# UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY

## Escuela de Ciencias Físicas y Nanotecnología

# TTTLE: PLA a comprehensive review, and the obtaining of its monomer from sugarcane bagasse

Trabajo de integración curricular presentado como requisito para la obtención del título de Ingeniero en nanotecnología

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# Dedication

I want to dedicate this thesis to God who gave me the wisdom, knowledge, and courage to keep going every time in my life.

I want to dedicate this thesis to my mother, my father, my sister and my brother, who were always with me in the hardest part of my life. They are the ones who know who I am and the ones that are giving me all the support I need to complete my career and this work.

Also, I want to dedicate this thesis to Juan Lobos and Veronica Lobos, who were helping me in every part of my career with words of encouragement.

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# Resumen

Poliácido láctico (PLA) es un polímero biodegradable con un gran rango de aplicaciones. Las propiedades del material son severamente afectadas por diferentes condiciones como la pureza del monómero, catalizadores, temperatura y más. Este trabajo presenta una revisión bibliográfica del PLA, la obtención de su monómero, polimerización, propiedades, aplicaciones y caracterización. El bagazo de caña de azúcar es presentado como fuente para la producción de ácido láctico, en el cual el pre-tratamiento recibido juega un papel determinante. Las aplicaciones van a depender de las propiedades del material, como sus propiedades mecánicas o térmicas. La síntesis del PLA fue estudiada por dos rutas diferentes, policondensación y polimerización por rompimiento de anillo; en el cual el peso molecular y el rendimiento fueron analizados bajo los efectos de diferentes parámetros.

**Palabras claves**: Bagazo de caña de azúcar, acido láctico, poliácido láctico, PLA, polimerización por rompimiento de anillo, policondensación directa.

# Abstract

Poly (lactic acid) (PLA) is a biodegradable polymer with a wide range of applications. The properties of the material are several affected by different conditions as it monomer purity, catalyst, temperature and more. This Work present a bibliographical revision of PLA, its monomer obtaining, polymerization, properties, applications and characterization. Sugarcane bagasse its presented as a source for lactic acid production, in which the pretreatment received plays a determinant role. The applications will be depending on the properties of the material, like mechanical or thermal properties. The synthesis of PLA was studied in two different routes, polycondensation and ring opening polymerization, in which the molecular weight and yield were analyzed under the effect of different parameters.

**Keywords:** Sugarcane bagasse, lactic acid, Poly(lactic acid), PLA, Ring Opening Polymerization, Direct Polycondensation.

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# Chapter 1

# Introduction

One of the most common synthetic biopolymer that has been studied is poly(lactic acid) (PLA), since it was first discovered in 1800[1]. It can be produced from several kinds of agricultural waste (any lignocellulosic biomass,) like sugarcane bagasse[2–5]. The main process to its production can be explained in two parts: The first, related to the fermentation of feedstock into lactic acid; the second being the polymerization of lactic acid into Poly(lactic acid). In the first part, the amount of lactic acid produced will vary according to the pre-treatment received by the feedstock[6]. Then, the fermentation takes place for the transformation of sugar (glucose, xylose, etc) into lactic acid[7]. In the second part, the lactic acid is polymerized, which can be done in two different ways: Polycondensation or Ring Opening Polymerization (ROP)[8]; polycondensation is a relatively simple method, but with the perk of usually obtaining a low molecular weigh polymer[9] (this problem has been studied in order to be overcomed), while for ROP it is needed to have an intermediate product prior to the process (lactide) which will be then polymerized into PLA[10], this method is the most used one because of the facilities to obtain a higher molecular weight polymer[11].

PLA has lots of applications: as food packaging, bone implant, drug delivery systems, in the automotive industry, among others[12]. One of the most used ones is in the food industry as packaging, increasing the demand of this particular method during the past years[13]. Another industrial interest for the application of PLA is in the textile industry, as in the fabrication of antimicrobial fabrics to be used in hospitals[14]. The properties of PLA can be adjusted and controlled, which makes this polymer a good candidate to replace many fuel-based plastics being used nowadays[15]

In the following chapter the process for the synthesis of PLA from sugarcane bagasse is explained. The theoretical framework starts with general information about waste management, and a description of sugarcane bagasse. Then follows information about lactic acid and different ways to ferment sugarcane bagasse into lactic acid, PLA properties (chemical, mechanical) and a market studio. Three different applications of PLA are provided for each industry they are relevant for: pharmaceutical, textile and food industries. This thesis will be focusing in two methods of polymerization through a table containing different synthesis parameters that affect the polymer for each method. Furthermore, four different characterization techniques for the analysis of PLA are presented. This article ends with a conclusion of which method can be applied in Ecuador to obtain PLA from the sugarcane bagasse.

# Chapter 2

# Motivation

## 2.1 Problem Statement

According to studies, the amount of plastic production is going to double for the next 20 years[16]. During 2011, plastic became the most common type of waste[17]. South America was placed in the top 5 regions that generate more mismanaged plastic (5.81 Mt/year) waste in 2015[16]. It is observed that as plastic production increases, the waste and contamination due to plastics will also increase. This leads to the challenge of finding solutions applicable to this region. One way to manage the contamination due to petroleum based plastics is the use of biodegradable polymers, like poly (lactic acid). This biodegradable polymer can be used as a replacement for many petroleum based plastics, specially in the area of food packaging and disposable plastics. PLA can be obtained from different kinds of agro-industrial waste, one of them being sugarcane bagasse. By learning the process of how to synthesize this material and the characteristic that can be obtained, it can be implemented in Ecuador, been the first in the production of plastics in its primary form in this country.

## 2.2 Objectives

**General objective:**

1. To study PLA and the use of sugarcane bagasse for obtaining its monomer.

**Specific objectives:**

1. To analyze PLA polymerization and its monomer obtaining conditions.
2. To choose a suitable method for PLA synthesis.
3. To analyze the possibilities to implement PLA synthesis in Ecuador.

# Chapter 3

# Theoretical Framework

Waste management from agro-industries is a topic that has been in development for a long time by implementing a variety of techniques. The main ideas for the different treatments are focused in energy production, bio-polymers or other products of added value[3,18,19]. The waste from industries can be from either animal or vegetable origin (lignocellulosic biomass), which are not involved in primary production[3,20,21]. Treatments for these kind of material will depend of the final product that is desired to obtain. Anaerobic Digestion (AD) has been experiencing an increase of attention in the industry during latter years[22]. This way of waste treatment is usually used to obtain bio gas for energy production[23]. AD can be classified according to the technology used: Anaerobic Co-digestion, Solid State Anaerobic Digestion (SS-AD), and Rumen microorganisms (RM)[24]. Anaerobic Co-digestion is described as the anaerobic digestion of two substrates from different origin (livestock and biomass)[25], this method requires achieving a ratio of C/N of 20/1 - 30/1 to obtain a higher production of bio-gas or energy[26]; the most used main substrate for this process is animal manure, while the industrial waste and agro-industrial waste is used as co-substrate[27]. Solid State Anaerobic Digestion comes from a classification according to the amount of solid contained in the sample, it can go from Liquid (L-AD), semi-solid (S-AD) and solid state (SS-AD)[24]. In SS-AD it is found to contain a total 10% to 20% of solid or higher, according to the solids present in lignocellulosic biomass[28,29]; the main substrates used for this process are corn stover, wheat straw, yard trimmings, forestry waste and energy crops[30]. SS-AD has an advantage over L-AD due to the reduction of material volume in the reactor, SS-AD can obtain the same yield in bio-gas production than L-AD but in a shorter volume, and requires lower energy demand for heating[29]. Lastly, Rumen microorganisms (RM) are bacteria specifically present in the ruminant animals which helps with the fermentation of their food[31], industrially being used to decompose lignin into methane and carbon dioxide[32]. This way of digestion have shown higher degradation efficiency and conversion rate compared to traditional techniques of AD[33].

## 3.1 Sugarcane bagasse

Sugarcane bagasse is considered a crop residue[34], it is the result of crushing the sugar cane and extracting the liquid contained. The composition of the sugarcane bagasse used in different researches is found in Table 3.1. It was found that cellulose is in the range of 35.00% - 50%, hemicellulose is in the 20.60% - 35.80% range, 16.10 % - 25.15% for lignin and, ashes 1.00% - 2.84%. The components of the bagasse can vary because of many factors, been one of them the geographical location as it is shown in Table 3.1.

Table 3.1: Sugarcane composition

| Sugarcane Bagasse | Cellulose | Hemicellulose | Lignin | Others | Reference |
|---|---|---|---|---|---|
| Not specified | 50.00% | 25.00% | 25.00% | – | [35] |
| Ingenio Azucarero de Mante,Mexico | 38.90% | 20.60% | 23.90% | 16.6% | [36] |
| Kaset Thai Sugar, Thailand | 40.19 % | 22.54% | 25.15% | 12.12% | [37] |
| Not specified | 35.00% | 35.80% | 16.10% | 13.1% | [38] |
| Horacio Rodriguez sugar mill, Cuba | 36.10 % | 20.80% | 17.80% | 25.3% | [39] |
| Nanning Sugar Industry Co. Ltd., China | 44.98% | – | 18.45% | 36.57% | [40] |
| Sugar–alcohol mill, Brazil | 45.00% | 25.80% | 19.10% | 10.1% | [41] |
| Sugar mill, Brazil | 45.50% | 27.00% | 21.10% | 6.4% | [42] |
| Sugar and ethanol mills, Brazil | 43.10% | 25.20% | 22.90% | 8.8% | [43] |
| sugar and ethanol mills, Brazil | 42.19% | 27.60% | 21.56% | 8.65% | [44] |

Sugarcane bagasse has been studied for several years, leading to a wide window of applications. For example, it can be used for cellulose film preparation after a chemical process involving the addition of acetyl groups, it was shown that the remaining cellulose acts as a plasticizer for the film preparation[45]. Sugarcane bagasse is usually burned and derives in two products: the steam, which is used for electrical energy co-generation in sugarcane mills, and the ashes, which can be used as fertilizers[46]; the ashes of the biomass can also be used to improve the mechanical properties of compact soil blocks since the ash acts as a stabilizer, making for a promising alternative when energy consumption and pollution issues are considered[47]. Because of the contents of cellulose in sugarcane bagasse, it is used to obtain whiskers that can act as reinforcing elements in polymeric matrices; cellulose nanofibers of $255 \pm 55$nm of length in average and 4 ± 2nm of diameter in average were obtained after a pre-treatment with alkaline peroxide (bleaching), following with acid hydrolysis[48]. Sugarcane bagasse can be used too to produce bio-ethanol, or turned into bio-gas that can be used for energy generation, or in different industrial heating applications[49,50]; it has shown adsorption properties in cationic dyes such as Rhodamine B (RhB) or Basic Blue 9 (methylene blue), the absorption rate will vary according to the surface area of the bagasse[51]. It is possible to ferment the sugarcane bagasse to transform it into diverse products, one of them being the lactic acid which can be transformed by simultaneous hydrolysis and fermentation of the lignocellusic biomass by using *Bacillus sp.* with a yield of 99%[52].

According to the research center of sugarcane for Ecuador (CINCAE by its initials in Spanish, "CENTRO DE INVESTIGACIÓN DE LA CAÑA DE AZÚCAR DEL ECUADOR"), the generation of sugarcane bagasse was estimated to be 1 300 000 tones and 140 000 tones of cachaza (which is basically composed by cellulose, hemicellulose and lignin) in 2008[53].

## 3.2 Lactic Acid

Lactic acid is a three carbon organic acid (CH3-CH(OH)-COOH) known chemically as 2-hydroxypropanoic acid[54]. It was first isolated in 1780 by Carl Wilhelm Scheele, and first produced commercially in 1881 by Charles E. Avery[54]. There exists two optical isomers for lactic acid, L-lactic acid (also know as (S)-Lactic acid) and D-Lactic acid (also (R)-Lactic acid), as it is shown in Figure 3.1. L-lactic acid enantiomer has greater demand in pharmaceutical industry due to it is a compound generated by the human body[55].

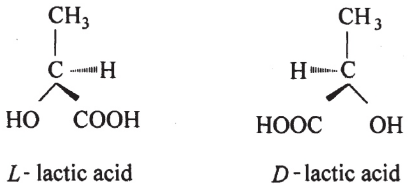

Figure 3.1: Optical isomers of lactic acid

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In addition, two routes for the synthesis of lactic acid exist: chemical synthesis and biological synthesis (microbial fermentation), as shown in Figure 3.2 .

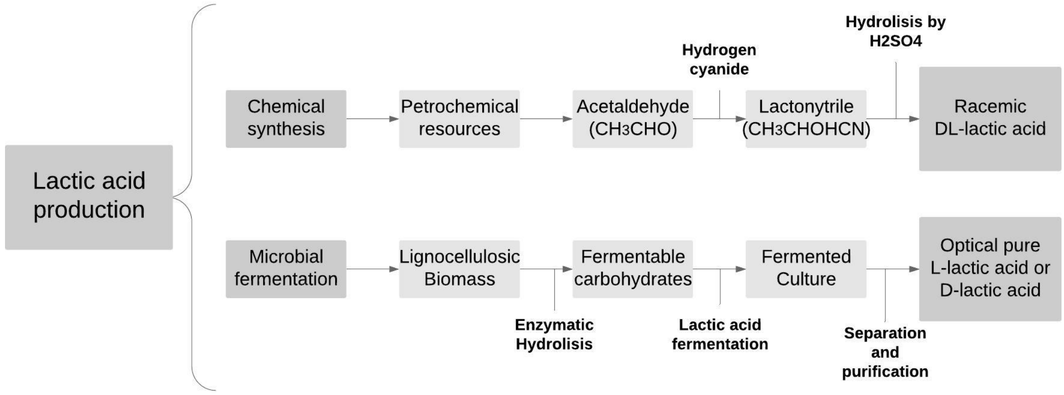

Figure 3.2: Synthesis of lactic acid

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The chemical synthesis is based on lactonitrile[57]. The process is followed by the following series of reactions[57]:

a) Addition of hydrogen cyanide

$$\underset{\text{Acetaldehyde}}{\mathrm{CH_3CHO}} + \underset{\text{Hydrogen Cyanide}}{\mathrm{HCN}} \xrightarrow{\text{catalyst}} \underset{\text{Lactonitrile}}{\mathrm{CH_3CHOHCN}} \tag{3.1}$$

b) Hydrolysis by sulphuric acid

$$\underset{\text{Lactonitrile}}{\mathrm{CH_3CHOHCN}} + \mathrm{H_2O} + \underset{\text{Sulphuric acid}}{1/2\mathrm{H_2SO_4}} \rightarrow \underset{\text{Lactic acid}}{\mathrm{CH_3CHOHCOOH}} + \underset{\text{Ammonium salt}}{1/2\mathrm{(NH_4)_2SO_4}} \tag{3.2}$$

c) Esterification

$$\underset{\text{Lactic acid}}{\mathrm{CH_3CHOHCOOH}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}} \rightarrow \underset{\text{Methyl lactate}}{\mathrm{CH_3CHOHCOOCH_3}} + \mathrm{H_2O} \tag{3.3}$$

d) Hydrolysis by water

$$\underset{\text{Methyl lactate}}{\mathrm{CH_3CHOHCOOCH_3}} + \mathrm{H_2O} \rightarrow \underset{\text{Lactic Acid}}{\mathrm{CH_3CHOHCOOH}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}} \tag{3.4}$$

Esterification and hydrolysis by water (step c and d) are the steps of the purification for the prior lactic acid obtained in step b[54].

The microbial fermentation process is the most used one on the market[58]. This process is based on the transformation of carbohydrates into lactic acid by microorganisms[58]. The process is done in an environment without oxygen (Anaerobic process)[58]. There are some organisms reported in literature capable of producing lactic acid, like *Lactobacillus (Lb.) casei, Lb. rhamnosus, Lb. delbrueckii, Lb. salivarius, Lb. zeae, Lb. coryniformis, Lb. amylovorus, Lb. plantarum, Lb. kefir, Lb. acidophilus, Le. lactis, Streptococcus (Str) thermophilus, Lactococcus (Lc) lactis* sp. lactis, *Lb. pentosus, Enterococus faecium, Pediococcus acidilactici*, etc[59,60].

The process of microbial fermentation can be spread in four steps: first, a pre-treatment in which the lignocellulosic matrix is breaking down, second, an Enzymatic hydrolysis to depolymerize lignocellulose into fermentation sugars like glucose and xylose, third, fermentation takes place by microorganisms transforming the sugars into lactic acid, and finally, the lactic acid is separated and purified[60]. The reactions for each process are[54,57]:

a) Fermentation and neutralization

$$\underset{\text{Carbohydrate}}{\mathrm{C_6H_{12}O_6}} + \underset{\text{Calcium hydroxide}}{\mathrm{Ca(OH)_2}} \xrightarrow{\text{fermentation}} \underset{\text{Calcium lactate}}{\mathrm{(2CH_3CHOHCOO^-)Ca^{2+}}} + 2\mathrm{H_2O} \tag{3.5}$$

b) Hydrolysis by sulphuric acid

$$\underset{\text{Calcium lactate}}{\mathrm{(2CH_3CHOHCOO^-)Ca^{2+}}} + \underset{\text{Sulphuric acid}}{\mathrm{H_2SO_4}} \rightarrow \underset{\text{Lactic acid}}{2\mathrm{CH_3CHOHCOOH}} + \underset{\text{Calciun sulpahte}}{\mathrm{CaSO_4}} \tag{3.6}$$

c) Esterification

$$\underset{\text{Lactic acid}}{\mathrm{CH_3CHOHCOOH}} + \underset{\text{Methanol}}{\mathrm{CH_3OH}} \rightarrow \underset{\text{Methyl lactate}}{\mathrm{CH_3CHOHCOOCH_3}} + \mathrm{H_2O} \tag{3.7}$$

d) Hydrolysis by water

$$\underset{\text{Methyl lactate}}{CH_3CHOHCOOCH_3} + H_2O \rightarrow \underset{\text{Lactic Acid}}{CH_3CHOHCOOH} + \underset{\text{Methanol}}{CH_3OH} \tag{3.8}$$

Step c and d are refeared to the purification of lactic acid that was obtained in step b[54].

Lactic acid has many uses in different industries. The principal application is in food-related industries (85% of the demand)[61]; another is the use of lactic acid derivatives as lactate ester which can be used in electronics and precision cleaning, this product was classified by the Environmental Protection Agency (EPA) as a negligible toxic with a high environmental profile[61]. One of the most notorious applications for lactic acid is in the production of polymers, specially a biodegradable polymer known as poly(lactic acid) which has promising properties for its use in several areas, as in surgical sutures, orthopedic implants, drug delivery, and an good alternative for petrochemical derivative plastics[60,62].

## 3.3 Fermentation of sugarcane bagasse

The fermentation of sugarcane bagasse generally requires a process in which the substrate is saccharified or hydrolyzed as a previous treatment[63]. Hydrolysis can be done by the addition of acid (acid hydrolysis) or the uses of enzymes (enzymatic hydrolysis); that can be combined by different parameters as temperature (steam explosion)[63]. Acid hydrolysis allows to break the hemicellulose and cellulose chains to transform into fermentable sugars as xylose or glucose[64,65]. Potential acids in this type of hydrolysis are $H_2SO_4$ and HCl[65], which must be at low concentration and used at low temperature to avoid degradation of sugars[37]. Enzymatic hydrolysis is the process in which enzymes enhance the break of bonds by adding elements of water[66]. One enzymes used to hydrolyze the lignocellulosic substrate is the cellulase[67]. The conditions of temperature of acid hydrolysis can be consider as pre-treatment for the enzymatic hydrolysis[37]

Both method can be combined with pre-treatments in order to increase the reactivity of acids or enzymes[68]. Two promising pre treatment are steam explosion and wet oxidation[68]. Steam explosion consist in heat the lignocellulosic material by high-pressure steam followed by an explosive decompression[68]. Wet oxidation consist in the treatment of the lignocellulosic material with water and air or oxygen at temperatures above 120°C[68].

In table 3.2 are presented different pre-treatment for the hydrolysis of sugarcane bagasse. As it is shown $NH_4OH$ is very used for lignin removal; the same with HCL and $H_2SO_4$. Temperature affect the yield of the sugar obtained in the same way that the concentration of the acid; in example too much acid with too much temperature will degrade the bagasse.

Lactic acid bacteria is one of the most studied microorganism for the production of lactic acid[60,71]. This bacteria is classified in two types, the homofermentative and the heterofermentative[63]. The homofermentative produces only one single product, while the heterofermentative produces other byproducts like ethanol, acetic acid, diacetyl, etc. in addition to lactic acid[63]. The formation of lactic acid is the result of piruvic acid truning into lactate by the effect

Table 3.2: Pre-treatment of sugarcane bagasse for sugar obtention

| **Pre-treatment** | **Temperature (°C)** | **Sugar obtained** | **Yield (% w/w bagasse)** | **Reference** |
|---|---|---|---|---|
| NH4OH & HCl | 100 | Glucose<br>Xylose | 1,69<br>25,49 | [65] |
| C2H5OH & NaOH | 90 | Glucose<br>Xylose | 26,2<br>8,6 | [69] |
| Steam explossion & Meicellase (enzymatic hydrolysis) | 50 | Glucose | 73,7 | [70] |
| NH4OH & H2SO4 | 121 | Glucose | 32 | [6] |

or either D-Lactate dehydrogenase or L-Lactate dehydrogenase enzymes[63]; depending on which bacteria is chosen, D-Lactic acid or L-lactic acid will be obtained[63]. The most commonly used homofermentative lactic acid bacteria for lactic acid production are[63]:

- *Lactococcus lactis*
- *Lactobacillus delbruecki*
- *Lactobacillus helveticus*
- *Lactobacillus casei*

There exist more homofermentative bacteria, such as *Lactobacillus amylophilus* or *Lactobacillus manihotivorans*, that have been studied to directly transform complex carbohydrates like starch or cellulose into lactic acid[63,72,73]. This gives an additional value to this bacteria because starch is a product that can be digested by humans, while cellulose cannot[74] (starch appears in higher quantities in a regular diet, cellulose usually is less than the 10% of the starch weight depending on the kind of food, for example, White bread presents 77.5% of starch and 0.13% of cellulose for each 100g of dry matter)[75]. Starch can be used as a energy source by humans because of the presence of amylase, which decomposes starch into glucose[74,76]; this does not happen with cellulose since the enzyme required for its decomposition is only found in ruminant animals (cellulose breaks the $\beta$ (1,4) glycosidic linkage)[74,76]. For these reasons, the use of cellulose for the production of lactic acid is a viable option.

In table 3.3 are presented different results gathered from the literature of lactic acid production. It can be observed that different microorganism have been used in order to ferment the sugars obtained from the sugarcane bagasse. Every substrate was previously treated in order to take out the lignocellulosic biomass and other residues, and to obtain sugars like cellulose or xylose. The pre-treatment for each substrate can be found in the respective reference for each microorganism. The are noted different yields for each microorganism, which can be affected by the reaction time, the amount of sugars present in the sample, and the system used for the fermentation.

Table 3.3: Data of sugarcane bagasse fermentation by different microorganism

| **Microorganism (Bacteria)** | **Source** | **Enantiomer** | **Time (hours)** | **System** | **Yield (%)** | **Reference** |
|---|---|---|---|---|---|---|
| Lactococus lactis IO-1 | Glucose, Xylose | L-lactic acid | 64 | Batch | 71 | [65] |
| Lactobacillus delbrueckii mutant Uc-3 | Cellulose | L-lactic acid | 72 | Batch | 83 | [77] |
| Lactobacillus lactis NCIM 2368 | — | D-Lactic acid | 48 | Batch | — | [78] |
| Lactobacillus lactis NCIM 2368 | — | D-Lactic acid | 120 | Batch | — | [78] |
| Lactobacillus casei | Glucose | L-lactic acid | 96 | Batch | ~103 | [69] |
| Lactobacillus plantarum | Glucose | L-lactic acid | 96 | Batch | ~103 | [69] |
| Lactobacillus lactis | Glucose | L-lactic acid | 96 | Batch | ~50 | [69] |
| Lactobacillus delbrueckii | Glucose | L-lactic acid | 96 | Batch | ~42 | [69] |
| Lactobacillus delbrueckii NBRC 3534 | Glucose | D-Lactic acid | 72 | static incubator | 90 | [79] |
| Bacillus sp. P38 | — | L-lactic acid | 100 | Fed-Batch | 99 | [80] |
| Lactococcus lactis | Glucose, Xylose | L-Lactic acid | 72 | Fed-Batch | 1.4 | [6] |
| Bacillus coagulans SIM-7 | Glucose | L-lactic acid | 10 | Batch | 92 | [81] |
| Lactobacillus delbrueckii DSM 20073 | Glucose | L-lactic acid | 24 | Batch | 86 | [81] |
| Lactobacillus casei LA-04-1 | Glucose | L-lactic acid | 84 | Batch | 88.6 | [82] |
| Bacillus sp. strain 17C5 | — | L-lactic acid | 192 | Batch | 89 | [83] |
| Bacillus coagulans DSM 2314 | Lignocellulosic sugars | L-lactic acid | 68 | SSF | 83 | [84] |

SSF (simultaneous saccharification and fermentation)

## 3.4 Poly(lactic acid)

Poly(lactic acid), or PLA, is a biodegradable polymer first discovered in 1800 by Pelouze when he condensed the lactic acid through distillation obtaining PLA of low molecular weigh[1]. In this process two different products were obtained, PLA of low molecular weight and lactide (a prepolymer for the polymerization of high molecular weigh PLA)[1]. Poly(lactic acid) can degrade by different mechanisms, whether chemical or biological, that will be affected by the characteristics of the polymer, like crystallization, molecular weight, melting point, etc.[54]. The polymer will change its properties according to its composition. As it was mentioned before, there are different stereoisomers for PLA (L-lactic acid and D-lactic acid). The polymer can have this conformation also, polymerizing into poly(L-lactic acid) (PLLA), poly(D-lactic acid) (PDLA), or a mixture of both, poly(D,L-lactic acid) (PDLLA)[58]. PLLA and PDLA are mirror images which present semicrystalline structure, while PDLLA is an amorphous polymer[85]. The crystallinity of the material will be affected by the optical isomers presented, for high optical purity the PLA have a higher percentage of crystallinity while for less optical pure material it present an amorphous phase[86]. In Figure 3.3 can be found the available product in the market. For the semicrystalline structure, PDLA and PLLA, the material looks opaque; while for the amorphous phase, PDLLA, the material looks transparent. When different frequencies of light interact with the surface of a material, the atomic response of the subject will be in form of vibrations that can be selectively absorbed, transmitted or reflected[58]. PDLLA looks transparent because the vibrations of the electron are transmitted to the neighboring atoms and them remitted to the opposite side of the material[58].In the other hand, PDLA and PLLA looks opaque because the vibration of the atoms do not pass to the neighboring atoms, producing in short periods of time vibrations that are remitted as reflected light[58].

Figure 3.3: PLA available in the market
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Poly(lactic acid) has been of interest during the former years, showing an exponential growth of publications about this polymer from 1990 to 2009[1]. The main reason of this behaviour comes from the variety of applications that this particular polymer has, which can go from the food industry, as in food packaging, to the pharmaceutical industry, like composites for drug delivery systems.[88,89]. Among the biggest companies producing and exporting poly(lactic acid) that can be found in USA there is NatureWorks, which in addition to producing high quality PLA, reduces pollution, decreasing the amount of $CO_2$ emitted to 0.27 kg $CO_2$ eq./kg PLA in 2006 (a 85% reduction compared to 2003) and also the amount of fossil energy required to 27.2 MJ/kg PLA on 2006 (50% reduction over

2003)[2]

### 3.4.1 Chemical properties

Poly(lactic acid), as forementioned, can be formed in different configurations. According to an specific configuration, the polymer will have different properties. PLA structure is shown in Figure3.4 and the empirical formula is $(C_3H_4O_2)_n$[90]. PLLA is polymerized from L-Lactic acid, PDLA is polymerized from D-Lactic acid, and PDLLA is polymerized from D-Lactic acid and L-Lactic acid[91].

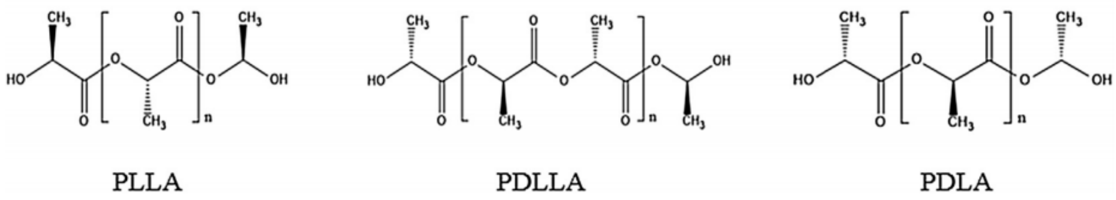

Figure 3.4: PLA Structure (PLLA, PDLA, PDLLA)

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The solubility of a material will depend on the Hildebrand solubility parameter[92,93]:

$$\delta = \left( \frac{(\Delta E_V)}{(V)} \right)^{\frac{1}{2}} \tag{3.9}$$

where $\delta$ is the Hildebrand solubility parameter, $\Delta E_V$ is the cohesive energy and $V$ is the molecular volume. When the magnitude of this parameter (for some substances) is equal or similar, it is said that they are miscible or soluble[92]. The Hildebrand solubility factor for PLA and some other substances are presented in table3.4. Poly(lactic acid) in its amorphous phase can be soluble in most organic solvents, for example, Tetrahydrofuran (THF), chlorinated solvents, benzene, acetonitrile and dioxane[94]. Crystalline PLA is soluble in chlorinated solvents and benzene at high temperatures[94].

Afterwards, a new parameter was introduced linked with properties, like polarity and hydrogen bond system (known as Hansen solubility parameter), which is a sum of $\delta_D$ (non polar), $\delta_p$ (polar) and $\delta_h$ (hydrogen bond)[1]. Under this criteria, PLA can only dissolve in a solvent when this parameter is less than 2.5[1]. PLA can be used for containers or storage systems for different liquids, as in water, ethanol, hexane, because they have a difference grater than 2.5 in Hansen parameter[1,95].

Another important property to keep in mind is the barrier that PLA has over other substances, which is determinant for packaging applications. PLA barrier properties was compared to Low density Polyethylene (LDPE) and polystyrene (PS) with $N_2$, $O_2$, $CO_2$ and $CH_4$. The permeation of $N_2$ in LDPE was 1.9 barrers, in PS was 4.1 barrers and in PLA 5.4 barres[96]. PLA shows better permeation of $N_2$ increasing 184.21% and 31.71% in comparison of LDPE and PS respectively. The permeation of $O_2$ was 6.9 barrers for LDPE and 9.5 barrers for PS and 12.8 for PLA[96]. PLA shows better permeation of $O_2$ with respect LDPE (85.51% more) and PS (34.73% more). $CO_2$

Table 3.4: Hildebrand solubility factor

| Substance | Solubility parameter ($cal^{0.5}cm^{-1.5}$) |
|---|---|
| Toluene | 8.9 |
| Ethyl acetate | 9.1 |
| Chloroform | 9.3 |
| Methylene chloride | 9.7 |
| Dioxane | 10.0 |
| Acetophenone | 10.6 |
| Acetonitrile | 10.9 |
| PLA | 9.8 - 10.2 |

permeation was 28 barres for LDPE, 38.5 barrers for PS and 48.7 barrers for PLA[96]. PLA present higher permeation of $CO_2$ compared to LDPE (73.93% more) and PS (26.49% more). $CH_4$ has a permeation of 4 barrers for LDPE, 6.3 barrers for PS and 7.3 barrers for PLA[96]. PLA present better permeation of 82.5% more with respect LDPE and 15.87% more with respect PS.

### 3.4.2 Mechanical properties

Poly(lactic acid) is a plastic, so in general it present in properties of plastics as it is shown in Figure 3.5[97]. Although this generality, PLA vary its mechanical properties according its composition, chirality, molecular weigh, crystallinity, etc.[1,98,99]. In Figure 3.5 is shown how the addition of crosslinkers change the mechanical properties of PLA without losing its plastic properties[97]. In another example, the elongation at break in tensile tests of PLLA shows that it increases according the molecular weight is increased; for PLLA with a molecular weight of 23 000 g/m the elongation at break is at 1.5%, while for PLLA of a molecular weight of 67 000 g/mol the elongation at break is at 7.0%[58]. The elongation at break for flexural test present that is going to be higher as the molecular weight increase[58]. The tensile strength of PLLA after annealing at 105°C is going to increase as the molecular weight is higher[58].

In general, semicrystalline PLA has a tensile modulus (Young modulus) around 3000-4000 MPa, a tensile strength around 50-70 MPa, an elongation at break around 2-10%, a flexural strength around 100 MPa and a flexural modulus about 4000-5000 MPa[58]. In table 3.5 the young modulus is observed in function of the molecular weight. Depending on the polymerization conditions, the young modulus will have different behaviour respect the molecular weight[100]. It is not a clear tendency that relate the young modulus and the molecular weight, it can be observed in Table 3.5 that the young modulus remain the same for PLLA of a molecular weight of 23000 g/mol and 31000 g/mol. Degradation affect the young modulus, but there is not a tendency[100]. After hydrolytic degradation (60 weeks) the young modulus decrease from 1.34 GPa to 0.9 GPa for PLLA with a molecular eight of 490000 g/mol; in the other hand for PLLA with a molecular weight of 122000 the young modulus increase from 0.86 GPa to 1.04 GPa[100].

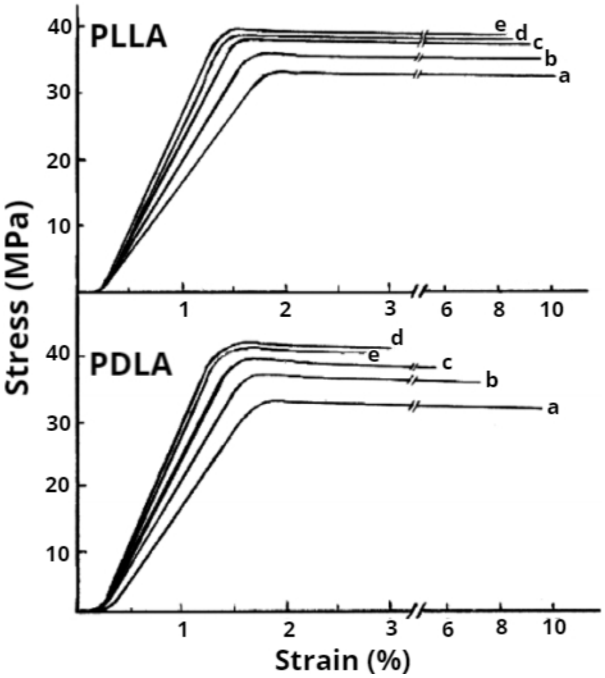

Figure 3.5: Strain stress curve of pure PLLA and PDLA (a) with the addition of a cross linker (triallyl isocyanurate) at 3% irradiated at an energy of 10kGy (b), 20 kGy (c), 30 kGy (d) and 50 KGy (e).

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By annealing PLA, the crystallinity can increase considerably; as an example a sample of PLLA with a molecular weight of 23000 can have a crystallinity of 9% before annealing, but PLLA with a molecular weight of 20000 can have a crystallinity of 70% after annealing at 150°C[58]. The increment in crystallinity produce a reduction in the elongation at break[58]. Furthermore, a higher degree in crystallization means a lower content of free volume, and in consequence, a general stiffness increase[105].

Toughness of poly(lactic acid) can be improved by four different ways: biaxial stretching, external plasticizing with plasticizers, blending with other polymers, and internal plasticizing by reactive extrusion[106].Biaxial stretching is a technique in which a specific orientation of the polymer is generated by changes in the microstructure[106]. Among the techniques used for the orientation of the polymer are found film blowing or cable drawing[106]. As an example, it was shown that by producing orientation on PLA, the strength at break goes from 62.9 MPa to 95.4 MPa and the elongation at break goes from 5.4 ±0.9% to 114 ±5% (the orientation was done by the elongation of PLA at a temperature of 60 °C[107].

Plasticizers as poly(ethylene glycol) (PEG) or acetyl tributyl citrate (ATBC) have been studied for the improvement of mechanical properties of PLA[106]. It was studied that the addition of PEG and organic montmorillonite (OMMT) to PLA can increase the elongation at break of the polymer from 10.83 ±0.50% to 183.09 ± 15.67%; while the

Table 3.5: Young modulus values of PLA studied by different autors according its molecular weight

| PLLA origin | Molecular Weight (g/mol) | Young's Modulus (GPa) | Reference |
|---|---|---|---|
| Synthesized by Peregeo et al. | 23000 | 3,55 | [101] |
| Synthesized by Peregeo et al. | 31000 | 3,55 | [101] |
| 4032D, NatureWorks | 52000 | 1,4 | [102] |
| Synthesized by Peregeo et al. | 58000 | 3,75 | [101] |
| Synthesized by Peregeo et al. | 67000 | 3,75 | [101] |
| 3051D, NatureWorks | 70000 | 3,25 | [103] |
| Synthesized by saha et al. | 80700 | 1,07 | [100] |
| Unitika Ltd. | 122000 | 0,86 | [100] |
| Ingeo™2003D, NatureWorks | 180000 | 3,04 | [104] |
| Polysciences Inc. | 409000 | 1,34 | [100] |

thermal stability was improved by the promotion of heat transfer in the matrix of the material[108]. Plasticizers also are studied for the improvement of ductility in PLA[96]. For blending polymers with PLA, biodegradable polyesters are the most used[106].It have been studied the addition of poly(3-hydroxybutyrate) (PHB) and poly(butylene succinate) (PBS) to obtain a ternary blend with higher elongation at break. PLA presented an elongation at break of 7.6 ±0.5% while the ternary blend presented 49.3 ±17.8%[109]. Reactive extrusion consist on the blending of polymers and the reactivity of the the hydroxyl and carboxyl group of PLA to improve the compatibility between polymers[106]. As an example, the addition of tris(nonylphenyl) phosphite (TNPP) as stabilizer was studied for the blending of PLA with Polyamide11 (PA11). The addition of PA11 shows a improvement in the blend avoiding the degradation of PLA at the moment of the blending, thus mechanical properties as tensile strength and young modulus increased in the blend[110].

### 3.4.3 Thermal properties

The thermal properties of PLA will vary according to its composition, molecular weight, polymerization method, and thermal history among other parameters[1]. The crystallinity can be measured with Differential Scanning Calorimetry (DSC) by applying the following equation:

$$X_c(\%) = \frac{\Delta H_m - \Delta H_{CC}}{\Delta H_{mT}} * 100 \tag{3.10}$$

where $\Delta H_m$ is the melting enthalpy, $\Delta H_{CC}$ is the cold crystallization value (from DSC), and $\Delta H_{mT}$ is the melting enthalpy of the totally crystallized sample; that in the case of PLA is 93 $J/g$.[111]

Commonly used PLA have a low crystallization rate and a crystallinity of 16% with a melting temperature T$_m$ = 155°C[112]. In comparison with PDLLA, the stereoisomers PLLA and PDLA usually are highly crystalline, which will depend on its purity[112]. As an example, PLLA with an optical purity of 97% will have a degree of crystallinity approximately of 37% with a melting point ($T_m$) around 137 °C - 178 °C, and a glass transition temperature ($T_g$) of 53 °C - 63 °C[112]. Crystallinity in PLA can be improved by blending PLLA with PDLA, forming an stereocomplex of PLA and increasing too the melting point of the polymer (which is maximized when 50/50 blend is used)[112]. As a comparison, the melting temperature of PLLA, obtained from Purac, is 188 °C, while their PDLLA is amorphous and in consequence its melting temperature is not defined, and lastly, for the stereocomplex of Poly(lactic acid) (scPLA), obtained from Teijin, it shows a melting temperature about 200 °C - 230 °C[112].

The molecular weigh has a strong effect in the melting temperatures and the glass transition temperatures as it is shown in Table 3.6[98]. According to the molecular weigh increase, the melting temperature and glass transition temperature will increase too[98]. The highest molecular weight indicate the formation of partly-crystalline structure[98].

Table 3.6: Glass transition temperature and Melting temperature on function of the average molecular weight for PLA

| **Average molecular weight ($M_n$) (g/mol)** | **Glass transition temperature ($T_g$) (°C)** | **Melting temperature ($T_m$) (°C)** |
|---|---|---|
| 12 930 | 34,07 | 112,76 |
| 23 363 | – | 114,69 |
| 24 799 | 42,10 | 118,65 |
| 25 004 | 42,67 | 125,95 |
| 26 348 | – | 136,93 |
| 28 823 | 50.92 | 147,44 |

Thermal conductivity is an important property for polymers because of its applications in technology as energy dissipators and as electrical insulators[113]. Ingeo PLA from NatureWorks presents different values for thermal conductivity. For an amorphous PLA sheet: at -8°C the thermal conductivity is 0.127 $J/(mKs)$; for 25°C, 0.130$J/(mKs)$; for 58°C, 0.131$J/(mKs)$, for 124°C, 0.126$J/(mKs)$; and for 190°C, 0.121$J/(mKs)$. For instance, thermal conductivity crystalline pellets (25% of crystallinity) at 25°C is 0.160$J/(mKs)$ (data obtained from Engineering Properties of Ingeo Biopolymer, technical data sheet from NatureWorks)[114]. There have been observed that the thermal conductivity can increase significantly by the addition of nanostructures such as graphene or carbon nanotubes[115].

The cooling processes can change the properties in the PLA. It was shown that PLA with nanoparticles of coir fibres increase its crystallinity when the cooling temperature ramp is small[111]. When the cooling ramp was 10 k/min the crystallinity was 9%; in the other hand when the cooling ramp was 3 K/min the crystallinity was 48.1%[111]. Shape and dimensional injected part instability is the result of intense cooling in a material which is a result of cold crystallization[111]. By reducing the cooling ramp, it was possible to eliminate the cold crystallization of the composite injected parts[111].

### 3.4.4 Degradation

The degradation of PLA is one of the most important properties to study since it is one of the primary functions for this polymer[116], this process will vary according to the conditions to which it has been subjected to. It can be described as abiotic degradation and biotic degradation as it is shown in Figure 3.6[54]. For abiotic degradation 4 different mechanisms exist: mechanical degradation, photo degradation, thermal degradation and chemical degradation, while for biotic degradation two mechanism are studied: microorganism degradation and enzymatic degradation.

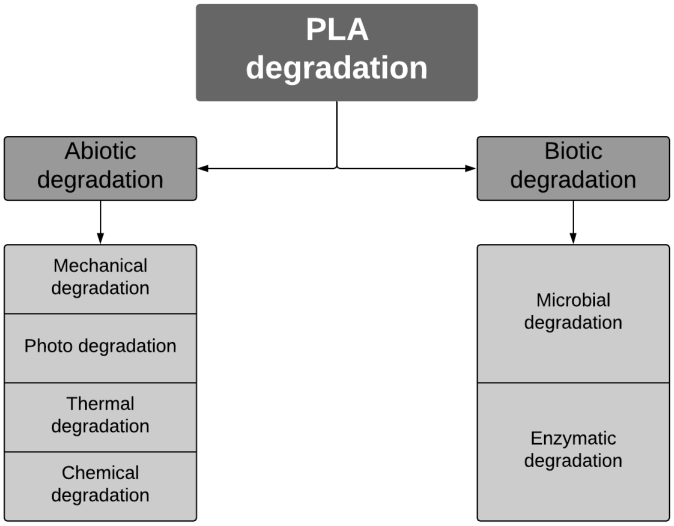

Figure 3.6: PLA Degradation
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#### Mechanical degradation

The mechanical degradation is a process involving the application of several forces (compression, tension, shear, agitation, grinding or extrusion) in order to break the plastic and thus obtaining a size reduction[54,117]. This mechanism of degradation is not the most predominant for Biodegradable polymers, but it can increase the rate of degradation for the previously mentioned methods[54,117]

#### Photo degradation

The mechanism of photo degradation is shown in Figure 3.7 which makes reference to the Norris II mechanism of carbonyl polyester[118]. This process usually leads to a loss of mechanical properties, in particular stiffness and strength[118]. UV rays are absorbed by the carbonyl groups, which in exchange will generate free radicals leading to a lower molecular weigh kind[1,117]. The Norris II mechanism shows the chain scission (low molecular weigh), and consequent formation of a C=C double bond, and hydroperoxide O-H in the new terminals[117]

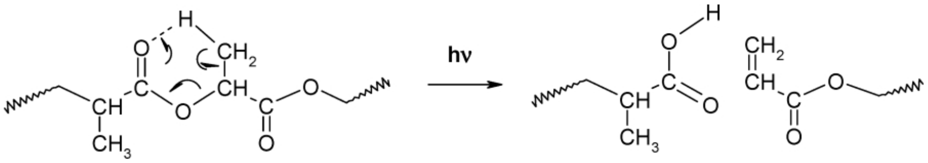

Figure 3.7: photo degradation of PLA
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For the photo degradation process there are available photo-sensitive additives, under the effect of UV rays these release free radicals, which will attack and brake randomly the polymeric bonds[54]. This process can be monitored by Fourier Transform Infrared spectroscopy (FT-IR) allowing an analysis of the differences in absorbance corresponding to the peak of hydroxyl and carbonyl[116].

### Thermal degradation

Thermal degradation is based on the use of heat to promote oxidation of the carbon in the plastic constituting polymer backbone[54]. For poly(lactic acid) the temperature at which thermal degradation occurs between 159°C and 178°C[54]. The process used to introduce PLA will require to subject it to a different temperature, as it is shown in table 3.7. PLA V is the raw material and presents the maximum degradation temperature required. PLA-I stands for poly(lactic acid) which undergoes injection, PLA-IA for injected and annealed PLA, PLA-EI for extruded and injected poly(lactic acid), PLA-EIA for extruded, injected, and annealed PLA[1].

Table 3.7: Thermal degradation temperature of PLA samples under different process

| **Sample** | **$T_5$ (°C)** | **$T_{50}$ (°C)** | **$T_{95}$ (°C)** | **$T_p$ (°C)** |
|---|---|---|---|---|
| PLA-V | 331 | 358 | 374 | 362 |
| PLA-I | 325 | 356 | 374 | 359 |
| PLA-IA | 323 | 353 | 370 | 357 |
| PLA-EI | 325 | 357 | 374 | 358 |
| PLA-EIA | 324 | 352 | 369 | 356 |

### Chemical degradation

Chemical degradation is related to the interaction of atmospheric pollutants or agrochemicals in order to change the properties of the polymer[54]. Oxygen is considered the most powerful element to cause degradation as it attacks the covalent bonds, producing free radicals[54].

Hydrolysis is another way of chemical degradation and can be analyzed by Differential scanning calorimetry, thermogravimetric analysis, or Fourier transform infrared spectroscopy[117]; the mechanism is shown in Figure 3.8[54]. This process is an auto catalyst process in which the lactic acid boosts the catalysis of the hydrolytic reaction[1]. There are three possibilities of hydrolysis, one being surface erosion, another bulk degradation and also bulk degradation with auto catalysis[1]: in surface erosion the material starts to degrade from the surface to the center of the polymer; for bulk degradation, the whole material degrades at the same rate; in bulk degradation with auto catalysis, the plastic starts to degrade from the inner areas to the surface, generating in first instance a hole in the center of the material. Usually, bulk degradation occurs at a higher rate than the surface erosion since in surface erosion the lactic acid diffuses in the buffer where PLA is located, furthermore, in bulk erosion the lactic acid remains inside the PLA sample, producing a higher auto catalysis and leading to a higher rate of degradation (that was observed in a experiment at 37°C with a buffer at pH of 7.4)[1,119]

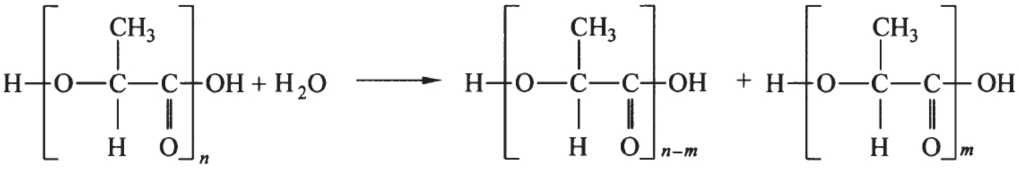

Figure 3.8: Hydrolysis of PLA
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**Microbial degradation**

Polymers can be degraded by being exposed to different kinds of microbes, selected depending on the specific polymer being degraded. Environmental conditions will be determinant to the degradation of the material since the microbial degradation rate is highly affected by microbial population, and parameters like humidity, temperature, pH, salinity, oxygen content, and nutrients supply[120]. For the microbial degradation of PLA, most *Amycolatopsis* genus members can degrade it[121]. PLA is hard to degrade under its glass transition temperature because of its inactivity, but with *Amycolatopsis sp.* it was shown that PLA can be degraded even at a temperature below the glass transition temperature[122]. Other microorganisms have been used in order to prove the degradation of PLA by microorganism, for example, *Saccharothrix waywayandensis* is an actinomycete that degrades poly(lactic acid)[121], in an study it was shown that mass loss for PLA was of 95% after 4 days[121]. The culture conditions are critical at the moment of degradation considering that it can improve the degradation rate of the material, plus crystallinity, which plays an important role at the moment of degradation (PLA with high degree of crystallinity is resistant to biological attack)[121,121].

**Enzymatic degradation**

Hydrolysis is one of the major degradation mechanisms for PLA[1]. This process can be improved by the addition of enzymes[1]. These enzymes can be secreted by microorganism that are found in the environment[123]. The enzymatic degradation of polymers can also be observed in the human body: in contact with tissues and body fluids, several enzymes (as horseradish peroxidase, catalase, xanthine oxidase among others,) leads to an oxidative or hydrolysis process[123]. Depending of the microorganism used during degradation, the process can be classified as aerobic or anaerobic and each will be highly affected by the conditions in which the degradation is taking place[117].

For PLA degradation, the key enzymes are protease and lipase, both have been observed to attack the amorphous parts first, and then the crystalline parts[123–125]. In particular, for the case of proteinase K, the ester bond connecting the L-Lactyl units is hydrolyzed prior to D-Lactyl units[123]. Enzymatic action can be also affected by the aging of the polymer: mobility decrease in the polymer chain due to the aging, makes the enzymatic attack less efficient[124]. Additionally, it has been shown that for proteinase K. the rate of degradation can be reduced when PDLA is added to PLLA[126].

PLA degradation is slow when the crystallinity is high (more than 26%) and if the molecular weigh is high[99,127]. Normally PLA is attacked by fungi and bacteria that segregate enzymes that brake the polymer in fragments of around 500 g/mol which can be digested by microorganism[99]. In the body, PLA is depolymerized by chemical hydrolysis which leads to loose of molecular weight, then a loss of mass, and finally a decomposition into monomers by macrophages; finally the lactic acid is degrade by lactates and pyruvates to be then eliminated in form of $CO_2$[99].

## 3.5 Market information of Poly(lactic acid)

The annual production of plastic in 2015 was of 381 millions of tonnes, being most commonly used (146 millions of tonnes) in the packaging sector[128,129]. In Figure 3.9 is shown the amount of plastic produced by different industrial sectors in 2015. Specifically for PLA, the largest industry segment was packaging, with a 37% of the total production destined to it[130]. The second largest segment of the PLA use is in the textile industry[130].

Poly(lactic acid) market was valued at 247.2 millions of dollars in 2014, with a dominant use in packaging[130]. Compound annual growth rate (CAGR) is estimated at of 19.5% during the period of 2013-2020 (according to Sarah Clark and Ranjan Singh in the report "Polylactic Acid (PLA) Market by Application (Packaging, Agriculture, Electronics, Textiles, Bio-Medical), By Geography (North America, Europe, Asia-Pacific, LAMEA) - Global Opportunity Analysis and Industry Forecast, 2012 - 2020"[131].)

The mayor production of PLA in the world was done by NatureWorks, followed by Pyramid technologies in 2014[132]. The three top countries exporting PLA are the United States, Netherlands, and China[132].

### 3.5.1 Market in Ecuador

Ecuador has non production of Poly (lactic acid), this material is imported with a value around $ 2.55K (approx 0.2% of total importations in Ecuador) according to the Observatory of Economic Complexity (OEC)[133]. About 0.16% of

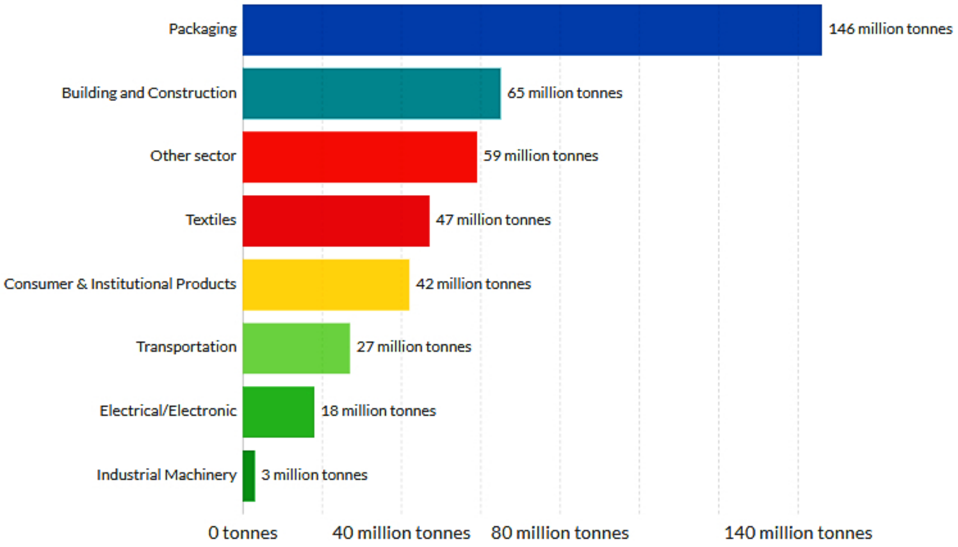

Figure 3.9: Plastic production by Industrial sector in 2015, obtained from (https://ourworldindata.org/plastic-pollution)

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total importations in Ecuador correspond to Lactic Acid with a value of $ 932K[133]. Ecuador does not export neither PLA or lactic acid[133]. This polymer is well used by Ecuadorian companies as "*Innova 3D*" and "*TAICED*" in 3D printing as base material for their designs[134,135].

According to OEC in 2017, the total importations value for Ecuador in plastic and rubber is $ 1.28B, from which 16% is occupied by Ethylene polymers ($ 205M), and 9% by Propylene polymers ($ 115M)[133]. Total exports for Ecuador in plastics and rubber is $ 168M, from which 2.5% is occupied by Propylene polymers ($ 4.14M), and 0.8% by Ethylene polymers ($ 1.35M)[133].

According to "Cámara de Industrias de Guayaquil" (Guayaquil Chamber of Industries) in 2017, from the total importations of plastics in primary form, 33% correspond to Ethylene polymers and 18% correspond to Propylene polymers[136]. In 2017 Ecuador had not petrochemical Industry, which is the supplier of raw material of the plastic products manufacturing sector[136]. This leads to the country to import all the raw material for plastic products generation which had a total value of $ 602.92M in 2017.

## 3.6 Applications of Poly(lactic acid)

PLA have been a material of interest because its characteristics like mechanical properties, thermal properties, chemical properties, degradation, and also its way of manufacture. This material have been proved to replace a petrochemical based plastics which lead us to a wide options for its use[96]. The most studied applications of PLA are in the Pharmaceutical industry, in the textile industry, and in the food industry. This section is going to review those three industries explained different examples that have been under research.

### 3.6.1 Pharmaceutical Industry

Because of the biodegradability, bio compatibility and bioresorbable ability of the Poly(lactic acid), is one of the materials that can be leader in this area[96]. There exist many applications in the medical field, since cancer treatment, drug delivery systems, prosthesis, etc.

Along different ways of cancer treatment, Chemotherapy is still used in patients with different type of cancer like ovarian cancer or breast cancer[137–139]. Fisetin is an natural flavonoids used for cancer treatment of different types like prostate cancer, melanoma (skin cancer), colorectal cancer, bladder cancer, breast cancer, leukemia and cervical cancer[140]. It affects multiple molecular and signaling pathways depending on the cancer type[140]. It have been studied the possibilities that PLA nanoparticles can encapsulate fisetin in order to delivered controlled in the body[141]. The nanoparticles were prepared by the spontaneous emulsification solvent diffusion method[141]. For this method four different parameter will affect the nanoparticles properties, the first is the concentration of poloxamer 188, the second is the oil to water phase ratio, the third is the drug to PLA mass ratio, and the fourth is the acetone to ethanol volume ratio[141]. The particles were analyzed by Transmission Electron Microscopy (TEM) in which it was noticed that the particles were spherical and monodispersed[141]. The PLA nanoparticle filled with fisetine showed a higher anti-tumor effect than the free fisetin solution[141].

Another compound for chemotherapy have been reported to be encapsulated by PLA and poly glicol acid (PGA)[142]. L-asparaginase (ASNase) which is a key chemotherapeutic agent for acute lymphoblastic leukemia was loaded into nanospheres of a co polymer compound by PLA and poly glycolic acid[142]. The method of preparation was the water-in-oil-in-water solvent evaporation technique[142]. The particles prepared were spherical monodispersed with a mean diameter of 390 ± 88 nm[142]. It was showed that the release rate for this compound changed according the ratio of PLA and PGA and its molecular weigh[143]. In 14 days, 81.9% of the compound was released when the molecular weigh was 12 Kda (low molecular weigh) whereas 46.3% of the compound was release when the molecular weigh was 30 Kda[143]. Finally it was demonstrated that the specific activity of the encapsulated compound was higher than the compound freely delivered[142]. It have been studied also the encapsulation

It have been reported also that encapsulation of baricitinib (drug used for rheumatoid arthritis treatment) into the co polymer of poly(lactic acid - glicolic acid) PLGA[144]. The preparation of the nanoparticles loaded with the drug was by precipitation method in which the insoluble drug is precipitated in an aqueous phase with the addition of the polymer mixture slowly in moderated stirring[144]. The nanoparticles were spherical and dispersed with a diameter in the scale of nanometers (the diameter will vary according the different conditions of the preparation for the nanoparticles), the smallest diameter obtained was of 88 nm[144]. It was demonstrated that the drug was effectively released resulting in 89% of release after 12 hours and 94% of release in 24 hours[144]. Those results suggest that this configuration can be used for management of chronic rheumatoid arthritis by reducing the side effects of baricitinib because of its low concentration[144].

Along other application it has been studied the synthesis of PLLA nanofibers for medical applications [145,146]. The preparation of these nanofibers can be done by using the method of electrospinning [145]. Nanofibers of PLA can be combined with polyglutamic acid $\gamma$-PGA for treatment of wounds [146]. There were tasted in-vivo experiment by using the fibers in mice wounds [146]. After 14 days of the wound creation, the mice with nanofibers treatment resemble normal skin and the re-epithelialization was significantly increased compared to the control group [146]. The resulting nanofibers had a diameter around 120 ± 31 nm [146].

There are also some applications in the macro scale. PLA has been used as a matrix with hydroxyapatite loading with gentamicin [147]. This composite was intended to use in dental and orthopedic implants to prevention of bacterial infection [147]. The drug (antibiotic) loaded in the composite is released in three different stages. The first stages is in the first week in which the drug is released from the surface of the prosthesis, the second stage (week 1 to 5) the material start to degrade and the liquid medium penetrate the matrix where the drug is stored and them released, in the final stage (week 5 to 15) the drug was released completely with the total degradation of the material [147]. The release mechanism of this material is affected by the degradation rate that can be tuneable to specific applications [147].

A lot of different applications exist in the pharmaceutical industry for PLA in the nano, micro and macro scale [148–150]. They can go from encapsulating different compounds for its respective delivery [151,152], till macro devices for tissue engineering [153] or prosthesis (3D printing) [154,155].

### 3.6.2 Textile Industry

Another field in which PLA can be applied is in the textile industry [54]. It has been reported the fabrication of cotton fabric by the addition of PLA and chitosan nanoparticles [156]. The PLA and chitosan nanoparticles were prepared by the ionic gelation technique [156]. The method consisted in dissolve chitosan into acetic acid, then PLA is dissolved in chloroform which was added drop by drop to the chitosan solution; after that, the solution is sonicated and a cross linking agent is added [156]. Finally the solution is stirrer vigorously and centrifuged to obtain the desired product [156]. The nanoparticles were spherical shape with a average diameter of 88.02 nm [156]. Finally the nanoparticles were added to the cotton fabric to analyze its properties [156]. The final fabric treated with nanoparticles showed improvement in stiffness, and in the tensile strength compared to the untreated fabric [156]. The material also showed antibacterial effects which can opened a way of investigation in textile for cosmetics or agricultural products [156].

PLA have been studied also for the design of flame retardant or heat resistance materials [157,158]. Polylactic acid exhibit certain flame retardant properties, but are insufficient for some applications; so it is necessary to improve it by making blends or composites with other materials [157]. It was reported that PLA can be mixed with Kraft lignin and ammonium polyphosphate in order to improve the flame retardant properties of PLA [157]. It was obtained that by mixing 5% of Kraft lignin and 5% of ammonium polyphosphate the flame retardant properties of PLA are increased [157]. The material was mixed with a Thermo Haake co-rotating and them extruded to produce finally filaments by melt spinning [157]. The results present filaments with an diameter around 100 $\mu$ when it was composed only by PLA (95%) and Kraft lignin (5%) [157]. PLA can be also combined with silicon oxide nanoparticles in order to study the heat resistance of the material [158]. The silicon oxide nanoparticles are first mixed with 3-Aminopropyltriethoxysilane silane to stabilize them and attached to the PLA [158]. The treated nanoparticle was mixed with PLA by a screw extruder and them some filaments were prepared in which the concentration 1% of silicon oxide nanoparticles with respect PLA[158]. The structural analysis showed that the nanoparticles were evenly distributed in the polymer staying in the nano scale[158].The results indicates that the thermal decomposing temperature, the glass transition temperature and the melting point temperature increases due to the effect of silicon oxide nanoparticles[158].

Aloe Vera fibers have been recently used in India in the textile industry[159]. These fibers can be incorporates into biopolymers as PLA in order to improve their properties[159]. In this investigation was remarked the method to remove the non-cellulosic content of the Aloe Vera fibers with sodium bicarbonate replacing the conventional method using sodium hydroxide[159]. The composite was prepare by melting the fibers with PLA in a single strew extruder in a ration of 30:70 by weigh of fibers:PLA[159]. The reinforced material showed better mechanical properties than pure PLA (tensile strength for pure PLA was 43.9 MPa while for PLA with the fibers was 54.7 MPa)[159]. According to Chaitanya S. et al this materials can be used for preparation of automobile interior trims, consumers electronics (phone body parts), non-toxic toys for children, etc[159]

It has been also studied the effect of PLA with a layer of titanium oxide ($TiO_2$) deposited[14]. The deposition of Titanium was made by sputtering system in a environment of argon[14]. The analysis showed that the nanoparticles of $TiO_2$ were interacting physically with PLA substrate[14]. It was tested the antibacterial effect of the material. As the time in the sputtering increased, the percentage of nanoparticles also increased, which leads to higher antibacterial properties (for 10 min in sputtering the PLA with $TiO_2$ nanoparticles showed a reduction of 90% for *E. Colli* and 82% for *S.aureus*)[14]. This material can be used in the production of textiles for disposable hospital clothing with the additional value of decreasing the energy used for the elimination of hospital clothing[14].

Hydrolysis of PLA have been studied in order to improve properties like hydrophilicity[160]. For this, the PLA was treated with the enzyme alcalase from under shaking at 150 rpm *Bacillus licheniformis*. It was obtained that the moisture regain was of 0.72 ± 0.3% for PLA untreated while the treated PLA fabric was 1.36 ± 0.17%[160]. It was showed that when the carboxyl groups concentrations increases, the hydrophilicity of PLA also increases[160]. SEM images demonstrated that there was not damage in the surface of the sample which allows the use of the material in the textile industry[160].

This industries allows the use of PLA in different ways as it was shown. More investigation have been done in this area as the generation of garnet by 3D printing[161] or the green manufacturing of fabrics[162]. By using biopolymer in these industries the emission of fossil fuel derived $CO_2$ dropped representing a clear advantage over petroleum based polymers[162].

### 3.6.3 Food Industry

An interesting field for PLA uses is the food industry, because as a biodegradable polymer it can offer a huge amount of advantages over petroleum derived plastics. One study before goes to the application is to know if PLA is safe in contact with food. It was shown in 1995 that PLA was safe for the contact with food even if it was short term, or long term, with the only condition that the temperature will no exceed the 60°C[163]. The only migrants from PLA is lactic acid or it dimers and oligomers (which will hydrolyze into lactic acid) that in small quantities are completely safe[163].

Cellulose nanocrystals have been studied in order to improve the properties of PLA for food packaging[164,165]. It was found that with only the 3% of nanocellulose content in PLA the water permeability was reduced by a 82% and the oxygen permeability up to 90%[164]. PLA reinforced showed good transparency and good reduction of UV light, a critical parameter for materials intended to be used in food packaging[164]. Because of the crystallinity of the cellulose nanocrystals, when they are combined with PLA the mechanical properties are improved[164]. It was also shown that the migration of compounds were under the allowed limit making an excellent candidate for food packaging[164].

It has been studied about the blending of PLA and poly(butylene adipate-co-terephthalate) (PBAT)[166]. The synthesis of the blend was made by extrusion using a single-screw extruder[166]. The results showed that the rate of degradation vary according the percentage of PLA, when the amount of PLA was 17% the composite presented a faster deterioration than the composite with an amount of PLA of 40%[166]. The biocomposite with 17% of PLA was completely degraded after 42 days[166]. It can be concluded that the biocomposite can be used for disposable materials because the degradation rate can be manipulated by varying the amount of PLA in the sample.

PLA fibers has been also used for the encapsulation of allyl isothiocyanate (AITC) to used as food packaging[13]. AITC was added in different volumes to a solution of PLA with dichloromethane[13]. The fibers were prepared by electrospining which were grafted into PLA films[13]. The amount of AITC plays a important role in the morphology of the fibers, when the content of AITC was low the fibers were of a diameter from 0.5 - 2.5 $\mu$m, in the other hand when the content of AITC was high the fibers were of a diameter less that 100 nm[13]. It was reported the antibaterial activity of the film in contact with food. For *E. coli* the cells on grape increased to 3000 CFU/g after 40h without AITC film, while the grapes with AITC film only had 30 CFU/g. Also in turkey meat after 40h without AITC film the cells of the bacteria increased to 63000 CFU/g while the sample with AITC film only reported 630 CFU/g demonstrating that they are good candidates for food packaging[13].

The polymerization of lactic acid with PEG have been studied Sahan Y. et al[167]. The preparation was by opening ring polymerization of lactic acid with Sn(II)-ethyl hexanoate with the addition of PEG[167]. The polymer had an organic structure with no negative effect for human health[167]. The bioactive polymer presented significant antimicrobial properties[167]. Finally it was concluded that because the polymer was not hazardous for the human health and its antimicrobial properties it can be used for the preservation of raw food and processed food[167].

There exist more applications for PLA in different fields. The properties of the polymer as its biodegradability, mechanical properties, thermal properties, and chemical properties allows to use for our daily life. It can be used in the agriculture as pesticides encapsulation or protective clothes for farmers[168]. PLA can be applied also in the cosmetic industry as controlled delivery system for essential oils used in the health care[169,170]. Finally PLA is used for home furnishing as carpets, tiles, rug, curtains, pillow, etc[171,172].

## 3.7 Synthesis of poly(lactic acid)

There exist two general methods of polymerization, the first is the polycondensation and the second is the chain polymerization[173]. PLA can be synthesized by two methods, the first is polycondensation and the second is ring opening polymerization method[1] (which is a method that belongs to chain polymerization[173]).

Polycondensation is defined as "Polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all degrees of polymerization"[174]. The growth step is represented as:

$$P_x + P_y \rightarrow P_{x+y} + L \tag{3.11}$$

where $P_x$ and $P_y$ are the chains of degree of polymerization x and y respectively, and L is a lower mass byproduct[174].

ROP is defined as the "polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer"[174].

### 3.7.1 Polycondensation

Polycondensation of PLA is a relative simple and inexpensive process[9] because not intermediate products need to be formed and it can be done without catalyst or solvents[175]. By doing this is very hard to obtain a polymer of high molecular weigh because of the equilibrium between free acids, polyesters and water (It is very difficult to obtain water as a byproduct)[176]. In order to obtain a high molecular weight polymer and overcome this problem, the addition of some catalyst (preferable of tin) are needed[177].The process can be done by the same monomer because it has -OH and -COOH groups which are necessary for the polymerization[178].

In this process two different methods can be studied. The first is the solution polycondensation and the second is the melt polycondensation[178]. In solution polycondensation an organic solvent capable to dissolve the PLA without interfering in the reaction is used[178]. This process allow to obtain a polymer with high molecular weight (more than 200 000 g/mol) but with the problem that some impurities due to the solvent used[177,178]. The properties of the polymer by this method are very similar to the properties of the polymer synthesized by ROP[177,178]. In melt polycondensation, no solvent are needed to the polymerization process, it only requires that the temperature is higher than the melting temperature of the polymer[178]. Three main factor should be controlled in this process to obtain high molecular weigh, the reaction kinetics, the water formed removal, and the degradation of PLA prevention[178].

The scheme of polycondensation of PLA is shown in Figure 3.10. In step one the distillation allows to obtain low molecular weight oligomers of lactic acid, then the polymerization starts until a higher molecular weight is obtained. Lactide can be formed in any step if parameters as pressure or temperature are not controlled[176].

In Table 3.8 are shown different results that have been obtained from literature for the Polycondensation of PLA. Temperature plays an important parameter because of the equilibrium that exist between the poly (lactic acid) formation and lactide formation. The reaction time also is crucial at the moment of polymerization because it can lead in different molecular weigh polymers. With ZnO as catalyst was observed that when the time was increased a higher molecular weigh polymer was obtained with a higher yield when the temperature was the same. The entries in table 3.8 that are with "—" in the temperature section (entries 6, 7, 9, 10) means that there were different stages in which the temperature was changed along the polymerization. In general it can be observed that polycondensation of lactic acid (LA) or L-lactic acid (L-LA) can result in the polymerization of PLA with high molecular wight.

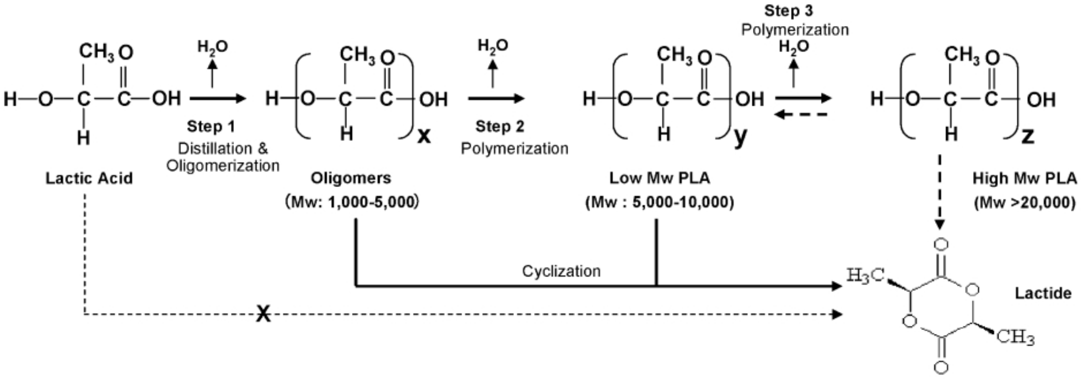

Figure 3.10: Polycondensation method for PLA

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Table 3.8: Results reported of Polycondensation for PLA with different catalyst

| **Monomer** | **Catalyst** | **Temperature (°C)** | **Time (h)** | **Yield (%)** | **Average molecular weight $M_n$ (g/mol)** | **Molecular weight $M_w$ (g/mol)** | **References** |
|---|---|---|---|---|---|---|---|
| LA | Tin chloride/ phthalic anhydride | 160 | 30 | – | 6 900 | 22 100 | [179] |
| LA | Tin chloride/ maleic anhydride | 160 | 30 | – | 13 400 | 61 700 | [179] |
| LA | Tin chloride/ p-toluene sulfonic acid | 160 | 30 | – | 18 300 | 81 500 | [179] |
| LA | ZnO | 180 | 40 | 65 | – | 84 300 | [180] |
| LA | ZnO | 180 | 30 | 63 | – | 79 400 | [180] |
| L-LA | TSA | — | 153 | – | 133 000 | 180 000 | [181] |
| L-LA | EBSA | — | 153 | – | 206 000 | 247 000 | [181] |
| L-LA | CSA | 180 | 24 | – | 5 234 | 14 875 | [182] |
| L-LA | TSA | — | 15 | 62.75 | 14 794 | 32 400 | [183] |
| L-LA | TSA | — | 53 | 72.25 | 11 111 | 24 000 | [183] |

TSA (p-Toluenesulfonic acid monohydrate); EBSA (4-ethylbenzenesulfonic acid); CSA (Cellulose sulfuric acid)

The binary catalyst of Tin Chloride with it respective anhydride or acid allows to have high molecular weight PLA; the best catalyst of those three is Tin chloride/p-toluene sulfonic acid (TSA) which leads to a molecular weight of 81500 g/mol[179].

ZnO catalyst was used to produce high molecular weight PLA, it was shown that molecular weight increase as the time of reaction increase[180]. ZnO was compared with the catalytic activity of $\gamma$-$Al_2O_3$ in which was demonstrated that ZnO produced higher molecular weight under the same conditions but with lower conversion percentage[180]. This study concluded that pressure also played an important roll in the polymerization of PLA by Polycondensation, as the pressure is reduced, more water can be removed and as the water is removed, the polymer chain length increase[180]. Finally it was stated that catalyst with higher solubility in water are better to the polymerization of PLA[180].

As it was shown before, organic acids as TSA and 4-ethylbenzen sulfonic acid (EBSA) are promising in the PLA synthesis of high molecular weight[181]. Organic acids have catch the attention in investigation because they are friendly with environment and only requires 1% of catalyst weight with respect the monomer, unfortunately it requires a long time for the whole process to be completed[181]. TSA allowed to obtain a polymer with higher molecular weight in comparison with EBSA, but TSA showed lower efficiency compared to EBSA; this occur because TSA is more volatile than EBSA[181].

The catalyst of cellulose sulfuric acid presented a polymerization of low molecular weight PLA[182]. The process involving this catalyst was sensible to change of time and temperature, at higher temperature and longer time, the polymer obtained had higher molecular weight than the polymer at low temperature and shorter time[182]. By using this process the polymer presented a crystallinity of 53% and it started to degrade at a temperature of 252,12°C[182].

Finally Polycondensation of PLA was done by TSA[183]. It was demonstrated in this study the scalability from 5g of lactic acid used to 100Kg of lactic acid used[183]. No significant decreasing in molecular weight was present, but at high scale it was shown that longer time is required to obtain a polymer as good as in the laboratory test[183]. Even though the longer time required in the scaled process, this presented a higher yield that in the laboratory test[183]. Also it was found that at higher time and temperature the molecular weight and the melting temperature increase[183].

It is possible to obtain high molecular weight PLA by polycondensation, but in general it requires long time for the reactions to occur in the best conditions. In Figure 3.11 (a) is shown the different molecular weights as function of the different catalyst studied. It has been found that in Polycondensation organic acids as TSA or EBSA can be used for the PLA synthesis of higher molecular weight. Also in Figure 3.11 (b) is shown the time necessary for the reaction to occur. For Polycondensation several hours are necessary to complete the process which can be unfavorable at the moment of scaling the process to an industrial process.

### 3.7.2 Ring opening polymerization

This second method of polymerization requires an extra step. This step consist on the production of a prepolymer called lactide which structure is shown in Figure 3.12. Lactide has its respective stereoisomer that will depend of the source (lactic acid)[1]. D-Lactic acid will polymerize into D-Lactide, L-Lactic acid will polymerize into L-Lactide and also it exist the possibility to have meso-lactide that is a combination of D,L-Lactic acid[1]. The process to obtain lactide consist in few steps[1]:

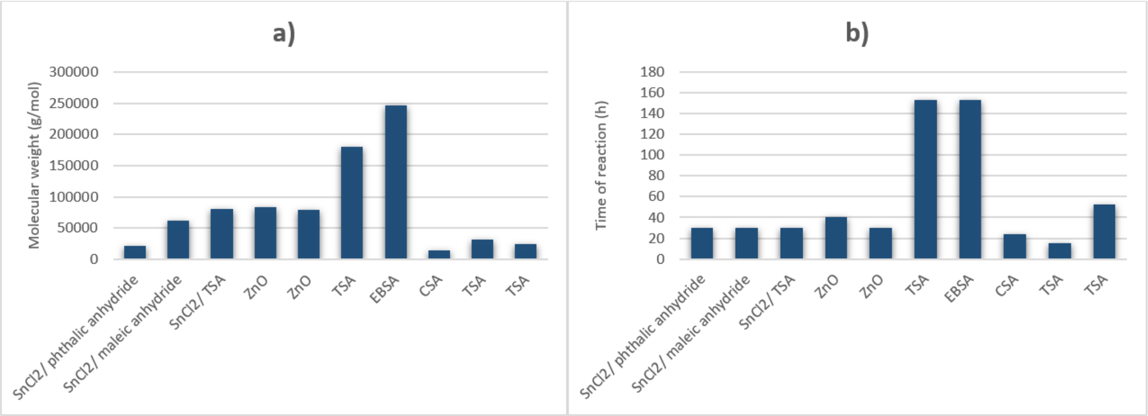

Figure 3.11: Catalyst used in polycondensation. (a) Molecular weight of final polymer as a function of different catalyst. (b) Time of reaction required for each catalyst to complete the polymerization

1. Feeding Lactic acid into a Evaporator
2. Removal of water and solvents from crude lactic acid
3. Feeding the concentrated lactic acid with catalyst into lactide reactor
4. Removal of lactide as vapor from the reactor
5. Condensation of lactide vapor
6. Purification of Lactide by distillation system

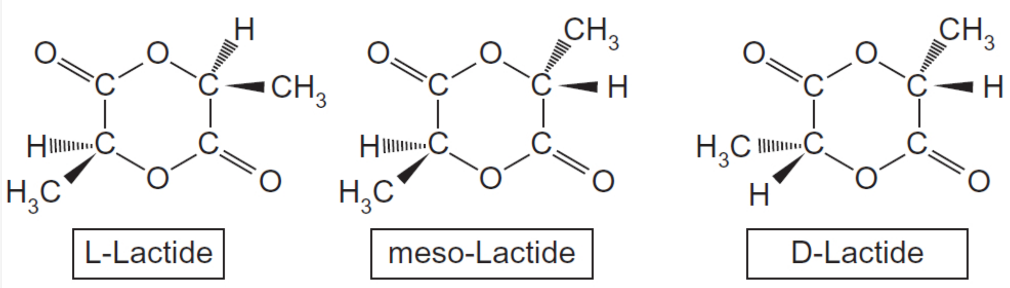

Figure 3.12: Lactide stereocomplex

1

After the lactide is obtained, the polymerization into poly(lactic acid) takes place. ROP can occur in three different ways (anionic, cationic, or through coordination-insertion mechanism) depending of the catalyst used[184]. One catalyst very used in Ring opening polymerization of lactide is the Tin (II) (ehtylhexanoate) or Sn(octanoate)$_2$ [185,186] because of its catalytic activity and its solubility in lactide [184]. The catalyst mentioned operates in the coordination-insertion mechanism [184]. The mechanism of the reaction is shown in Figure 3.13 [187]. First it is shown a proton migration of from the methanol to the octanoate ligand (the alcohol ligand is converted into alkoxide) [187]. Then the insertion process occurs and it is described in two steps, the first is the nucleophilic attack of the alkoxide on the coordination lactide and the second is ring opening [187]. This last step results in the insertion of lactide into the O-H bond of a coordinated methanol [187].

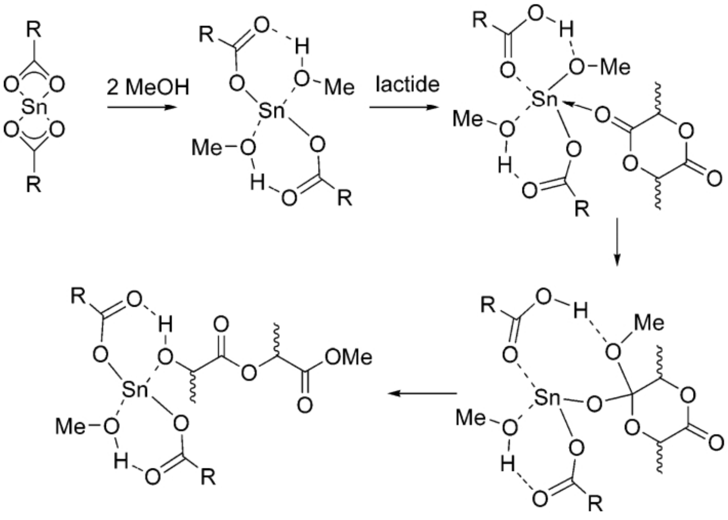

Figure 3.13: Ring opening polymerization of lactide with Sn(octoate)$_2$ as catalyst
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In table 3.9 it is shown different results from the polymerization by ring opening. The table describes the source (L-lactic acid (L-LA); L-Lactide; D-Lactide or D,L-Lactide (rac-Lactide) for the polymerization. It is shown the catalyst used in each process, the polymerization time, the yield, the average molecular weigh and the molecular weigh.

Table 3.9: Results reported of ROP for PLA with different catalyst

| **Monomer** | **Catalyst** | **Reaction Time (h)** | **Yield (%)** | **Average molecular weight Mn (g/mol)** | **Molecular weight Mw (g/mol)** | **Reference** |
|---|---|---|---|---|---|---|
| L-LA | Magnesium Complex | 2 | 95 | 16600 | 24070 | [188] |
| L-LA | Magnesium Complex | 2 | 98 | 21300 | 33228 | [188] |
| D-Lactide | DBU | 1 | 59 | 12900 | 17400 | [189] |
| D-Lactide | TBD | 1 | 85 | 19900 | 33500 | [189] |
| rac-Lactide | DBU | 0.5 | 94 | 45181 | 89006 | [190] |
| rac-Lactide | Potassium naphthalenolate | 0.5 | 98 | 70400 | 82368 | [191] |
| L-lactide | Sodium Complex | 0.5 | 98 | 29150 | 34105 | [192] |
| rac-Lactide | Sodium Complex | 0.5 | 98 | 28900 | 33813 | [192] |
| L-lactide | Sodium Complex | 1.58 | – | 113900 | 137819 | [192] |
| L-lactide | Potassium Complex | 1.75 | – | 108750 | 139200 | [192] |
| L-lactide | Lithium Complex | 2 | – | 100560 | 133744 | [192] |
| L-LA | Aluminium methyl complex | 0.5 | 99 | 12800 | 13696 | [193] |
| rac-Lactide | Aluminium methyl complex | 0.5 | 99 | 13700 | 14659 | [193] |
| rac-Lactide | Aluminium methyl complex | 48 | 93 | 106400 | 118104 | [193] |
| rac-Lactide | Aluminium methyl complex | 60 | 95 | 233600 | 273312 | [193] |
| L-Lactide | Tin (II) ethylhexanoate | 44 | 84 | 16000 | 24000 | [194] |
| Lactide | Tin (II) ethylhexanoate | 0.41 | 81.09 | – | 151127 | [195] |
| Lactide | Tin (II) ethylhexanoate | 0.75 | 82.59 | – | 127065 | [195] |

DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene); TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene)

Magnesium complexes were studied for the polymerization of poly(lactic acid) with 4-fluorophenol as co-catalyst[188]. It was shown that in few hours a high yield was obtained[188]. The differences in molecular weight and yield for each one of the complexes is the radical position between CH3 and H[188].

DBU and TDB were used for mechanochemical ROP, in which at a lower time of polymerization, it was obtained PLA with a molecular weight compared to magnesium complexes, but with a lower yield. It was shown that TDB produce a higher molecular weight polymer with a higher yield than DBU[189]. The use of initiator improved the polymerization, giving a polymer with a molecular weight that reach an order of $10^5$ g/mol[189]. It was shown that as the time of polymerization increased, the polymer increase its molecular weight and the conversion percentage[189]. For DBU with toluene as initiator at one hour was obtained a polymer with a molecular weight of 100 000 with a conversion of 55% while at two hours the molecular weight was 188 000 with a conversion of 81%[189]. The liquid-assisted griding produce a higher molecular weight polymer because it prevent the chain degradation[189].

DBU is also used for the polymerization of rac-lactide.The results will vary according the monomer used, as it is shown in Table 3.9 DBU catalyst better rac-lactide that D-lactide; for rac-lactide the molecular weight was 89 006 g/mol with a yield of 94% while for D-lactide the molecular weight was 17 400 with a yield of 59%[190]. In this study was tasted the addition of alcohol as macroinitiator. monohydroxy-terminated polyethylene glicol (PEG-OH) was used as initiator for PLA polymerization[190]. It was shown that the PEG-OH did not improve the polymerization, as the ratios between the concentration of alcohol and the catalyst ([PEG-OH]:[DBU]) increase, the molecular weight and the yield were reduced[190].

Rac-lactide also can be polymerized with potassium naphthalenolate for the synthesis of PLA with high molecular weight and high yield at room temperature[191]. In this study it was used the addition of Benzyl alcohol (BnOH) at the same ratio of the catalyst compared to lactide. It was demonstrated the at a ratio between [rac-lactide]:[catalyst]:[BnOH] of 1000:1:1 the higher molecular weight and yield was achieved[191]. As the time of reaction and the concentration of rac-lactide with respect catalyst and BnOH increase, the molecular weight and yield rises[191]. Moreover Potassium naphthalenolate was compared with sodium naphthalenolate in which was demonstrated that potassium complex were better for ROP of PLA in comparison of sodium complex. At 3 min for potassium complex it was obtained a molecular weight of 34 450 with a yield of 99% while for sodium complex at 3 min the molecular weight was 4 500 g/mol with a yield of 57%[191]. At higher temperature Sodium complex works better than potassium complex[192]. Swarup Ghosh et al. studied the polymerization of PLA by ROP using sodium, potassium and lithium complexes. It was shown that at a temperature of 140° Sodium complexes worked better than potassium complexes and this last one worked better than lithium complexes[192]. It was also tasted the activity of BnOH which demonstrated that lowered the molecular weight of the final product. It was demonstrated that when the concentration of the monomer increased, the molecular weight increase too[192]. When the ratio of [monomer]:[catalyst] is 200, the molecular weight for the three different complexes were in the order of $10^4$ g/mol[192]. When the ratio of [monomer]:[catalyst] is 800, the molecular weight for the three complexes were in the order con $10^5$ g/mol[192]. All complexes were used for the polymerization of L-lactide and rac-lactide; and worked with both lactide, obtaining molecular weights of the same order of magnitude[192].

Aluminium methyl complexes were used for PLA synthesis by ROP. As it happen in the last mentioned complexes for PLA polymerization, the molecular weight of the polymer will increase as the concentration of [Lactide]:[catalyst] increase[193]. When the ratio is 100, the molecular weight is in the order of $10^4$ g/mol; while when the ratio is 800 or 1600, the molecular weight is in the order of $10^5$ (it requires longer time of polymerization)[193]. Aluminium complexes worked well for the polymerization of rac-lactide and L-lactide resulting in polymers with similar molecular weights[193].

Tin (II) ethylhexanoate ($Sn(Oct)_2$) was used for the synthesis of PLA, it was combined with different initiators to observe the effect of them in the polymerization[194]. two different initiators were used with $Sn(Oct)_2$, poly(butylene succinate (PBS) and 1-dodecanol[194]. PBS was the best initiator because it was required in less quantity (0.001% of the monomer weight) while 1-dodecanol requires 0.1% of the monomer weight[194]. PBS (at 0.001% of monomer weight) presented an increase in molecular weight when the temperature of polymerization was raised; at 120°C and 4 hours the molecular weight was 7700 g/mol, while at 160°C and 4 hours the molecular weight was 24000 g/mol[194]. 1-dodecanol was less effective because the PLA synthesized had a molecular weight of 6200 at 160°C and 4 hours[194]. It has been studied the use of initiators for $Sn(oct)_2$ as polyglycerol-10 or toluene to improve the molecular weight of the final product[195]. According to Yunzi Hu et al. toluene was not effective as polyglycerol-10 because using toluene as initiator result in a polymer of molecular weight in the order of $10^4$ g/mol while with polyglycerol-10 the molecular weight was in the order of $10^5$ g/mol[195]. It was shown that molecular weight reduces when time goes more than 25 minutes and less than 25 minutes; but the yield increment when the time is more that 25 minutes[195].

In Figure 3.14 is shown the catalyst studied and the molecular weights of the final product. It can be observed that the highest molecular weigh was reached with Aluminium methyl complex, but it requires too much time of reaction in comparison with other catalyst. Then sodium, potassium and lithium complex with Tin (II) ethylhexanoate are the catalyst which gave higher molecular weight PLA (molecular weight in the order of $10^5$)

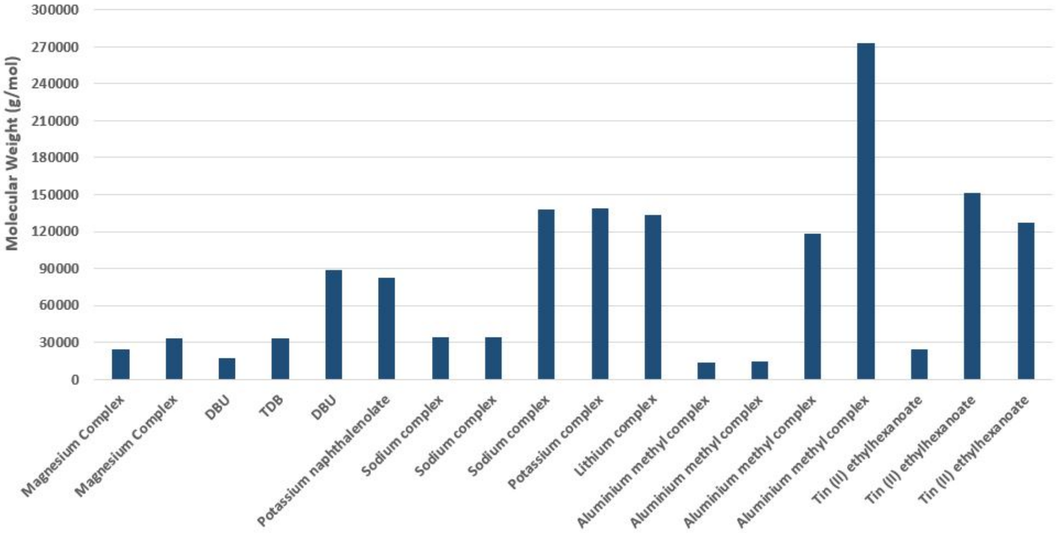

Figure 3.14: Molecular weight of PLA synthesized by ROP as function of different catalyst

## 3.8 Characterization techniques of Poly(lactic acid)

### 3.8.1 Fourier Transform Infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy is a vibrational spectroscopic technique which study the vibrations produced by molecules. The transition between quantized vibrational energy states results into infrared spectra[196]. The analysis of Infrared (IR) spectra tells which molecules (functional groups) are present in the sample and it respective concentrations[197]. The technique born in 1891 with an interferometer made by A. Michelson[198]. Then Rayleigh discover that the interferogram obtained by that equipment was related to the spectrum by a serie of mathematical operations (Fourier transform)[198]. In 1949 Peter Fellgett was credited to be the first to transform the interferogram to a spectra in the infrared region[198]. This technique is well known to be a non destructive technique, which gives information about functional groups, bonding types and molecular conformations[199]. Lately it has been used to analyze surface of polymer after certain treatment or weathering[200,201].

The working principle for FTIR is detailed in Figure 3.15. First the source of infrared light goes through an interferogram. The signal obtained from the interferogram is them directed to the sample. The response corresponding to the samples is then detected.

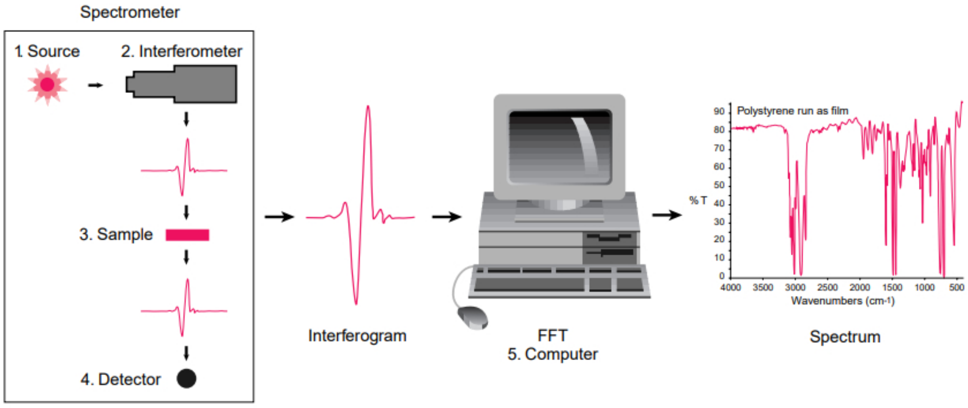

Figure 3.15: Fourier transform infrared spectroscopy working principle.

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FTIR data of PLA is shown in Table 3.10[180]. The data presented are the functional groups vibrations with its respective wavenumber of PLA synthesized by the two methods explained before (Polycondensation and Ring Opening Polymerization). In Figure A.1 is shown the FTIR spectra from which the data was obtained.

Table 3.10: FTIR absorption peaks of PLA

| **Functional Group** | **Wave number (cm-1)** | |
|---|---|---|
| | PLA polycondensation | PLA ROP |
| -OH stretch | 3508.52 | 3504.66 |
| -CH stretch | 2999.31, 2949.16 | 2995.45, 2945.30 |
| -C=O carbonyl stretch | 1755.22 | 1757.15 |
| -CH3 bend | 1456.26 | 1454.33 |
| -CH- deformation | 1384.89, 1363.67 | 1361.74, 1381.03 |
| -C=O bend | 1269.16 | 1267.23 |
| -C-O stretch | 1134.14, 1091.71 | 1186.22, 1130.29, 1091.71 |
| -OH bend | 1045.42 | 1047.35 |
| -C-C- stretch | 954.76, 920.05 | 954.76, 867.97 |

### 3.8.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a technique in which the weigh of a material is recorded as a function of temperature[203].According to the International Confederation for Thermal Analysis, TGA is defined as a technique where the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program[204]. It is generally used for measure physical and chemical properties, like crystalline transitions, vaporization, sublimation, fusion, oxidative degradation, activation energies of pyrolysis, thermal degradation[205–207]. Polymers can be used for different application according the thermal degradation they have, so TGA become an ideal technique to analyze them[208]. From thermogravimetric analysis a curve is obtained called TGA curve in which mass or percentage of mass is plotted against temperature or time[209]. This output must of the times shows the first derivative of the TGA curve with respect the time or temperature and it is know as differential thermogravimetric (DTG) curve, which represent the rate of the mass change[209].

The instrumentation of this equipment is a balance, a furnace, atmosphere control, crucibles, thermocouples as it is detailed in Figure 3.16[210]. The balance is the essential part of the equipment. It should be able to measure difference of mg because in modern equipment it is used samples of 1g[211]. The furnace bust work in the range from room temperature until 1100 °C or 1600 °C according the configuration of the equipment[211]. The simple way to perform the experiment is under environmental conditions (air), but as it can react oxidizing the sample, a inert gas as nitrogen or argon can be used[211] (normally for polymer, a reducing atmosphere is rarely needed[212]). The crucible is found between the heaters where the sample is deposited and are normally of platinum due to is lack of interaction with the sample and its fusion point (1769 ∘C)[211].Thermocouples consist of two metals fussed, which produces a fixed and standart EMF across the junction that vary with temperature[211]. The measurement can be affected by different parameters, as the heating rate or atmosphere, the morphology of the sample, the material of the crucible, etc.[209].

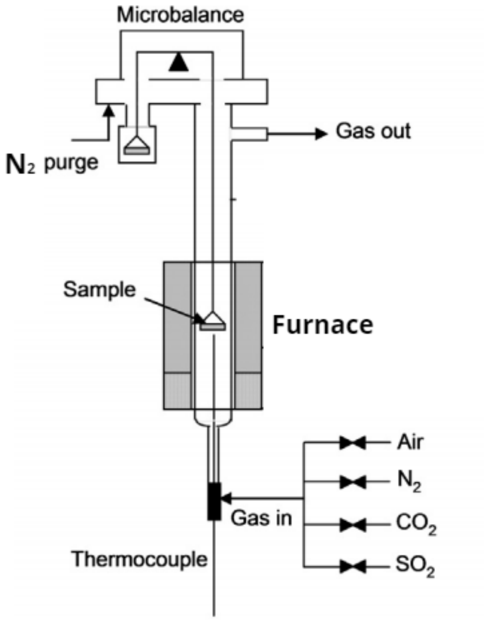

Figure 3.16: Thermogravimetric analysis configuration.
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The degradation temperature of PLA vary according the method used for its preparation as the monomer used and the parameters applied. As an example PDLA can have a degradation temperature around 255°C - 327°C[182,214]. Thermal properties of PLA can be affected by blending it with other materials. PLA 2003D Haake shows a degradation temperature around 356 °C while PLA 1 wt% Biosilicate shows a degradation temperature around 319°C; a decreasing in the degradation temperature of 37°C[215]. Also, PLA can be mixed with halloysite nanotubes (HNT) and polyethylene glycol (PEG) showing an increasing in the degradation temperature around 24°C (PLA was 346°C and PLA/PEG/HNT was 370°C)[216]

### 3.8.3 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry is technique used for the study of thermal behaviour of different materials, like polymers, copolymers, composites[217]. In this technique the heat flux is monitored against the time or the temperature in a specific atmosphere[218]. The configuration of the equipment is shown in Figure 3.17 in which a difference of temperature between the sample and a reference (Aluminum) is recorded to obtain the heat flux of the material[219]. The principal use of this technique is to determine first order transitions (melting) and second order endothermic transitions (glass transitions)[217]. A heating process analysis in DSC is shown in Figure 3.18[220]. In this heating stage, the behaviour in the first point ($T_g$) indicates that there exist an increase in the heat capacity of the polymer because it has gone trough a glass transition[220]. The peak observed in the second point of Figure 3.18 ($T_c$) is an exothermic transition in which the polymer crystallize[220]. Finally When a depression is observed as in $T_m$ (Endothermic process) means that a first order transition is happening, in this case the polymer absorbs heat and melts[220].

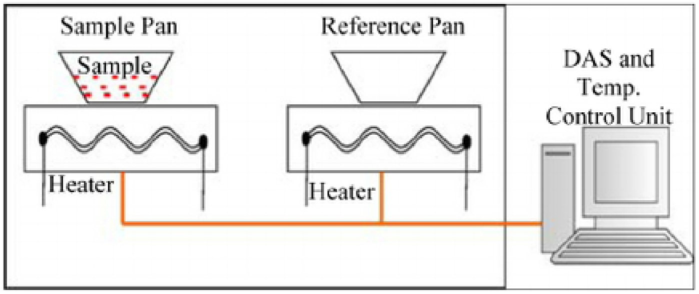

Figure 3.17: DSC equipment configuration.

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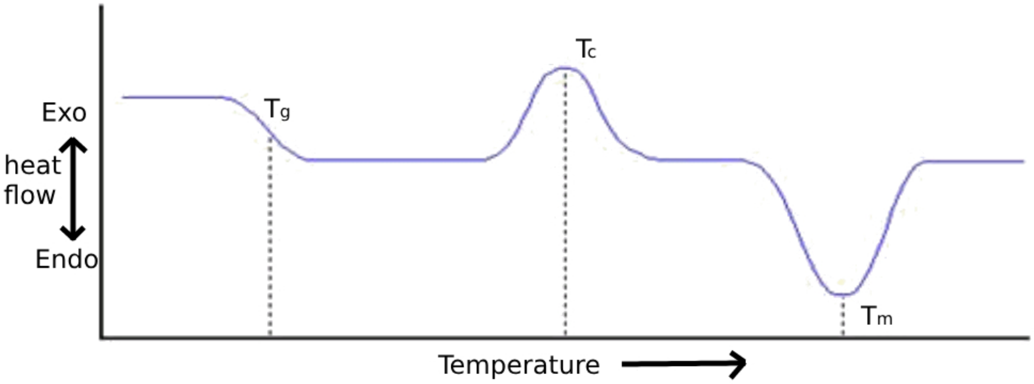

Figure 3.18: Representation of a heating process in DSC analysis

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The thermal history of a material can be studied by DSC under a series of heating and cooling processes. In Figure A.3 is shown a heating/cooling cycle of PLA and PLA/banana fiber composite (endothermic up, exothermic down)[111]. In the heating stage, PLA exhibit glass transition at a temperature approximately 59°, and a cold crystallization in a temperature interval of 80° to 120° and 150° to 159°[111]. Also in the heating stage it is presented an endothermic peak at approximately 169° which represent the melting temperature. In the cooling stage it is observed that not exist a clear peak of crystallization for PLA, while the composite exhibit melt crystallization[111].

In Figure 3.19 is shown how the thermal properties of PLA reinforced with coir fibers change depending on the cooling ramp applied[111]. In the first heating it is shown the glass transition temperature, two exothermic peaks (cold crystallization), and the melting peak[111]. In the cooling process it can be observed in shadow the melt crystallization which vary as the cooling ramp change; for lower cooling ramp the area of the peak becomes larger[111]. In the second heating process, it can be observed that the glass transition peak become smoother and the cold crystallization peaks reduce its areas as the cooling ramp decrease[111]. Also, as the crystallinity of the material is dependent on the enthalpies, by changing it (as the cold crystallization enthalpy), the degree of crystallinity will be altered.[111].

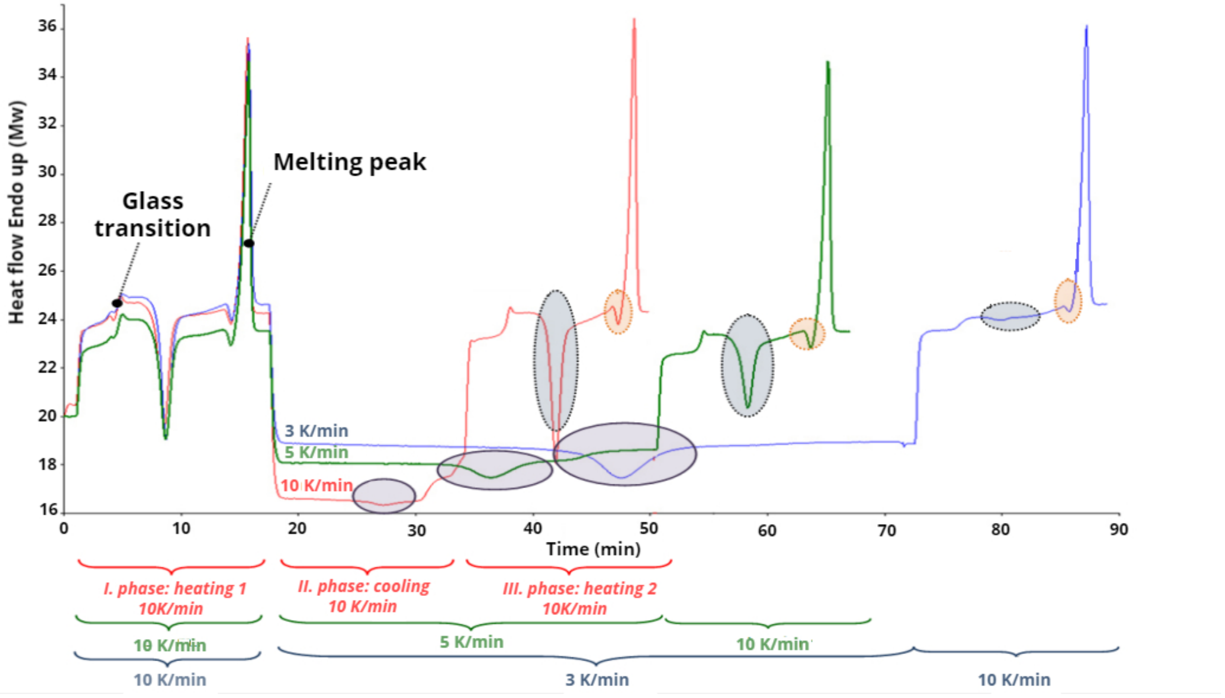

Figure 3.19: Differential Scanning Calorimetry of PLA reinforced with coir fibers with different temperature ramp in the cooling stage. Cooling temperature ramp at 10 K/min (red), 5 K/min (green) and 3 K/min (blue) [111]

Glass transition temperature and melting temperature will vary according the method of preparation and also according the parameters like time of reaction, temperature of polymerization or catalyst used[214].

As an example it is shown in Table 3.11 the variation of melting temperature according the reaction time and the temperature of polymerization[214]. The DSC curve is shown in the Appendix in Figure A.4.

Table 3.11: PLA melting temperature in function of the time and temperature of reaction

| **Reaction Time (h)** | **Temperature (°C)** | **Melting temperature Tm (°C)** |
|---|---|---|
| 5 | 130 | 155.98 |
| 10 | 145 | 163 |
| 15 | 150 | 164 |
| 20 | 155 | 169.46 |
| 30 | — | 177.56 |
| >30 | — | 165.55 |

### 3.8.4 Scanning Electron Microscopy (SEM)

Scanning electron microscope is a technique which allow to resolve image in the order of nanometers. Human eyes can resolve images until 0.2mm, while light microscope can do it until $0.2\mu m$[221]. The working principle is represented in Figure 3.20, where an electron beam (high energy) is generated from a filament and them focused through a lens system to the specimen to analyze[222]. The detectors then will acquire the emitted electrons to direct them into a signal amplifier to be finally displayed into an image of the specimen[222].

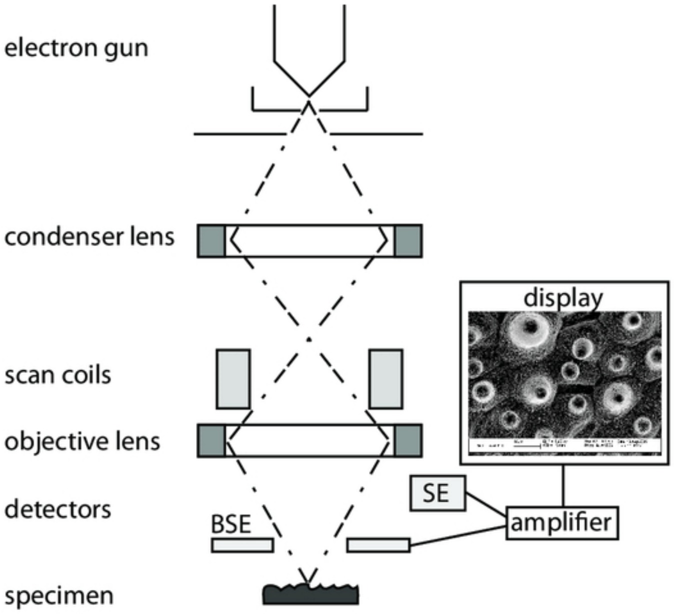

Figure 3.20: SEM working principle

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It is very useful to analyze structure comparing topography or elemental composition present in the sample[223–225].

In this technique, the image system will have a dependence in the nature of the sample (it must be conductive in order to obtain an image from the microscope)[226]. If the sample is not conductive, it mus be coated by a conductive material, must of the time the sample is covered with a thin layer (some nm) of gold[227]. If the sample is in suspended or dispersed in a solution, normally a drop of the sample is dried in the holder and them if it requires (sample not conductive) is coated with gold[228]. Several parameters of measurement will matter in the image obtained. The probe size is fundamental for the resolution; the smallest the probe size is, the higher the resolution in the image is obtained (it needs to be consider enough beam current in order to see the image)[229]. Electron probe current is another parameter that will affect the quality of the image; higher probe current will give higher quality of the image (small values for probe current can give noise in the image as an result)[229]. Electron probe convergence angle will affect the depth of focus; when the angle is shorter, the best depth of focus is obtained which mean that features on the surfaces at different high will appear all in focus[229]. Electron beam accelerating voltage will affect the interaction of the electron beam with the sample. When the accelerating voltage is low (Low-Voltage mode) the information acquired will be mostly of the surface (obtaining a surface detailed image)[229]. When the accelerating voltage is high, the information obtained will be mostly from the interior if the sample[229].

For polymers, SEM is a technique that allows to follow and confirm several process in the surface of the material[230–232]. In PLA foams, SEM is used to measure the pore size (in average) in which was shown that for poly(lactic acid) foams the average pore size decrease as the concentration of PLA increase[230]. PLA foams prepared in a solution of tetrahydrofuran/methanol (THF/MeOH) at different concentrations produce morphological changes in the structure which were analyzed with SEM[230]. It was shown that according the methanol concentration of the solution decrease, larger crystalline structure are obtained[230]. PLA properties can be improved by the addition of fillers in its matrix, in which the dispersion on the material can affect the properties[231]. SEM can be used to analyze the dispersion of fillers in PLA composites as it was demonstrated by Battegazzore et al.[231]. PLA functionalization can be observed also with scanning electron microscopy. Hila Shalom et al. presented in PLA functionalization with nanotubes of tungsten disulfide that circles appear around the nanotube in the cross-section of the polymer, which indicate a relative poor adhesion between polymer and nanotube[232].

# Chapter 4

# Conclusions & Outlook

PLA present different properties that can be tuned for specific applications in many fields like in medicine, food industry and textile industry. Mechanical and thermal properties of PLA can be modified by physical or chemical routs, as the addition of different materials or by a serie of heating and cooling process. PLA is a sensible material for enzymatic attack and it have the disadvantage in its glass transition temperature that is around 50°C.

The route for the synthesis of PLA can be simplified in three steps: 1) Sugarcane pre-treatment, 2) Sugars fermentation into lactic acid, 3) Polymerization of lactic acid. Sugarcane bagasse pre-treatment is determinant for the final yield of the polymer. It is normally used acids, like $H_2SO_4$, or bases, like NaOH, for the lignin removal; but enzymatic hydrolysis has been tasted with the inconvenient of the time (it requires long time). The use of $NH_4OH$ and $H_2SO_4$ is a good option in this step because it takes a short period of time and high conversion of glucose from the bagasse.

The fermentation into lactic acid will strongly depend on the bacteria used. For each bacteria the optimal conditions were used and the one with higher yield was *Lactococus lactis*. In the third step (polymerization), two routes were studied with different catalyst under their optimal conditions of time and temperature. Ring Opening Polymerization is the chosen route of polymerization as the most effective, because it can be obtained high molecular weight and the time of reaction is very short in comparison of direct polycondensation. In ROP the best catalyst was Tin (II) ethylhexanoate which allows obtaining a polymer with high molecular weight in a period of time less than an hour.

In Ecuador, because of the generation of sugarcane bagasse, the production of Poly (lactic acid) can be implemented in the sugars mills. It is well known that sugarcane bagasse is used for co-generation of energy, but as not all the sugarcane bagasse is used with that purpose, it can be tapped for the production of a high value material as it is the PLA. The synthesis of PLA can be done in Ecuador because it is a country that generates millions of tones of sugarcane bagasse. Some mechanical properties of PLA are comparable with polyethylene and polypropylene; even the disadvantage of the glass transition temperature and the sensibility to enzymatic attack, the implementation of PLA manufacturing in sugars mills will open a new window for the production of plastic products in Ecuador which will be able to obtain the raw material for different products without the need to import. In addition, as it was shown in the market information, there is not petrochemical industry in Ecuador which provides raw material for the production of plastics products; this give the opportunity to start the production of raw material in a environmental friendly way.

# Appendix A

# Characterization techniques

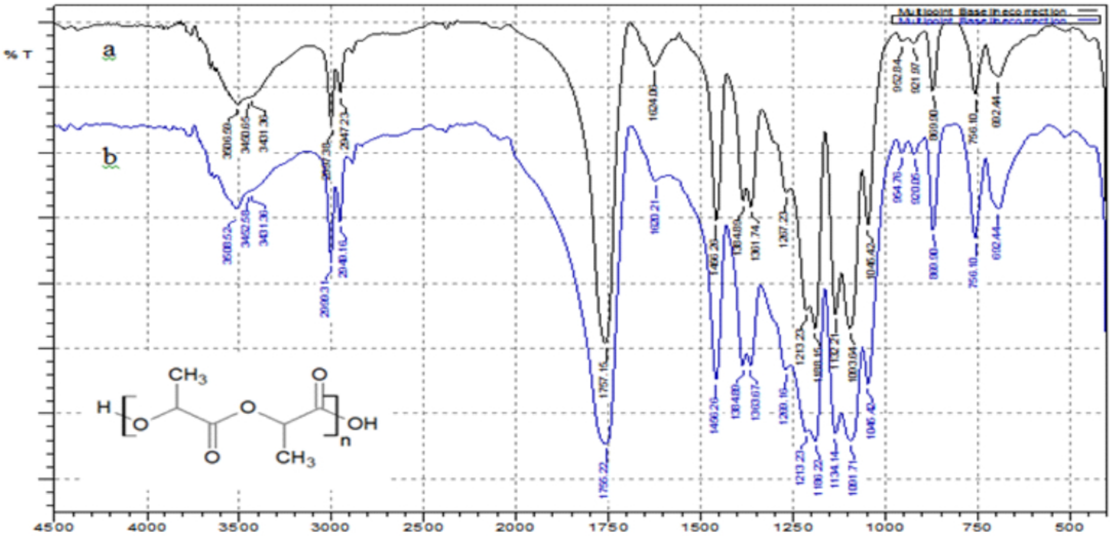

Figure A.1: FTIR spectra of PLA synthesized by Polycondensation with a) $\gamma$-$Al_2O_3$ and b) ZnO

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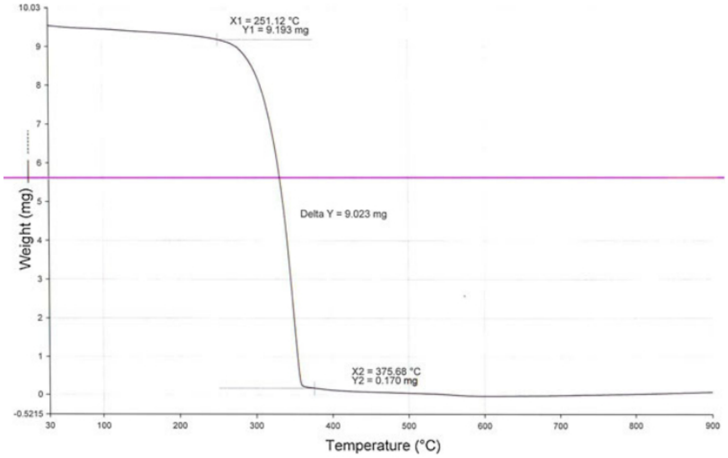

Figure A.2: TGA curve of PLLA synthesized by polycondensation

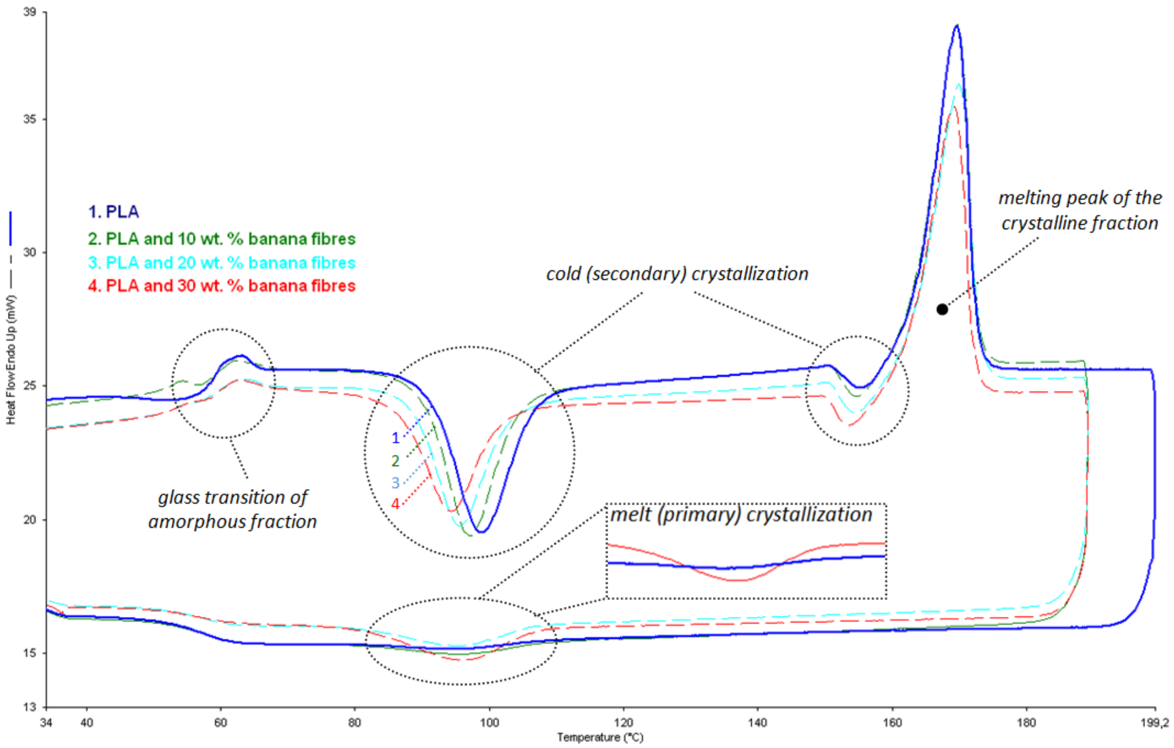

Figure A.3: DSC of PLA and PLA composite with banana fibers

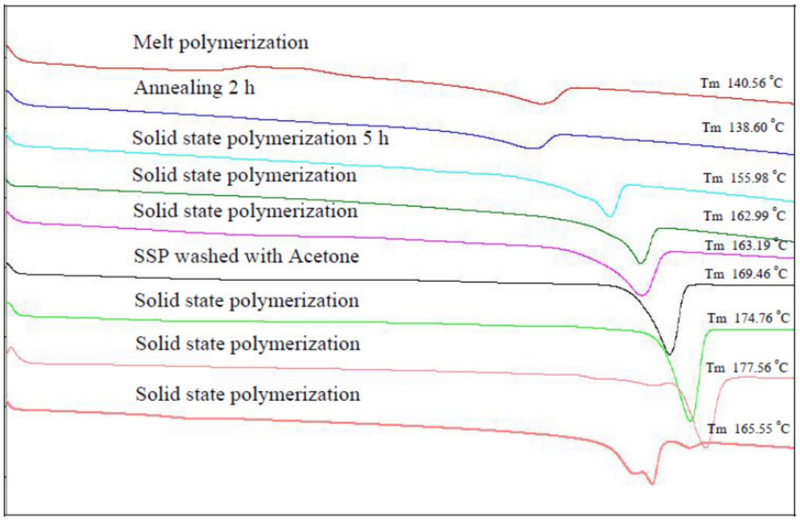

Figure A.4: Melting point temperature of PLA produced by polycondensation in function of reaction time and temperature of polymerization

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