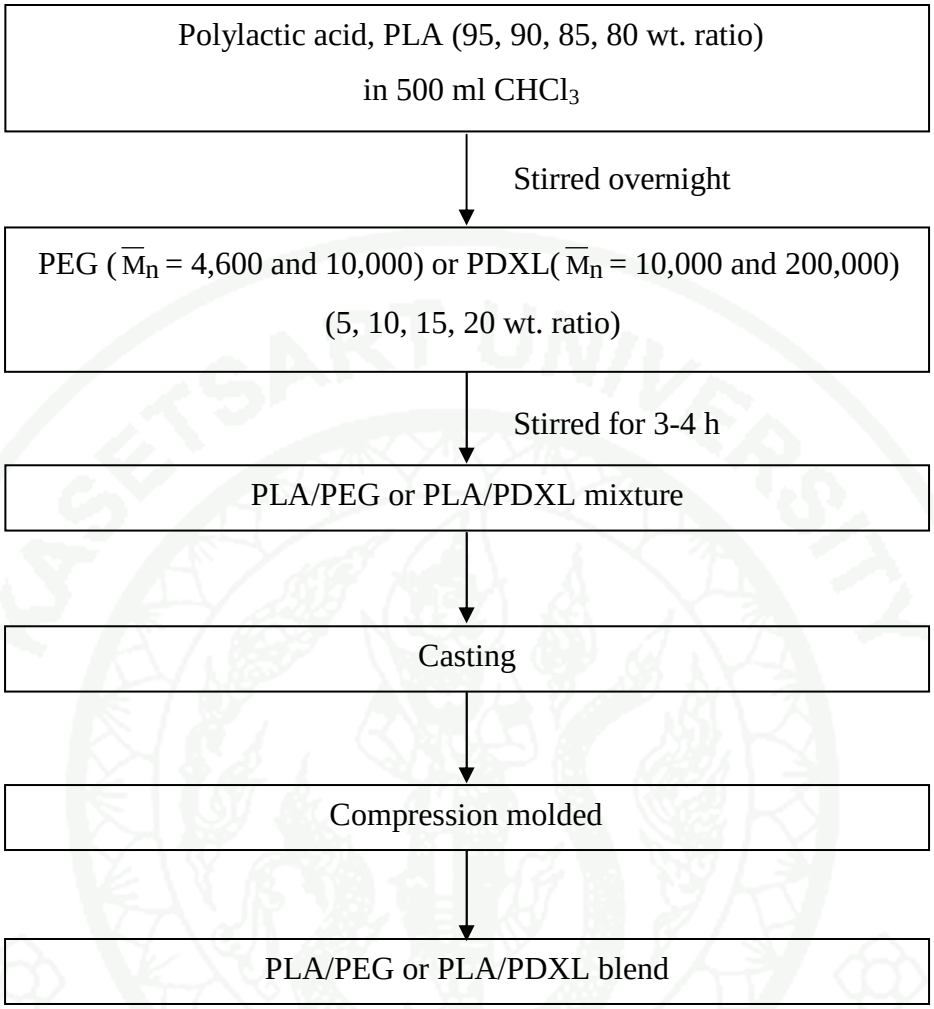


Figure 37 Flow chart for preparation of PLA/PEG and PLA/PDXL blends.

1.2 PLA/DF blends

PLA/DF blends vary from 95/5, 90/10, 85/15 and 80/20 wt. ratio were prepared as shown in Table 17 and Figure 38. The desired weight of dried PLA (95, 90, 85 and 80 wt. ratio) was first dissolved in 500 ml of chloroform and stirred on magnetic stirrer at room temperature for 24 h. Then, the desired weight of dried duck feather fiber, DF (5, 10, 15 and 20 wt. ratio) was added and the mixture was further stirred at room temperature for 30 min or until the mixture was well dispersed. The mixture was laid undisturbed before casting to assure no more bubbles in the mixture for approximately 1-1½ h. After casting, the PLA/DF sheet was laid undisturbed

again at room temperature to evaporate off the chloroform for 24 h and the PLA/DF sheet obtained was divided into two portions equally. The first portion of PLA/DF sheet was cut into small pieces and kneaded by a two roll mill. Both PLA/DF sheet obtained from the second portion of casting and from two roll mill were cut into small pieces, compression molded and then cut into dumbbell-shaped pieces for further characterization.

1.3 PLA/DF/PEG and PLA/DF/PDXL blends

PLA/DF/PEG and PLA/DF/PDXL blends, by varying the weight ratio (wt. ratio) of PLA, DF and PEG or PDXL from 80-95, 5-20 and 10-15 wt. ratio respectively, were prepared as shown in Table 17 and Figure 38. The desired weight of dried PLA (95, 90, 85 and 80 wt. ratio) was first dissolved in 500 ml of chloroform and stirred on magnetic stirrer at room temperature for 24 h. Then, the desired weight of dried PEG2 ($\overline{M}_n$ = 10,000), PDXL1 ($\overline{M}_n$ = 10,000) and PDXL2 ($\overline{M}_n$ = 200,000) (10, 10 and 15 wt. ratio respectively) was added and the mixture was stirred at room temperature for 3-4 h. Lastly, the desired weight of duck feather fiber, DF (5, 10, 15 and 20 wt. ratio) was added and the mixture was further stirred at room temperature for 30 min or until the mixture was well dispersed. The mixture was laid undisturbed before casting to assure no more bubbles in the mixture for approximately 1-1½ h. After casting, the PLA/DF/PEG or PLA/DF/PDXL sheet was laid undisturbed again at room temperature to evaporate off the chloroform for 24 h and the PLA/DF/PEG or PLA/DF/PDXL sheet obtained was divided into two portions equally. The first portion of PLA/DF/PEG or PLA/DF/PDXL sheet was cut into small pieces and kneaded by a two roll mill. PLA/DF/PEG or PLA/DF/PDXL sheet obtained from the second portion of casting and from two roll mill were cut into small pieces, compression molded and then cut into dumbbell-shaped pieces for further characterization.

Table 17 PLA/DF, PLA/PEG2/DF, PLA/PDXL1/DF, and PLA/PDXL2/DF blends.

Samples: weight ratio	PLA (g)	PEG (g)/ $\overline{M}_n$		PDXL (g)/ $\overline{M}_n$		DF (g)
		4,600	10,000	10,000	200,000	
PLA/DF:95/5	95	-	-	-	-	5
PLA/DF:90/10	90	-	-	-	-	10
PLA/DF:85/15	85	-	-	-	-	15
PLA/DF:80/20	80	-	-	-	-	20
PLA/ PEG2/DF:95/10/5	95	-	10	-	-	5
PLA/ PEG2/DF:90/10/10	90	-	10	-	-	10
PLA/ PEG2/DF:85/10/15	85	-	10	-	-	15
PLA/ PEG2/DF:80/10/20	80	-	10	-	-	20
PLA/PDXL1/DF:95/10/5	95	-	-	10	-	5
PLA/PDXL1/DF: 90/10/10	90	-	-	10	-	10
PLA/PDXL1/ DF:85/10/15	85	-	-	10	-	15
PLA/PDXL1/DF:80/10/20	80	-	-	10	-	20
PLA/PDXL2/DF:95/15/5	95	-	-	-	15	5
PLA/PDXL2/DF: 90/15/10	90	-	-	-	15	10
PLA/PDXL2/ DF:85/15/15	85	-	-	-	15	15
PLA/PDXL2/DF:80/15/20	80	-	-	-	15	20

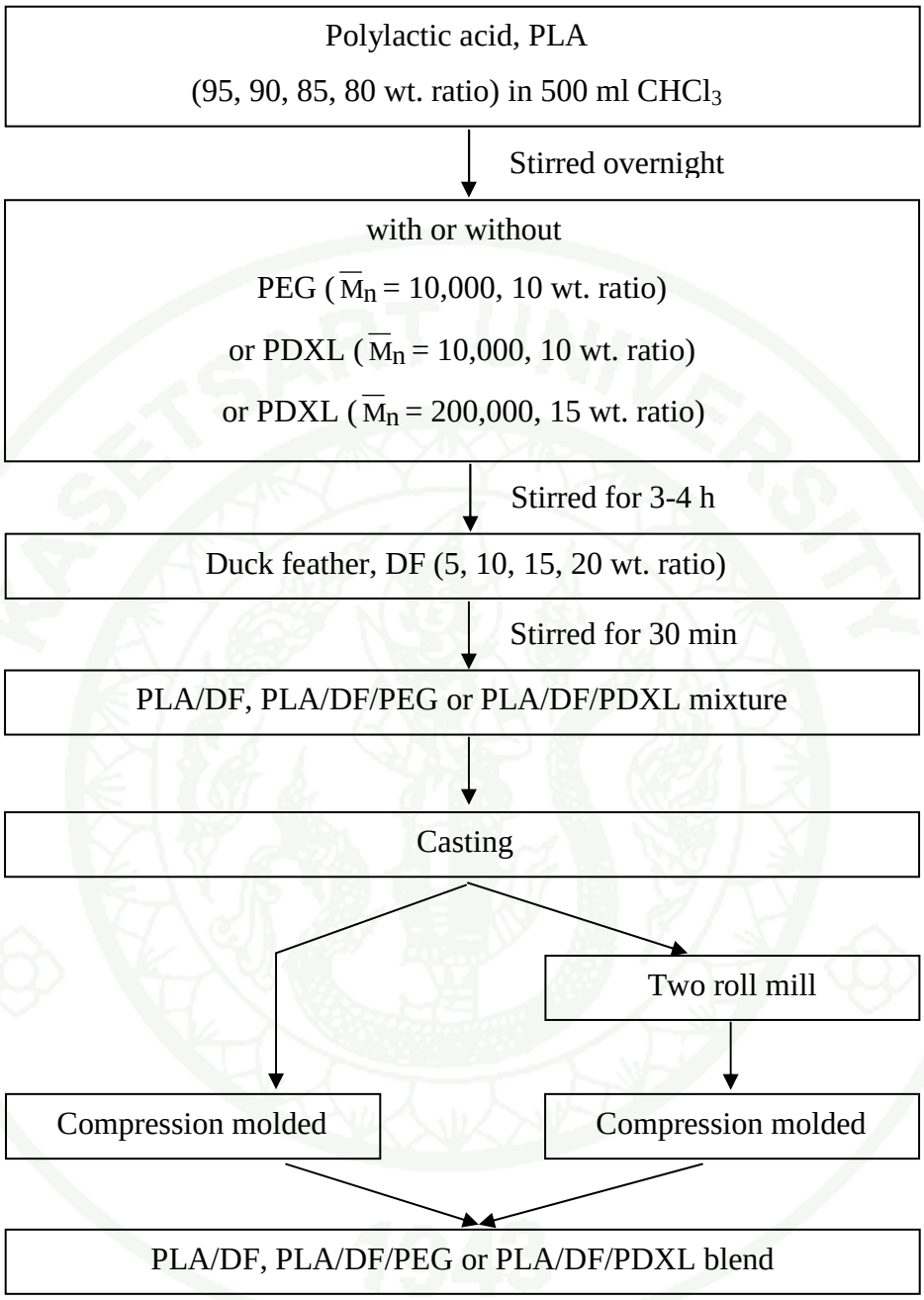


Figure 38 Flow chart for preparation of PLA/DF, PLA/DF/PEG and PLA/DF/PDXL blends.

2. PLA/impact modifier blends

PLA/impact modifier blends containing five impact modifiers: household gloves latex (LT1), concentrated natural rubber latex (LT2), poly(*cis*-1,4-isoprene) rubber (IR), poly(acrylonitrile-*co*-butadiene) rubber (NBR), and poly(ethylene-*co*-vinyl acetate) (PEVA) vary from 95/5 and 90/10 wt. ratio were prepared as shown in Table 18 and Figure 39. The desired weight (95 and 90 wt. ratio) of PLA was first dissolved in 500 ml of chloroform and stirred on magnetic stirrer at room temperature for 24 h. Impact modifiers, LT1, LT2, IR, NBR and PEVA, vary from 5 and 10 wt. ratio were dispersed in the prepared PLA chloroform solution using the two speed laboratory Waring 8010s blender at 18,000 rpm for 10 min at room temperature. The mixture was laid undisturbed before casting to assure no more bubbles in the mixture for approximately 1-1½ h. After casting, the PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA sheet was laid undisturbed again at room temperature to evaporate off the chloroform for 24 h, and PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA sheet was further dried in vacuum oven at room temperature for 24 h. PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA sheet obtained from casting was then cut into small pieces, compression molded and then cut into dumbbell-shaped pieces for further characterization.

Table 18 PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA blends.

Samples: weight ratio	PLA (g)	LT1 (g)	LT2 (g)	IR (g)	NBR (g)	PEVA (g)
PLA/LT1:95/5	95	5	-	-	-	-
PLA/LT1:90/10	90	10	-	-	-	-
PLA/LT2:95/5	95	-	5	-	-	-
PLA/LT2:90/10	90	-	10	-	-	-
PLA/IR:95/5	95	-		5	-	-
PLA/IR:90/10	90	-		10	-	-
PLA/NBR:95/5	95	-		-	5	-
PLA/NBR:90/10	90	-		-	10	-
PLA/PEVA:95/5	95	-		-	-	5
PLA/PEVA:90/10	90	-		-	-	10

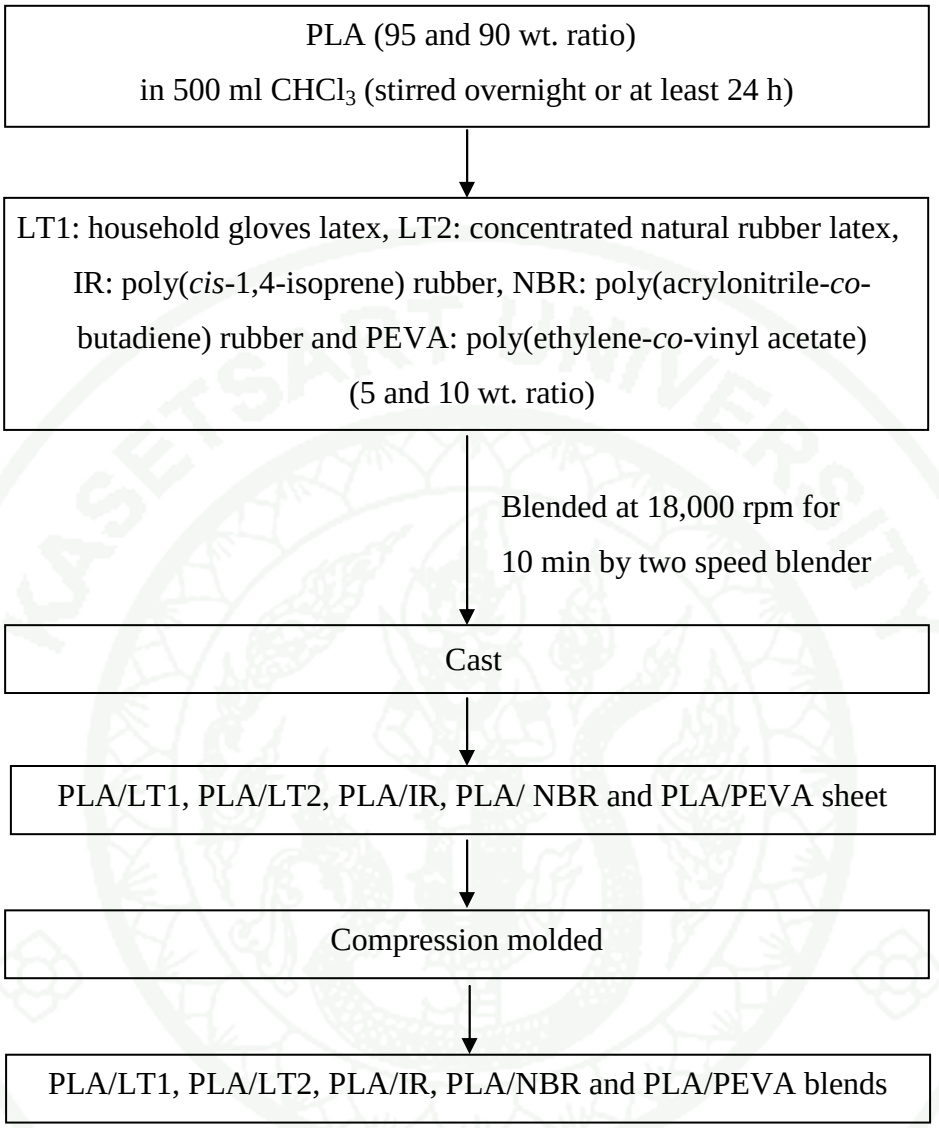


Figure 39 PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA blends.

RESULTS AND DISSCUSSION

Part I: Direct melt polycondensation of lactic acid

Polylactic acid is commonly classified as aliphatic polyester; therefore, it can be synthesized via a well known esterification reaction. One of the disadvantages of esterification from carboxylic acid with alcohol in the presence of homogeneous acid catalysts is that they are miscible with the reaction medium; as a result, it is difficult in separation off PLA obtained from the catalyst and from the reaction medium. Thus, heterogeneous catalysts such as cationic ion exchange resins or supported acid catalysts are preferred over homogeneous acid due to the ease of products separation and catalyst recovery. Two cationic ion exchange resins: catalyst A and catalyst B were chosen for this study and their structures and properties were shown in Figure 40 and Table 19 respectively.

Table 19 Properties of catalysts used in this study.

	Catalyst A	**Catalyst B**
Functional group	$-SO_3^- H^+$	$-SO_3^- H^+$
Standard ionic form	H^+	H^+
Maximum operating temperature (°C)	190°C	150°C
Total exchange capacity (eq/kg)	2.55	4.7
Surface area (m^2/g)	36	52

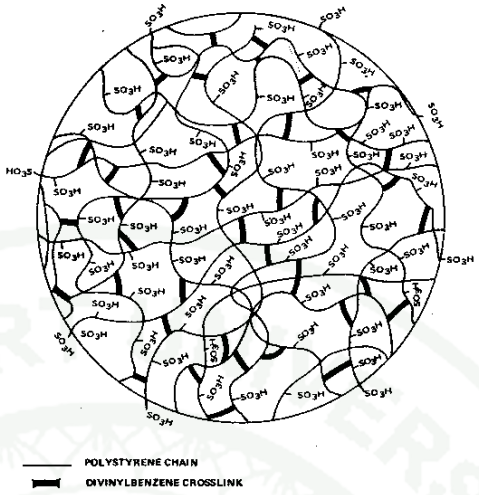


Figure 40 Structure of cationic ion exchange resins catalysts containing sulfonic acid group used in this study (Phruksaphithak, 2007).

Polylactic acid was synthesized by direct melt polycondensation of L-lactic acid catalyzed either with catalyst A or catalyst B via cationic mechanism as shown in Figure 41. The direct melt polycondensation was carried out by varying the temperature from 135°C (T_0), 160°C (T_1), 170°C (T_2) to 180°C (T_3); mole ratio of L-lactic acid and catalyst (catalyst A and catalyst B) from 100:1, 500:1 to 1000:1 and maintaining the reaction condition by alternating between under N_2 atmosphere and under reduced pressure (15 mmHg) for the required period of time. The PLA obtained were characterized as followed: structure by 400 MHz ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and fourier transforms infrared spectroscopy (FT-IR), molecular weight by gel permeation chromatography (GPC), and thermal properties by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

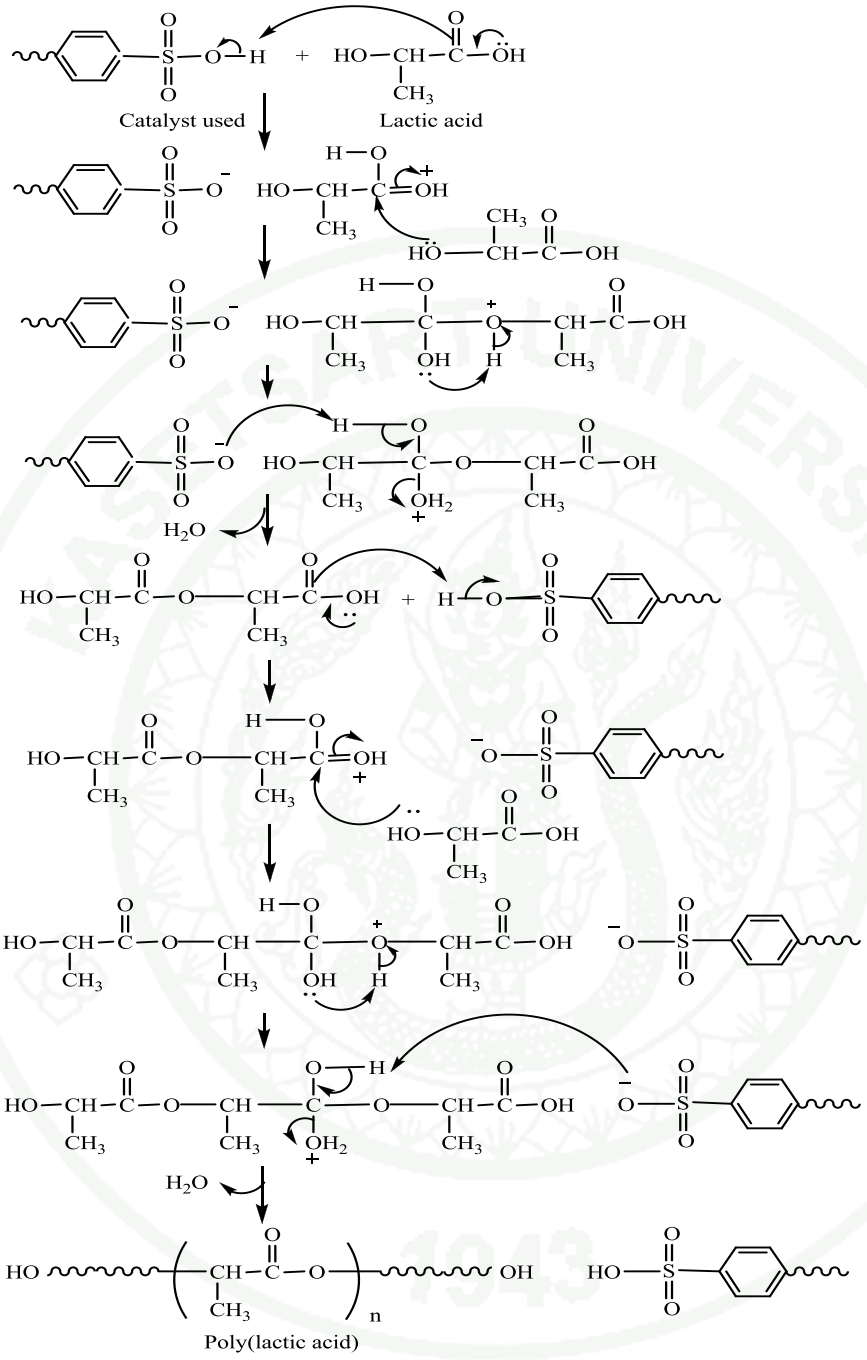


Figure 41 The mechanism for synthesis of PLA using cationic ion exchange resins catalysts containing sulfonic acid group used in this study.

Appearance of white pellets or powdered of the PLA obtained is shown in Figure 42. The results from FT-IR, ^{1}H and ^{13}C NMR analysis of PLA obtained in this

study having the same spectra as shown in Figure 43- Figure 45 respectively. Figure 43 shows that FT-IR spectrum of PLA obtained exhibited characteristics absorption peaks (ν_{max}) in cm^{-1} in the region of 2850−2998 (asymmetric -C-H stretching in $-CH_3$ and -CH), at 1761 (-O-C=O), in the region of 1400-1200 (ester sequence O=C-O-) and at 1187-1044 (-HC-O-). Figure 44 shows peaks (δ) in ppm at 1.6 (d, 3H, -CH-CH_3) and 5.2 (q, 1H, -CH-CH_3**)** and Figure 45 shows peaks (δ) in ppm at 18 (CH_3), 68.5 (-CH-CH_3), and 170 (-C=O). These indicated that pure PLA was formed. The typical DSC and TGA thermograms together with the GPC chromatogram of PLA obtained are shown in Figure 46 to Figure 48 respectively.

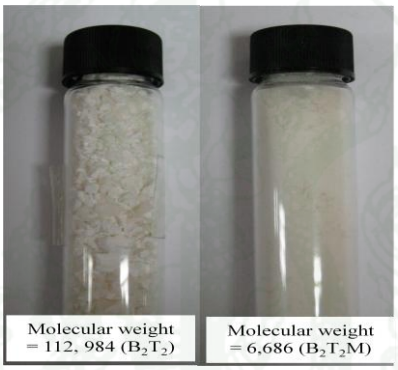


Figure 42 Example of appearance of PLA obtained in this study (sample code).

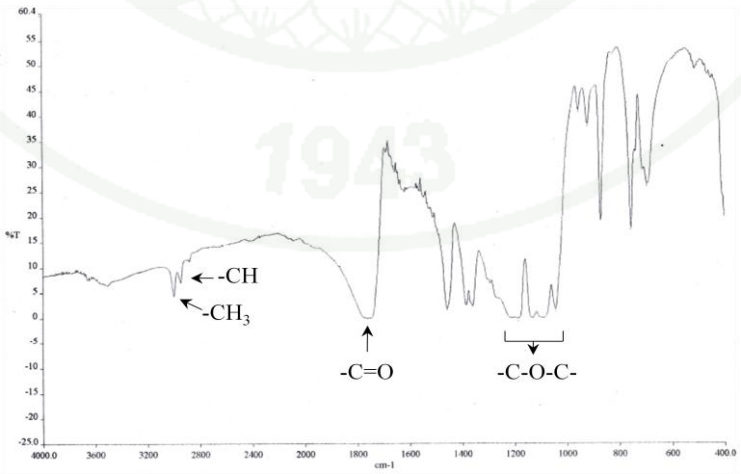


Figure 43 Example of FT-IR spectrum of PLA obtained in this study (KBr).

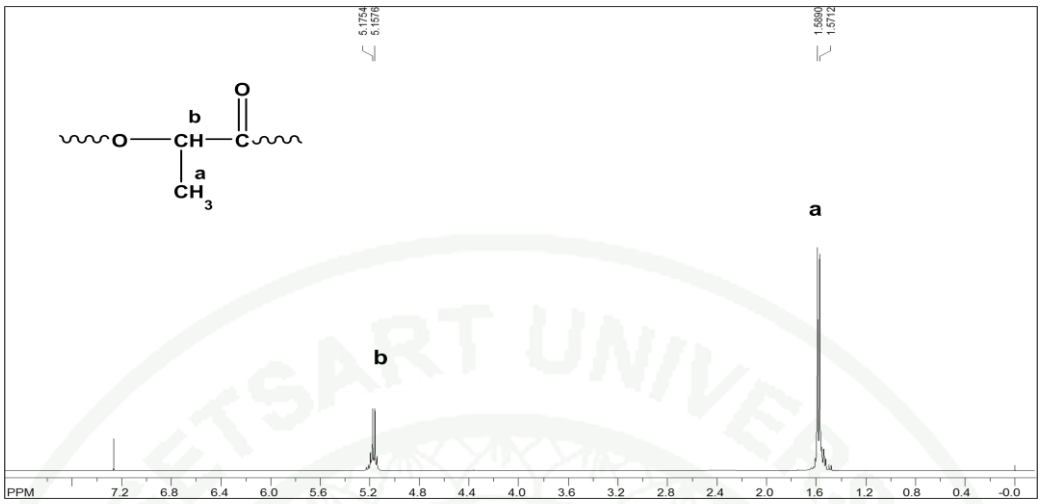


Figure 44 400 MHz ^{1}H NMR spectrum of PLA obtained from this study ($CDCl_3$).

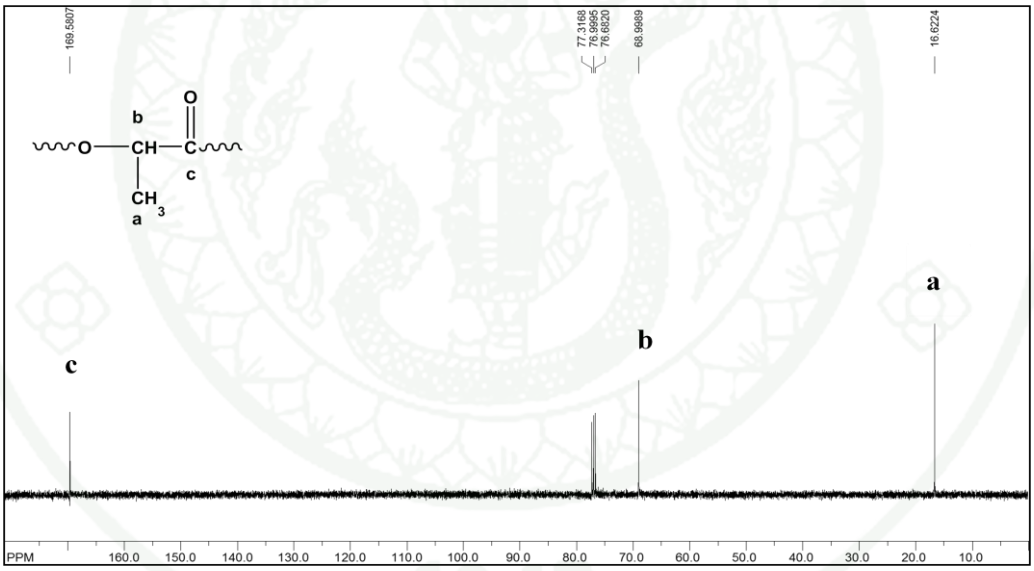
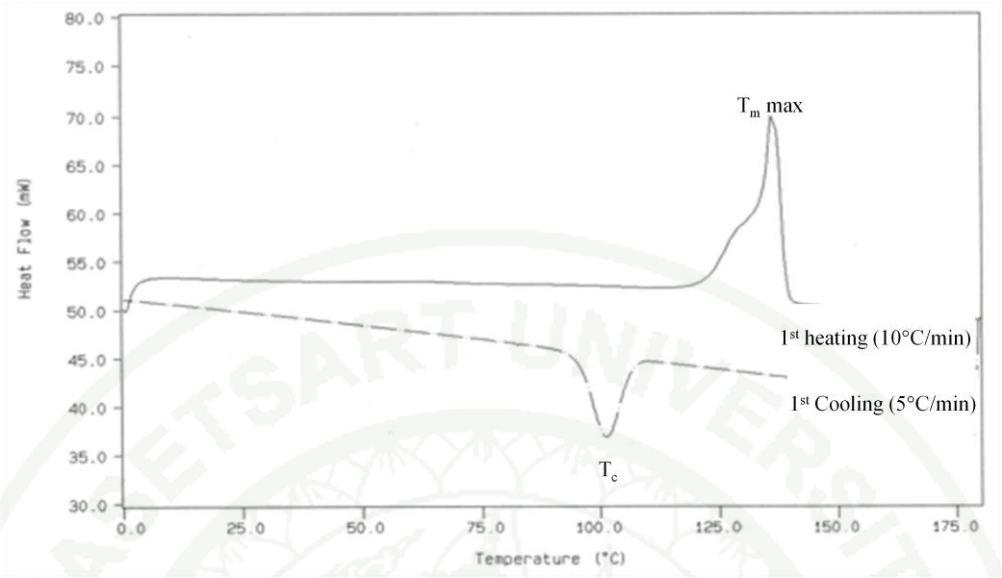
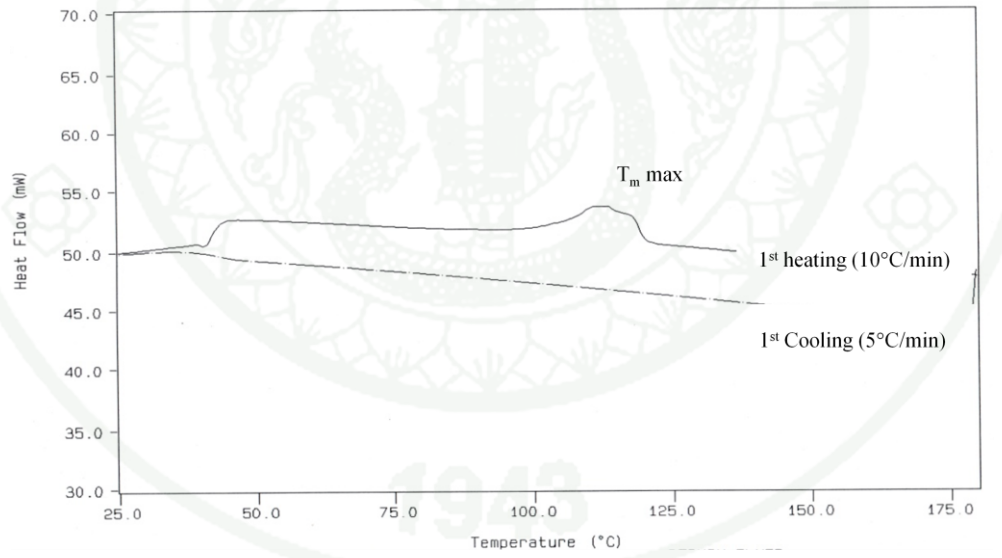


Figure 45 400 MHz ^{13}C NMR spectrum of PLA obtained from this study ($CDCl_3$).



(a)



(b)

Figure 46 Typical DSC thermogram of PLA obtained in this study (a) with T_c (A_1T_2M) and (b) without T_c (B_2T_3S).

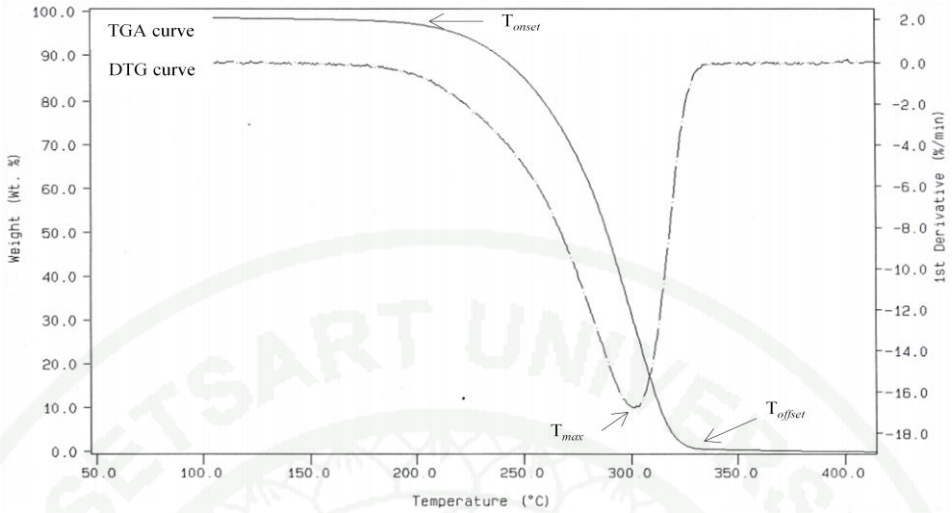


Figure 47 Typical TGA-DTA thermogram of PLA obtained in this study (B_2T_3S).

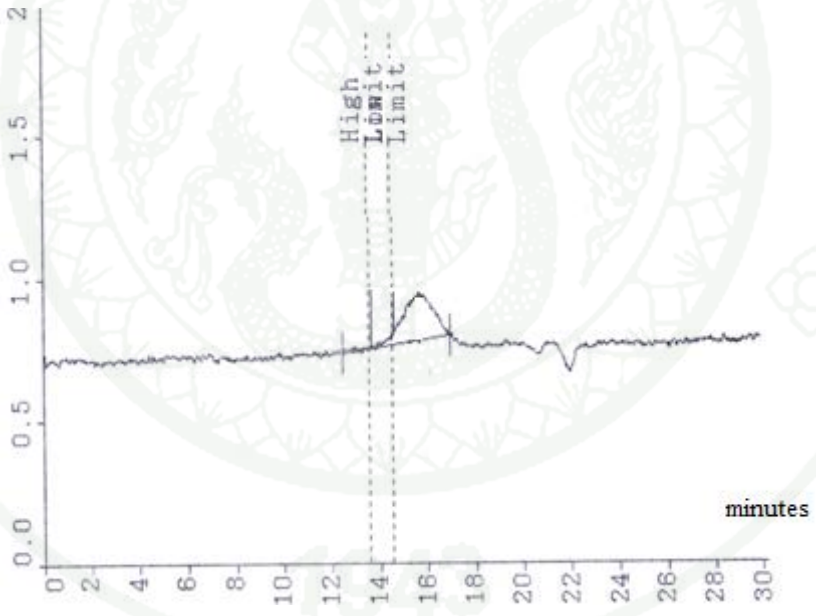


Figure 48 Typical GPC chromatogram of PLA obtained in this study ($C_{12}B_2T_2$-2, $\overline{M}_W$ = 8,900).

1. Synthesis of polylactic acid (PLA) with 100 g of lactic acid (LA)

1.1 By direct melt polycondensation (DMPC) for 12 h

Results of molecular weight, thermal properties and thermal decomposition of PLA obtained from DMPC using catalyst A and catalyst B with mole ratio of LA: catalyst = 100:1 (A_1 or B_1), 500:1 (A_2 or B_2) and 1000:1 (A_3 or B_3) at 160^{o}C (T_1), 170^{o}C (T_2) or 180^{o}C (T_3) for 12 h by alternating between under nitrogen atmosphere for 3 h and under reduced pressure (15 mmHg) for 1 h with 100 g of lactic acid are summarized in Table 20 - Table 22 and Table 23 - Table 25 respectively. PLA obtained from using catalyst A has weight average molecular weight ($\overline{M}_W$) from 28,000 to 104,000, % yield from 6.0 to 35.7%, melting temperature (T_m*max*) from 121^{o}C to 127°C, degree of crystallization (χ_c) 46 to 62, thermal decomposition (decomposition temperature, T_{max}) from 267°C to 308°C and % decomposition from 75 to 88%; and from using catalyst B has $\overline{M}_W$ from 51,000 to 113,000, % yield from 0.8 to 31.8%, T_m*max* from 127°C to 136°C, χ_c from 56 to 72, T_{max} from 293°C to 327°C and % decomposition from 73 to 96%.

Table 20 Characteristics of PLA obtained with 100 g of LA by DMPC using catalyst A for 12 h.

Codes	Characteristics	Yield (%)	$\overline{M}_w$	PD*
A_1T_1	White powder	12.7	54,000	1.0
A_1T_2	White powder	25.8	52,000	1.0
A_1T_3	White powder	19.3	28,000	1.1
A_2T_1	White powder	6.0	54,000	1.0
A_2T_2	White powder	9.2	52,000	1.1
A_2T_3	Brown viscous gel	27.1	-**	-
A_3T_1	White powder	9.0	52,000	1.1
A_3T_2	White powder	7.7	104,000	1.1
A_3T_3	Brown viscous gel	35.7	-**	-

* Polydispersity index

** No precipitate was formed when adding the PLA/$CHCl_3$ solution into methanol

Table 21 Thermal properties by DSC analysis of PLA obtained with 100 g of LA by DMPC using catalyst A for 12 h.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
A_1T_1	-*	125	-	55.8	60
A_1T_2	-	124	-	57.0	61
A_1T_3	-	122	-	43.4	46
A_2T_1	-	123	-	44.8	60
A_2T_2	-	125	-	51.2	55
A_2T_3	-	-	-	-	-
A_3T_1	-	127	-	56.5	60
A_3T_2	-	121	-	58.6	62
A_3T_3	-	-	-	-	-

* Not detect

Table 22 Thermal decomposition by TGA analysis of PLA obtained with 100 g of LA by DMPC using catalyst A for 12 h.

Codes	T_{onset} (°C)	T_{offset} (°C)	T_{max}(°C)	% Decomposition
A_1T_1	248	322	308	80
A_1T_2	252	320	299	83
A_1T_3	250	299	267	77
A_2T_1	261	309	275	79
A_2T_2	268	316	282	75
A_2T_3	-	-	-	-
A_3T_1	255	322	301	80
A_3T_2	261	324	304	88
A_3T_3	-	-	-	-

Table 23 Characteristics of PLA obtained with 100 g of LA by DMPC using catalyst B for 12 h.

Codes	Characteristics	Yield (%)	$\overline{M}_w$	PD
B_1T_1	White powder	9.7	51,000	1.0
B_1T_2	White powder	24.5	52,000	1.1
B_1T_3	White powder	31.8	52,000	1.0
B_2T_1	White powder	18.7	54,000	1.0
B_2T_2	White powder	19.5	113,000	1.1
B_2T_3	Brown viscous gel	-*	-	-
B_3T_1	White powder	15.7	51,000	1.0
B_3T_2	White powder	13.2	104,000	1.1
B_3T_3	White powder	0.8	56,000	1.0

* No precipitate was formed when adding the PLA/$CHCl_3$ solution into methanol

Table 24 Thermal properties by DSC analysis of PLA obtained with 100 g of LA by DMPC using catalyst B for 12 h.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
B_1T_1	-*	130	105	67.2	72
B_1T_2	-	130	95	58.5	62
B_1T_3	-	136	-	56.1	60
B_2T_1	-	130	-	58.9	63
B_2T_2	-	130	-	54.6	58
B_2T_3	-	-	-	53.1	57
B_3T_1	-	130	-	62.1	66
B_3T_2	-	127	-	52.4	56
B_3T_3	-	127	-	53.4	57

* Not detect

Table 25 Thermal decomposition by TGA analysis of PLA obtained with 100 g of LA by DMPC using catalyst B for 12 h.

Codes	T_{onset} (°C)	T_{offset} (°C)	T_{max}(°C)	% Decomposition
B_1T_1	226	324	310	87
B_1T_2	253	320	307	83
B_1T_3	263	338	327	96
B_2T_1	256	322	310	84
B_2T_2	244	310	300	73
B_2T_3	-	-	-	-
B_3T_1	227	325	298	86
B_3T_2	246	329	309	96
B_3T_3	230	323	293	88

In case of catalyst A was used, results showed that $\overline{M}_w$ of PLA obtained decreases with increasing the temperature for mole ratio of LA: catalyst A = 100:1 and 500:1 and decreases sharply to the point only brown viscous liquid is obtained at 180°C for mole ratio of LA: catalyst A = 500:1. On the contrary, $\overline{M}_w$ of PLA obtained increases with increasing the temperature from 160°C to 170°C but decreases to only brown viscous liquid is obtained with increasing the temperature to 180°C for mole ratio of LA: catalyst A = 1000:1 (Figure 49).

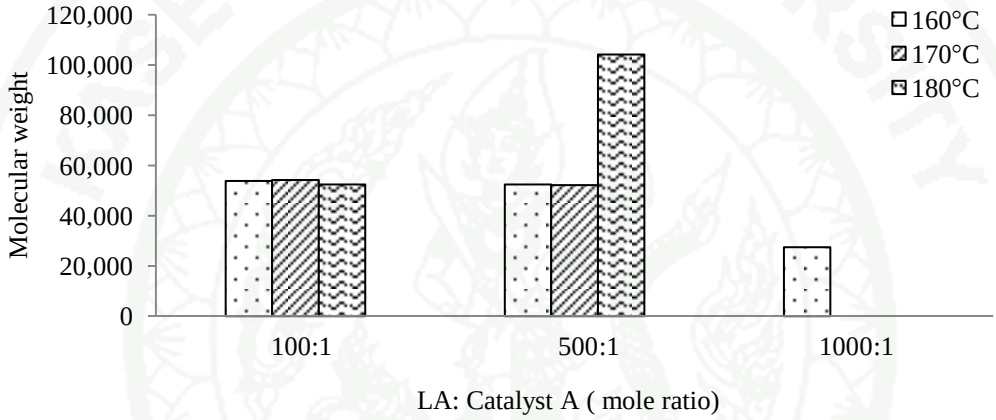


Figure 49 Comparison of molecular weight of PLA obtained with 100 g of LA by DMPC using catalyst A for 12 h.

In case of catalyst B was used, results showed that $\overline{M}_w$ of PLA obtained increases slightly with increasing the temperature for mol ratio of LA: catalyst B = 100:1. For mole ratio of LA: catalyst B = 500:1 and 1000:1, $\overline{M}_w$ of PLA obtained increases with increasing the temperature from 160°C to 170°C and then decreases when increasing the temperature to 180°C, especially, only brown viscous liquid is obtained for mole ratio of LA: catalyst B = 500:1 (Figure 50).

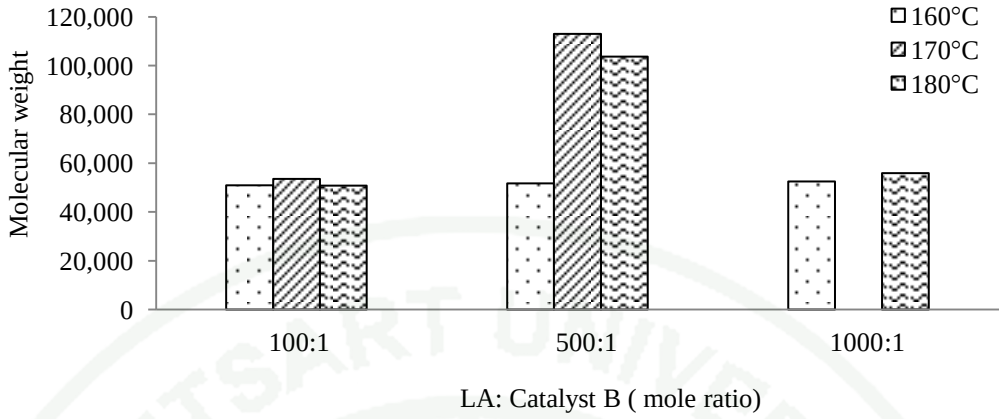


Figure 50 Comparison of molecular weight of PLA obtained with 100 g of LA by DMPC using catalyst B for 12 h.

Thus, temperature at 180°C is too high to synthesize PLA using catalyst A and catalyst B for mole ratio of LA: catalyst A or catalyst B = 500:1 and using catalyst A for mole ratio of LA: catalyst A = 1000:1. In addition, although PLA obtained using catalyst B has a slightly higher molecular weight ($\overline{M}_w$) than using catalyst A, most of $\overline{M}_w$ from both catalyst A and B of PLA obtained is in the range of 50,000. The highest $\overline{M}_w$ of PLA can be obtained from catalyst A or catalyst B by carrying the reaction at 170°C with the mole ratio of LA: catalyst A and LA: catalyst B = 1000:1 ($\overline{M}_w$ = 104,000) and 500:1 ($\overline{M}_w$ = 113,000) respectively.

1.2 By DMPC for 6, 6 h

Instead of carrying the reaction from DMPC by alternating between under nitrogen atmosphere for 3 h and under reduced pressure (15 mmHg) for 1 h at 160°C, 170°C or 180°C for 12 h, the reaction was heated by alternating between under nitrogen atmosphere for 2 h and under reduced pressure (15 mmHg) for 1 h at 135°C for 6 h and at 160°C, 170°C or 180°C for 6 h. Results of molecular weight, thermal properties and thermal decomposition of PLA obtained from direct melt polycondensation using catalyst A and catalyst B with mole ratio of LA: catalyst = 100:1 (A_1 or B_1), 500:1 (A_2 or B_2) and 1000:1 (A_3 or B_3) at 135°C (T_0) for 6 h and at

160°C (T_1), 170°C (T_2) or 180°C (T_3) for 6 h with 100 g of lactic acid are summarized in Table 26 - Table 28 and Table 29 - Table 31 respectively. PLA obtained from using catalyst A has $\overline{M}_W$ from 4,000 to 53,000, % yield from 0.3 to 10.4%, T_m*max* from 111°C to 136°C, χ_c from 31 to 68, T_{max} from 302°C to 323°C and % decomposition from 77 to 97%; and from using catalyst B has $\overline{M}_W$ from 70,000 to 104,000, % yield from 3.1 to 25.2%, T_m*max* from 125°C to 134°C, χ_c from 49 to 86, T_{max} from 293°C to 323°C and % decomposition from 75 to 96 %.

Table 26 Characteristics of PLA obtained with 100 g of LA by DMPC using catalyst A for 6, 6 h.

Codes	Characteristics	Yield (%)	$\overline{M}_W$	PD
A_1T_1M	White powder	8.3	53,000	0.9
A_1T_2M	White powder	7.4	4,000	1.0
A_1T_3M	White powder	4.5	38,000	2.2
A_2T_1M	White powder	6.2	5,000	0.9
A_2T_2M	White powder	5.6	7,000	1.0
A_2T_3M	White powder	0.4	11,000	1.6
A_3T_1M	White powder	3.9	5,000	0.9
A_3T_2M	White powder	10.4	7,000	1.0
A_3T_3M	White powder	0.3	10,000	1.0

Table 27 Thermal properties by DSC analysis of PLA obtained with 100 g of LA by DMPC using catalyst A for 6, 6 h.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
A_1T_1M	-*	133	110	63.6	68
A_1T_2M	-	136	109	57.4	61
A_1T_3M	-	132	101	62.2	66
A_2T_1M	-	130	97	52.9	56
A_2T_2M	-	133	97	52.7	56
A_2T_3M	-	111	-	28.7	31
A_3T_1M	-	133	111	63.4	68
A_3T_2M	-	135	103	56.4	60
A_3T_3M	-	127	-	34.3	37

* Not detect

Table 28 Thermal decomposition by TGA analysis of PLA obtained with 100 g of LA by DMPC using catalyst A for 6, 6 h.

Codes	T_{onset} (°C)	T_{offset} (°C)	T_{max}(°C)	% Decomposition
A_1T_1M	266	324	308	93
A_1T_2M	265	333	317	91
A_1T_3M	251	318	302	93
A_2T_1M	262	322	310	91
A_2T_2M	274	328	312	95
A_2T_3M	266	331	308	97
A_3T_1M	256	325	313	91
A_3T_2M	272	326	308	95
A_3T_3M	254	346	323	77

Table 29 Characteristics of PLA obtained with 100 g of LA by DMPC using catalyst B for 6, 6 h.

Codes	Characteristics	Yield (%)	$\overline{M}_w$	PD
B_1T_1M	White powder	21.4	100,000	1.0
B_1T_2M	White powder	3.1	92,000	1.1
B_1T_3M	White powder	10.4	96,000	1.0
B_2T_1M	White powder	7.7	98,000	1.1
B_2T_2M	White powder	18.9	99,000	1.0
B_2T_3M	White powder	17.0	70,000	1.0
B_3T_1M	White powder	25.2	97,000	1.1
B_3T_2M	White powder	3.9	104,000	1.0
B_3T_3M	White powder	19.3	93,000	1.2

Table 30 Thermal properties by DSC analysis of PLA obtained with 100 g of LA by DMPC using catalyst B for 6, 6 h.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
B_1T_1M	-*	134	100	54.1	58
B_1T_2M	-	128	98	80.6	86
B_1T_3M	-	125	88	57.2	61
B_2T_1M	-	130	-	62.8	67
B_2T_2M	-	125	-	58.6	63
B_2T_3M	-	130	-	54.6	58
B_3T_1M	-	128	-	52.9	56
B_3T_2M	-	128	-	46.2	49
B_3T_3M	-	127	-	56.8	61

* Not detect

Table 31 Thermal decomposition by TGA analysis of PLA obtained with 100 g of LA by DMPC using catalyst B for 6, 6 h.

Codes	T_{onset} (°C)	T_{offset} (°C)	T_{max}(°C)	% Decomposed
B_1T_1M	269	333	321	96
B_1T_2M	276	337	323	89
B_1T_3M	267	341	322	87
B_2T_1M	250	312	293	91
B_2T_2M	270	333	318	89
B_2T_3M	252	320	311	81
B_3T_1M	241	315	297	76
B_3T_2M	248	323	300	89
B_3T_3M	241	308	297	75

In case of catalyst A was used, results showed that $\overline{M}_W$ of PLA obtained decrease from 160°C to 170°C, then increases from 170°C to 180°C for mole ratio of LA: catalyst A = 100:1; but $\overline{M}_W$ of PLA obtained increases with increasing the temperature from 160°C to 180°C for mole ratio of LA: catalyst A = 500:1 and 1000:1 (Figure 51).

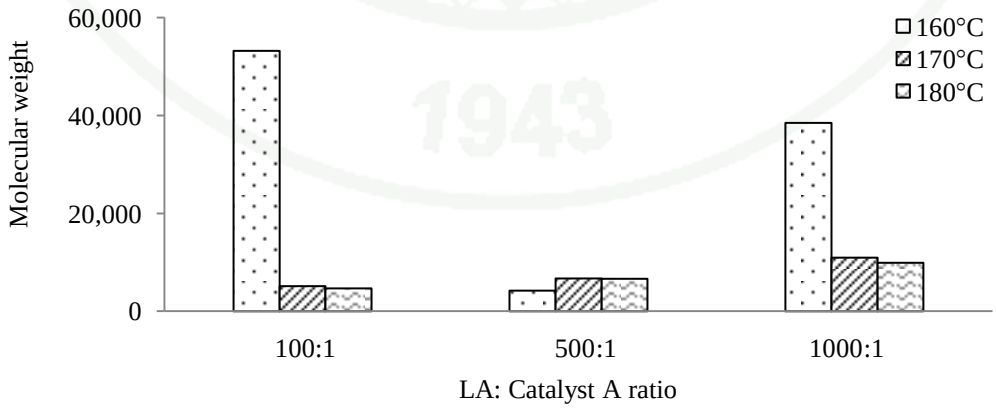


Figure 51 Comparison of molecular weight of PLA obtained with 100 g of LA by DMPC using catalyst A for 6, 6 h.

In case of catalyst B was used, results showed that $\overline{M}_w$ of PLA obtained is not depended on both temperature and mole ratio of LA: catalyst B. Most of $\overline{M}_w$ from catalyst B of PLA obtained is in the range of 90,000 and PLA obtained using catalyst B has a much higher molecular weight ($\overline{M}_w$) than using catalyst A. It can also be concluded that PLA can be obtained in all temperature from 160°C to 180°C using both catalyst A and B (Figure 52). The highest $\overline{M}_w$ of PLA can be obtained from catalyst A when carrying the reaction at 160°C with the mole ratio of LA: catalyst A 100:1 ($\overline{M}_w$ = 53,000), and from catalyst B when carrying the reaction at 170°C with the mole ratio of LA: catalyst B = 1000:1 ($\overline{M}_w$ = 104,000).

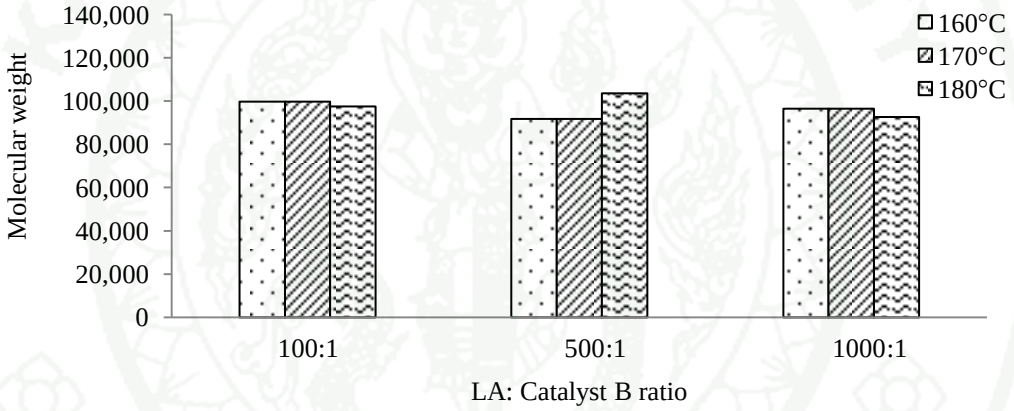


Figure 52 Comparison of molecular weight of PLA obtained with 100 g of LA by DMPC using catalyst B for 6,6 h.

1.3 By solution polycondensation (SP) for 6, 6 h

The reaction condition from DMPC by alternating between under nitrogen atmosphere for 2 h and under reduced pressure (15 mmHg) for 1 h at 135°C for 6 h and at 160°C, 170°C or 180°C for 6 h was further studied using SP in toluene and 1-methyl pyrrolidone (NMP) mixture in order to compare the results of PLA obtained from the 6, 6 h condition by DMPC. It was found that PLA cannot be obtained, and only brown viscous liquid are formed in all conditions when catalyst A was used (Figure 53 and Table 32). Results of molecular weight, thermal properties and thermal

decomposition of PLA obtained from SP using catalyst B with mole ratio of LA: catalyst = 100:1 (A_1 or B_1), 500:1 (A_2 or B_2) and 1000:1 (A_3 or B_3) at 135^{o}C (T_0) for 6 h and at 160^{o}C (T_1), 170^{o}C (T_2) or 180^{o}C (T_3) for 6 h with 100 g of LA are summarized in Table 33 - Table 35. PLA obtained from using catalyst B has $\overline{M}_w$ from 4,600 to 10,000, % yield from 1.3 to 21%, T_m*max* from 113^{o}C to 133°C, χ_c from 32 to 68, T_{max} from 290°C to 313°C and % decomposition from 82 to 96%.

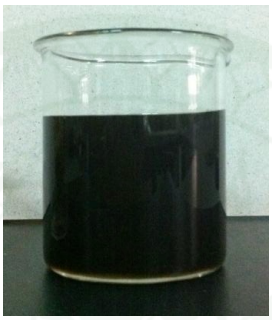


Figure 53 Brown viscous gel obtained by SP**.**

Table 32 Characteristics of PLA obtained with 100 g of LA by SP using catalyst A for 6, 6 h.

Code	Characteristics	Yield (%)	$\overline{M}_w$	PD
A_1T_1S	Brown viscous gel	10.3	-	-
A_1T_2S	Brown viscous gel	12.3	-	-
A_1T_3S	Brown viscous gel	16.9	-	-
A_2T_1S	Brown viscous gel	9.5	-	-
A_2T_2S	Brown viscous gel	11.7	-	-
A_2T_3S	Brown viscous gel	15.7	-	-
A_3T_1S	Brown viscous gel	7.4	-	-
A_3T_2S	Brown viscous gel	17.1	-	-
A_3T_3S	Brown viscous gel	14.8	-	-

Table 33 Characteristics of PLA obtained with 100 g of LA by SP using catalyst B for 6, 6 h.

Codes	Characteristic	Yield (%)	$\overline{M}_w$	PD
B_1T_1S	White powder	1.7	4,600	1.0
B_1T_2S	White powder	9.7	5,200	1.0
B_1T_3S	White powder	21	5,800	1.3
B_2T_1S	White powder	3.0	4,800	1.0
B_2T_2S	White powder	6.8	5,300	1.0
B_2T_3S	White powder	1.3	9,700	1.5
B_3T_1S	White powder	3.3	5,500	1.1
B_3T_2S	White powder	7.5	5,800	1.1
B_3T_3S	White powder	2.5	10,000	1.6

Table 34 Thermal properties by DSC analysis of PLA obtained with 100 g of LA by SP using catalyst B for 6, 6 h.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_C
B_1T_1S	-*	133	107	63.8	68
B_1T_2S	-	131	-	45.0	48
B_1T_3S	-	134	-	30.3	32
B_2T_1S	-	118	76	40.5	43
B_2T_2S	-	128	94	56.0	60
B_2T_3S	-	113	-	33.4	36
B_3T_1S	-	125	-	44.6	44
B_3T_2S	-	128	80	50.5	54
B_3T_3S	-	123	-	30.5	33

* Not detect

Table 35 Thermal decomposition by TGA analysis of PLA obtained with 100 g of LA by SP using catalyst B for 6, 6 h.

Codes	T_{onset} (°C)	T_{offset} (°C)	T_{max}(°C)	% Decomposition
B_1T_1S	241	328	300	87
B_1T_2S	265	321	290	88
B_1T_3S	257	321	306	96
B_2T_1S	243	316	293	86
B_2T_2S	258	320	313	88
B_2T_3S	254	318	301	96
B_3T_1S	242	301	309	82
B_3T_2S	238	315	299	86
B_3T_3S	283	326	309	96

The brown viscous gel from using catalyst A was characterized by FT-IR as shown in Figure 54. An additional band at 3473 cm^{-1} related to the stretching of OH group of lactic acid is still observed. This band is an indication that only the oligomer residual of PLA is contained in the brown viscous gel (Kaitian *et al*., 1996). Moreover, $\overline{M}_W$ of all PLA that can be obtained using catalyst B by SP is much lower than PLA obtained by DMPC, and the highest $\overline{M}_W$ is ~10,000 from mole ratio of LA: catalyst B = 1000:1 at 180°C.

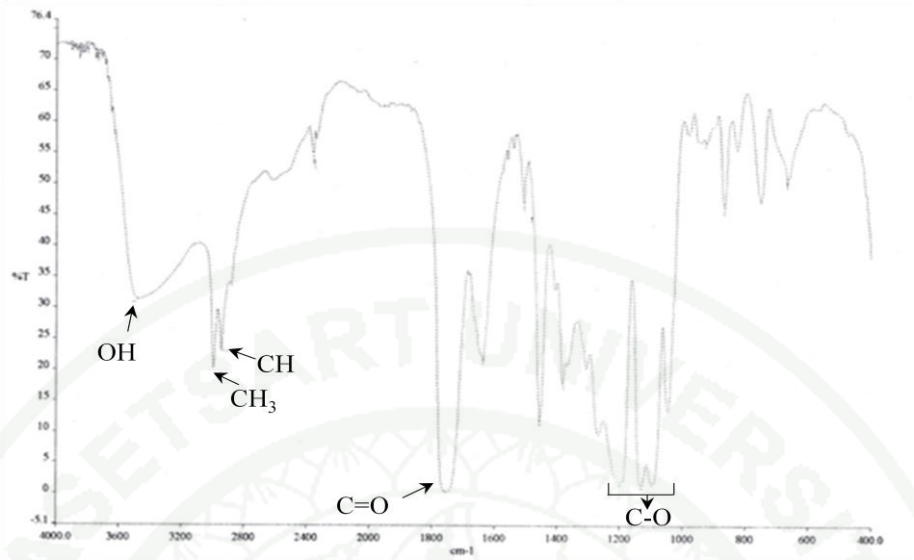


Figure 54 FT-IR spectrum of brown viscous gel obtained from catalyst A by SP.

Finally, $\overline{M}_w$ of PLA obtained using catalyst A and catalyst B with 100 g of lactic acid is compared as shown in Table 36 and Table 37 respectively. All PLAs obtained by DMPC have $\overline{M}_w$ higher than by SP, and PLA obtained using catalyst B has a much higher $\overline{M}_w$ than using catalyst A (Figure 55). Therefore, factors of temperature and mole ratio of LA: catalyst are closely related in effecting the $\overline{M}_w$ of PLA obtained by both DMPC and SP. Conditions for obtaining the highest $\overline{M}_w$ and the $\overline{M}_w$ range of PLA obtained in each condition are summarized in Table 38.

When using catalyst A, it is found that PLA cannot be obtained by SP, and the majority $\overline{M}_w$ of PLA obtained by DMPC when carrying the reaction for 12 h or dividing into two steps 6, 6 h are 50,000 and <10,000 respectively with the highest $\overline{M}_w$ of PLA obtained = 104,000 for 12 h at 170^{o}C with the mole ratio of LA: catalyst A = 1000:1 and = 53,000 for two steps 6, 6 h at 160^{o}C with the mole ratio of LA: catalyst A = 100:1.

When using catalyst B, it is found that PLA can be obtained by both DMPC and SP, and the majority $\overline{M}_w$ of PLA obtained by DMPC when carrying the reaction for 12 h or dividing into two steps 6, 6 h and by SP for 6, 6 h are 50,000,

90,000 and <10,000 respectively with the highest $\overline{M}_w$ of PLA obtained = 113,000 for DMPC 12 h at 170°C with the mole ratio of LA: catalyst B = 500:1, $\overline{M}_w$ = 104,000 for DMPC in two steps 6, 6 h at 170°C with the mole ratio of LA: catalyst B = 1000:1 and = 10,000 for SP in two steps 6, 6 h with the mole ratio of LA: catalyst B = 1000:1 when catalyst B was used.

In addition, all PLAs obtained gave the same melting temperature ($T_m max$) range in between 115°C to 130°C, and the thermal decomposition temperature (T_{max}) range in between 270°C to 320°C.

Table 36 Comparison of $\overline{M}_w$ of PLA obtained with 100 g of LA using catalyst A.

Codes	$\overline{M}_w$	Codes	$\overline{M}_w$	Code	$\overline{M}_w$
A_1T_1	54,000	A_1T_1M	53,000	A_1T_1S	-
A_1T_2	52,000	A_1T_2M	4,000	A_1T_2S	-
A_1T_3	28,000	A_1T_3M	38,000	A_1T_3S	-
A_2T_1	54,000	A_2T_1M	5,000	A_2T_1S	-
A_2T_2	52,000	A_2T_2M	7,000	A_2T_2S	-
A_2T_3	-	A_2T_3M	11,000	A_2T_3S	-
A_3T_1	52,000	A_3T_1M	5,000	A_3T_1S	-
A_3T_2	104,000	A_3T_2M	7,000	A_3T_2S	-
A_3T_3	-	A_3T_3M	10,000	A_3T_3S	-

Table 37 Comparison of $\overline{M}_w$ of PLA obtained with 100 g of LA using catalyst B.

Codes	$\overline{M}_w$	Codes	$\overline{M}_w$	Codes	$\overline{M}_w$
B_1T_1	51,000	B_1T_1M	100,000	B_1T_1S	4,600
B_1T_2	52,000	B_1T_2M	92,000	B_1T_2S	5,200
B_1T_3	52,000	B_1T_3M	96,000	B_1T_3S	5,800
B_2T_1	54,000	B_2T_1M	98,000	B_2T_1S	4,800
B_2T_2	113,000	B_2T_2M	99,000	B_2T_2S	5,300
B_2T_3	-	B_2T_3M	70,000	B_2T_3S	9,700
B_3T_1	51,000	B_3T_1M	97,000	B_3T_1S	5,500
B_3T_2	104,000	B_3T_2M	104,000	B_3T_2S	5,800
B_3T_3	56,000	B_3T_3M	93,000	B_3T_3S	10,000

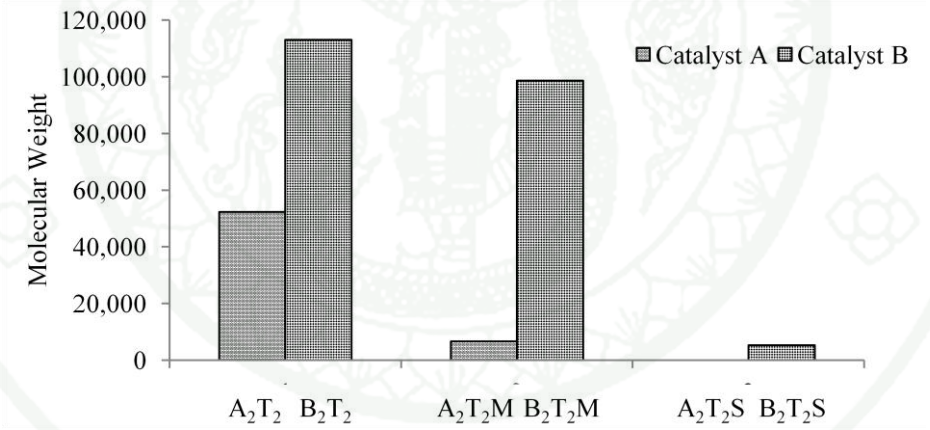


Figure 55 Effect of catalysts and methods (either by DMPC or SP) on the $\overline{M}_w$ of PLA obtained with 100 g of LA.

Table 38 Conditions for obtaining the highest $\overline{M}_w$ and the $\overline{M}_w$ range of PLA obtained in each condition.

Catalyst	Method	Highest $\overline{M}_w$				Majority $\overline{M}_w$
		Sample	LA: catalyst	Temp.	$\overline{M}_w$	
A	Melt 12 h	A_3T_2	1000:1	170°C	104,000	50,000
	Melt 6,6 h	A_1T_1M	100:1	160°C	53,000	<10,000
	Solution	PLA cannot be obtained				
B	Melt 12 h	B_2T_2	500:1	170°C	113,000	50,000
	Melt 6,6 h	B_3T_2M	1000:1	170°C	104,000	90,000
	Solution	B_3T_3S	1000:1	180°C	10,000	<10,000

2. Synthesis of polylactic acid (PLA) by DMPC with 1 kg of lactic acid (LA)

It was found from the synthesis of PLA with 100 g lactic acid that $\overline{M}_w$ of PLA obtained by DMPC gave higher $\overline{M}_w$ than by SP, PLA obtained using catalyst B has a much higher $\overline{M}_w$ than using catalyst A, and mole ratio of LA: catalyst B = 500:1 at 170°C for 12 h gave the highest $\overline{M}_w$ (113,000). Therefore, DMPC and catalyst B with emphasizing the mole ratio of LA: catalyst B = 500:1 at 170°C were chosen to scale up the synthesis of PLA with 1 kg of lactic acid.

DMPC with 1 kg of lactic acid (C_x, the subscript x indicating the number of trial) were carried out using catalyst B with mole ratio of LA: catalyst B = 500:1 (B_2) or 1000:1 (B_3) at 135°C (T_0), 160°C (T_1), 170°C (T_2) or 180°C (T_3) with different time periods. In order to complete the dehydration process, the DMPC is carried out in a series of steps at different temperatures and different time periods by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg) as shown in Table 14. At the end of the each designed time period, PLA (~100-200 g) was withdrawn from the reaction mixture and characterized. All white powder PLAs obtained (Figure 56) were confirmed from ^{1}H and ^{13}C NMR spectra as shown in

Figure 44 and Figure 45 respectively. Results of molecular weight and thermal properties of PLA obtained are summarized in Table 39 and Table 40.

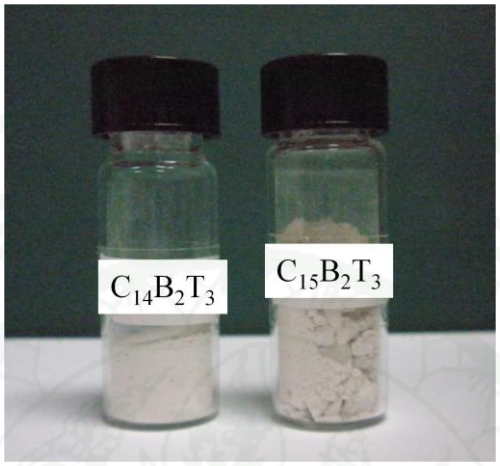


Figure 56 Examples of white powder PLA obtained with 1 kg of LA by DMPC using catalyst B.

Table 39 Characteristics of PLA obtained with 1 kg of LA by DMPC using catalyst B with different time periods.

Codes	Starter*	Time (h)	Characteristics	Yield (%)	$\overline{M}_w$	PD
$C_1B_2T_2$-1	LA1	12	Brown gel	-	-	-
$C_1B_2T_2$-2	$C_1B_2T_2$-1	(12,12) =24	Brown gel	-	-	-
$C_1B_2T_2$-3	$C_1B_2T_2$-2	(24,12) = 36	Brown gel	-	-	-
$C_2B_2T_2$-1	LA1	16	Brown gel	-	-	-
$C_2B_2T_2$-2	$C_2B_2T_2$-1	(16,16) =32	Brown gel	-	-	-
$C_3B_2T_2$-1	LA1	24	White powder	4.2	4,000	1.0
$C_3B_2T_2$-2	$C_3B_2T_2$-1	(24,10) = 34	White powder	7.7	4,400	1.0
$C_3B_2T_2$-3	$C_3B_2T_2$-2	(34,10) = 44	White powder	9.9	4,600	1.1
$C_3B_2T_2$-4	$C_3B_2T_2$-3	(44,10) = 54	White powder	16.5	4,700	1.1
$C_3B_2T_2$-5	$C_3B_2T_2$-4	(54,10) = 64	White powder	15.8	4,800	1.0
$C_4B_2T_1$-1	LA1	72	White powder	16.0	3,000	1.1
$C_4B_2T_1$-2	$C_4B_2T_1$-1	(72,25) = 97	White powder	42.3	4,400	1.0
$C_5B_2T_2$-1	LA1	72	White powder	30.2	6,500	1.1
$C_5B_2T_2$-2	$C_5B_2T_2$-1	(72,25) = 97	White powder	36.7	6,800	1.1
$C_6B_3T_2$-1	LA1	72	White powder	26.0	4,200	1.0
$C_6B_3T_2$-2	$C_6B_3T_2$-1	(72,25) = 97	White powder	40.6	9,700	1.3
$C_7B_2T_0$-1	LA1	72	White powder	10.5	2,600	1.1
$C_7B_2T_2$-2	$C_7B_2T_0$-1	(72,25) = 97	White powder	25.1	5,300	1.1
$C_8B_2T_0$-1	LA1	72	White powder	18.9	3,200	1.1
$C_8B_2T_2$-2	$C_8B_2T_0$-1	(72,25) = 97	White powder	20.6	4,600	1.1
$C_9B_2T_1$	LA1	24	Brown gel	-	-	-
$C_{10}B_2T_1$	LA1	24	Brown gel	-	-	-
$C_{11}B_2T_2$-1	LA1	24	Brown gel	-	-	-
$C_{11}B_2T_2$-2	$C_{11}B_2T_2$-1	(24,24) = 48	Brown gel	-	-	-

Table 39 (Continued)

Codes	Starter*	Time (h)	Characteristics	Yield (%)	$\overline{M}_w$	PD
$C_{12}B_2T_2$-1	LA1	24	White powder	6.4	6,200	1.2
$C_{12}B_2T_2$-2	$C_{12}B_2T_2$-1	(24,24) = 48	White powder	2.2	8,900	1.1
$C_{13}B_2T_3$	LA1	24	Brown gel	-	-	-
$C_{14}B_2T_3$**	LA2	24	White powder	10.4	7,000	1.4
$C_{15}B_2T_3$**	LA1	24	White powder	15.4	146,000	1.1
$C_{16}B_2T_3$	LA2	24	Brown gel	-	-	-

* LA1 (Lactic acid from Aldrich), LA2 (Lactic acid from Purac)

** Surrounding with dry ice

The most important factor to obtain high molecular PLA is to remove the water produced during the polycondensation. It can be seen that PLA cannot be obtained consistently with the same mole ratio of LA: catalyst B, the same temperature and the same amount of reaction time (Table 39). This might due to the efficiency of each polycondensation to remove the water produced. Most of the PLAs obtained with 1 kg of LA by DMPC have rather low molecular weight ($\overline{M}_w$) with the majority $\overline{M}_w$ of ~4,000 and melting temperature (T_m*max*) range of the PLA obtained is in between 111°C to 142°C. Increasing the reaction time slightly increases $\overline{M}_w$ of PLA obtained. $\overline{M}_w$ of PLA obtained from both temperature at 170°C and 180°C, and from both mole ratio of LA: catalyst B = 500:1 and 1000:1 is almost comparable. It was found that purity of lactic acid used has significant effect on $\overline{M}_w$ of PLA obtained with the same condition, for example, at mole ratio of LA: catalyst B = 500:1 at 180°C, lactic acid purchased from Aldrich ($\overline{M}_w$ of $C_{15}B_2T_3$ = 146,000) gave higher $\overline{M}_w$ than from Purac ($\overline{M}_w$ of $C_{14}B_2T_3$ = 7,000). Surprisingly, high $\overline{M}_w$ PLA ($\overline{M}_w$ = ~146,000) was formed unexpectedly when carrying the reaction surrounding with dry ice atmosphere in order to eliminate the humidity of the surrounding.

Table 40 Thermal properties of PLA obtained with 1 kg of LA by DMPC using catalyst B.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
$C_1B_2T_2$-1	-	-	-	-	-
$C_1B_2T_2$-2	-	-	-	-	-
$C_1B_2T_2$-3	-	-	-	-	-
$C_2B_2T_2$-1	-	-	-	-	-
$C_2B_2T_2$-2	-	-	-	-	-
$C_3B_2T_2$-1	-	122	-	68.63	73
$C_3B_2T_2$-2	-	124	-	63.78	68
$C_3B_2T_2$-3	-	123	-	61.25	65
$C_3B_2T_2$-4	-	130	-	64.20	68
$C_3B_2T_2$-5	-	128	-	52.75	56
$C_4B_2T_1$-1	50	122	-	56.76	61
$C_4B_2T_1$-2	-	130	-	58.14	62
$C_5B_2T_2$-1	-	124	-	55.28	59
$C_5B_2T_2$-2	-	128	-	50.11	54
$C_6B_3T_2$-1	-	123	-	48.13	51
$C_6B_3T_2$-2	-	122	-	45.21	48
$C_7B_2T_0$-1	48	126	-	50.34	54
$C_7B_2T_2$-2	-	132	-	57.89	62
$C_8B_2T_0$-1	-	125	-	45.51	49
$C_8B_2T_2$-2	-	142	-	49.91	53
$C_9B_2T_1$	-	-	-	-	-
$C_{10}B_2T_1$	-	-	-	-	-
$C_{11}B_2T_2$-1	-	-	-	-	-
$C_{11}B_2T_2$-2	-	-	-	-	-

Table 40 (Continued)

Codes	T_g (°C)	T_m (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
$C_{12}B_2T_2$-1	-	121	97	25.83	28
$C_{12}B_2T_2$-2	54	111	-	16.74	18
$C_{13}B_2T_3$	-	-	-	-	-
$C_{14}B_2T_3$	-	133	-	53.06	57
$C_{15}B_2T_3$	-	128	-	40.97	44
$C_{16}B_2T_3$	-	-	-	-	-

3. Synthesis of polylactic acid (PLA) by DMPC with 10 kg of lactic acid (LA)

Synthesis of PLA was further studied with 10 kg LA from the results obtained from 100 g of LA as shown in Figure 57. DMPC with 10 kg of LA (D_x, the subscript x indicating the number of trial) were carried out using catalyst B in a stainless steel jacketed cylindrical reaction kettle with open cover (Figure 58) with mole ratio of LA: catalyst B = 500:1 (B_2) or 1000:1 (B_3) at 160°C (T_1) and 170°C (T_2) at different time period. $\overline{M}_w$ of PLA obtained from both temperature at 170°C and 180°C when carrying the DMPC with 1 kg LA is almost comparable, and because of difficulty in maintaining the temperature at 180°C from the designed power control panel, PLA synthesis by DMPC with 10 kg LA was not carried out at this temperature.

The same as when carrying the synthesis with 1 kg LA, in order to complete the dehydration process, the dehydration is also carried out in a series of steps at different temperatures and different time periods by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg) as shown in Table 15. All white powder PLAs obtained (Figure 59) were confirmed from ^{1}H and ^{13}C NMR spectra as shown in Figure 44 and Figure 45 respectively. Results of molecular weight and thermal properties of PLA obtained are summarized in Table 41 and Table 42.

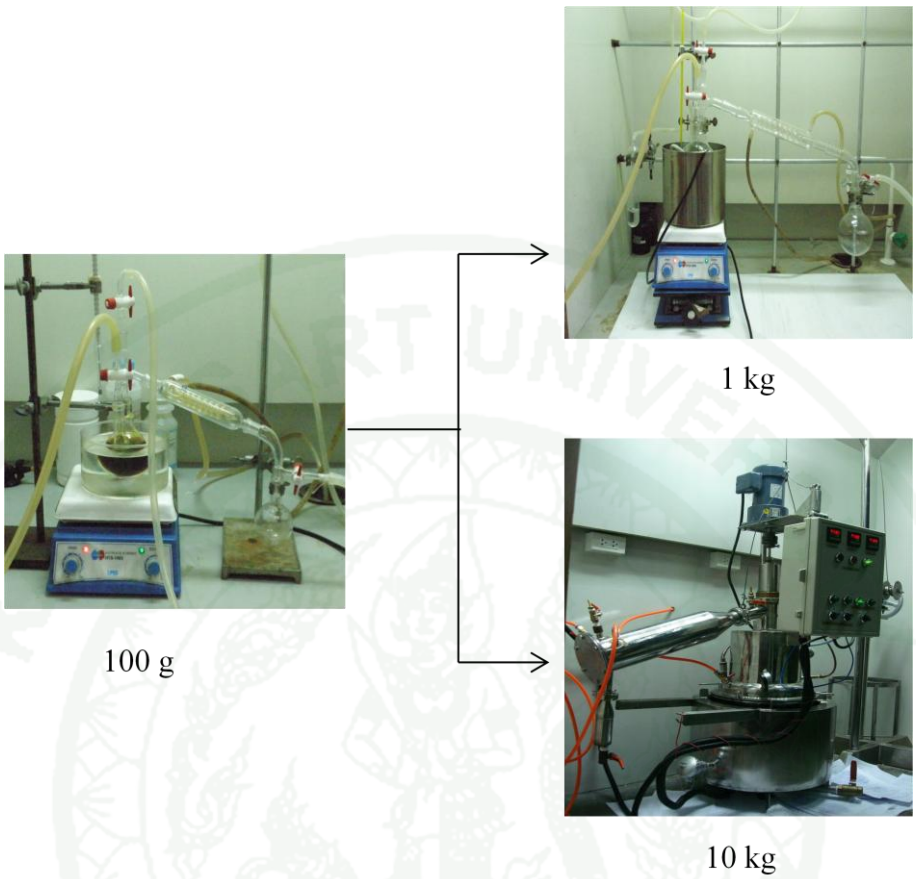


Figure 57 Systems setup for carrying the DMPC in this study.

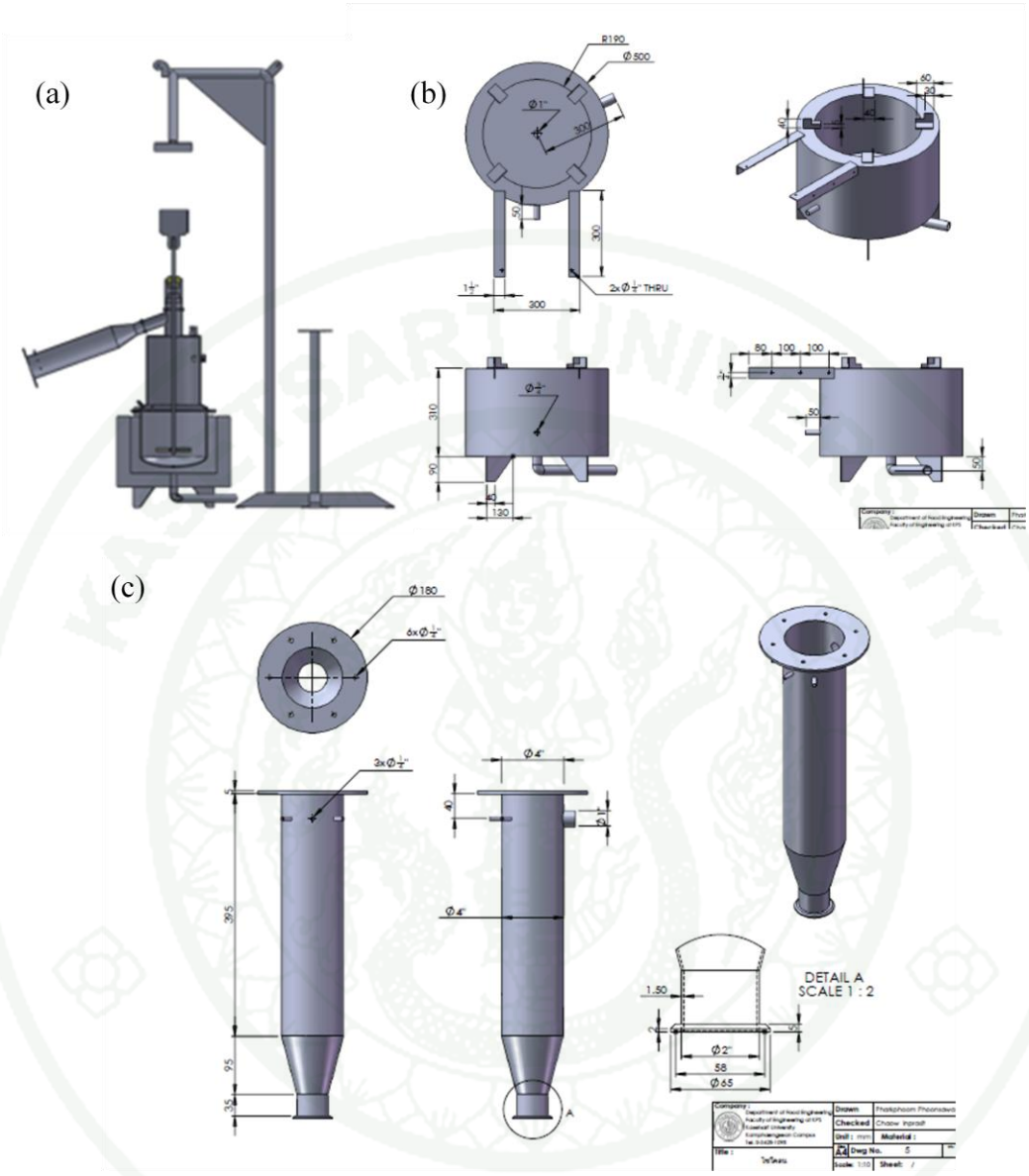


Figure 58 Drawing of (a) system setup (b) cylindrical kettle with open cover with heating jacket reactor and (c) condenser.

Figure 59 Examples of white powder PLA obtained with 10 kg of LA by DMPC using catalyst B.

Table 41 Characteristics of PLA obtained with 10 kg of LA by DMPC using catalyst B with different time periods.

Codes	Starter*	Time (h)	Characteristics	Yield (%)	$\overline{M}_w$	PD
$D_1B_2T_0$-1	LA2	72	White powder	10.5	2,600	1.1
$D_1B_2T_2$-2	$D_1B_2T_0$-1	(72,25) = 97	White powder	25.1	5,300	1.1
$D_2B_3T_0$-1	LA2	72	White powder	18.9	3,200	1.1
$D_2B_3T_2$-2	$D_2B_3T_0$-1	(72,25) = 97	White powder	20.6	4,600	1.1
$D_3B_2T_2$	LA2	12	-	-	-	-
$D_4B_2T_2$	LA2	16	-	-	-	-
$D_5B_2T_1$-1	LA2	72	White powder	16.0	3,000	1.1
$D_5B_2T_1$-2	$D_5B_2T_1$-1	(72,25) = 97	White powder	42.3	4,400	1.0
$D_6B_2T_2$-1	LA2	24	White powder	4.2	4,000	1.0
$D_6B_2T_2$-2	$D_6B_2T_2$-1	(24,10) = 34	White powder	7.7	4,400	1.0
$D_6B_2T_2$-3	$D_6B_2T_2$-2	(34,10) = 44	White powder	9.9	4,600	1.1
$D_6B_2T_2$-4	$D_6B_2T_2$-3	(44,10) = 54	White powder	16.5	4,700	1.1
$D_6B_2T_2$-5	$D_6B_2T_2$-4	(54,10) = 64	White powder	15.8	3,000	1.1
$D_7B_2T_2$-1	LA2	72	White powder	30.2	6,500	1.1
$D_7B_2T_2$-2	$D_7B_2T_2$-1	(72,25) = 97	White powder	36.7	6,800	1.1
$D_8B_3T_2$-1	LA2	72	White powder	26.0	4,200	1.1
$D_8B_3T_2$-2	$D_8B_3T_2$-1	(72,25) = 97	White powder	40.6	9,700	1.3
$D_9B_2T_2$	LA2	48	White powder	20.4	57,000***	1.3
$D_{10}B_2T_2$**	LA2	48	White powder	9.2	87,000***	1.3
$D_{11}B_2T_2$	LA2	48	White powder	66.0	66,000***	1.1

* LA1 (Lactic acid from Aldrich), LA2 (Lactic acid from Purac)

** Surrounding with dry ice

***Only a small percentage at this $\overline{M}_w$ obtained (see Table 43)

Table 42 Thermal properties of PLA obtained with 10 kg of LA by DMPC using catalyst B.

Codes	T_g (°C)	$T_m max$ (°C)	T_c (°C)	Heat of fusion (J/g)	χ_c
$D_1B_2T_0$-1	47	126	-	50.34	54
$D_1B_2T_2$-2	-	132	-	57.89	62
$D_2B_3T_0$-1	-	125	-	45.51	49
$D_2B_3T_2$-2	-	142	-	49.91	53
$D_3B_2T_2$	-	-	-	-	-
$D_4B_2T_2$	-	-	-	-	-
$D_5B_2T_1$-1	50	122	-	56.76	61
$D_5B_2T_1$-2	-	130	-	58.14	62
$D_6B_2T_2$-1	-	122	-	68.63	73
$D_6B_2T_2$-2	-	124	-	63.78	68
$D_6B_2T_2$-3	-	123	-	61.25	65
$D_6B_2T_2$-4	-	130	-	64.20	68
$D_6B_2T_2$-5	-	128	-	52.75	56
$D_7B_2T_2$-1	-	124	-	55.28	59
$D_7B_2T_2$-2	-	128	-	50.11	53
$D_8B_3T_2$-1	-	123	-	48.13	51
$D_8B_3T_2$-2	-	122	-	45.21	48
D_9B2T_2	-	135	-	61.68	66
$D_{10}B_2T_2$	-	130	91	55.08	59
$D_{11}B_2T_2$	-	145	98	46.90	53

The melting temperature ($T_m max$) range of the PLA obtained with 10 kg LA by DMPC is in between 122°C to 145°C. Most of the PLAs obtained have rather low molecular weight ($\overline{M}_w$) with the majority $\overline{M}_w$ of ~4,000 the same as obtaining from the 1 kg scale. High $\overline{M}_w$ PLA = 57,000, 87,000 and 66,000 in only a small percentage of 6.2%, 13.0% and 5.3% from $D_9B_2T_2$, $D_{10}B_2T_2$ and $D_{11}B_2T_2$ can be obtained respectively as shown in Figure 60 and Table 43.

Table 43 Molecular weight distribution of PLA obtained with 10 kg of LA by DMPC using catalyst B.

Codes	$\overline{M}_w$	**Area (%)**	$\overline{M}_w$	**Area (%)**
$D_9B_2T_2$	57,000	6.2	2,900	93.8
$D_{10}B_2T_2$	87,000	13.0	2,900	87.0
$D_{11}B_1T_2$	66,000	5.3	3,600	94.7

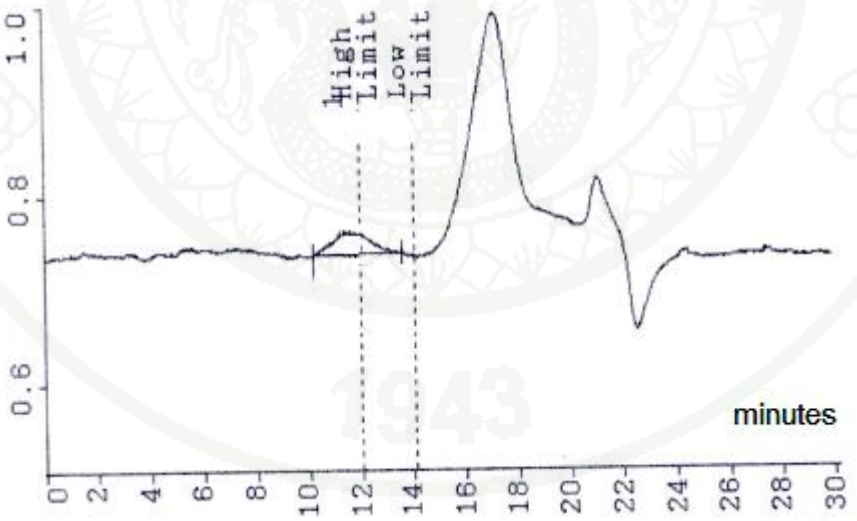


Figure 60 GPC chromatogram showing two molecular weights (small peaks for $\overline{M}_w$ = 87,000 with 13% area and a larger peak for $\overline{M}_w$ = 2,900 with 87% area) of PLA obtained with 10 kg LA by DMPC ($D_{10}B_2T_2$).

In synthesis of PLA from 10 kg LA by DMPC, various factors must be considered such as impurities of LA used, reactor design and heat transfers (reaction temperature, reaction time and synthesis condition). Although, it was found that $\overline{M}_w$ of PLA obtained from LA purchased from Aldrich (LA1) gave higher $\overline{M}_w$ than LA purchased from Purac (LA2), LA2 was used for carrying the PLA synthesis with 10 kg scale since LA1 cost is too high from the available limited budget. When compared the price of LA purchased, price of LA from Aldrich (LA1, 1 kg/8,000 Baht) is much higher than from Purac (LA2, 25 kg/8,000 Baht). Both LA1 and LA2 used for PLA synthesis by DMPC contain about 85-90 wt% L-LA (LLA) and 10-15% water respectively, along with trace of D-LA (DLA) and other impurities. This necessitates the removal of water from LA used, before the commencement of the reaction. This is done by distilling off the excess water in LA at 105^{o}C and then under reduced pressure (15 mmHg) at the same temperature with different time periods. It was found out that $\overline{M}_w$ of PLA obtained is not depended on the time periods for dehydration the LA2 used as can be seen when comparing sample $D_{10}B_2T_2$ and $D_{11}B_2T_2$ with the rest of the samples.

During DMPC, LA is converted to PLA along with the formation of condensate water as a byproduct. Usually, DMPC is carried out above T_m of PLA and under reduced pressure with a continuous flow of N_2 (under inert N_2 atmosphere). Removal of water vapor is comparatively more rapid with the help of continuous flow of N_2 and the reduction of pressure in the system to drive out water molecules. In addition, higher temperature increases the vapor pressure of water and helps water molecules to escape from the polymer melt and thereby enhances the rate of the forward reaction. It is found that $\overline{M}_w$ of PLA obtained with 10 kg LA cannot be increased by increasing the steps of DMPC at different temperatures and different time periods by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg).

Direct polycondensation rate depends on both chemical (chemical reaction) and physical processes (heat treatment, crystallization). The possible rate-determining steps are (i) chemical reaction control (a reversible chemical reaction), (ii) interior diffusion control (diffusion of the volatile reaction products such as water and oligomer (lactic acid) in the viscous polymer) and (iii) surface diffusion control (diffusion of the volatile reaction product from the surface of the polymer to the surrounding inert gas). At equilibrium, PLA produced, condensate water and unreacted LA are all presented. In order to synthesize a sufficient high molecular weight PLA, the equilibrium constant of polycondensation (K_c) has to be high enough to shift the equilibrium to the direction of PLA formation and further enhance the chain extension since condensate water prefer to hydrolyze PLA produced reverse back into LA (Figure 61). Thus, the condensate water must be removed effectively to shift the equilibrium to PLA formation (Le Chatelier's principle). However, it is getting more and more difficult to remove water from the system as the polycondensation proceeds due the severe increase of melt viscosity; therefore higher operating temperature is required. Although, high reaction temperature was useful to promote the removal of water, various side reactions such as depolymeriztion, thermal degradation, hydrolytic action, and intramolecular esterification of oligomer (lactic acid) can occur. If reaction temperature was too high, it would also cause partial or full carbonization of reactants, especially when the reaction time was longer (Zhang *et at*. 2008). Moreover, an increase in temperature to increase the polymerization rate or the dehydration process can generate additional heat to dissipate besides the heat generates from the polycondensation. Heat transfer and removal become particularly difficult when melt viscosity is high, because high melt viscosity limits both the interior and surface diffusion of volatile reaction products such as water and low molecular weight PLA. It is found that thermal control of the reaction is very difficult and the rate of thermal transfer is insufficient to remove the heat of polymerization with the stirrer from the designed reactor in this study, particularly with large volume of 10 kg of LA which requires reasonable rates of polymerization. As a result, the temperature of the reaction increases from 170^{o}C to almost 200^{o}C as the DMPC proceeded. It had been reported that it was not possible to prepare PLA at temperature higher than 200°C because a severe oxidation occurred which was observed by the

formation of the dark brown color, and molecular weight of polymer decreased dramatically (Zhu *et al*., 1990; Kaitain *et al.*, 1996). As the consequent from all the mentioned reasons, only low PLA is obtained by the DMPC with 10 kg LA in this study.

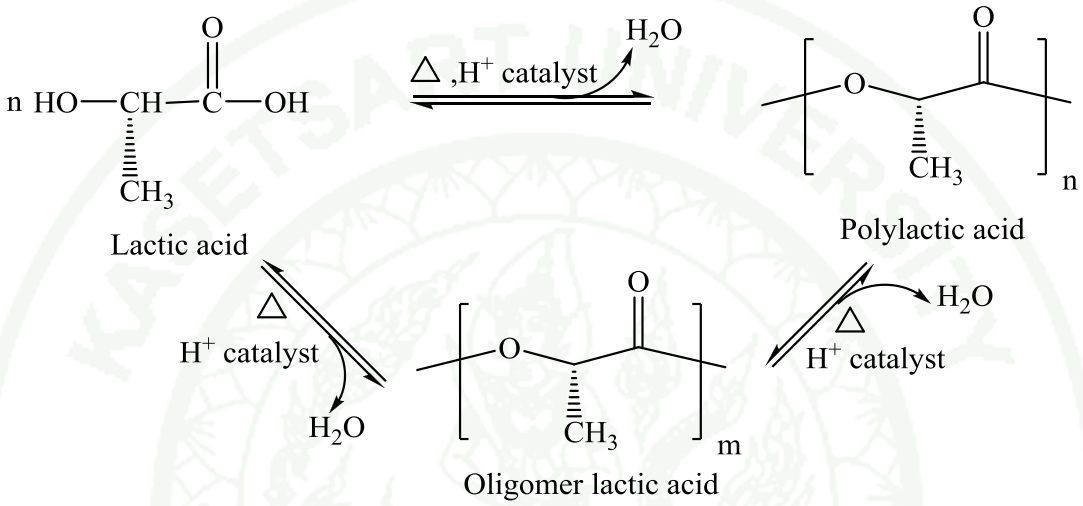


Figure 61 Formation of PLA from LA with the reversible reaction.

Part II: PLA modification by blending

PLA blends with two plasticizers: polyethylene glycol (PEG1 and PEG2 having $\overline{M}_n$ = 4,600 and 10,000 respectively) and polydioxolane (PDXL1 and PDXL2 having $\overline{M}_n$ = 10,000 and 200,000 respectively); with duck feather fiber (PLA/DF); with duck feather fiber and compatibilizer (PLA/DF/PEG or PLA/DF/PDXL); and with four rubbery impact modifiers: household gloves latex (LT1), concentrated natural rubber latex (LT2), poly(*cis*-1,4-isoprene) (IR), poly(acrylonitrile-*co*-butadiene) (NBR) and one eco-friendly, non toxic and biodegrability polymer impact modifier: poly(ethylene-*co*-vinyl acetate (PEVA) (PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA) were investigated as followed.

1. PLA/PEG and PLA/PDXL blends.

PLA/PEG and PLA/PDXL blends by varying the wt. ratio of PLA and PEG or PDXL from 95/5, 90/10, 85/15 and 80/20 were prepared. Characteristics of the PLA/PEG and PLA/PDXL blends at wt. ratio = 90/10 was shown in Table 44. Results of the effect of PEG and PDXL as plasticizers on the mechanical properties, including tensile strength (T.S.) at max load and at break; elongation at max load and at break; Young's modulus and ductility; of PLA blends were summarized in Table 45 and Figure 62. The results showed that increasing the molecular weight of both PEG and PDXL can increase the T.S. at break, % elongation and ductility of PLA/ PEG and PLA/PDXL blends. T.S. at break and modulus all decreased with increasing the wt. ratio of plasticizers. On the contrary, elongation at break and ductility dramatically increased and reached the optimum at 90/10 wt. ratio for PLA/PEG2 (213 % elongation) and PLA/PDXL1 (176 % elongation) and at wt. ratio 85/15 for PLA/PDXL2 (101 % elongation) blends. These indicated that PEG2, PDXL1 and PDXL2 can toughen the PLA at the wt. ratio of 10, 10 and 15 respectively and these proportions were used to further study as compatibilizers in PLA/DF blends.

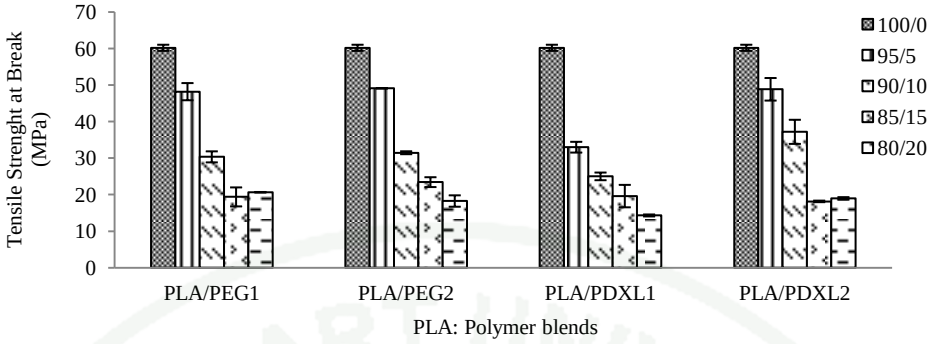
Table 44 Characteristics of PLA/PEG and PLA/PDXL blends at 90/10 (wt. ratio).

Codes	Characteristics	Photograph
PLA/PEG1: 90/10	White, dim	
PLA/PEG2: 90/10	White, dim	
PLA/PDXL1: 90/10	White, dim	
PLA/PDXL2: 90/10	White, dim	

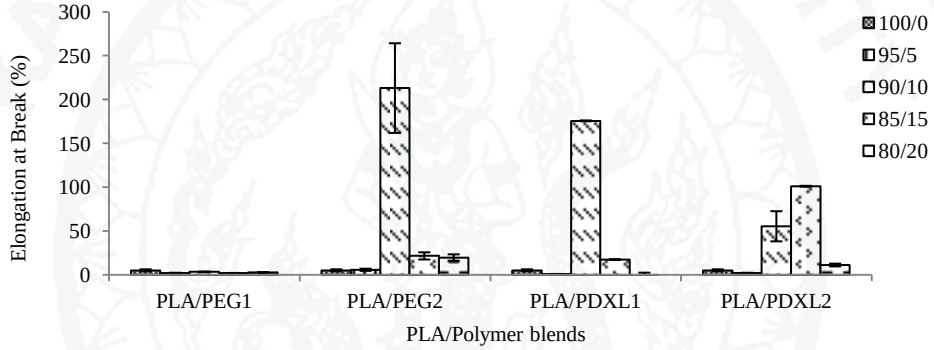
Results of thermal properties including the glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) of PLA/PEG and PLA/PDXL blends were shown in Table 46. Figure 63 represented DSC thermogram of the PLA/PEG and PLA/PDXL blends. It can be seen that PLA/PEG and PLA/PDXL blends exhibited slightly lower T_g but slightly higher T_m than pure PLA. Thus, PEG and PDXL can improve the brittleness of PLA with the lower T_g.

Table 45 Mechanical properties of PLA/PEG and PLA/PDXL blends.

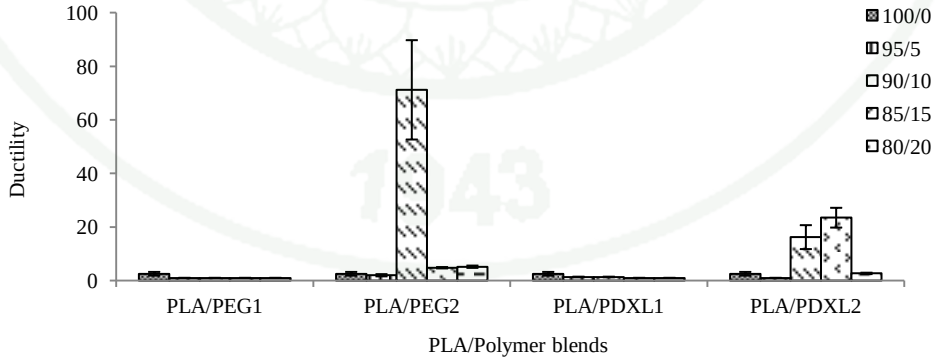
Codes	T.S. at max load (MPa)	Elongation at max load (%)	T.S. at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)	Ductility
PLA	60.2±0.8	2.1±0.1	47.5±2.8	5.2±1.2	3.9±0.2	2.5±0.7
PLA/PEG1						
95/5	48.2±2.4	2.2±0.3	48.2±2.4	2.2±0.3	20.5±3.3	1.0±0.0
90/10	30.3±1.5	3.4±0.4	30.3±1.5	3.4±0.4	9.7±1.1	1.0±0.0
85/15	19.4±2.6	2.0±0.3	19.4±2.6	2.0±0.3	9.9±1.8	1.0±0.0
80/20	20.6±0.1	2.7±0.1	20.6±0.1	2.7±0.1	7.1±0.1	1.0±0.0
PLA/PEG2						
95/5	49.1±0.0	3.0±0.0	31.3±0.2	5.8±1.2	20.6±0.7	2.0±0.4
90/10	31.5±0.4	3.0±0.2	20.8±4.7	213.2±51.2	0.0±0.0	71.2±18.5
85/15	23.4±1.4	4.6±1.1	21.2±2.8	21.7±4.1	3.8±0.5	4.8±0.3
80/20	18.2±1.7	3.9±1.0	13.2±1.4	19.8±3.7	3.9±0.3	5.2±0.4
PLA/PDXL1						
95/5	33.0±1.5	0.87±0.2	33.0±1.5	0.87±0.2	1.4±0.1	1.0±0.0
90/10	25.0±1.0	3.8±0.5	20.2±1.9	175.8±0.5	5.2±0.4	47.6±12.4
85/15	19. 6±0.3	17.5±2.2	19. 6±0.3	17.5±2.1	2.5±1.9	1.0±0.0
80/20	14.3±3.1	0.4±0.1	14.3±3.1	20.4±0.1	1.8±0.2	1.0±0.0
PLA/PDXL2						
95/5	48.8±3.1	2.3±0.1	48.8±3.1	2.3±0.1	21.1±2.4	1.0±0.0
90/10	37.2±3.3	3.4±0.1	15.1±0.5	55.5±17.1	14.4±0.4	16.2±4.5
85/15	18.2±0.2	4.4±0.7	14.3±0.2	101.2±0.5	4.4±0.4	23.5±3.7
80/20	19.0±0.3	4.2±0.2	20.1±0.1	11.3±1.6	5.6±0.1	2.7±0.3



(a)



(b)



(c)

Figure 62 The effect of PEG and PDXL on (a) tensile strength at break (b) elongation at break and (c) ductility of PLA/PEG and PLA/PDXL blends.

Table 46 Thermal properties of PLA/PEG and PLA/PDXL blends.

Codes	1st Heating (rate 10°C/min)				1st Cooling (rate 10°C/min)
	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)
PLA	57.9	-	148.8	7.1	-
PLA/PEG1					
95/5	50.3	99.7	149.8	22. 7	-
90/10	52.6	84.2	155.1	23.0	88.9
85/15	51.9	-	150.4	17.5	94.3
80/20	54.6	85.6	150.4	28.2	93.4
0/100	-*	-	56.1	104.1	-
PLA/PEG2					
95/5	54.7	93.1	154.3	22.6	-*
90/10	52.2	85.1	149.9	20.6	88.4
85/15	-	-	151. 8	24.7	84.9
80/20	54.7	85.6	150.4	28.7	93.4
0/100	-	-	67.7	181.2	-
PLA/PDXL1					
95/5	53.3	104.2	155.3	52.9	84.7
90/10	51.4	84.8	153.5	50.7	-
85/15	50.6	84.1	149.8	28.0	92.4
80/20	-	-	150.6	26.9	86.47
0/100	-	-	56.1	104.1	-

Table 46 (Continued)

Codes	1st Heating (rate 10°C/min)				1st Cooling (rate 10°C/min)
	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)
PLA/PDXL2					
95/5	53.2	102.9	154.1	30.2	-
90/10	50.3	99.4	151.9	24.0	-
85/15	-	77.1	157.3	20.4	85.3
80/20	-	-	153.0	24.8	86.8
0/100	-	-	63.9	97.4	-

* Not detect

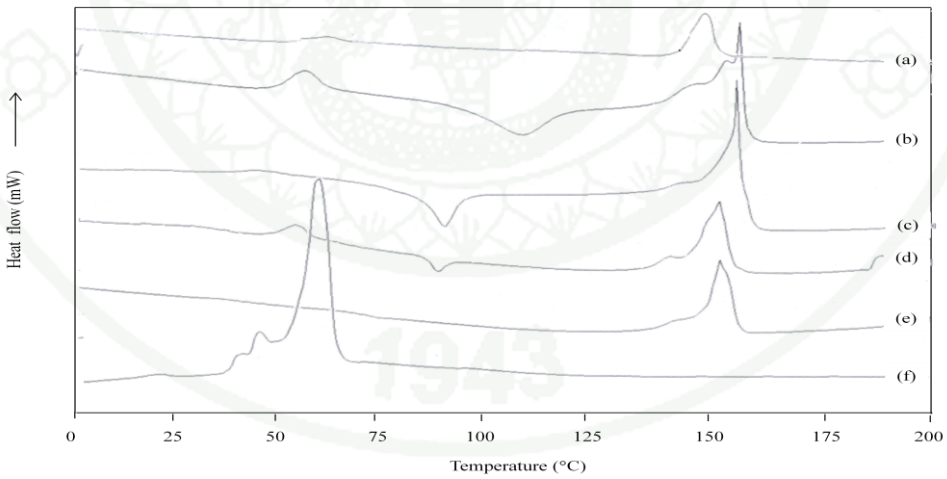


Figure 63 DSC thermogram of (a) pure PLA, (b) PLA/PDXL1: 95/5, (c) PLA/PDXL1: 90/10, (d) PLA/PDXL1: 85/15, (e) PLA/PDXL1: 80/20 and (f) pure PDXL1 (1st heating at 10°C/min).

Morphology of PLA/PEG2, PLA/PDXL1 and PLA/PDXL2 observed from SEM were shown in Figure 64 to Figure 66 respectively. Pure PLA showed a relatively smooth surface without any sign of plastic deformations of the brittle fracture characteristics (Figure 64(a)). SEM morphology of PLA/PEG and PLA/PDXL blends showed that PEG and PDXL dispersed uniformly in the PLA matrix showing no phase separation occurred in PLA/PEG and PLA/PDXL blends. Results were in agreement with thermal properties showing that PEG and PDXL can indeed improve the brittleness of PLA.

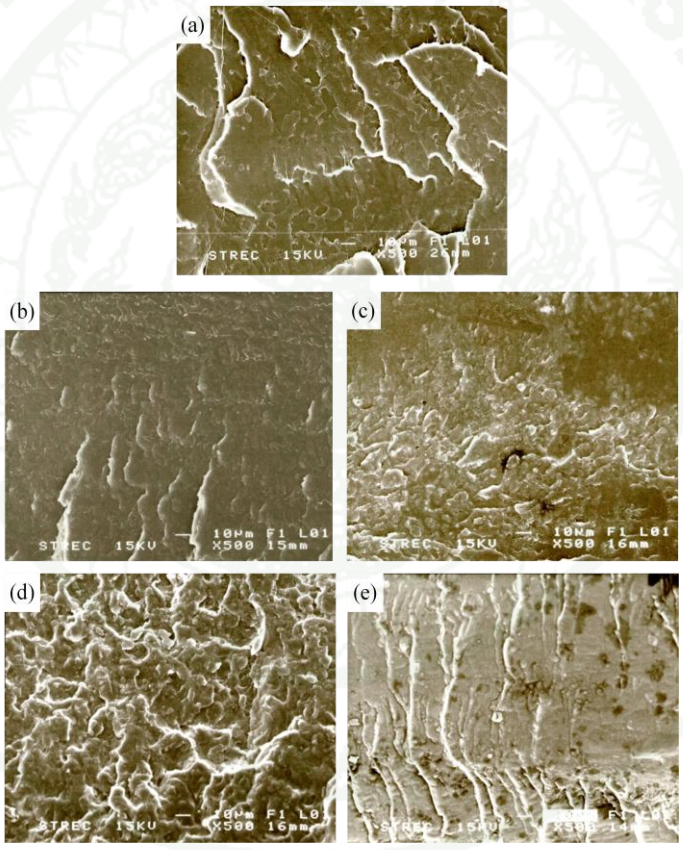


Figure 64 SEM cross section morphology (500x) of (a) pure PLA, (b) PLA/PEG2: 95/5, (c) PLA/PEG2: 90/10, (d) PLA/PEG2: 85/15 and (e) PLA/PEG2: 80/20.

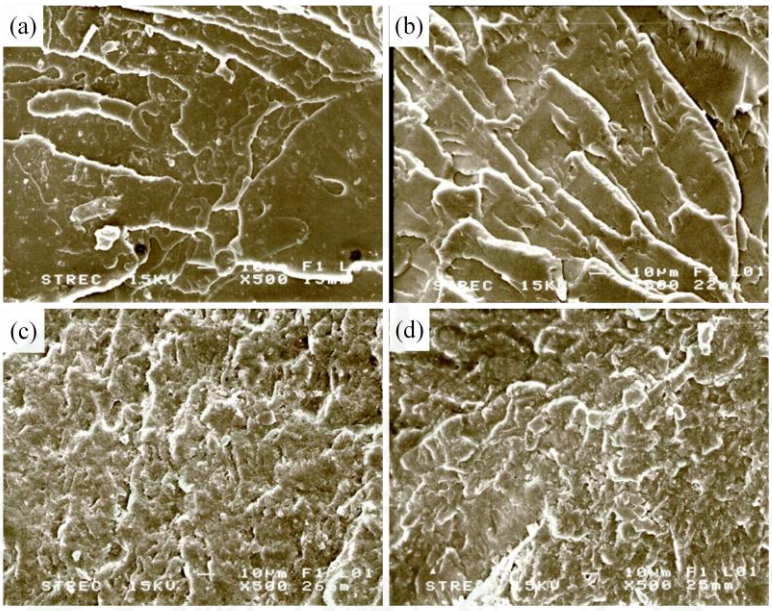


Figure 65 SEM cross section morphology (500x) of (a) PLA/PDXL1: 95/5, (b) PLA/PDXL1: 90/10, (c) PLA/PDXL1: 85/15 and (d) PLA/PDXL1: 80/20.

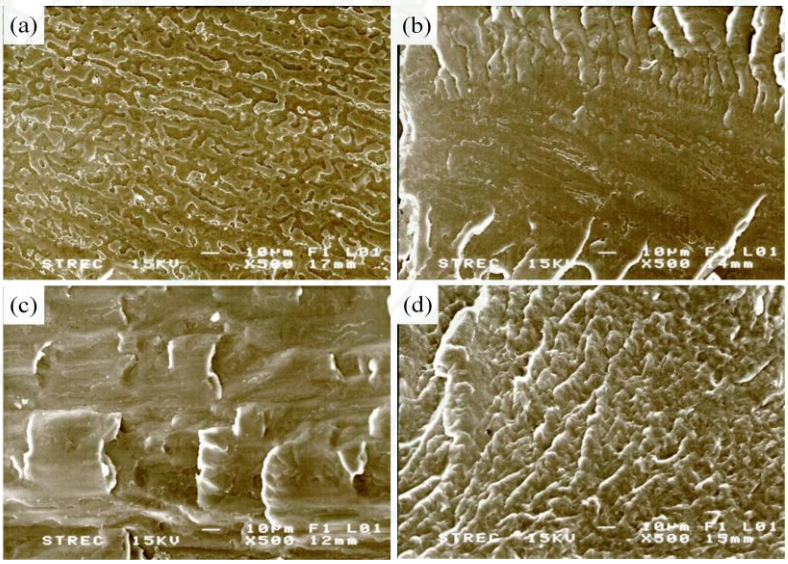


Figure 66 SEM cross section morphology (500x) of (a) PLA/PDXL2: 95/5, (b) PLA/PDXL2: 90/10, (c) PLA/PDXL2: 85/15 and (d) PLA/PDXL2: 80/20.

2. PLA/DF blends

PLA/DF blends by varying the wt. ratio of PLA and DF from 95/5, 90/10, 85/15 and 80/20; and PLA/PEG2/DF, PLA/PDXL1/DF and PLA/PDXL2/DF with the wt. ratio 95-80/10/5-20, 95-80/10/5-20 and 95-80/15/5-20 respectively were prepared. Characteristics of the PLA/DF blends at wt. ratio = 95/5 was shown in Table 47. It can be seen that the PLA/DF blends obtained by kneading with a two roll mill had a smoother surface than from casting. Results of the PLA/DF blends and the effect of PEG and PDXL as compatibilizer on the PLA/PEG/DF and PLA/PDXL/DF blends on the mechanical properties including tensile strength (T.S.) at max load and at break, elongation at max load and at break, Young's modulus and ductility of PLA blends were summarized in Table 48 and Figure 67- Figure 68. The results showed that mechanical properties of PLA/DF, PLA/PEG/DF and PLA/PDXL/DF blends from kneading with a two roll mill were all higher than from casting. Results showed that tensile strength and elongation at break of PLA/DF decreased with increasing the DF content. Moreover, tensile strength and elongation at break of all PLA/DF blends from both kneading and casting was lower than pure PLA, but the modulus of PLA/DF from kneading was higher than pure PLA in all proportions. When blending PLA/DF with PEG and PDXL as compatibilizer in PLA/DF blends, results showed that PDXL exhibited higher tensile strength and modulus than PEG (PDXL1> PEG2) at same molecular weight ($\overline{M}_n$ = 10,000). This may due to the more compatibility from the addition methylene group (-CH_2-O-) of PDXL with PLA. Although, the tensile strength and elongation at break of PLA/PEG/DF and PLA/PDXL/DF blends were higher than PLA/DF, they were still lower than pure PLA. These indicated that DF is not suitable to toughen PLA property even with the help of good compatibilizer as PEG and PDXL.

Table 47 Characteristics of PLA/DF and PLA/PEG or PDXL/DF blends at 95/5 (wt. ratio).

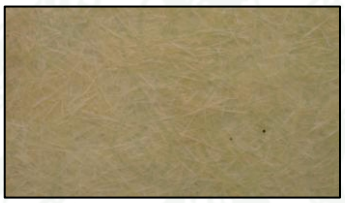
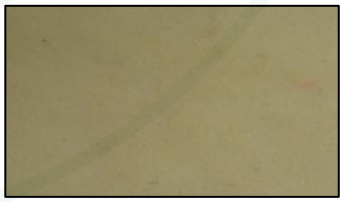
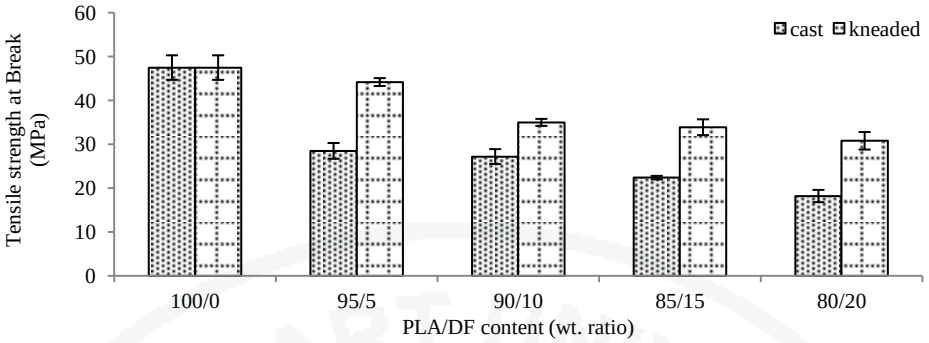
Codes	Photograph	
	By casting	**By two roll mill (knead)**
PLA/DF: 95/5		
PLA/PEG2/DF: 95/10/5		
PLA/PDXL1/DF: 95/10/5		
PLA/PDXL2/DF: 95/10/5		

Table 48 Mechanical properties of PLA/DF and PLA/PEG2/DF, PLA/PDXL1/DF and PLA/PDXL2/DF blends.

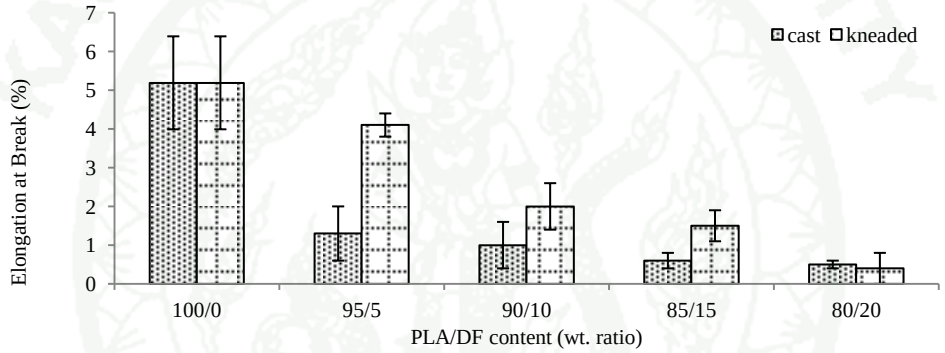
Codes	T.S. at max load (MPa)	Elongation at max load (%)	T.S. at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)	Ductility
PLA	60.2±0.8	2.1±0.1	47.5±2.8	5.2±1.2	3.9±0.2	2.5±0.7
PLA/DF-cast:						
95/5	28.5±1.8	1.3±0.7	28.5±1.8	1.3±0.7	0.0±0.0	1.0±0.0
90/10	27.2±1.7	1.0±0.6	27.2±1.7	1.0±0.6	0.0±0.0	1.0±0.0
85/15	22.4±0.4	0.6±0.2	22.4±0.4	0.6±0.2	0.0±0.0	1.0±0.0
80/20	18.2±1.4	0.5±0.1	18.2±1.4	0.5±0.1	0.0±0.0	1.0±0.0
PLA/DF-knead:						
95/5	44.2±0.9	4.1±0.3	44.2±0.9	4.1±0.3	8.8±0.8	1.0±0.0
90/10	35.0±0.8	2.0±0.6	35.0±0.8	2.0±0.6	14.2±3.5	1.0±0.0
85/15	33.9±1.8	1.5±0.4	33.9±1.8	1.5±0.4	8.8±0.3	1.0±0.0
80/20	30.8±2.0	0.4±0.4	30.8±2.0	0.4±0.4	16.6±0.6	1.0±0.0
PLA/PEG2/DF-cast:						
95/10/5	7.1±0.2	1.0±0.0	7.1±0.2	1.0±0.0	6.8±0.2	1.0±0.0
90/10/10	10.2±0.5	0.2±0.1	10.2±0.5	0.2±0.1	14.1±1.2	1.0±0.0
85/10/15	18.1±1.7	2.4±0.4	18.1±1.7	2.4±0.4	7.1±1.3	1.0±0.0
80/10/20	17.6±1.1	2.0±0.2	17.6±1.1	2.0±0.2	9.3±1.4	1.0±0.0
PLA/PEG2/DF-knead:						
95/10/5	24.4±0.9	3.3±0.1	24.4±0.9	3.3±0.07	9.3±0.9	1.0±0.0
90/10/10	15.2±0.3	0.7±0.0	15.2±0.3	0.7±0.0	19.9±0.7	1.0±0.0
85/10/15	13.2±2.5	0.3±0.4	13.2±2.5	0.3±0.4	21.5±0.6	1.0±0.0
80/10/20	11.2±0.6	0.9±0.17	11.2±0.6	0.9±0.17	27.7±0.8	1.0±0.0

Table 48 (Continued)

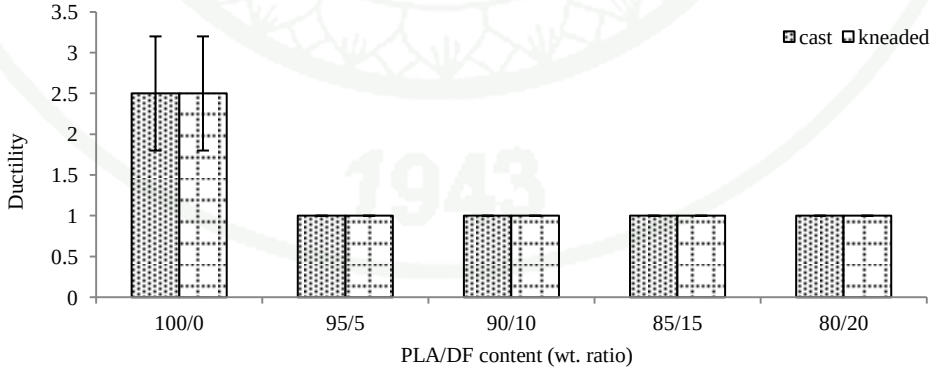
Codes	T.S. at max load (MPa)	Elongation at max load (%)	T.S. at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)	Ductility
PLA/PDXL1/DF-cast:						
95/10/5	27.2±1.2	1.2±0.2	27.2±1.2	1.2±0.2	23.5±6.0	1.0±0.0
90/10/10	23.3±4.7	1.8±0.2	10.8±9.4	4.2±4.2	35.0±1.1	2.3±2.2
85/10/15	18.9±1.9	1.1±0.5	0.0±0.0	0.4±0.4	17.7±1.6	0.45±0.4
80/10/20	14.8±1. 7	0.0±0.0	15.0±1.7	0.0±0.0	41.3±1.4	1.05±0.1
PLA/PDXL1/DF-knead:						
95/10/5	36.1±1.6	1.8±0.1	35.7±1.5	2.3±0.3	22.5±2. 9	1.3±0.2
90/10/10	23.4±0.2	1.2±0.2	23.4±0.2	1.2±0.2	18.0±2.9	1.0±0.0
85/10/15	16.9±3.1	0.7±0.1	16.9±3.1	0.7±0.1	19.7±1.5	1.0±0.0
80/10/20	nd	nd	nd	nd	nd	nd
PLA/PDXL2/DF-cast:						
95/15/5	14.3±1.3	2.0±0.2	14.1±1.4	2.1±0.2	7.50±58	1.0±0.0
90/15/10	17.6±0.5	3.2±0.1	17.1±0.5	3.3±0.1	6.0±0.3	1.0±0.0
85/15/15	14.0±3.3	2.4±0.2	14.0 ±3.3	2.5±0.3	6.1±1.9	1.0±0.0
80/15/20	12.4±1.2	0.8±0.1	12.4±1.2	0.8±0.1	1.9±0.9	1.0±0.0
PLA/PDXL2/DF-knead:						
95/15/5	16.7±0.6	3.8±0.4	15.3±0.5	5.5±1.3	4.2±1.0	1.4±0.2
90/15/10	17.5±0.8	1.9±0.1	17.5±0.8	1.9±0.1	8. 8±0.5	1.0±0.0
85/15/15	13.6±0.3	1.6±0.4	13.6±0.3	1.8±0.3	7.8±0.78	1.1±0.2
80/15/20	17.3±2.0	2.4±0.4	17.1±2.2	2.5±0.4	1.6±0.3	1.0±0.1



(a)

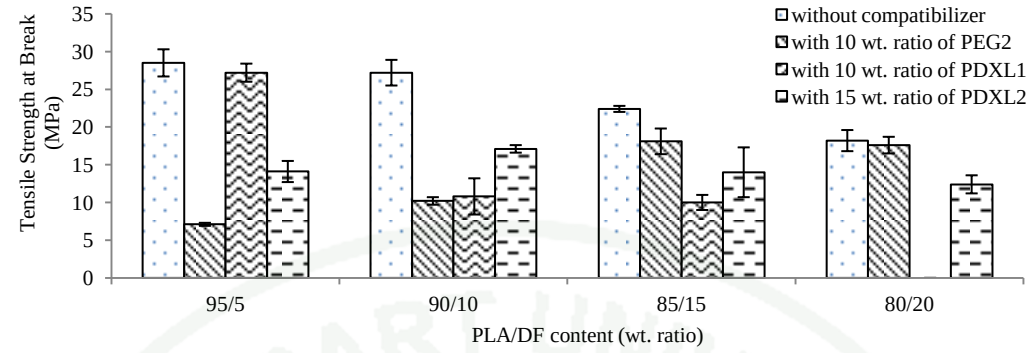


(b)

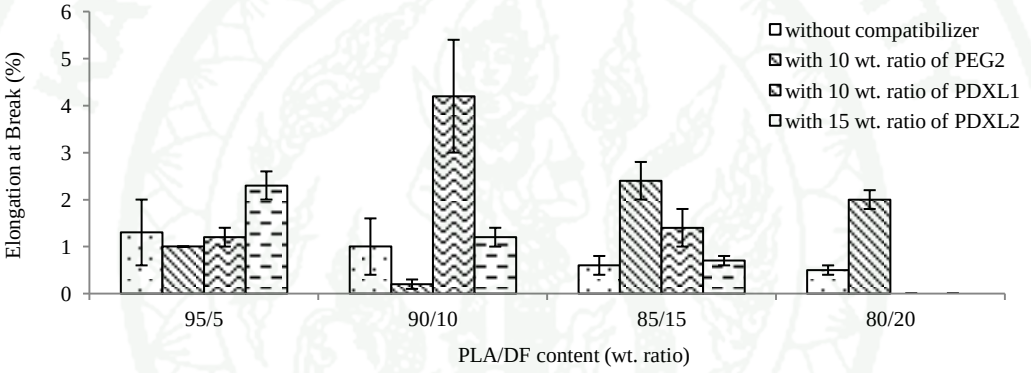


(c)

Figure 67 Comparison the effect of DF content on mechanical properties of PLA matrix.



(a)



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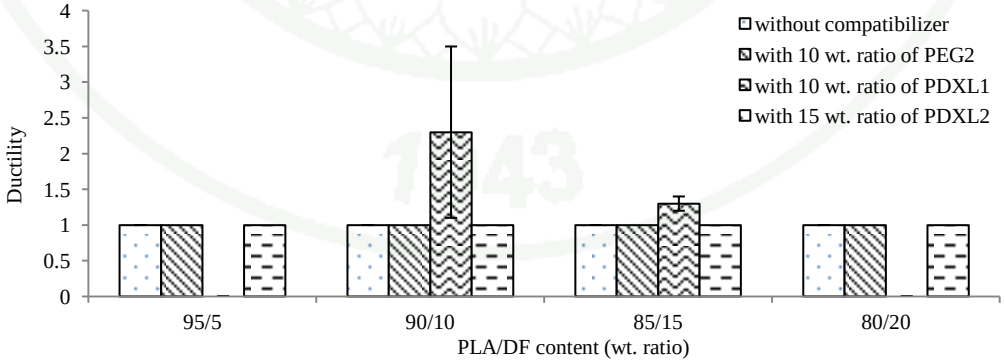


(c)

Figure 68 Comparison the effect of compatibilizer on PLA/DF composite.

Further adding the same 10 wt. ratio and the same molecular weight ($\overline{M}_n$ = 10,000) of PEG2 and PDXL1 into PLA/DF blends are also observed. At 95/5 of PLA/DF blend, both PEG2 and PDXL1 cannot increase the elongation at break (EB), but instead it is found that the EB decrease. At 90/10 of PLA/DF blend, only PDXL1 can increase the EB significantly. At 85/15 of PLA/DF blend, both PEG2 and PDXL1 can increase the EB and PEG2 has higher EB than PDXL1. Likewise, adding PEG2 into 80/20 of PLA/DF blends can increase the EB of the PLA/DF blends.

Results of thermal properties including the glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) of PLA/DF, PLA/PEG/DF and PLA/PDXL/DF blends were shown in Table 49. Figure 69 represented DSC thermogram of the PLA/PDXL1/DF blend. It can be seen that increasing the DF content of PLA/DF, slightly increased the melt temperature of the PLA/DF blends. The same result of PLA/PEG and PLA/PDXL blends also extended to the PLA/PEG/DF and PLA/PDXL/DF blends which exhibited slightly lower T_g but slightly higher T_m than pure PLA.

Table 49 Thermal properties of PLA/DF, PLA/PEG/DF and PLA/PDXL/DF blends.

Codes	1st Heating (rate 10°C/min)				1stCooling (rate 10°C/min)
	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)
PLA	57.9	-	148.8	7.1	-
PLA/DF-cast:					
95/5	55.1	-*	150.0	8.7	-
90/10	56.4	-	148.2	9.3	-
85/15	58.0	-	147.5	11.8	-
80/20	60.8	-	150.8	10.2	-
PLA/DF-knead:					
95/5	57.0	-	148.8	7.1	-
90/10	59.3	-	147.4	9.6	-
85/15	58. 6	-	149.6	9.0	-
80/20	58.1	-	151.5	11.3	-
PLA/PEG2/DF-cast:					
95/10/5	55.9	86.4	151.2	22.8	89.3
90/10/5	50.0	-*	150.1	22.4	92.8
85/10/15	54.1	85.8	150.4	22.2	90.0
80/10/20	55.9	89.7	158.5	23.2	85.2
PLA/PEG2/DF- knead:					
95/10/5	49.9	85.9	153.6	27.2	93.4
90/10/10	45.8	85.2	152.9	36.1	93.1
85/10/15	47.9	85.4	151.0	24.5	92.4
80/10/20	54.1	85.3	157.6	19.1	90.2
PLA/PDXL1/DF-cast:					
95/10/5	52.6	99.2	155.1	24.9	-

Table 49 (Continued)

Codes	1st Heating (rate 10°C/min)				1st Cooling (rate 10°C/min)
	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)
90/10/10	45.2	83.2	153.6	19.2	-
80/10/15	46.6	83.9	157.4	20.5	-
80/10/20	-	77.9	158.7	16.9	-
PLA/PDXL1/DF-knead:					
95/10/5	50.2	93.0	157.6	23.0	-
90/10/10	-	81.5	160.8	24.7	89.9
85/10/15	48.5	79.4	159.5	20.6	89.3
80/10/20	42.7	-*	150.8	21.9	93.0
PLA/PDXL2/DF-cast:					
95/15/5	-	82.8	150.5	24.2	84.6
90/15/10	-	74.0	153.2	21.6	84.8
85/15/15	-	73.5	151.3	18.6	84.6
80/15/20	-	74.8	151.6	21.0	88.8
PLA/PDXL2/DF-knead:					
95/15/5	-	-	153.8	22.7	87.3
90/15/10	-	-	153.4	22.9	84.6
85/15/15	-	-	152.5	28.9	90.1
80/15/20	-	-	155.5	19.9	87.3

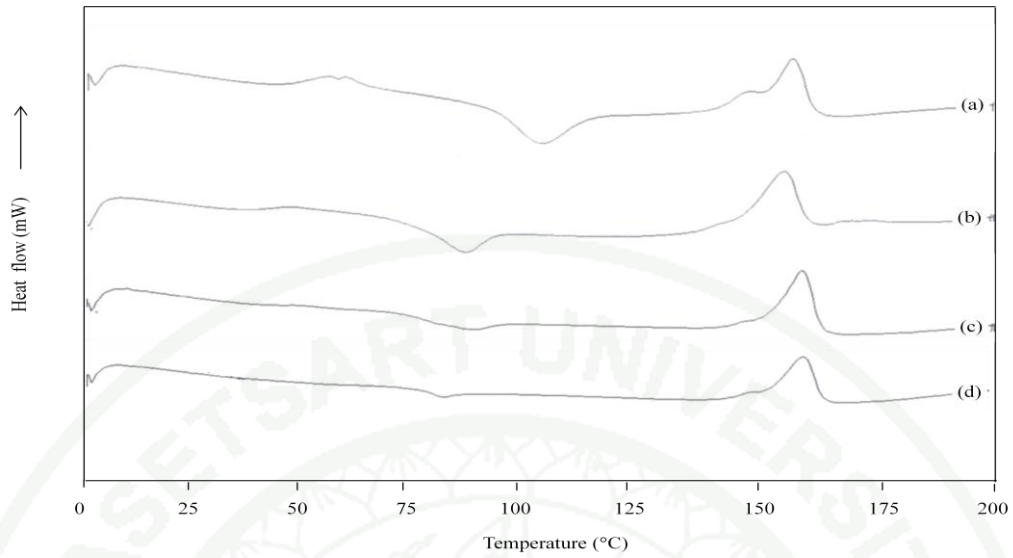


Figure 69 DSC thermogram of PLA/PDXL1/DF cast at ratio of (a): 95/10/5, (b) 90/10/10, (c) 85/10/15 and (d) 80/10/20 (cast) at heating rating 10°C/min.

Duck feather fiber (DF) morphology was taken as shown in Figure 70. The fibers are cylindrical in shape (Figure 70(a)), and a hollow cross-section, (Figure 70(b) while the latter has a solid core, with little protrusions at certain intervals along its length (Figure 70(c)).

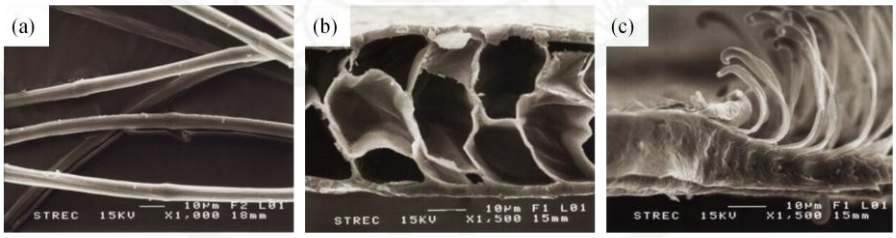


Figure 70 SEM images (1500x) of the duck feather fiber

The morphology of fracture surfaces of PLA/DF was investigated by SEM as shown in Figure 71 and Figure 72. It can be observed that DF can be moderately dispersed in the PLA matrix at low DF content. Pull out DF and voids were found on the fracture surface, as the fibers are trapped by the PLA matrix forming a network having DF inside the PLA matrix as reinforcement (pointed by the arrows). Thus, DF

adhere at the interface between PLA matrix can prevent crack and enable effective stress transfer between PLA matrix and DF and hope that DF can lead to a better mechanical tensile properties. In this studying, PLA/DF blends were not broken off together, instead of DF pull out and voids observed around DF which indicated poor adhesion between DF and PLA matrix. Possibility voids and pull out of DF in PLA matrix were reduced by kneading PLA/DF. SEM of sheet using two roll mills before compression molded is shown in Figure 72. Figure 72 showed small size and moderate dispersed of DF in PLA matrix, but showed small void enclose DF fiber indicated that kneading has not enough on the improvement of PLA properties as corresponding with the mechanical properties confirming that mechanical properties of PLA/DF were lower than pure PLA. Adding compatibilizer is one selection to modify the fiber interfacial adhesion between DF and PLA matrix. The effects of PEG and PDXL as compatibilizers in PLA/DF blends were shown in Figure 73- Figure 75. It showed moderate dispersion of the DF in PLA matrix. Besides, it also showed voids and DF pull out enclose DF and polymer matrix that may contribute for the reduction of mechanical properties of the PLA/DF blends than the pure PLA.

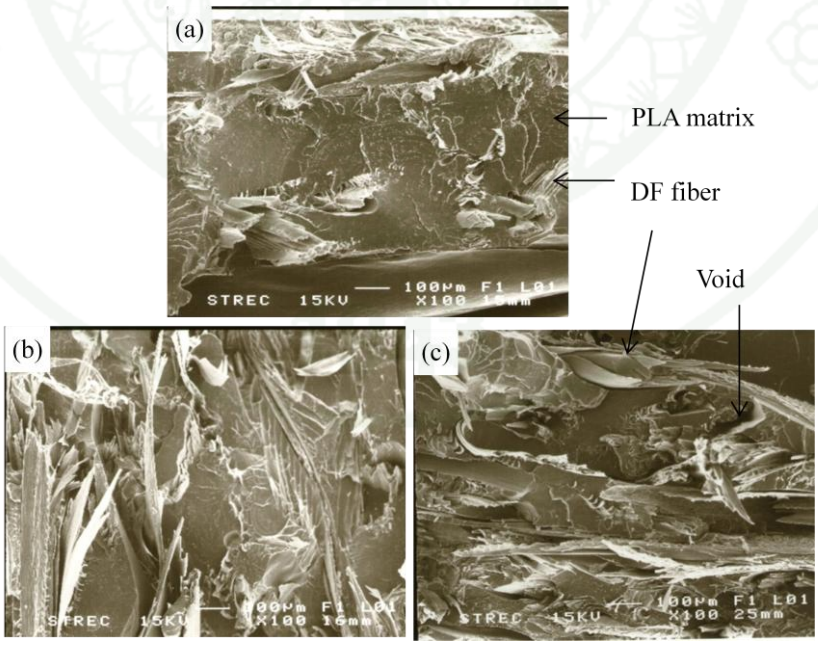


Figure 71 SEM cross section morphology (x100) of (a) PLA/DF: 95/5, (b) PLA/DF: 90/10 and (c) PLA/DF: 80/20

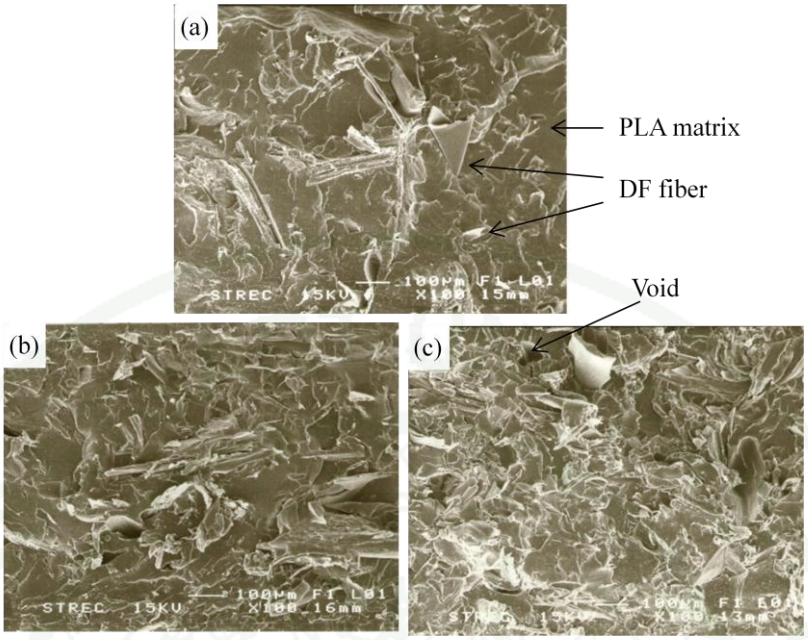


Figure 72 SEM cross section morphology (x100) PLA/DF was knead with two roll mill (a) PLA/DF: 95/5, (b) PLA/DF: 90/10 and (c) PLA/DF: 80/20

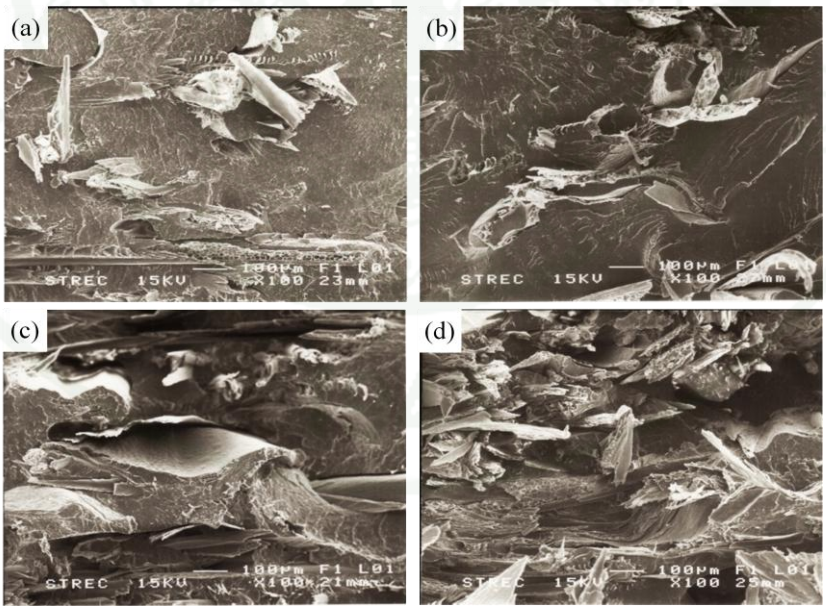


Figure 73 SEM cross section morphology (x100) of (a) PLA/PEG(2)/DF: 95/10/5, (b) PLA/PEG2/DF: 90/10/10, (c) PLA/PEG2/DF:85/10/15 and (d) PLA/PEG2/DF: 80/10/20.

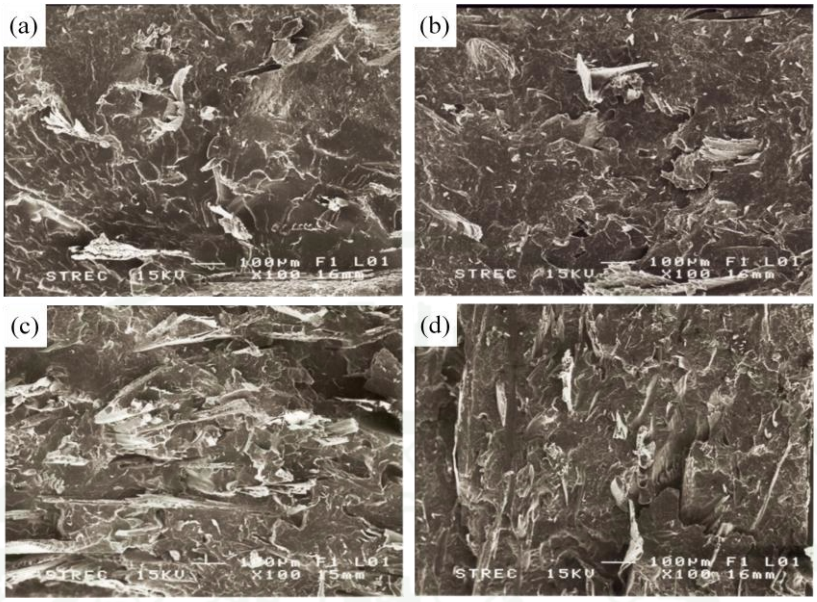


Figure 74 SEM cross section morphology (x100) of (a) PLA/PEG2/DF: 95/10/5-knead, (b) PLA/PEG(2)/DF: 90/10/10-knead, (c) PLA/PEG2/DF: 85/10/15-knead and (d) PLA/PEG2/DF: 80/10/20-knead.

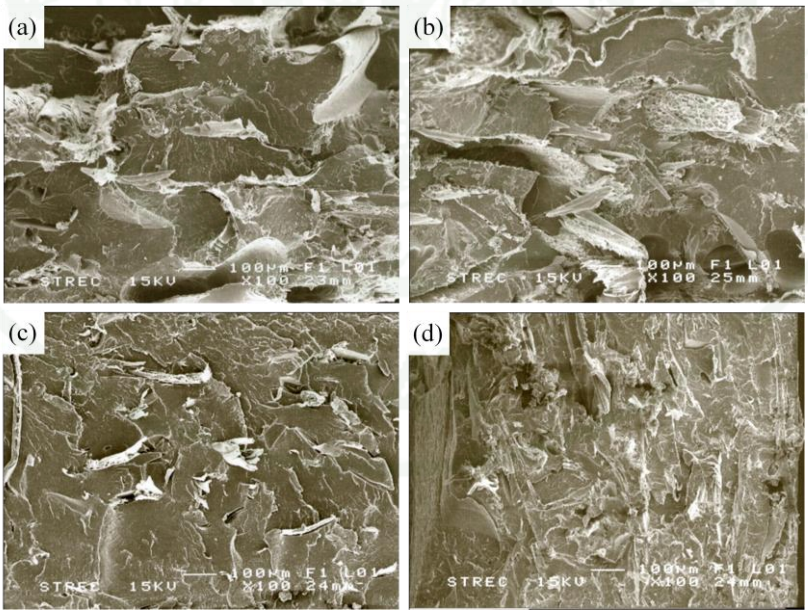


Figure 75 SEM cross section morphology (x100) of (a) PLA/PDXL1/DF: 95/10/5, (b) PLA/PDXL1/DF: 90/10/10, (c) PLA/PDXL1/DF: 95/10/5-knead and (d) PLA/PDXL1/DF: 90/10/10-knead.

3. PLA/ impact modifier blends

Figure 76 shows SEM fractured surfaces micrographs of compression molded pure PLA and PLA/impact modifier: 90/10 wt. ratio blends. The fractured surface of pure PLA showed the relatively smooth surface without any signs of plastic deformation which indicated the brittle fracture characteristics. Phase separation morphology of each PLA/impact modifier blend showing a uniform dispersion of impact modifier in PLA matrix indicating poor interfacial adhesion were observed. Additionally, rough fractured surfaces of PLA/impact modifier blends were also observed which indicated the ductile fracture characteristics.

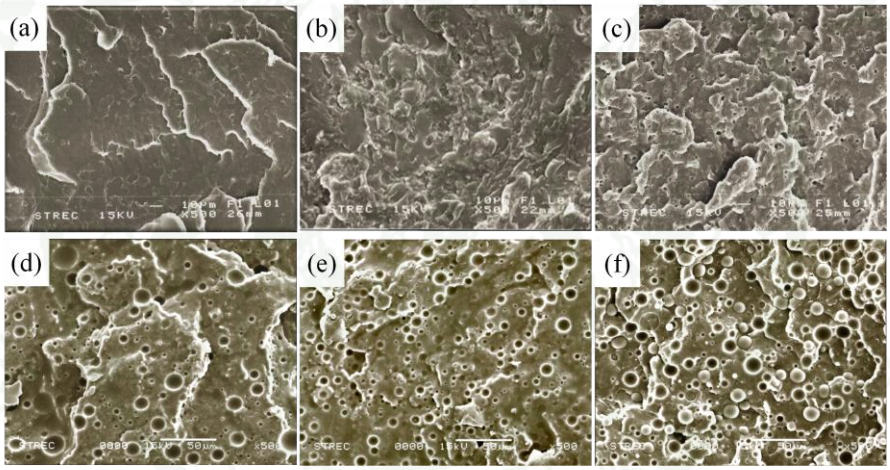


Figure 76 SEM fractured surfaces micrographs of (a) pure PLA, (b) PLA/LT1: 90/10, (c) PLA/LT2: 90/10, (d) PLA/IR: 90:10 (e) PLA/NBR: 90/10 and (f) PLA/PEVA: 90/10.

The DSC results of the first heating scan of compression molded of pure PLA and PLA/impact modifier blends are summarized in Table 50 and Figure 77. The pure PLA showed a glass transition temperature (T_g) at 55.9°C and a melting temperature (T_m) at 151.3°C. It can be seen that PLA in the PLA/impact modifier blends exhibited almost the same T_g and T_m as pure PLA. PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA blends showed a T_g at 54.1 and 53.0°C; 56.3 and 57.1°C; 55.8 and 56.7°C; 55.7 and 55.4°C; and 53.5 and 57.5°C by adding 5 and 10 wt. ratio of impact

modifiers, respectively. PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA blends showed a T_m at 151.4 and 154.9°C; 150.6 and 155.2°C; 151.7 and 152.8°C; 152.0 and 151.4°C; and 153.7 and 151.4°C by adding 5 and 10 wt. ratio of impact modifiers, respectively. This suggested that there was no molecular interaction between PLA and impact modifiers; therefore, the PLA/impact modifier blends were immiscible. This result was in agreement with the SEM obtained previously.

Table 50 Thermal properties of PLA/impact modifier blends.

Codes	1st Heating (rate 10°C/min)				1st Cooling (rate 10°C/min)
	T_g (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)
PLA/LT1:					
95/5	54.1	102.2	151.4	21.6	-
90/10	53.0	-	154.9	25.0	-
PLA/LT2:					
95/5	56.3	111.5	150.6	19.1	-
90/10	57.1	116.0	155.2	16.5	-
PLA/IR:					
95/5	55.8	-	151.7	-	-
90/10	56.7	-	152.8	-	-
PLA/NBR:					
95/5	55.7	-	152.0	-	-
90/10	55.4	-	151.4	-	-
PLA/PEVA					
95/5	53.5	-	153.7	-	-
90/10	57.5	-	151.4	-	-

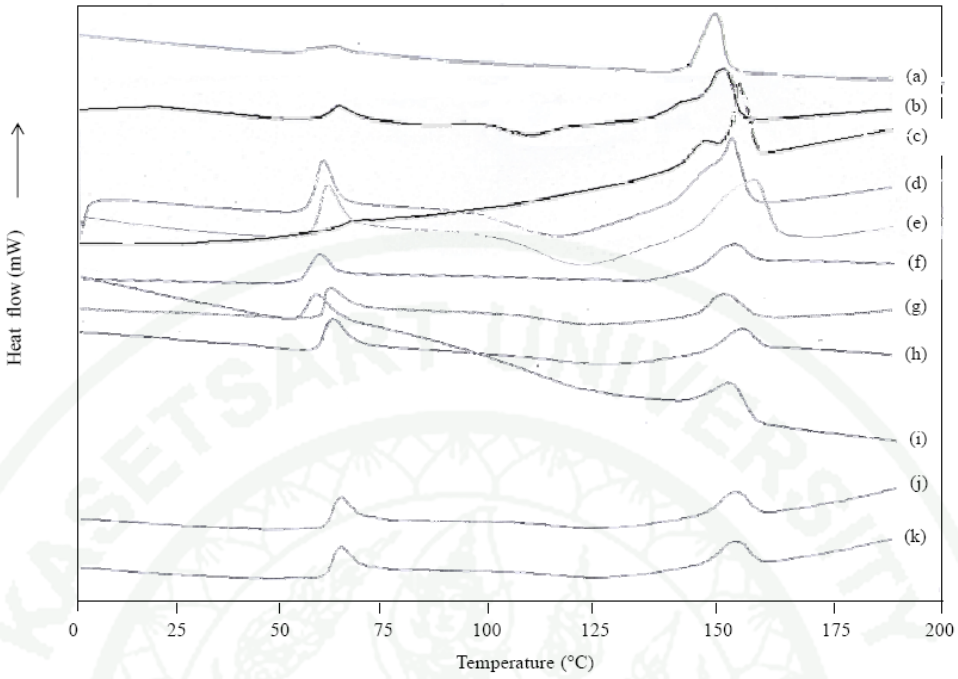


Figure 77 DSC thermograms of (a) PLA, (b) PLA/LT1: 95/5, (c) PLA/LT1: 90/10, d) PLA/LT2: 95/5, (e) PLA/LT2: 90/10, (f) PLA/IR: 95/5, (g) PLA/IR: 90/10, (h) PLA/NBR: 95/5, (i) PLA/NBR: 90/10, (j) PLA/PEVA: 95/5 and (k) PLA/PEVA: 90/10.

Table 51 illustrates tensile properties including tensile strength (T.S.) and elongation at maximum load, tensile strength and elongation at break, Young's modulus and ductility of pure PLA and its blends with 5 and 10 wt. ratio of 5 impact modifiers, LT1, LT2, IR, NBR and PEVA. Figure 78 shows the stress/strain curves of pure PLA and it blends with 5 and 10 wt. ratio of all impact modifiers. Results indicated that the fracture behavior changed from brittle fracture in pure PLA to ductile fracture in all PLA/impact modifier blends. All PLA/impact modifier blends show distinct yielding and stable neck growth through cold drawing and finally broke at significantly increased elongation. Figure 79 shows the effect of impact modifier type and content on tensile strength at break, elongation and ductility of pure PLA and PLA/impact modifier blends. The T.S. at break decreased in all PLA/impact modifier blends; PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA (Figure 79(a)). T.S. at break decreased by about 69.2% in PLA/LT2:95/5 wt. ratio and 57.2% in

PLA/PEVA:90/10 wt. ratio when compared with pure PLA. Table 51 showed that modulus in all blends and T.S. at break in PLA/LT1, PLA/LT2, PLA/IR and PLA/NBR blends was not significantly affected by the type and content of impact modifiers in the blends, but T.S. at break in PLA/PEVA blends was decreased by increasing the PEVA content from 5 to 10 wt. ratio. These results were in agreement with the results obtained by Ishida *et al*. (2009). By contrast, the elongation at break significantly increased in all PLA/impact modifier blends from about 16% in PLA/LT2:90/10 to about 102% in PLA/NBR:95/5 when compared with pure PLA and only PLA/NBR blends was affected by the content of impact modifier added (Figure 79(b)). This might be explained from the compatibility enhancement between the increasing of polar segment of cyano groups when increase the NBR content with the hydroxyl polar segment in PLA. Finally, the increase in ductility of all PLA/impact modifier blends (Figure 79(c)) from all five types of impact modifiers confirmed the toughening capability of all impact modifiers. Thus, it is evident from tensile properties obtained indicated that PLA/impact modifier blends exhibit greater flexibility with all impact modifiers.

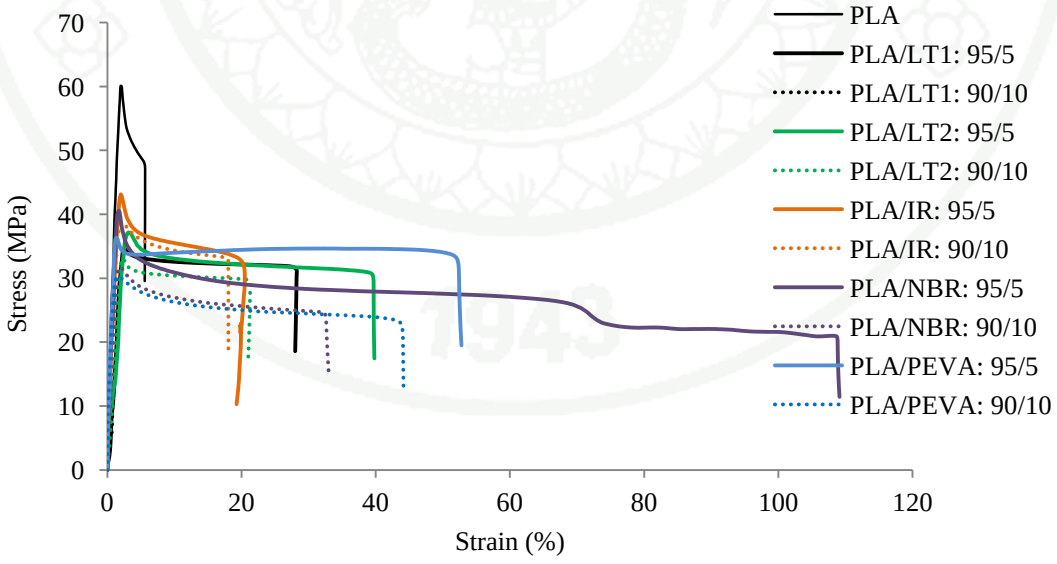
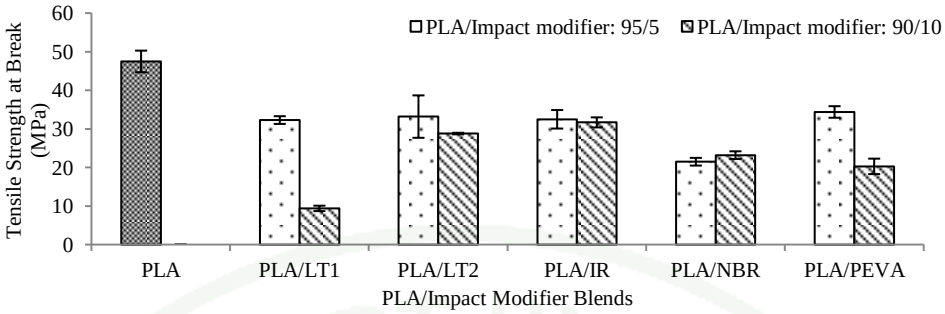


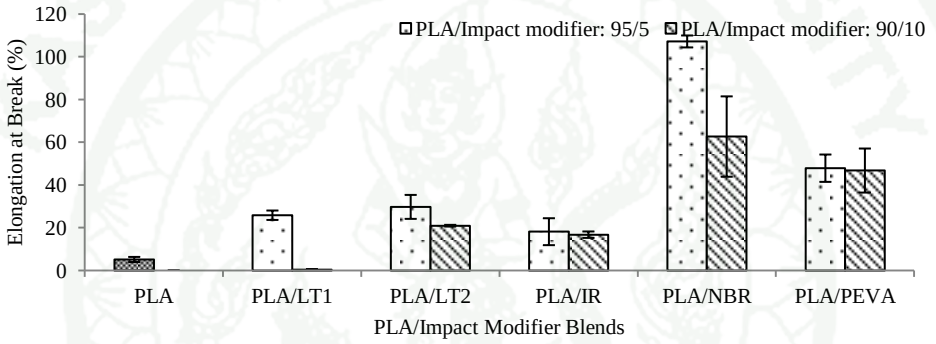
Figure 78 Effect of impact modifier content on the tensile stress/strain curves of PLA/impact modifier blends.

Table 51 Mechanical properties of PLA and PLA with the different of impact modifier blends.

Codes	T.S. at max load (MPa)	Elongation at max load (%)	T.S. at break (MPa)	Elongation at break (%)	Young's Modulus (GPa)	Ductility
PLA	60.2±0.8	2.1±0.1	47.5±2.8	5.2±1.2	3.9±0.2	2.5±0.7
PLA/LT1:						
95/5	35.7±1.3	2.0±0.2	32.3±1.0	25.9±2.2	19.1±2.5	12.8±1.0
90/10	9.4±0.7	0.5±0.2	9.4±0.7	0.5±0.2	15.4±2.3	1.0±0.0
PLA/LT2:						
95/5	35.5±5.9	2.9±0.4	33.2±5.5	29.8±5.6	1.2±0.1	10.3±0.7
90/10	33.4±1.1	2.0±0.4	28.8±0.2	21.0±0.4	1.9±0.3	10.8±2.2
PLA/IR:						
95/5	42.9±2.7	1.7±0.4	32.5±2.4	18.2±6.3	3.2±0.9	10.5±3.2
90/10	37.9±0.8	2.1±0.2	31.7±1.3	16.8 ±1.5	2.8±0.2	8.2±0.1
PLA/NBR:						
95/5	41.3±0.8	1.8±0.2	21.5±1.0	107.2±2.8	3.0±0.3	60.2±6.5
90/10	31.4±0.9	1.7±0.3	23.2±1.0	62.7±18.8	2.5±0.5	38.0±14.4
PLA/PEVA:						
95/5	36.9±1.9	1.6±0.4	34.4±1.5	47.9± 6.4	3.2±0.6	30.2±6.9
90/10	29.7±0.6	1.8±0.2	20.3±2.0	46.8±10.3	2.6±0.4	26.8±5.0



(a)



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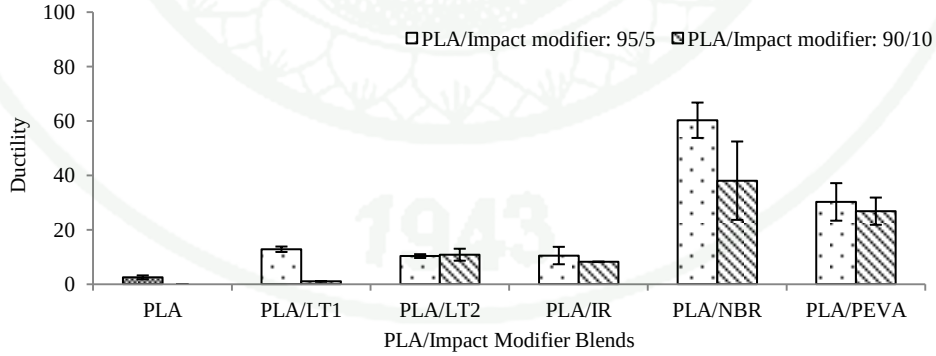

(c)

Figure 79 Effect of impact modifier content on the (a) tensile strength at break, (b) elongation at break and (c) ductility of pure PLA and PLA/impact modifier blends.

CONCLUSIONS

Part I: Direct melt polycondensation of lactic acid

Synthesis of polylactic acid (PLA) by direct polycondensation using two cationic exchange resin catalysts (A and B) with 100 g, 1 kg and 10 kg of commercial lactic acid (LA) were studied. Direct polycondensation was carried out by varying the mole ratio of LA: catalyst = 100:1, 500:1 and 1000:1 at temperature from 160^{o}C, 170^{o}C to 180^{o}C under alternating between N_2 atmosphere and reduced pressure (15 mmHg) for different time periods. The structure of white powder PLA obtained was confirmed by 400 MHz ^{1}H and ^{13}C NMR.

Synthesis of PLA with 100 g of LA (from Aldrich) was carried out by both direct melt polycondensation (DMPC) and solution polycondensation (SP). DMPC was carried out for 12 h at 160°C, 170°C or 180°C by alternating between purging nitrogen for 3 h and reduced pressure (15 mmHg) for 1 h; and by preheating at 135^{o}C for 6 h and heating at 160^{o}C, 170^{o}C or 180^{o}C for another 6 h by alternating between purging nitrogen for 2 h and reduced pressure (15 mmHg) for 1 h. SP was carried out by quantitatively removing the condensate water byproduct under toluene-water azeotropic distillation and then heating at 160^{o}C, 170^{o}C or 180^{o}C for 6 h by alternating between purging nitrogen for 2 h and reduced pressure (15 mmHg) for 1 h. It was found that temperature and mole ratio of LA: catalyst are closely related in effecting the $\overline{M}_W$ of PLA obtained by both DMPC and SP. $\overline{M}_W$ of PLA obtained by DMPC gave higher $\overline{M}_W$ than by SP and PLA obtained using catalyst B has a much higher $\overline{M}_W$ than using catalyst A. The highest $\overline{M}_W$ (=113,000) of PLA obtained was from catalyst B by DMPC with mole ratio of LA: B = 500:1 at 170^{o}C for 12 h. Thus, this condition was used for synthesis of PLA with 1 kg and 10 kg of LA. In addition, all PLAs obtained gave the same melting temperature (T_m*max*) range in between 115^{o}C to 130^{o}C, and the thermal decomposition temperature (T_{max}) range in between 270^{o}C to 320^{o}C.

Synthesis of PLA with 1 kg of LA (from Aldrich and Purac) was carried out by DMPC using catalyst B with mole ratio of LA: catalyst B = 500:1 and 1000:1 in a series of steps at 160^{o}C, 170^{o}C or 180^{o}C with different time periods by alternating between under nitrogen atmosphere and under reduced pressure (15 mmHg). It was found that purity of lactic acid used has significant effect on $\overline{M}_W$ of PLA obtained. As the result, chemical grade lactic acid from Aldrich gave PLA with higher $\overline{M}_W$ than bulk lactic acid from Purac at the same condition. $\overline{M}_W$ ~146,000 of PLA was obtained with of LA:B = 500:1 (mole ratio) at 180^{o}C for 24 h for 1 kg system when carrying the DMPC surrounding with dry ice atmosphere.

Synthesis of PLA with 10 kg of LA (from Purac) was carried out by DMPC using catalyst B with mole ratio of LA: catalyst B = 500:1 and 1000:1 in a series of steps at 160^{o}C or 170^{o}C with different time periods by alternating between purging nitrogen and reduced pressure (15 mmHg). Because of difficulty in maintaining the temperature from the designed reactor together with the LA used was from Purac, most of the PLAs obtained had rather low $\overline{M}_W$ and small percentage of 6.2%, 13.0% and 5.3% of PLA having $\overline{M}_W$ = 57,000, 87,000 and 66,000 was obtained respectively.

Part II: PLA modification by blending

Modification of PLA properties was carried out by blending with 5, 10, 15 and 20 wt. ratio of polyethylene glycol (PEG) and polydioxolane (PDXL). The results showed that increasing the molecular weight of both PEG and PDXL can increase the T.S. at break, % elongation and ductility of PLA/ PEG and PLA/PDXL blends. T.S. at break and modulus all decreased with increasing the wt. ratio of PEG and PDXL in the blends. It was found that % elongation of PLA/PEG and PLA/PDXL blends was higher than pure PLA, thus PEG and PDXL can be used as plasticizers to toughen PLA.

Modification of PLA properties was carried out by blending with 5, 10, 15 and 20 wt. ratio of duck feather fibers by kneading from two roll mill and by solution

casting. The results showed that mechanical properties of PLA/DF blends from kneading were all higher than from casting. Results also showed that tensile strength and % elongation at break of PLA/DF decreased with increasing the DF content. Moreover, tensile strength and % elongation at break of all PLA/DF blends from both kneading and casting was lower than pure PLA. The effect of PEG and PDXL as compatibilizer in PLA/DF blends was studied. Although, the tensile strength and % elongation at break of PLA/PEG/DF and PLA/PDXL/DF blends were higher than PLA/DF, they were still lower than pure PLA. These indicated that DF together with PEG and PDXL is not suitable to toughen PLA.

Finally, the properties of PLA were modified by blending with 5 and 10 wt. ratio of four rubbery impact modifiers (household gloves latex (LT1), concentrated natural rubber latex (LT2), poly(*cis*-1,4-isoprene) (IR), poly(acrylonitrile-*co*-butadiene) (NBR)) and one eco-friendly, non toxic and biodegradability polymer impact modifier (poly(ethylene-*co*-vinyl acetate (PEVA)). Results showed that % elongation at break in all PLA/impact modifier blends (PLA/LT1, PLA/LT2, PLA/IR, PLA/NBR and PLA/PEVA) significantly increased from about 16% in PLA/LT2: 90/10 to about 102% in PLA/NBR: 95/5 when compared with pure PLA and only PLA/NBR blends was affected by the NBR content. This indicated that LT1, LT2, IR, NBR and PEVA can be used as impact modifier to toughen PLA.

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