

SCHOOL OF SCIENCE
Department of Industrial Chemistry “Toso Montanari”

Second cycle degree in

**Low Carbon Technologies and Sustainable
Chemistry**

Classe LM-71 - Scienze e Tecnologie della Chimica Industriale

**Study of the absorption of organic
compounds on biopolymers**

Experimental degree thesis

CANDIDATE

Francesca Martino

SUPERVISOR

Prof. Luca Bernardi

CO-SUPERVISOR

Prof. Matteo Minelli

Dott. Giacomo Foli

TABLE OF CONTENTS

Abstract	10
Chapter 1. Introduction	11
1.1 Objective	11
Chapter 2. Polylactic acid	14
2.1 Introduction	14
2.1.1 PLA advantages	14
2.1.2 PLA limitations	15
2.2 Structure	17
2.3 Cycle in nature.	18
2.4 Properties	19
2.4.1 Crystallinity and thermal properties	20
2.4.2 Solubility	21
2.4.3 Barrier properties	21
2.4.4 Mechanical properties	21
2.5 Synthesis	22
2.5.1 Direct condensation	23
2.5.2 Azeotropic dehydration	24
2.5.3 Ring Opening Polymerization	25
2.5.4. Comparison of Poly (Lactic Acid) Synthesis	25
2.6 Modification	26
2.6.1 Bulk modification	27
2.6.2 Surface modification	30
2.7 Processing	32
2.7.1 Injection molding	32
Chapter 3. Terpenes	34
3.1 Tested substances	36
3.1.1 α -Pinene	36

3.1.2 Linalool	38
3.1.3 L-Linalool	39
3.1.4 β -Citronellol	40
Chapter 4. Fundamental of mass transport	41
4.1. Mathematical approach to evaluate mass transfer	41
4.1.1 Solubility	45
4.1.2 Diffusivity	46
4.2 Equipment	49
4.3.1 Differential scanning calorimetry (DSC)	49
4.3.2 High Performance Liquid Chromatography (HPLC)	52
4.3.3 Soxhlet extractor	58
Chapter 5. Experimental Part	60
5.1 Materials	60
5.1.2 Introduction	60
5.1.3 PLA – Ingeo 4060D	61
5.1.4 PLA – Ingeo HP3100	61
5.2 PLA films preparation and thermal treatment	62
5.3 Gravimetric methods: determination of absorption kinetics and transport parameters of terpenes on PLA	63
5.4 Analysis	66
5.4.1 Evaluation of the thermal history of PLA films: DCS	66
	69
5.4.2 Evaluation of a possible enantiomeric excess of absorbed liquid: HPLC	69
Chapter 6. Results	70
6.1 Absorption kinetics of terpenes on poly (L-lactic acid) (PLLA)	70
6.2 Absorption of terpenes on poly (D, L-lactic acid) (PDLLA)	73
6.3 Solubility	74

6.3.1 PDLLA _____	74
6.3.2. PLLA _____	75
6.4 Diffusivity _____	76
6.4.2 PLLA _____	77
6.5 Comparison between PLLA and PDLLA _____	79
<i>Chapter 7. Conclusion</i> _____	81
<i>Bibliography</i> _____	83

LIST OF FIGURES

Figure (1). Applications of PLA	16
Figure (2). Stereoisomers of lactic acid.	17
Figure (3). Form of PLA: poly L-lactic acid (PLLA), poly D-lactic acid (PDLA) and poly D,L- lactic acid (PDLLA).	17
Figure (4). PLA cycle in nature.	18
Figure (5) Synthesis methods for Poly(Lactic Acid) [7].	23
Figure (6). Schematics of block copolymer structures: (a) diblock; (b) triblock; (c) alternating multiblock; (d); dendrimer-like copolymer; (e) star-like copolymer. [11]	30
Figure (7). Schematic illustration of entrapment process.	31
Figure (8). Major components of an injection molding machine showing the extruder (reciprocal screw) and clamp units [13].	33
Figure (9). Isoprene structure.	34
Figure (10). Isoprene units.	35
Figure (11). a. α -pinene. b. β -pinene.	37
Figure (12). Linalool.	38
Figure (13). a. (R)-(-)-linalool. b S-(+)-linalool.	38
Figure (14). β -Citronellol.	40
Figure (15). (S)-(-)-Citronellol. b (R)-(+)-Citronellol.	40
Figure (16). Permeation of small molecules from a higher to a lower chemical potential membrane or film side [19].	42
Figure (17). Diagram of diffusion through a polymer membrane.	47
Figure (18). Differential scanning calorimeter [24].	49
Figure (19). Schematic cooling (1) and heating (2) DSC curves of a typical polymer. [24].	50
Figure (20). Overview of HPLC [27].	53
Figure (21). HPLC Flow Diagram [26].	55
Figure (22). An example of HPLC separation [26].	56
Figure (23). Chromatogram and related terms [26].	57
Figure (24) Soxhlet extraction apparatus [29].	59

Figure (25). Example of absorption kinetic.	64
Figure (26). DSC curve of PDLLA.	67
Figure (27). DSC curve of PLLA.	68
Figure (28). Absorption kinetics of α -Pinene on PLLA.	70
Figure (29). Absorption kinetics of Linalool on PLLA treated at (95°C).	71
Figure (30). Absorption kinetics of Linalool on PLLA treated at 80°C.	71
Figure (31). Absorption kinetics of β -Citronellol on PLLA.	72
Figure (32). Absorption kinetics of L-Linalool on PLLA.	72
Figure (33). Absorption kinetics of α -Pinene on PDLLA.	73
Figure (34). Absorption kinetics of Linalool on PDLLA.	73
Figure (35). Absorption kinetics of β -Citronellol on PDLLA.	74
Figure (36). Solubility values for the tested substances in PDLLA.	75
Figure (37). Solubility values for the tested substances in PLLA.	76
Figure (38). Diffusivity values of terpenes in PDLLA.	77
Figure (39). Diffusivity values of terpenes in PLLA.	78

LIST OF TABLES

<i>Table (1). Effects of stereochemistry and crystallinity on mechanical properties [8].</i>	22
<i>Table (2). Advantages and disadvantages of different polymer synthesis methods.[8]</i>	26
<i>Table (3). Organic and inorganic fillers for the preparation of PLA composites. [11]</i>	29
<i>Table (4). Some terpenes and the plants they can be isolated from.</i>	36
<i>Table (5). Properties of α-pinene</i>	37
<i>Table (6). Properties of Linalool.</i>	39
<i>Table (7). Properties of L-Linalool.</i>	39
<i>Table (8). Properties of Citronellol.</i>	40
<i>Table (9) Typical material and application properties of Ingeo 4060D</i>	61
<i>Table (10). Typical material and application properties of Ingeo HP3100.</i>	62
<i>Table (11). PDLLA: a) Thermal treatment executed; b) crystallinity degree; c) data obtained from DSC analysis</i>	67
<i>Table (12). PLLA: a) Thermal treatment executed; b) crystallinity degree; c) data obtained from DSC analysis.</i>	69
<i>Table (13) sorption terpenes in PDLLA: solubility and diffusivity results obtained.</i>	80
<i>Table (14) Sorption of terpenes in PLLA: solubility and diffusivity results obtained.</i>	80

Abstract

This work has been conducted in order to determine the solubility and diffusion coefficients of different aromatic substances in two different grades of polylactic acid (PLA), Amorphous (PDLLA) and Crystalline (PLLA); in particular the focus is on the following terpenes: Linalool, α -Pinene, β -Citronellol and L-Linalool.

Moreover, further analysis, have been carried out with the aim to verify if the use of neat crystalline PLA, (PLLA), a chiral substrate, may lead to an enantioenrichment of absorbed species in order to use it as membrane in enantioselective processes.

The other possible applications of PLA, which has aroused interest in carry out the above-mentioned work, concerns its use in food packaging.

Therefore, it is interesting and also very important, to evaluate the barrier properties of PLA, focusing in particular on the transport and absorption of terpenes, by the packaging and, hence, by the PLA.

PLA films/slabs of one-millimeter thickness and with square shape, were prepared through the Injection Molding process.

On the resulting PLA films heat pretreatment process of normalizing were then performed to enhance the properties of the material.

In order to evaluate solubility and diffusion coefficient of the different penetrating species, the absorption kinetics of various terpenes, in the two different types of PLA, were determined by gravimetric methods.

Subsequently, the absorbed liquid was extracted with methanol (MeOH), non-solvent for PLA, and the extract analyzed by the use of High Performance Liquid Chromatography (HPLC), in order to evaluate its possible enantiomeric excess . Moreover, PLA films used were subjected to differential scanning calorimetry (DSC) which allowed to measure the glass transition temperature (T_g) and to determine the degree of crystallinity of the polymer (X_c).

Chapter 1. Introduction

1.1 Objective

The aim of this thesis is to determine the solubility and diffusion coefficients of different aromatic substances in two different grades of polylactic acid (PLA), Amorphous (PDLLA) and Crystalline (PLLA); in particular the focus is on the following terpenes:

- Linalool
- α -Pinene
- β -Citronellol
- L-Linalool

Moreover, further analysis, as reported below, have been carried out with the aim to verify if the use of neat crystalline PLA, (PLLA), a chiral substrate, may lead to an enantioenrichment of absorbed species. Therefore, a possible application is to use it as membrane in enantioselective processes in order to separate chiral compounds into their individual enantiomers.

The other possible applications of PLA, which has aroused interest in carry out the above-mentioned work, concerns its use in food packaging.

Food packaging represents a key factor in food preservation, used both as a simple container and, increasingly, as a means of reducing the rate of qualitative decay of the product, protecting it from microbiological and chemical contamination.

Among the various polymers that can be used for this purpose, PLA is certainly one of the most used. Therefore, in order to evaluate its application in the food field, it is interesting and also very important, for the achievement of the prefixed objectives, to evaluate the barrier properties of PLA, focusing in particular on the transport and absorption of terpenes, by the packaging and, hence, by the PLA.

Poly(lactic acid) (PLA) is a thermoplastic aliphatic polyester made up of lactic acid (2-hydroxy propionic acid) building blocks. Lactic acid has one stereocenter; hence two optically active stereoisomers are possible: L-lactic acid and D-lactic acid. PLA can be produced starting from pure L-lactic and D-lactic isomers, leading to the optically active homopolymers of poly-L-lactic acid (PLLA) and poly-D-lactic acid (PDLA), respectively. Furthermore, if a racemic mixture of L- and D-monomers is employed, poly-D, L-lactic acid (PDLLA) copolymer is obtained. The stereochemistry has a relevant impact on material properties, in particular on the degree of crystallinity. PLLA and PDLLA, employed in this study, are, in fact, semi-crystalline and amorphous polymer, respectively, and could possibly lead to enantio-enrichment of absorbed species.

PLA films/slabs of one-millimeter thickness and with square shape, were prepared through the Injection Molding process.

This process involves heating and injection, under pressure, of polymeric material, in this case PLA, into a closed metal mould. The melted PLA, cools and hardens in the shape inside the mould, which then opens to allow the material to be ejected for inspection or secondary operations.

Heat pretreatment process of normalizing, on the resulting PLA films, were then performed to enhance the properties of the material such as relieving internal stresses, improving toughness and uniform thermal history.

Normalizing is a three-step heat treatment process in which the material, being a semi-crystalline thermoplastic polymer, is firstly heated above its glass transition temperature (usually in a vacuum oven) after which the material is soaked in the temperature over a sufficient period for transformation to occur and finally it is taken out from the furnace and allowed to cool in atmosphere / room temperature [1].

Since two different types of PLA were used, heat treatments, performed on the specimens, have been optimized in order to ensure the repeatability of the measurements. PDLLA was treated under vacuum for one hour at a temperature of 80°C, while PLLA was treated overnight at a temperature of 95°C.

In order to evaluate solubility and diffusion coefficient of the different penetrating species, the absorption kinetics of various terpenes, in the two different types of PLA, were determined by gravimetric methods.

PLA films were thus immersed in the selected terpenes and, through the use of an analytical balance, the increase in mass over time was evaluated, until equilibrium is reached. The films were weighed at regular time intervals. Before being weighed, each film was dabbed with absorbent paper in order to remove excess liquid.

Once equilibrium was reached, absorbed liquid was extracted with methanol (MeOH), non-solvent for PLA, and the extract analyzed by analytical method, in order to evaluate a possible enantiomeric excess of absorbed liquid. In particular, High Performance Liquid Chromatography (HPLC) has been used to separate, identify and quantify each component of a mixture.

Moreover, PLA films used were subjected to differential scanning calorimetry (DSC) which allowed to measure the glass transition temperature (T_g) and to determine the degree of crystallinity of the polymer (X_c).

P(L, D-LA) and P(L-LA) were analyzed after heat treatment.

Chapter 2. Polylactic acid

2.1 Introduction

Poly lactide or else poly (lactic acid), PLA, is an aliphatic thermoplastic polyester extensively researched and utilized thanks to the wide range of its potential applications.

It is one of the most promising bioplastics because of its attractive mechanical properties, low emission of greenhouse gases, low amount of energy used for production, and high industrial production capacity.

Moreover, the methods for processing PLA are well-established polymer manufacturing techniques used for other commercial polymers such as PS and PET.

PLA is biobased, compostable and renewable; thus, it has been considered to be a promising alternative of petrochemical-derived polymers. In fact, it has found use in many applications for example in packaging, e.g., from packaging of electronic product to tableware and water cups, in biomedicine and pharmaceuticals and more lately in 3D printing.

However, there are numerous specific areas in which PLA exhibits in general some disadvantages such as poor melting strength, a low degradation rate, limited toughness etc.

Solutions for overcoming these disadvantages have been discussed in recent years. Enhancing the toughness of PLA, for example, has been systematically attempted by various strategies and technologies, such as by blending PLA with other polymers, modifying it with plasticizers, or reinforcing it by the addition of properly chosen nanofillers [2,3].

2.1.1 PLA advantages

- Eco-friendly — PLA derived from renewable resources (e.g., corn, wheat, or rice), is biodegradable, recyclable, compostable and for this reason it can help to reduce the dependence, of our society, on fossil fuels [4]. Moreover,

its production also consumes carbon dioxide [5]. Such characteristics make PLA an attractive biopolymer.

- **Biocompatibility** — is the most attractive aspect of PLA especially for the biomedical applications. PLA, when implanted in living organisms, hydrolyzes to its constituent α -hydroxy acid, then is incorporated into the tricarboxylic acid cycle and excreted. PLA degradation products, namely H₂O and CO₂, are non-toxic (at a lower composition) making it a natural choice for biomedical applications [5] including sutures, clips, and drug delivery systems (DDS).
- **Processibility** — PLA has better thermal processibility compared to other biopolymers such as poly (hydroxy alkanooates) (PHAs), poly (ethyene glycol) (PEG), etc. PLA can be processed by film casting, extrusion, blow molding, and fiber spinning.
- **Energy savings** — Compared to petroleum-based polymers, PLA requires 25–55% less energy to be produced, data that can be further improved in the future. It is also important to note that, for PLA production, the total amount of water required is competitive with the best performing petroleum-based polymers [4]. This energy-saving feature perfectly caters to the new concept of “low-carbon economy” which, recently emerged, response to the global warming and energy crisis concerns, making investment in PLA a necessary and wise strategy in the future [4].

PLA is, therefore, an eco-friendly bioplastic characterized by an excellent biocompatibility, processibility, and less energy dependence. In spite of all these advantages it shows some drawbacks as well, that limit its use in specific applications.

2.1.2 PLA limitations

- **Poor toughness** — PLA is a very brittle material with less than 10% elongation at break. For this reason, its use in the applications that need plastic deformation at higher stress levels, is limited.

- Slow degradation rate — PLA degrades through the hydrolysis of backbone ester groups. The degradation rate depends on the PLA crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content [6]. The slow degradation rate is often considered to be an important selection criterion for biomedical applications and serious problem to disposal of consumer commodities.
- Poor chemical modifiability — PLA is chemically inert with the lack of side-chain reactive groups that make its surface and bulk modifications a challenging task.

In figure 1 the main fields of PLA application are summarized. Taking into account the disadvantages of PLA stated above, it is not surprising that, in the past, PLA has not received the attention it deserves. Nevertheless, as reported in the following paragraphs, several methods have been examined in order to improve these properties and to expand its field of application.

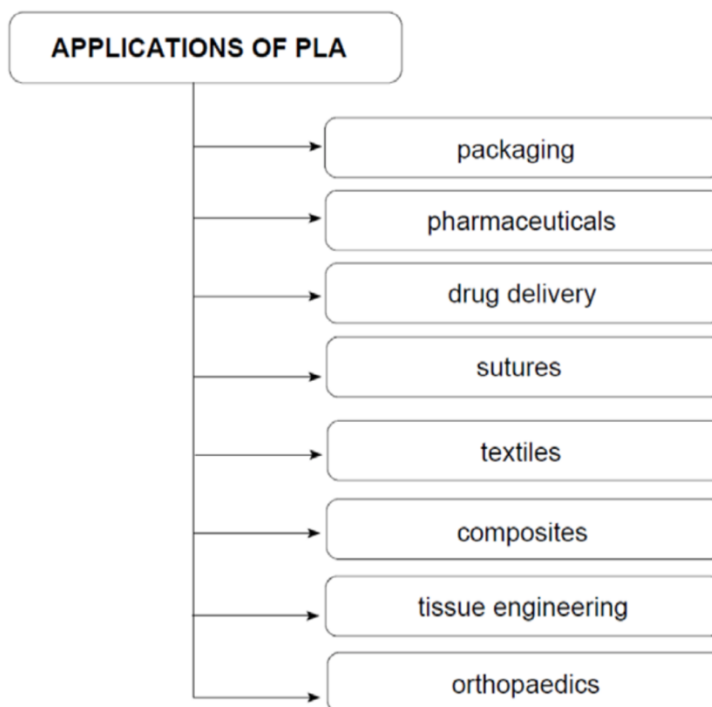


Figure (1). Applications of PLA

2.2 Structure

The basic building block for PLA is lactic acid, which was first isolated in 1780 from sour milk by the Swedish chemist Carl Wilhelm Scheele and first produced commercially in 1881.

Lactic acid (2-hydroxy propionic acid) is the simplest hydroxy acid with an asymmetric carbon atom; hence two optically active stereoisomers are possible: L-lactic acid and D-lactic acid (Figure 2).

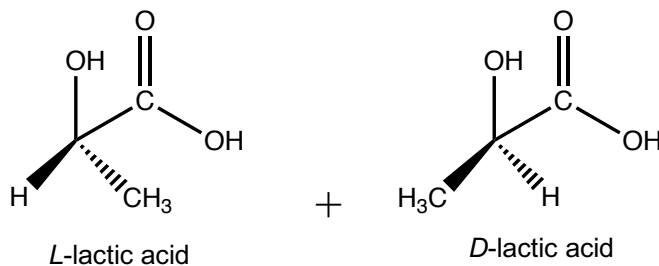


Figure (2). Stereoisomers of lactic acid.

L-lactic acid is produced in humans and mammals, a combination of both is produced in bacteria. Lactic acid is, however, also produced from corn, beet, sugarcane, etc, by bacterial fermentation of carbohydrates.

According to its structure, in particular on the L- and D-Lactic acid fraction, PLA can be categorized into three types, poly L-lactic acid (PLLA), poly D-lactic acid (PDLA) and poly D, L- lactic acid (PDLLA), if a racemic mixture of L- and D-stereoisomers is employed. (Figure 3).

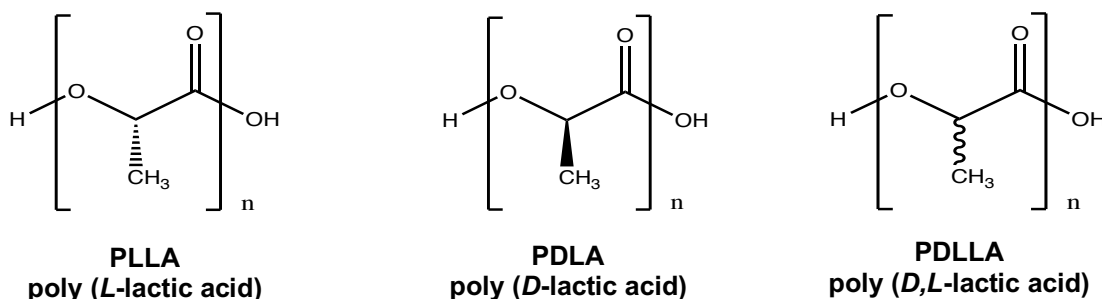


Figure (3). Form of PLA: poly L-lactic acid (PLLA), poly D-lactic acid (PDLA) and poly D,L-lactic acid (PDLLA).

2.3 Cycle in nature.

The production of PLA, as reported in the previous paragraph, presents four most attractive advantages that are renewability, biocompatibility, processability, and energy saving.

The natural cycle of PLA, shown in figure (4), starts with the photosynthesis in order to obtain the raw material (agricultural products) that is then subjected to the extraction of starch.

Through the simple process of hydrolysis, it is possible to obtain sugar from starch, that is then purified from any residue and is prepared for the next steps.

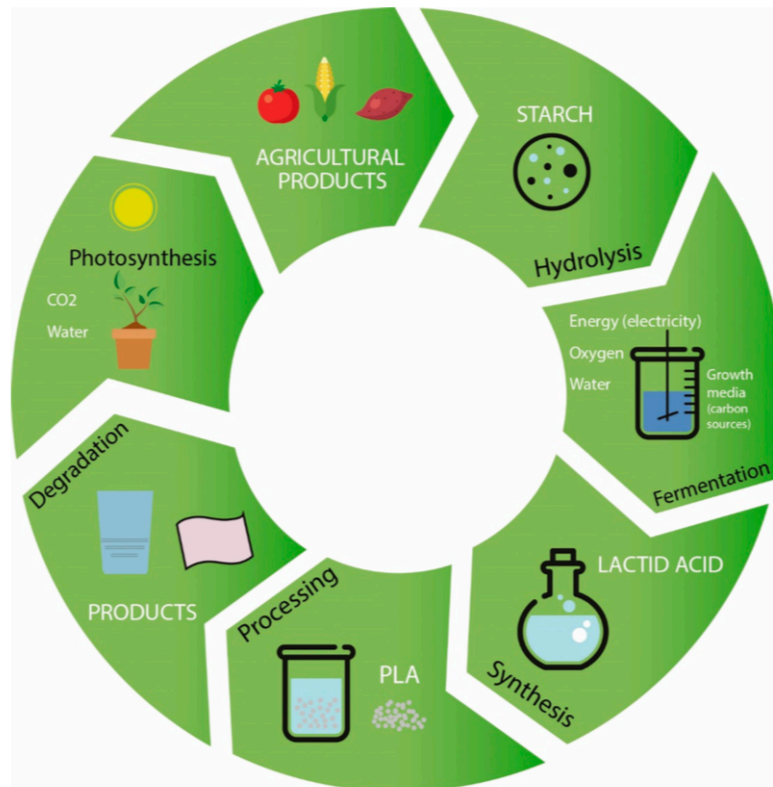


Figure (4). PLA cycle in nature.

Through a simple fermentation and distillation, lactic acid is obtained. This is the basic constitutional unit of PLA and can be manufactured by carbohydrate fermentation or chemical synthesis. Lactic acid (2-hydroxy propionic acid), as reported in paragraph 2.2 exists in two optically active configurations, the L(+) and D(-) isomers (Figure 2).

The majority of lactic acid is made by bacterial fermentation of carbohydrates through which, both L-(+) and D-(-) isomers are obtained. It is also produced by mammalian, however in this case only the L-(+) isomer is generate.

According to the type of bacteria used, bacterial fermentation processes can be classified in heterofermentative and homofermentative.

Heterofermentative bacteria are a type of lactic acid bacteria that, during the glucose fermentation, other than the lactic acid as the main product, produce a significant amount of other metabolites such as acetic acid, ethanol, glycerol, mannitol and carbon dioxide during the glucose fermentation.

On the contrary, homofermentative bacteria produce only lactic acid as a primary by-product in glucose fermentation. Consequently, since homofermentative pathways lead to greater yields of lactic acid and lower levels of byproducts, are mainly used by industry [6].

Nowadays the majority of the fermentation processes use a genus of *Lactobacilli*, classified as homofermentative, which yields to a high rate of lactic acid. These bacteria require general processing conditions include a pH of 5.4 – 6.4, a temperature of 38 – 42 °C and a low oxygen concentration [6].

Once lactic acid is obtained, through polymerization, it is first generated in the granular form and then further processed to be used as a basic component for the production of plastics and fibers for industrial use (PLA).

During the process, plants absorb CO₂ and release oxygen. Therefore, if on the one hand the production process emits carbon dioxide, on the other, using agricultural products, absorbs it.

In this way the cycle is closed making the process sustainable.

2.4 Properties

Properties of PLA essentially depend on some of its characteristics, such as molecular weight, stereochemistry, as well as on the processing conditions by which the melting point, the degree of crystallinity and the mechanical strength are particularly affected.

2.4.1 Crystallinity and thermal properties

In the solid state, PLA can be either amorphous or semicrystalline, depending on the stereochemistry and thermal history.

The degree of crystallinity, for a polymer, is a very important property that refers to the amount of crystalline region in the polymer with respect to amorphous content, determined by the proportion between D- and L-lactide in the polymer.

The degree of crystallinity, then, influences many properties among which the tendency of the polymer to give degradative hydrolysis. In fact, it has been shown that a highly crystalline PLA takes months, if not years, to be completely degraded to lactic acid, while an amorphous polymer can be degraded in a few weeks. This is due to the water impermeability of the crystalline region.

Crystallinity is strongly related to the glass transition temperature (T_g) since it reduces chain mobility of the neighboring amorphous regions; consequently, a growth of the crystal phase fraction leads to a corresponding increase in T_g .

Therefore, T_g is a very important property to take into consideration when considering polymers for a particular commercial application. This is because, above the T_g , PLA passes from a rigid glassy state to a rubbery softer one, while below the T_g , it behaves as a glass so, as a brittle polymer. The typical PLA glass transition temperature (T_g) ranges from 50°C to 80°C. This is because the glass transition temperature (T_g) of amorphous PLA ranges between 55 to 60 °C and is a function of the PLA molecular weight and stereochemistry while in semicrystalline PLA, the T_g is higher (60–80 °C) and depends on the crystallization conditions that determine both the morphology of the crystalline/amorphous phases and the degree of crystallinity [25].

Regarding the melting temperature, it ranges from 130°C to 180°C, but there are differences due to the different composition of PLA. In fact, PLA produced from L-lactide (PLLA) presents a melting temperature (T_m) that ranges between 170 °C and 180 °C, whose variation depends on the presence of impurities and a certain, albeit minimal, racemization.

In both poly-D lactic acid (PDLA) and poly-D, L-lactic acid (PDLLA), instead, irregularities within the chain, that cause disorganization, are introduced. In this

way, the tendency to crystallize is limited preventing the formation of perfect crystals and thus lowering the T_m .

Both of these transitions, T_g and T_m , are strongly affected by overall optical composition, primary structure, thermal history, and molecular weight.

2.4.2 Solubility

The solubility of lactic acid-based polymers is strongly dependent on the molecular weight, degree of crystallization, and whether other monomeric units are present in the polymer. In general, PLLA is soluble in chlorinated or fluorinated organic solvents while racemic-based PLA or PLA with high percentages of D- lactide are soluble in other organic solvents such as acetone, pyridine, xylene, ethyl acetate and others.

Lactic acid-based polymers are not soluble in water, alcohols (e.g., methanol, and ethanol) and alkanes (e.g., hexane and heptane).

2.4.3 Barrier properties

Because PLA finds a lot of applications in food packaging, its barrier properties (mainly to carbon dioxide, oxygen and water vapour) have been largely investigated [7]. The diffusion takes place mainly through the amorphous regions of a polymer, so an increase in the extent of crystallization will inevitably result in a decrease in permeability.

The analysis of the influence of crystallinity on the transport properties of gases and vapors through polymeric films, therefore, is very important from theoretical and technological point of view [7]. The permeability of a polymeric materials is determined by absorption and diffusion, and it strongly correlated to the solubility of the sample, parameters that will be discussed in the following chapters.

2.4.4 Mechanical properties

The mechanical properties of lactic acid-based polymers can be varied to a large extent ranging from soft and elastic plastics to stiff and high strength materials.

When higher mechanical properties are desired, semicrystalline PLA is preferred over the amorphous ones [8].

Mechanical properties and crystallization behavior of PLA are very dependent on the molecular weight and stereo chemical makeup of the backbone [9].

In Table 1 the effects of stereochemistry and crystallinity on the mechanical properties of amorphous L-PLA, annealed L-PLA, and amorphous D, L-PLA, are listed.

Annealing is a heat treatment process used in order to alter the material properties.

In this type of process, the polymer is thermally treated below its glass transition temperature, for a certain time before cooling, in order to relieve the internal stresses introduced during its fabrication (molding, cooling after molding, machining, etc.)

The ability to control the stereochemistry allows precise control over the speed and degree of crystallinity, the mechanical properties, and the processing temperatures of the material.

Table (1). Effects of stereochemistry and crystallinity on mechanical properties [8].

Properties		Annealed		
		PLLA	PLLA	PDLLA
Tensile strength	MPa	59	66	44
Elongation at break	%	7	4	5.4
Modulus of elasticity	MPa	3750	4150	3900
Yield strength	MPa	70	70	53
Flexural strength	MPa	106	119	88
Unnotched izod impact	J/m	195	350	150
Notched izod impact	J/m	26	66	18
Rockwell hardness		88	88	76
Heat deflection temperature	°C	55	61	50
Vicat penetration	°C	59	165	52

2.5 Synthesis

PLA synthesis is a multi-stage process that begins with the production of lactic acid and ends with its polymerization.

In the Figure 3 it is possible to observe the three main methods for PLA synthesis.

The lactic acid can be polymerized with direct condensation that leads to the obtainment of a fragile polymer, with low molecular weight and poor mechanical properties.

Another way to polymerize PLA is the azeotropic dehydration condensation of the lactic acid, a process that allow to obtain high molecular weights without the use of external agents.

Finally, the third way is the Ring Opening Polymerization (ROP), the most industrially used, by which high molecular weight PLA is produced.

Currently, direct polymerization and ring opening polymerization are the most used production techniques.

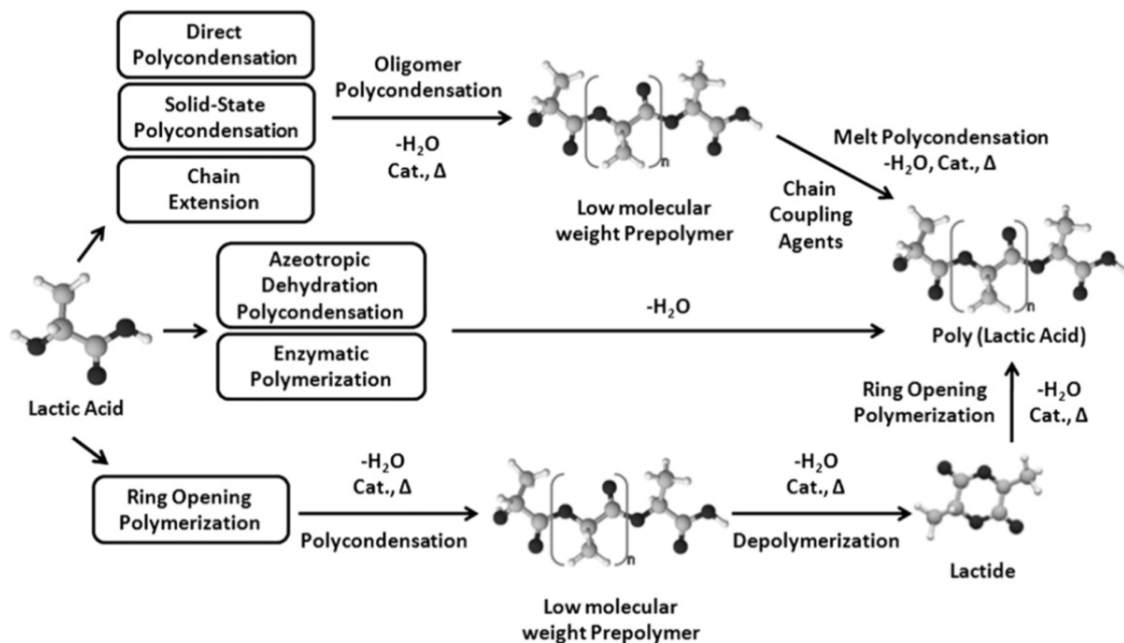


Figure (5) Synthesis methods for Poly(Lactic Acid) [7].

2.5.1 Direct condensation

Lactic acid direct condensation was the first method used to produce PLA and is also the least expensive route and easiest method to obtain it.

PLA production is carried out by connecting carboxyl and hydroxyl groups, present on the lactic acid monomer, with the production of water byproduct simultaneously.

Due to the difficulty in removing byproducts completely from the highly viscous reaction mixture, polymer produced through direct polycondensation is usually of low molecular weight ($<50,000 \text{ g}\cdot\text{mol}^{-1}$) and low quality [10].

In order to increase the molecular weight of the polymer, it is possible to use adjuvants that promote esterification or agents that promote chain extension. However, this involves an increase in both cost and process complexity, as well as the inclusion of external agents that must be carefully evaluated depending on the final scope of material use.

In order to overcome this main disadvantage, newly developed methods have been proposed.

2.5.2 Azeotropic dehydration

Azeotropic dehydration is a direct method for synthesis of high molecular weight PLA, therefore does not require the use of external agents as in the previous process.

In this route, the removal of water formed from the reaction medium becomes relatively easier. This is possible by the use of an aprotic solvent at high boiling temperature that, through the azeotropes formation, facilitates the removal of water from the system and allow to obtain polymer with a high molecular weight, even above $300,000 \text{ g/mol}$.

For this type of reaction, a temperature of $130 \text{ }^\circ\text{C}$ and reaction times of 30-40 hours are required.

Moreover, in order to obtain a satisfactory degree of polymerization, the catalyst concentration must be high.

However, in this way, a subsequent purification is necessary to avoid problems of degradation or hydrolysis in subsequent processing.

2.5.3 Ring Opening Polymerization

Ring-opening polymerization (ROP) is the most commonly route to achieve high molecular weight [11].

The first step of the process involves the lactose purification by the removal of water under moderate conditions and without the use of solvent. The product is a low molecular weight pre-polymer.

In the second step of the process, the pre-polymer is then depolymerized with the use of a catalyst in order to obtain a mixture of lactides.

Finally, in the third step of the process, the lactide is polymerized in a ring-opening reaction without the use of solvents.

The result is PLA with controlled molecular weight and, moreover, by controlling residence time and temperatures in combination with catalyst type and concentration, it is possible to control the ratio of D-and L-lactic acid units in the final polymer.

The polymerization mechanism involved can be ionic, coordination, or free-radical, depending on type of catalyst employed.

Numerous studies have examined the influence of different factors on the polymerization of lactide, such factors can be the concentration and type of catalyst, monomer purity, and temperature.

However, particular attention has been paid to the catalyst.

Currently the most widely used catalyst for the ring-opening polymerization of lactides is tin octanoate, but numerous novel efficient metal-free catalytic systems are emerging as valuable alternatives [12].

The problem of heavy metal-based catalysts is that they can contaminate the product, complicating the purification of the PLA obtained, and consequently, also limiting its applications in the fields of food packaging and biomedicine.

2.5.4. Comparison of Poly (Lactic Acid) Synthesis

In summary, polycondensation is the most used process to produce PLA with low molecular weight, using basic equipment and process. In contrast, ring opening polymerization leads to the production of a wider range of molecular

weight polymer by controlling the purity of lactide and its polymerization. Therefore, the selection of a specific method to produce PLA, should be based on the application, since each approach has its unique advantages and limitations. For example, in drug release materials, the use of low molecular weight PLA is preferred, as it could be degraded quickly. While for packaging and textile products, high molecular weight PLA is suitable.

The advantages and disadvantages of different methods are summarized in Table 2.

Table (2). Advantages and disadvantages of different polymer synthesis methods.[8]

Method	Advantages	Disadvantages
Azeotropic polycondensation	Low cost	Low yield
	Basic equipment	Low purity (usually with residual solvent and byproducts in polymer)
	Moderate temperature (<180 °C)	Solvent waste and pollution
Solid state polycondensation	High purity (suppression of side reactions)	Low yield
	High molecular weight	Long duration
	Moderate conditions	Complicated operation
Ring opening polymerization	High purity	Low overall yield
	Wide range of molecular weight (2×10^4 to $6.8 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$) [56]	Long duration
	Availability in high molecular weight	Demanding condition
	Controlled polymer properties	Complicated operation

2.6 Modification

The major drawbacks of PLA, as reported in paragraph 2.1, are its poor chemical modifiability, poor mechanical ductility, slow degradation rate and poor hydrophilicity.

In order to expand the field of application of PLA, it can be modified mainly concerning two aspects: bulk properties and surface chemistry.

2.6.1 Bulk modification

Biomaterials must possess bulk properties, in particular hydrophilic and mechanical properties, meeting special requirements [12]. Critical factors that influence these characteristics include chemical components, compositions and morphological structure.

In bulk modification of PLA, the focal points on which the researcher are concentrated, are the variety and number of hydrolytic groups, the flexibility and crystallinity of molecular chains, and the hydrophilic groups.

Blending, plasticization, composition and copolymerization method belong to this category.

- **Blending**

This method is effective, simple and versatile and allow to develop new materials with tailored properties without synthesizing new polymers.

In this way the properties of different polymers (biodegradable and non-biodegradable), such as poly (ethylene glycol) (PEG), poly(β -hydroxybutyrate) (PHB), poly(ϵ -caprolactone) (PCL), poly (butylene adipate-co-terephthalate) (PBAT), chitosan, and starch can be combined by blending with PLA.

Particularly blends of PLA with low-density polyethylene (LDPE), poly (vinyl acetate) (PVA), and polypropylene (PP) have been examined, while blends with biodegradable polymers have not been as extensively studied.

The blends obtained have shown better resistance to biodegradation and hydrolysis, but most of this are immiscible and, due to low interfacial adhesion between the polymer phases, display poor mechanical properties. Therefore, synthesis of new polymers, biodegradable or non-biodegradable, that can be compatibly blended with PLA, will represent an important objective in the future.

- **Plasticization**

PLA is a glassy polymer, rigid and brittle at room temperature (RT) due to its $T_g \sim 55\text{ }^\circ\text{C}$, with poor elongation at break (typically less than 10%).

Potentially, for most of the rigid objects, PLA fulfills the packaging industry's requirements but for the purpose of use it also as soft films, it needs to be plasticized.

Indeed, developing packaging materials requires high flexibility at room temperature and thus, there is no tolerance for the polymer film tearing or cracking when subjected to stresses during package manufacturing or use [12].

This has been achieved by the use of plasticizers, with low molecular weight, high boiling point and low volatility, that allow to lower the T_g and, therefore, increase the ductility and softness of PLA.

Other relevant requirements for these applications are transparency, low crystallinity and desired barrier properties.

- **Composites**

In order to enhance the thermal stability, the hydrolysis resistance, or the mechanical properties of PLA it is possible to use fibers as fillers in the formation of PLA composites. It has been demonstrated that the mechanical properties, for PLA composites prepared with natural and modified cellulose fibers, scale with the mass fraction of added fibers. In this way it is also possible to minimize their cost, tailor their biodegradability, and broaden their areas of application.

A comparison between some of the organic and inorganic material used as PLA fillers is shown in table 3.

Table (3). Organic and inorganic fillers for the preparation of PLA composites. [11]

Type	Filler	Result
Organic	Jute	Tensile stress and modulus increase with fiber volume fraction
	Flax fibers	Composite strength about 50% higher than for PP/flax composites
	Kenaf fibers	Greatly improved crystallization rate, tensile and storage moduli
	Bamboo fibers	Increased bending strength and improved thermal properties
	Silkworm silk fibers	Good wettability, increased elasticity modulus and ductility
	Microcrystalline cellulose	Poor mechanical properties and adhesion; increased storage modulus
	LA-modified microcrystalline cellulose	Higher tensile strength and elongation at break than neat PLA
	Acetylated bacterial cellulose	Considerable improvement in thermal and mechanical properties
Inorganic	Calcium metaphosphate	Narrow pore size distribution and high tensile strength
	Calcium carbonate	No brittle fracture behavior and comparably high bending strength
	Montmorillonite	Good affinity and improved thermal stability of the nanocomposites
	HAP	Improved elastic modulus and unchanged bending strength
	Carbon nanotubes	Dramatic enhancement in thermal and mechanical properties
	Nano/Micro-silica	Increased tensile strength, thermal stability, and hydrolysis resistance

- **Copolymerization**

PLA has carboxyl and hydroxyl groups that make possible its copolymerization with other monomers.

This can be done through polycondensation with lactone-type monomers such as ϵ -caprolactone, from which low molecular weight copolymers are obtained. Alternately, to produce high molecular weight copolymers, another method used is the ring-opening copolymerization of lactide with other cyclic monomers including glycolide, δ -valerolactone, and trimethylene carbonate, as well as with monomers like ethylene oxide (EO).

The hydrophobicity and crystallinity of the copolymers can be increased for low to moderate comonomer contents.

Block copolymers are formed by long sequences, also called blocks, of the same monomer unit, covalently bound to sequences of a different type.

Copolymers can have different structures according to the type of connection between different blocks, as shown in figure 6.

An example are PLA and PEG (polyethylene glycol) copolymers.

Diblock PLA-PEG and triblock PLA-PEG-PLA copolymers allow to modify the biodegradation rate, the hydrophilicity, and the mechanical properties of the copolymers; those PLA-PEG multi-block used to tailor phase separation; finally, to lower the T_g , T_m , and the crystallinity of the materials, star- and dendrimer-like PLA-PEG copolymers have also been synthesized [11].

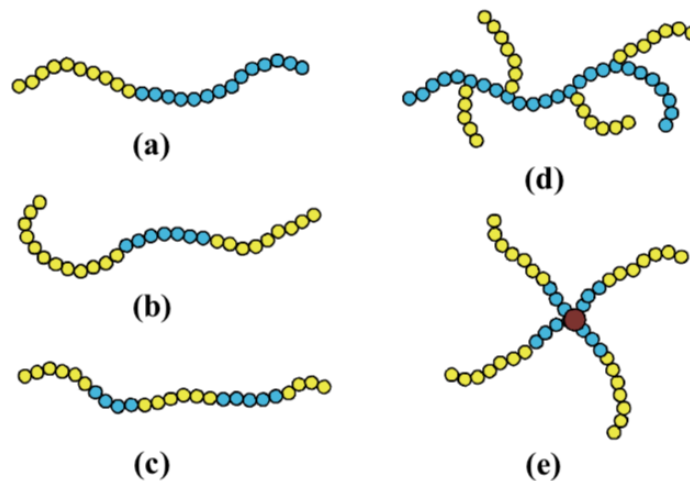


Figure (6). Schematics of block copolymer structures: (a) diblock; (b) triblock; (c) alternating multiblock; (d); dendrimer-like copolymer; (e) star-like copolymer. [11]

2.6.2 Surface modification

The surface properties of materials, such as hydrophilicity, roughness, surface energy, and topography, play a key role in determining their applications.

Different strategies of surface modification have been examined.

- **Entrapment**

This is a simple yet effective method, in which, as illustrated in figure 7, modifications are performed by incorporating altering species into the polymer surface region using the reversible swelling property in a categorical

solvent/non solvent substrate [13]. Therefore, the entrapment of modifying (e.g., PEG, alginate, gelatin, etc.) species requiring no specific functional groups in the polymer chains, as the modifying molecules accumulate merely on the surface of the material without modifying its bulk properties.

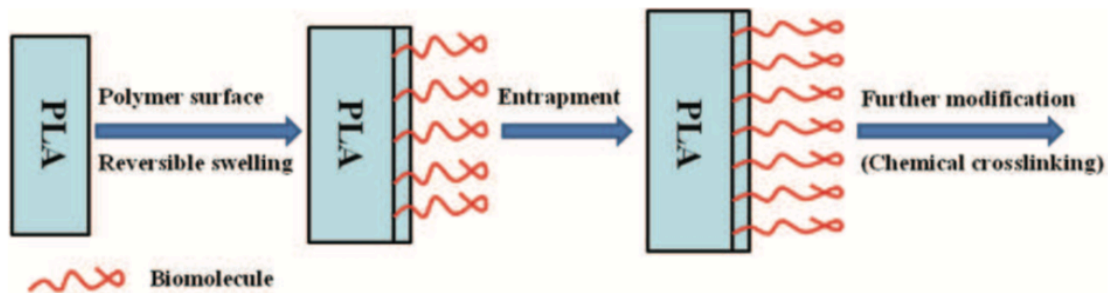


Figure (7). Schematic illustration of entrapment process.

- **Plasma treatment**

Plasma treatment are widely utilized to improve the hydrophilicity and cell affinity of PLA surfaces.

The advantages of this treatment, compared with other surface modification methods, are its ability to control the surface structure, energy and charge, and to uniformly modify the surface having no impact on bulk properties [11]. However, the effectiveness of the surface modification is partially lost due to surface rearrangement.

This is because the surface-modifying species, due to thermally activated macromolecular motions to minimize the interfacial energy, rearrange making the effect of plasma treatment non-permanent.

It was found that the modifying effects could be maintained by preserving samples at a low temperature (0–4 ° C), as the mobility of surface molecular chains decreases at temperatures much less than the T_g of PLA (55 ° C).

However, this approach might not be practical since this temperature range (0–4 ° C) is much lower than physiological as well as room temperature.

Another disadvantage of this treatment is that it can affect degradation of PLA that increases with an increase of plasma power and treatment time. These issues, related to non-permanent surface modification, potentially make it unsuitable for certain biomedical and consumer applications.

2.7 Processing

The methods for processing PLA are well-established polymer manufacturing techniques used for other commercial polymers such as PS and PET.

The main technique used for PLA production is the melt processing in which the PLA resin obtained is converted into end products such as consumer goods, packaging, and other applications. During the melting processing, the material is heated above its melting temperature, then the molten polymer is shaped into desired shapes, and finally is cooled to stabilize its final dimensions.

PLA is a hygroscopic material and very sensitive to the combined effect of high relative humidity (RH) and temperature, hence, before it can be processed, it should be dried to a water content less than 100 ppm (0.01%, w/w) to avoid hydrolysis (Mw reduction).

Once that the PLA resin is properly dried, the most important technique used for continuous processing of consumer goods of PLA of high Mw is the extrusion.

2.7.1 Injection molding

The first step in processing PLA is the extrusion in a heated screw.

The heat to melt the resins is provided by the extruder by the presence of heater bands wrapped around the barrel; however, the majority of heat input is provided by the friction of the resin between the screw and the barrel (Figure 8)

The molten polymer is injected by the screw into the mold cavities.

At the start of the process the molds close and the nozzle opens while the screw moves forward in order to inject the molten polymer into the mold cavity.

The polymer shrinks during cooling and for this reason, with a constant pressure, the screw is maintained in the injection position. Then, the nozzle is

closed, and the screw starts retracting, while the part continues to be cooled in the mold.

Injection molding is the most widely used converting process for thermoplastic articles, especially for those that are complex in shape and require high dimensional precision.

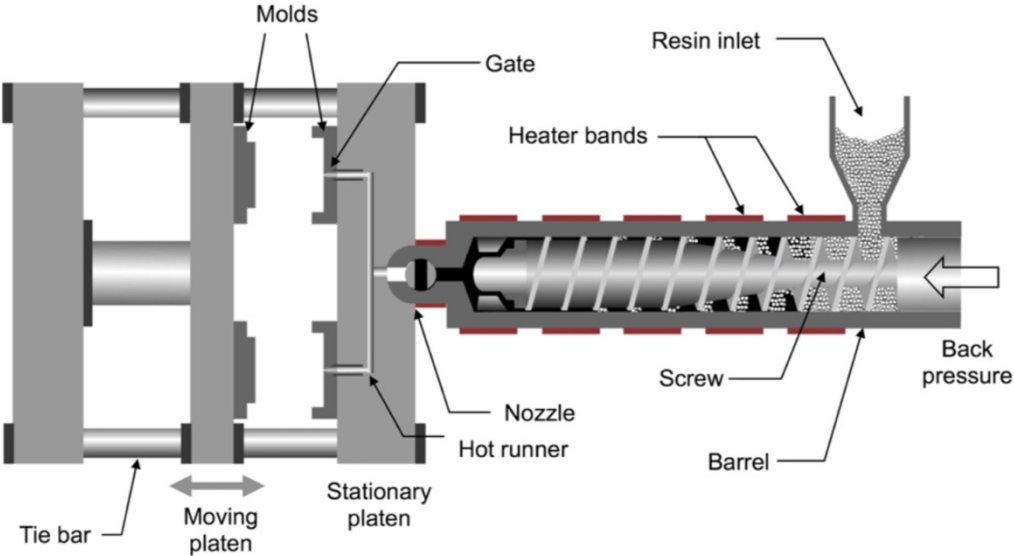


Figure (8). Major components of an injection molding machine showing the extruder (reciprocal screw) and clamp units [13].

Chapter 3. Terpenes

Terpenes are a large class of organic compound obtained from natural product and characterized by a remarkable structural diversity.

Natural products are isolated from different natural sources such as plants, animals, microbes and insects, but the focus of this work is on plant terpenes.

Plants are able to produce primary and secondary metabolites exploited by humans for their beneficial role in several applications. Primary metabolites, which include amino acids, simple sugars, nucleic acids, and lipids, are necessary for cellular processes. Secondary metabolites include compounds not essential for the growth of the microorganisms and often produced as defense strategy by the microbe producing them.

To date, about 8,000 terpenes and 30,000 terpenoids are known in the literature [14].

Despite both terms are sometimes used interchangeably, terpenes are simple hydrocarbons, while terpenoids are modified class of terpenes with different functional groups and oxidized methyl group moved or removed at various positions.

The structure of terpenes is based on repetition of isoprene units, each of which contain an isopropyl group defined as “head” and an ethyl residue defined as the “tail” (Figure 7). In terpenes, isoprene units are mostly condensed head-to-tail.

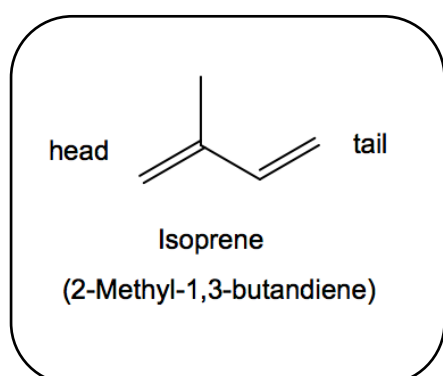


Figure (9). Isoprene structure.

According to the number of isoprene units, terpenes are classified in hemiterpenes (C_5), monoterpenes (C_{10}), sesquiterpenes (C_{15}), diterpenes (C_{20}), sesterterpenes (C_{25}), triterpenes (C_{30}), tetraterpenes (C_{40}) and polyterpenes (C_n) with n greater than 8 as reported in Figure 10.

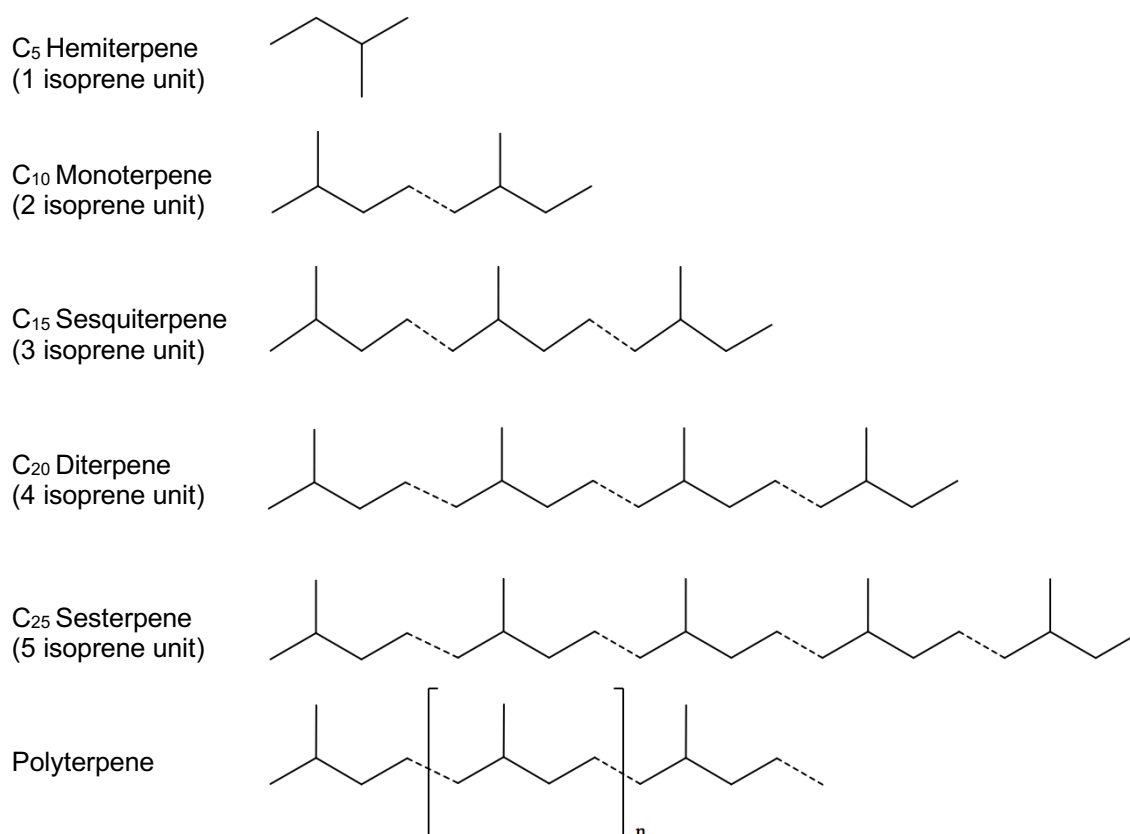


Figure (10). Isoprene units.

Terpenes are found in the resins of many plants as shown in the Table 4. The biological and biochemical functions of terpenes in plants are still under investigation. It is known that many plants produce terpenes to attract insects for pollination or in order to protect themselves from being eaten by certain animals.

Table (4). Some terpenes and the plants they can be isolated from.

Substance	Plant
Pinenes	Coniferous trees, terebinth
Limonene	Citric fruits (e.g. lemon, orange)
Citronellal	Citronella, eucalyptus
Citral	Lemongrass
Geraniol	Geranium
Citronellol	Citronella
Menthol	Peppermint
Eugenol	Clove
Linalool	Lavender

Pharmaceutical, food, agricultural, and chemical industries have exploited them for their potentials and effectiveness as medicines, flavor enhancers, pesticides, and fine chemicals, respectively [15]

In order to protect the environment, increasingly important nowadays, and due to the development of green chemistry, solvent use is to be avoided as much as possible.

An optimal alternative to petroleum solvents, in many industrial applications, could be the use of green solvents as terpenes, with extraordinary technical and chemical properties, recognized as environmentally safer.

3.1 Tested substances

3.1.1 α -Pinene

α -pinene, together with β -pinene, are the two isomers of pinene (Figure 11) and are among the best-known representatives of a broad family of monoterpenes.

Pinene is a bicyclic, double bond, terpenoid hydrocarbon [16].

α - and β -pinene are found in nature mainly in pine (coniferous trees) essential oils (EOs), but also in rosemary and orange peels.

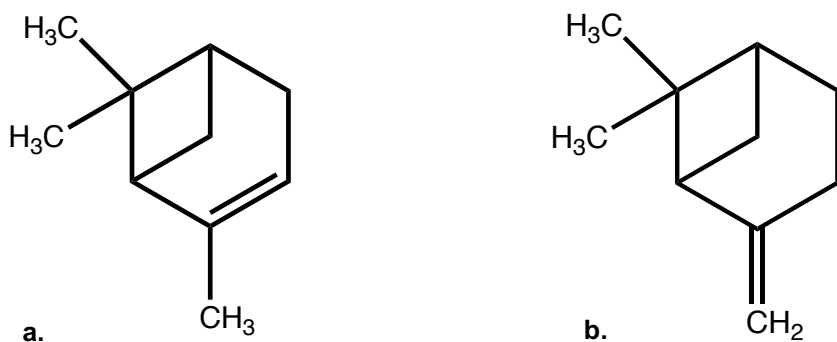


Figure (11). a. α -pinene. b. β -pinene.

They exhibit diverse biological activities, leading it to various applications and uses such as fungicidal agents, flavors, fragrances, and antiviral and antimicrobial agents [16].

Moreover, it is also used as antibacterial due to their toxic effects on membranes.

In this work the focus is on α -pinene, the tested substance, whose main properties are summarized in Table 5.

Table (5). Properties of α -pinene

Empirical Formula (Hill Notation)	$C_{10}H_{16}$
Molecular Weight	136.23 g/mol
Boiling point	155-156 °C
Density	0.858 g/ml (25 °C)
Vapour pressure	500 Pa (25 °C)

3.1.2 Linalool

Linalool (Figure 12), a naturally occurring acyclic monoterpene alcohol, is found in numerous aromatic plants, mainly in the families Lamiaceae (mint and other herbs), Lauraceae (laurels, cinnamon, rosewood), and Rutaceae (citrus fruits).

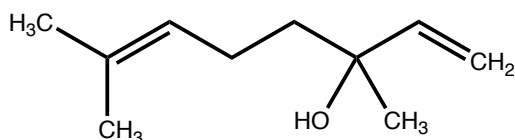


Figure (12). Linalool.

Linalool naturally exists in two isomeric configurations, (*S*)-(+)-linalool and (*R*)-(-)-linalool, depending on the configuration of the chiral carbon in position 3 (Figure 13).

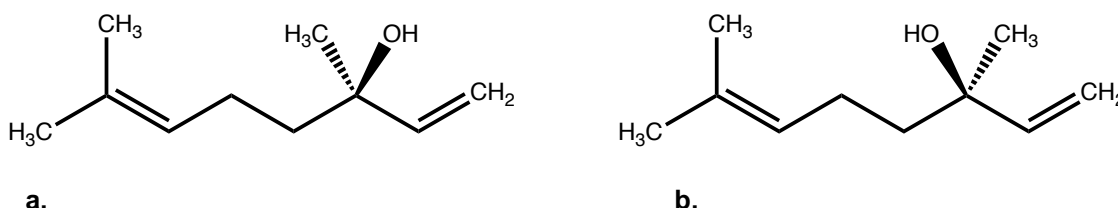


Figure (13). a. (*R*)-(-)-linalool. b. *S*-(+)-linalool.

Linalool exists in the plant essential oil as pure *S* or pure *R* isoform or as a racemic mixture (*SR*); however, many studies demonstrated that the *R* isomers are more common than the *S* ones [17].

Linalool possesses numerous pharmacological activities including analgesic, anxiolytic, sedative, anti-inflammatory, and antibacterial ones and it is often used in aromatherapy as natural relaxant.

It is also used as a scent in hygiene products and cleaning agents, including soaps, detergents, shampoos, and lotions.

Additionally, linalool is used by pest professionals as insecticide and some repellent products.

The main properties of linalool are shown in Table 6.

Table (6). Properties of Linalool.

Empirical Formula (Hill Notation)	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}=\text{CH}_2$
Molecular Weight	154.25 g/mol
Boiling point	194-197 °C
Density	0.87 g/ml (25 °C)
Vapour pressure	0.17 mmHg (25 °C)

3.1.3 L-Linalool

L-linalool or (*R*) - (-) -linalool (Figure 13), as reported in the previous paragraph, is one of the two enantiomers of linalool.

The properties of pure L-linalool differ only slightly from that of the racemate mixture and are reported in the Table 7.

The choice of using L-linalool was made in order to evaluate a possible enantio-enrichment of the absorbed species by the materials used, in particular PLLA, envisioning its possible applications in enantioselective membrane process.

Table (7). Properties of L-Linalool.

Empirical Formula (Hill Notation)	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}=\text{CH}_2$
Molecular Weight	154.25 g/mol
Boiling point	198 °C
Density	0.862 g/ml (25 °C)
Vapour pressure	0.20 mmHg (25 °C)

3.1.4 β -Citronellol

β -Citronellol (Figure 14) is an alcoholic monoterpene found in essential oil such as lemon grass, citronella grass and bushy matgrass and it is used as a flavoring agent in food and beverages due to its pleasant smell properties.

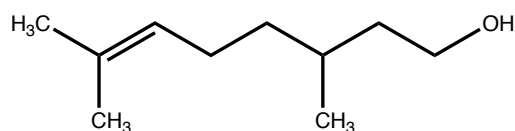


Figure (14). β -Citronellol.

The β -citronellol has a chiral center at carbon 3 and, for this reason, presents two isomeric forms that both occur in nature, (*R*)-(+)-isomer and (*S*)-(-)-isomer (Figure 15).

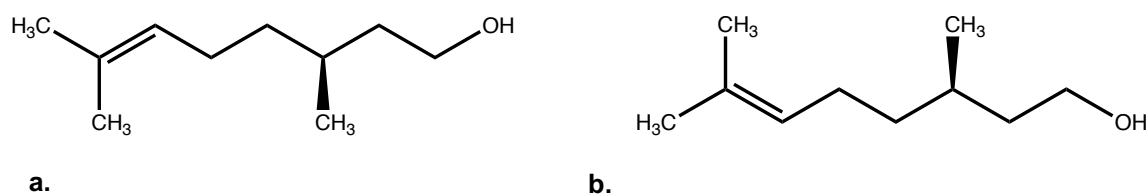


Figure (15). (*S*)-(-)-Citronellol. b (*R*)-(+)-Citronellol.

The main properties of citronellol are shown in Table 8.

Table (8). Properties of Citronellol.

Empirical Formula (Hill Notation)	$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$
Molecular Weight	156.27 g/mol
Boiling point	222 °C
Density	0.857 g/ml (25 °C)
Vapour pressure	~ 0.02 mmHg (25 °C)

Chapter 4. Fundamental of mass transport

Mass transfer properties play a crucial role in the research, development, and applications of polymers.

PLA, like any other polymer, is permeable to gases, vapors, liquids, including organic compounds, which may impact its end-use performance.

PLA barrier properties are affected by the enantiomer compositions of lactic acid, L-lactic acid and D-lactic acid. This is because, different configurations of lactic acid can result in PLA with different crystallinity and thermal properties.

On the other hand, temperature affects the mass transfer properties of PLA. The increase in temperature can enhance the diffusion of gases and vapors, resulting in glass to rubber transition, plasticization, and deterioration of a polymer [19].

Consequently, to improve the properties of PLA, modifications such as blending with other polymers, incorporation of additives, formation of composites and nanocomposites, are necessary. However, this may impact mass transfer properties of PLA in different ways.

So, a comprehensive understanding of the factors affecting PLA mass transfer properties is critical.

4.1. Mathematical approach to evaluate mass transfer

In the mass transfer through membranes, small molecules I (i.e., permeants) permeate through a polymer from high to low chemical potential (μ_i) in order to maintain thermodynamic equilibrium. The difference in μ_i is the fundamental driving force for mass transfer through polymers [19].

For a permeant i , its chemical potential, μ_i , can be expressed as:

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (1)$$

where μ_i^0 is the chemical potential of the permeant i at a standard state, R is the universal gas constant, T is temperature in Kelvin, and a_i is the chemical activity.

Permeation in polymers consists of three steps [20] (Figure 18):

- a. Sorption
- b. Diffusion
- c. Desorption.

The first step (a) refers to the sorption of the permeant into the polymer matrix from the high concentration side. The second (b) regards the diffusion of the permeant through the polymer matrix along the concentration gradient towards the low concentration side. In the latter step (c) the penetrant is desorbed or evaporate from the low concentration surface.

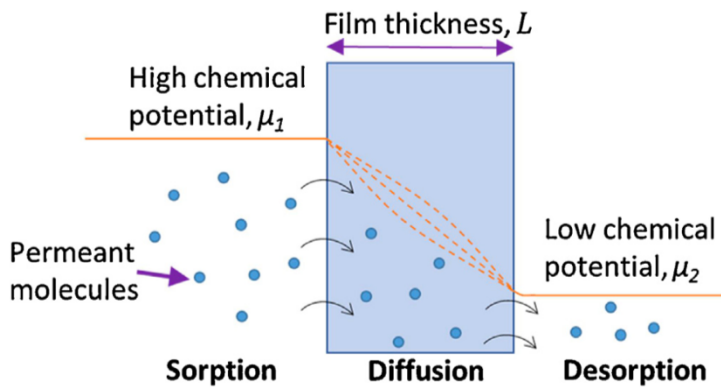


Figure (16). Permeation of small molecules from a higher to a lower chemical potential membrane or film side [19].

Assuming that in a polymeric membrane the diffusion of the permeant takes place only in x direction, from a mass balance point of view, the process can be described by Fick's first law of diffusion that shows a relationship between the flux (J) and the concentration gradient:

$$J = -D \frac{dc}{dx} \quad (2)$$

in this equation, D is the diffusion coefficient, c is the concentration and dc/dx is the concentration gradient in the direction of the flow.

Eq. (2) can be used when the permeant concentration does not change with time, this means at steady state.

The flux at steady state is defined as the amount of the permeant that passes through a surface of unit area per unit time:

$$J = \frac{q}{At} \quad (3)$$

where q is the amount of permeant, A is the area of the polymeric film, and t is the time.

At steady state, the permeant concentration, c_1 and c_2 , high and low concentration respectively, is constant on both sides of the film. Therefore, the equation (2) can be integrated across the total thickness of the film (L), resulting in:

$$J = D \frac{(c_1 - c_2)}{L} \quad (4)$$

Then, replacing J according to the equation (3), q can be describes as follow:

$$q = D \frac{(c_1 - c_2)At}{L} \quad (5)$$

When the permeant is a gas, it is more convenient to measure the partial pressure (p) of the gas that is in equilibrium with the polymer, rather than the concentration. At sufficiently low concentration and when the interaction between the permeant and the polymer is small, Henry's law is applied, and c is expressed as follow:

$$c = Sp \tag{6}$$

where (S) is the solubility coefficient of the permeant in the polymer. Then, assuming no interaction between the permeant and the polymer, Equation (5) can be expressed as:

$$q = DS \frac{(p_1 - p_2)At}{L} \tag{7}$$

which, can be rearranged as:

$$DS = \frac{qL}{(p_1 - p_2)At} \tag{8}$$

Introducing the permeability, P , of the permeant at steady state:

$$P = \frac{qL}{At\Delta p} \tag{9}$$

Therefore, from Equations (8) and (9), permeability can be expressed as the product of the diffusion coefficient D and the solubility coefficient S :

$$P = DS \tag{10}$$

Equations (8) and (9) are very simplistic and can be applied to penetrants in rubbery polymers that, at low concentration, typically show Fickian behavior. In contrast, for glassy polymers, due to their restricted polymer chain mobility, permeation phenomena may deviate from this relationship. Therefore, during the unsteady state portion of the mass transfer, the permeation process is described by Fick's second law [21]:

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad (11)$$

Where the first term of the equation is the rate of change of permeant concentration.

In the case in which there is a strong interaction between the penetrant and the polymer, D depends on time, position and concentration, and the equation (11) can be solved numerically. In contrast, when D is independent from time, position and concentration, the equation (11) can be rewritten as follow:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (12)$$

Therefore, diffusivity and solubility coefficient, are very important parameters to know, in order to evaluate the permeation coefficient. This is because the first indicates how fast the penetrant can penetrate in the polymer while the second, solubility coefficient, is an indication of how similar polymer and penetrant are.

4.1.1 Solubility

Solubility coefficient is a term that express the penetration and dispersion of a compound within the polymer matrix considered, hence, it is directly related to the absorption of such compound in the polymer.

On the other hand, solubility, a thermodynamic parameter, is a measure of how much penetrant can dissolve in the polymer at given condition.

Experimentally, the solubility coefficient (S) for a permeant within a polymer matrix can be calculated as follow:

$$S = \frac{M_{\infty}}{v p} \quad (13)$$

where M_{∞} is the total mass of permeant absorbed by the polymer during the absorption process, p is the partial pressure of the permeant, expressed in pascals, and v is the volume of the polymer film. This equation is used to calculate the solubility coefficient, in processes of permeation of vapors containing the chemical species of interest.

In processes where the permeant species, containing the molecule of interest, is a liquid the solubility coefficient is calculated as follow:

$$S = \frac{M_{\infty} - M_0}{V_0} \quad (14)$$

Where M_{∞} indicates the mass of the polymer at equilibrium, while M_0 and V_0 are, respectively, the mass and the volume of the polymer at the start of the process.

4.1.2 Diffusivity

Diffusion is the process by which matter, as result of random molecular motions, is transported from one part to another of a system.

As mentioned previously, in order to evaluate the permeability of a permeant it is necessary to assess the mechanism by which the substance diffuses within the membrane, therefore the diffusivity.

The flux of a substance through a polymer membrane is described by the Fick's first law of diffusion, reported in the paragraph 4.1 (equation 2), where the flux is function of gradient concentration.

Referring to a substance A, for example a terpene, this difference in concentration, c_{A0} and c_{AI} , where $c_{A0} > c_{AI}$, at the ends of the polymer membrane, is the driving force that generates the diffusive flow of component A (Figure 17) c_{A0} .

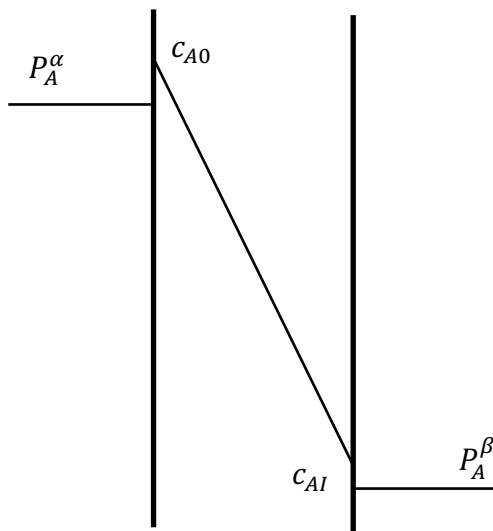


Figure (17). Diagram of diffusion through a polymer membrane.

Summarizing, the first Fick's law provides information regarding the flux of a substances through a polymer membrane along a given direction as a function of concentration.

While, in order to evaluate the diffusive flux variation or that of concentration of a component A, as function of the time as well, the second Fick's law have to be considered (equation 12).

In particular a diffusive process of molecules within a polymer film, object of this work, will be considered.

Suppose, hence, that an infinite sheet of uniform material of thickness $2l$ is placed in a solution and that the solute is allowed to diffuse into the sheet [22].

At this point, the boundary conditions for the resolution of Fick's second law that must be considered are reported in the following equations:

$$\frac{dc_A}{dt} = D \frac{d^2c_A}{dx^2} \quad (15)$$

$$t = 0, \quad -l < x < l, \quad C_A = C_{A,0} \quad (16)$$

$$t > 0, \quad \pm l, \quad C_A = C_{A,I} \quad (17)$$

where $C_{A,0}$ is the concentration of the species A, within the polymer, at time zero while $C_{A,I}$ is the concentration at the interface between polymeric film and permeant species.

The system presented above has been solved as follows [22]:

$$\frac{C - C_{A,0}}{C_{A,t} - C_{A,0}} = 1 - \left(\frac{4}{\pi^2}\right) \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \cdot \exp\left\{\frac{-D_A(2n+1)\pi^2 t}{4l^2}\right\} \cdot \cos\frac{(2n+1)\pi x}{2l} \quad (18)$$

If M_t denotes the total amount of diffusing substance which has entered the sheet at time t and M_∞ the corresponding quantity after infinite time [22], the following equation is obtained:

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot \exp\left\{\frac{-D(2n+1)\pi^2 t}{l^2}\right\} \quad (19)$$

With this equation it is possible use experimental values obtained in order to have an estimation of the diffusion coefficient of the permeant species in the polymeric film considered.

4.2 Equipment

4.3.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is the most popular thermal analysis technique, which provides accurate information, quickly and easily, about both physical and energetic properties of a material.

Differential scanning calorimeters (Figure 18) commonly have two sample positions, one for the sample under investigation and the other for a reference sample, which is often an empty crucible or one filled with an inert material [23].

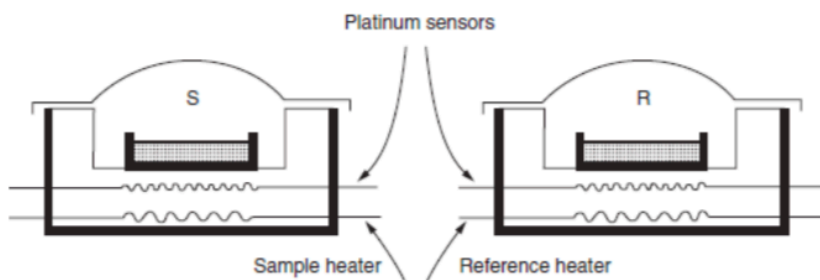


Figure (18). Differential scanning calorimeter [24].

This type of technique is based on the measurement of the difference in thermal flux, as a function of temperature, between the sample under examination and a reference while both chambers are under the same temperature program, at atmospheric pressure.

A typical DSC plots, with heat flow as a function of temperature, reveal a series of thermal effects. The actual temperature, or temperature range, at which each thermal event occurs is primarily determined by the polymer's structure.

As it is possible to observe in Figure 19, starting from the lowest temperature onward, the first discontinuity observed is the glass transition (T_g) which appears as a rounded step and which corresponds to the difference in heat capacity (ΔC_p) of the sample before and after the transition. The hysteresis peak

represents enthalpy relaxation that depends on the thermal history of the material.

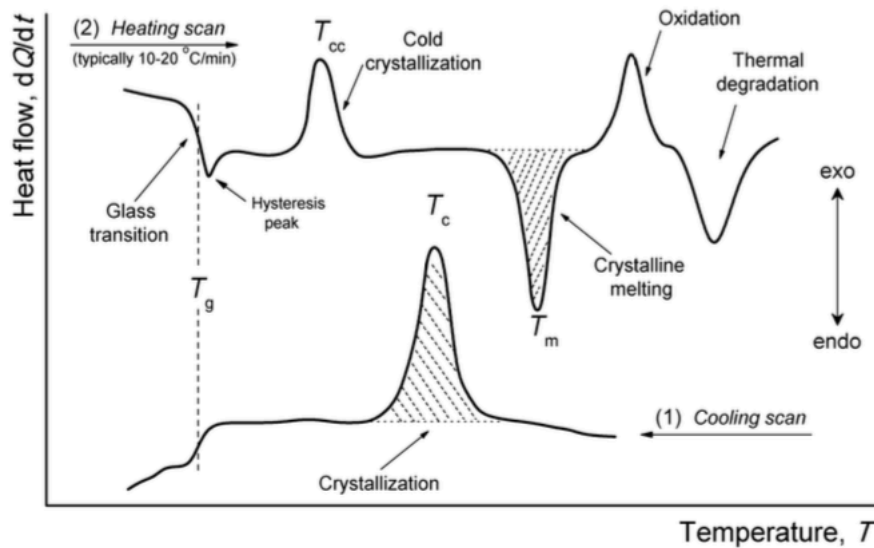


Figure (19). Schematic cooling (1) and heating (2) DSC curves of a typical polymer. [24].

After that, with the increase of temperature, it is possible to find a cold crystallization peak (T_{cc} , exothermic), which intensity depends on the ability of the sample to crystallize in the timescale of the experiment and on its history. Going on, there is a crystalline melting peak (T_m , endothermic).

Finally, at much higher temperatures, the polymer undergoes thermal degradation, resulting in main-chain scission, cross-linking, cyclization, or loss of volatile fragments [25].

In the course of heating, if the experiment is not conducted at inert atmosphere, oxidation reaction may appear.

Differential scanning calorimetry measures the heat flow entering or being released by a material, from which it is possible to calculate, at constant pressure, the heat capacity (C_p) according to the following equation:

$$C_p = (\partial q / \partial T)_p \quad (20)$$

where q is the heat input while T is the temperature.

Supposing that the temperature changes from T_0 to T_1 , the enthalpy of the reaction ΔH is:

$$\Delta H = \int_{T_0}^{T_1} C_p dT \quad (21)$$

ΔT is usually small and for this reason C_p can be considered independent of temperature.

Finally, the integral in the equation (20) is reduced obtaining the following equation:

$$\Delta H = C_p(T_1 - T_0) = C_p \Delta T \quad (22)$$

4.3.2 High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography or commonly known as HPLC is an analytical technique used to separate, identify or quantify each component in a mixture.

It can be applied to several types of sample, such as environmental, pharmaceuticals, food, forensic and industrial chemicals.

HPLC mainly utilizes a column that holds adsorbent packing material (stationary phase), a pump that moves the mobile phase(s) through the column, and a detector that shows the retention times of the molecules [26].

A brief description of these components is given below.

- **The column**

HPLC equipment uses steel or plastic columns with a length that ranges between 5 and 30 cm, and an internal diameter of 1-5 mm.

The columns are expensive and can be easily degraded by dust or by the irreversible adsorption of particles present in the sample and in the solvent. For these reasons the main entrance of the column is protected by a short guard column which is able to retain solutes and fine particles that adsorb strongly. The guard column, containing the same stationary phase as the main column and is periodically replaced.

The most common support with which the columns are filled is formed by high purity, spherical, microporous silica particles that are solvent permeable.

Most types of silica cannot be used at pHs greater than 8 because they are soluble in basic environments. Therefore, polymeric supports such as polystyrene can be used for chromatography of basic compounds with pHs ranging from 8 to 12.

- **The Pump**

The high-pressure pump generates a specified flow rate of mobile phase. It is electronically controlled and this is very important in order to have a

constant solvent flow during the analysis. Otherwise, the retention times are influenced inducing, therefore, errors in the identification of the sample.

- **The detector**

The detector, connected to the outlet end of the columns, has the role of monitor the column effluent in real time. Several types of detectors are available since sample compound characteristics can be very different. The most common is the UV-absorbance detector, useful for compounds that can absorb ultraviolet light. Another type of detector is the fluorescence detector used if the compound fluoresces. Otherwise, if the compound does not fit these characteristics, a more universal type of detector, such as an evaporative-light-scattering detector (ELSD), is used.

Once the mobile phase exits the detector it is collected as waste.

Figure 20 shows a basic overview of the HPLC process

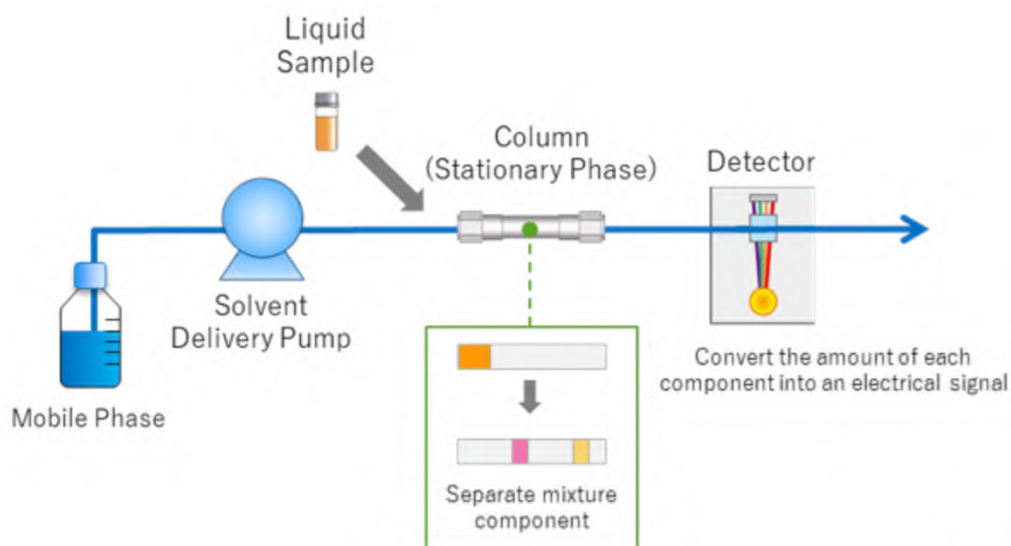


Figure (20). Overview of HPLC [27].

The separation of the sample is achieved introducing a small volume of it to the straw of the mobile phase that is then pumped in the column packed with the stationary phase. Each component in the sample interacts in a different way with

the adsorbent material due to the specific physical interactions. In this way the components of the sample are retarded, this means that they move through the column at different rates. The amount of retardation depends on the nature of the analyte and composition of both stationary and mobile phase.

At the end of the column is possible to find a detector that generates a signal proportional to the amount of sample component emerging from the column. In this way, with the help of a computer and a properly software, a quantitative analysis of the sample components ca be done.

According to the types of interactions between the analyte and the stationary phase, it is possible distinguish among different types of HPLC:

- **Normal phase chromatography**

The separation is based on the polarity. A polar stationary phase and a non-polar mobile phase are used. The polar analyte interacts with and is retained by the polar stationary phase.

- **Reversed-phase chromatography**

Is the most commonly used mode with a non-polar stationary phase and an aqueous, moderately polar mobile phase. It operates according to the principle of hydrophobic interactions, which result from repulsive forces between a polar eluent, the relatively non-polar analyte, and the non-polar stationary phase [28].

- **Size exclusion chromatography**

Molecules are separated according to the size. This technique is widely used for the molecular weight determination of polysaccharides.

- **Ion exchange chromatography**

Retention is based on the attraction between solute ions and charged sites bound to the stationary phase. Ions of the same charge are excluded [28].

Figure 20 show a basic overview of the HPLC process. Going into more detail, as it is possible to observe in the flow diagram in figure 21, an HPLC system consists of a variety of components, each of which have a specific role.

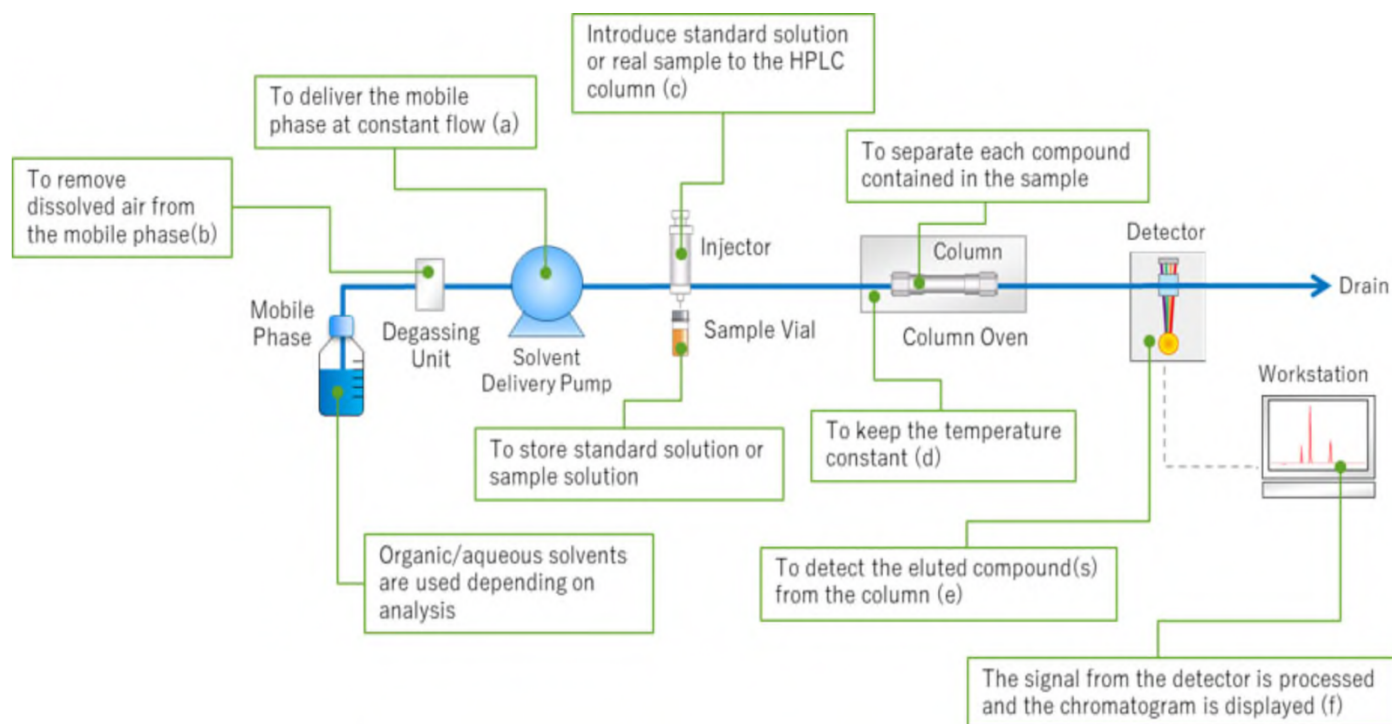


Figure (21). HPLC Flow Diagram [26].

As mentioned above, HPLC is able to separate and detect each compound according to their difference in elution rate through the column. In figure 22 an example of HPLC separation is shown.

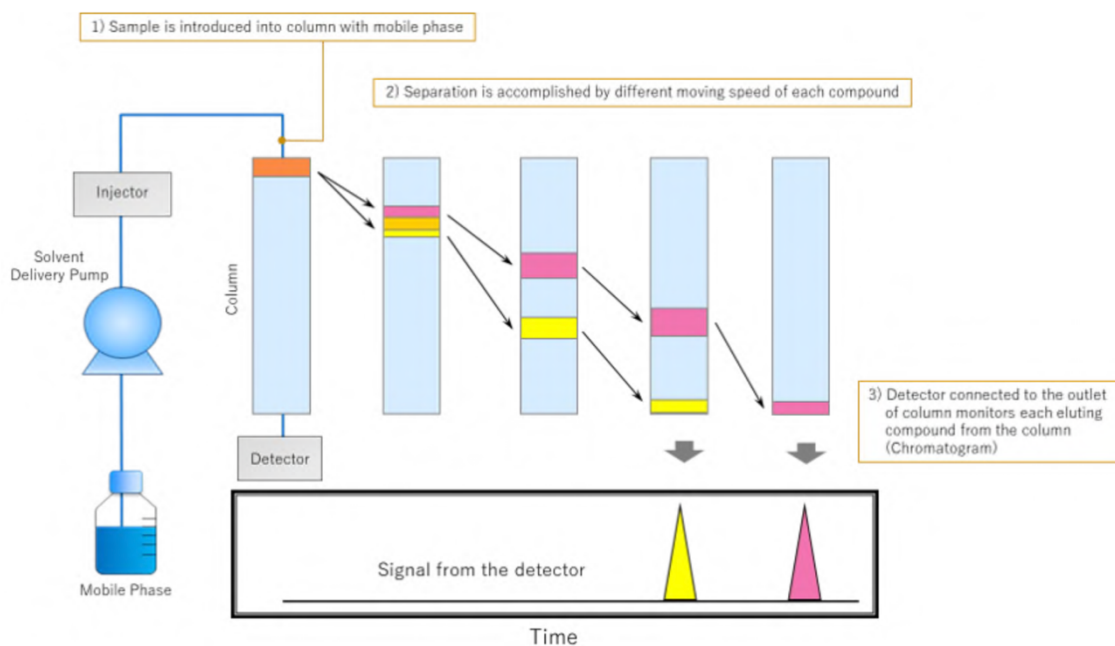


Figure (22). An example of HPLC separation [26].

There are two phases, mobile phase, that is the liquid that dissolves the target compound and the stationary one that interacts with the target compound.

The rates with which the component moves through the column with the mobile phase is directly proportional to its affinity with the mobile phase.

On the other hand, the stronger the affinity with the stationary phase, the slower it moves through the column [27].

In figure 22, the yellow component shows a strong affinity with the mobile phase e for this reason moves quickly through the column. The pink component, instead, moves slowly due to the strong affinity with the stationary phase.

Finally, as mentioned above, a detector monitors the column effluent in real time. The signal obtained in in this way processed and a chromatogram is displayed.

A chromatogram is a representation of the separation that has taken place in the column, an example is shown in figure 23.

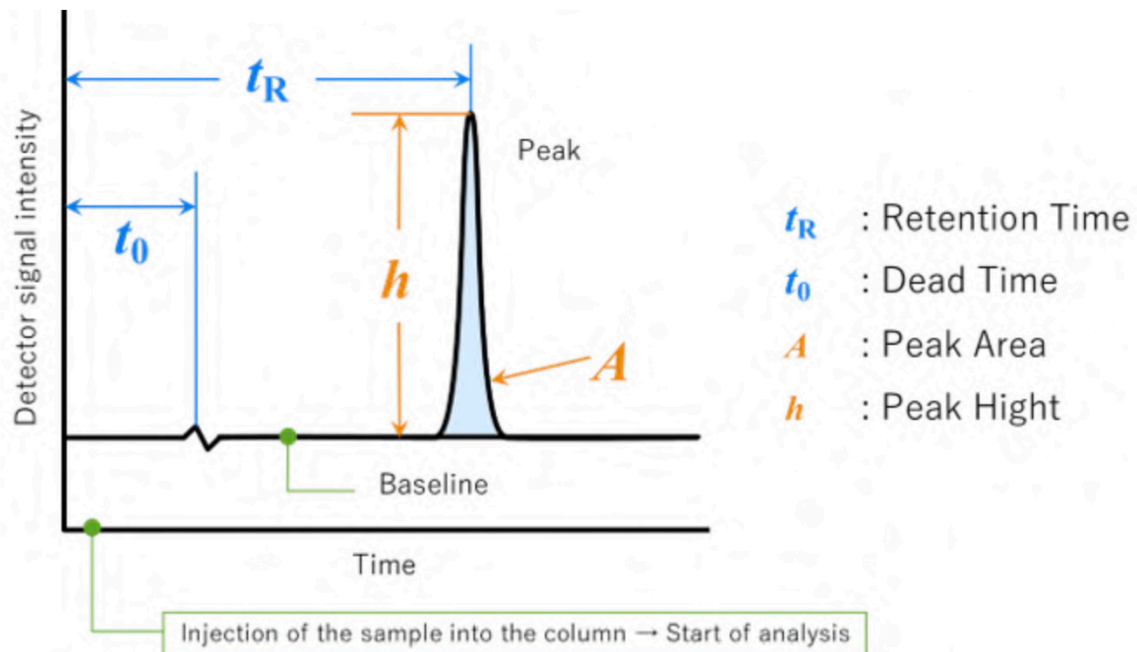


Figure (23). Chromatogram and related terms [26].

The chromatogram consists in a plot of two dimension in which the vertical axis shows the concentration in term of the detector signal intensity, while the horizontal axis is show the time of the analysis.

The baseline, a parallel line, is obtained when no compounds are eluted from the column. On the contrary, peak is obtained, representing the concentration of the target compound.

Retention time (t_R) indicates the interval of time between the injection and the apex of peak, while the t_0 , dead time, is the time required by a non-retained compound to from the injector to the detector.

The peak height (h) is the distance between a peak's apex and the baseline, and the area colored in light blue is the peak area (A). All of these results are used for the qualitative and quantitative analysis of a sample's components.

4.3.3 Soxhlet extractor

This technique was developed in 1879 by German chemist and nutritional physiologist, Franz Ritter von Soxhlet and, since then, has gained a widespread recognition in field of sample preparation [29].

The Soxhlet extractor is used for liquid-solid extractions when the compound to be extracted shows a limited solubility in the chosen solvent and the impurities are insoluble.

Solvent extraction of solid samples is one of the oldest techniques used for solid sample preparation, commonly known as 'solid-liquid extraction'.

In physicochemical terminology it is also known as leaching or lixiviation, a technique that enables to remove and separate analytes from solid matrices and also from other compounds that could interfere in the analytical process [30].

Three are the main parameters correlated to the efficiency of extraction: solubility, mass transfer and matrix effects. Consequently, it is important to consider the practical issues relating to extraction techniques, including solvent choice, matrix characteristics, liquid-solid ratio, pressure, temperature and extraction and evaporation times.

Regarding the choice of solvent, this should be done according to its ability to dissolve target analytes, not affecting the sample matrix [29]. For this reason, an important aspect is the polarity of the solvent that should be similar to that of the target analytes in the way to provide a sufficient contact with them.

This technique is widely used for several types of solid samples, particularly biological and environmental ones.

Figure 24 shows the conventional Soxhlet apparatus. It consists of a distillation flask, sample holder (thimble), siphon and condenser.

The stages that are usually involved in a Soxhlet extraction procedure are reported below.

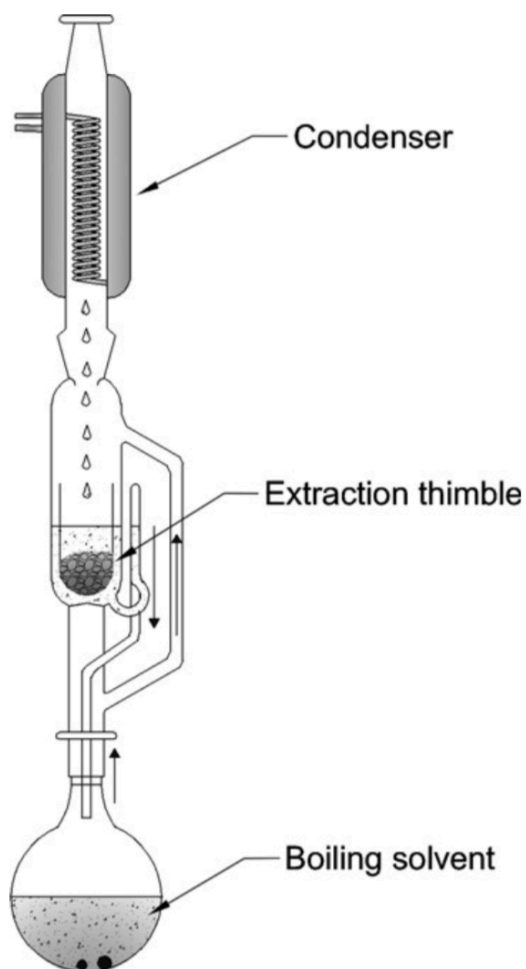


Figure (24) Soxhlet extraction apparatus [29].

The sample is first packed with a filter paper and placed in the thimble. After that, during the extraction, vapors of a fresh solvent, produced in a distillation flask, will flow through the thimble and are liquefied in the condenser.

Successively, when in the thimble the overflow level is reached, the siphon aspirates the solution, dropping the liquid back into the distillation flask. In this way the extracted analytes are carried in the bulk liquid. This operation is repeated until complete extraction is achieved.

Chapter 5. Experimental Part

5.1 Materials

5.1.2 Introduction

The PLA used in this work is of two type, both provided by NatureWorks and marketed under the Ingeo™ brand with the identifier of 4060D and HP3100. The former is a copolymer of PLA formed by 50 % of L-Lactide and 50% of D-Lactide while the second is almost entirely formed by the stereoisomer L. The 4060D, compared to HP3100, crystallizes with difficulty.

NatureWorks, with the use the best available technology, look at transform greenhouse gases into a range of polylactic acid performance.

In particular, today, they are focused on the use of plants like corn, cassava, sugar cane or beets that are able to capture and sequester CO₂ and finally to transform it into long-chain sugar molecules.

The first step in the production of PLA is a grinding process at which plants are subjected in order extract starch (glucose). Subsequently, enzymes are added and, through hydrolysis, glucose is converted into dextrose. Microorganisms then ferment this dextrose into lactic acid.

Then, a proprietary two-step process is carried out to transform lactic acid molecules into a lactose ring.

Finally, during the polymerization process, the lactose ring is opened and linked together with the aim to form the long chain of polylactide polymer called Ingeo. PLA produced is shipped around the world in form of pellets that are transformed by customers into a wide range of product such as coffee capsules, yogurt cups, baby wipes, and appliances.

5.1.3 PLA – Ingeo 4060D

Ingeo 4060D, amorphous, is available in pellet form. This polymer is stable in the molten state provided that the procedures of extrusion and of drying, the latter essential prior to processing, are followed. Typical material and application properties are shown in table 9.

Table (9) Typical material and application properties of Ingeo 4060D

Coex Film Properties		Ingeo 4060D	ASTM Method
Density		1.24	D1505
Optical Characteristics	Haze	2%	D1003
	Gloss, 20°	90%	D1003
Thermal Characteristics	Glass Transition Temp.	55- 60°C	D3418
	Seal Initiation Temp.	80°C	F88

5.1.4 PLA – Ingeo HP3100

Ingeo HP3100, crystalline, is a medium viscosity product designed for medium flow injection molding applications [31]. See Table (10) for properties.

This grade of PLA is used in several application including disposables such as cutlery, cups, plates, cosmetic packaging, and durables such as electronics housings and semi- durable building materials. Therefore, the range of product in widely varied and growing.

This grade of biopolymer can be processed on most conventional injection molding equipment [29]. Provided that drying procedures are followed the material is stable in the molten state.

Table (10). Typical material and application properties of Ingeo HP3100.

Physical Properties	Ingeo Resin	ASTM Method
Specific Gravity	1.24	D792
MFR, g/10 min (210°C, 2.16kg)	24	D1238
Relative viscosity ⁽²⁾	3.1	D5225
Mechanical Properties, molded amorphous with 26°C mold temperature		
Tensile Yield Strength, psi (MPa)	9,400 (65)	D638
Tensile Elongation, %	3.4	D638
Notched Izod Impact, ft-lb/in (J/m)	0.34 (18.2)	D256
Flexural Strength, psi (MPa)	16,200 (112)	D790
Flexural Modulus, psi (MPa)	520,000 (3585)	D790
Heat Distortion Temperature (°C) 66 psi, (0.455 MPa)	54	E2092
Molded Linear Shrinkage, %	0.2-0.4	
Clarity	Transparent	
Mechanical Properties, molded crystalline with 120°C mold temperature⁽³⁾		
Tensile Yield Strength, psi (MPa)	9,300 (64)	D638
Tensile Elongation, %	2.2	D638
Notched Izod Impact, ft-lb/in (J/m)	0.6 (32)	D256
Flexural Strength, psi (MPa)	15,700 (108)	D790
Flexural Modulus, psi (MPa)	632,000 (4357)	D790
Heat Distortion Temperature (°C) 66 psi, (0.455 MPa)	149	E2092
Molded Linear Shrinkage, %	1.7-1.8	
Clarity	Opaque	
Peak crystalline melting point (°C)	165-180	

(1) Typical properties; not to be construed as specifications

(2) RV measured at 1.0 g/dL in chloroform at 30°C

(3) Formula included 1wt% nucleating agent (LAK-301 from Takemoto Oil & Fat)

5.2 PLA films preparation and thermal treatment

PLA films were prepared by injection molding, a process that is described in Section 2.7.1.

All the samples used have the following measurements: 4 cm in height and width and approximately 1 mm in thickness.

Before being used, PLA films obtained by injection molding process, are subjected to a heat pretreatment, normalizing, with the aim to enhance the properties of the material such as relieving internal stresses, improving toughness and to uniform thermal history.

Normalizing is a three-step heat treatment process in which the material, being a semi-crystalline thermoplastic polymer, is firstly heated above its glass transition temperature (usually in furnace) after which the material is soaked in the temperature over a sufficient period for transformation to occur and finally it is taken out from the furnace and allowed to cool in atmosphere / room temperature [1].

Since two different types of PLA were used, two different types of pretreatment were performed, optimizing them in order to ensure the repeatability of the measurements. PDLLA was treated under vacuum for one hour at a temperature of 80 °C while PLLA was treated overnight at a temperature of 95°C. As far as PLLA is concerned, the almost exclusive high content of the stereoisomer L allows it to crystallize. Consequently, in order to ensure a better crystallization, it was subjected to longer heat treatment times and a higher temperature. In both cases, after the heat treatment and before to being used, the polymeric films obtained have been allowed to cool to room temperature.

5.3 Gravimetric methods: determination of absorption kinetics and transport parameters of terpenes on PLA

In order to evaluate the solubility and diffusion coefficient, gravimetric analysis on the polymeric films were performed, directly measuring the mass uptake with an analytical balance.

PLA films, in particular PDLA and PDLLA, prepared through the injection molding and opportunely pretreated, as indicated above, were first weighed to perform, subsequent, absorption tests with the chosen terpenes.

The absorption experiment was executed as follow. PLA films were immersed in Petri dishes, each of which filled with the chosen terpenes: α -Pinene, Linalool, L-Linalool β -Citronellol. Then Petri dishes are placed in a thermostatic oven and the PLA films are weighted at regular time intervals. To do this, the films were removed from the liquid, quickly dried with a paper towel, weighted on the analytical balance and finally re-immersed in the liquid [30].

In this way it is possible to obtain the mass uptake in function of time.

During this type of tests experimental errors can be made, in particular during the drying procedure that can be affected by the viscosity of the liquid and its surface tension.

At the end of the absorption test, therefore when the equilibrium is reached, and no weight increase is detected, it is possible to calculate solubility that correspond to the total amount of absorbed liquids per gram of polymer (Figure 25).

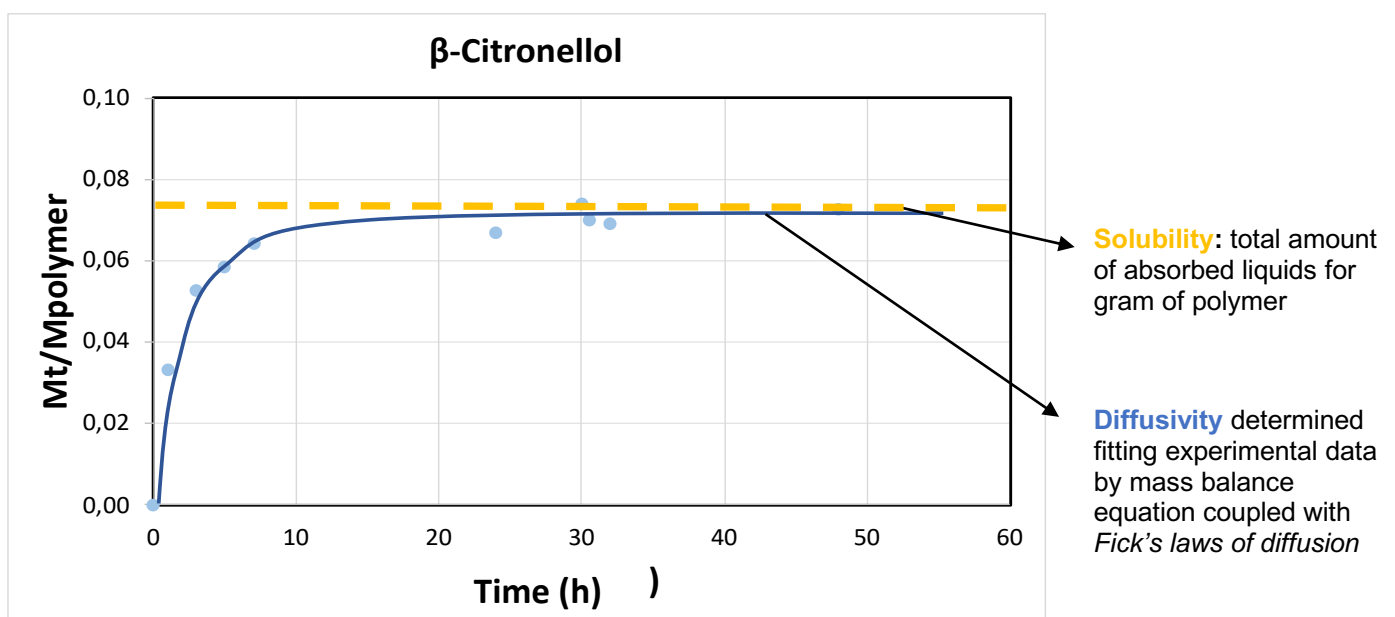


Figure (25). Example of absorption kinetic.

The diffusivity of a substances in a polymeric film must be calculated according to a suitable model to regress the mass uptake kinetics data [31]. In this study

the choice has relapsed on Fick's model (Equation 12) that provide an adequate representation of sorption of gases in rubbery and glassy polymers [30].

5.4 Analysis

5.4.1 Evaluation of the thermal history of PLA films: DCS

The thermal events of PLA films were determined by Differential Scanning Calorimetry (DSC). The temperature range investigated was from 10 to 190 °C. Films were weighed (around 10 mg), sealed into aluminum dishes and then heated from 10 to 190 °C. Next, the samples were cooled down and reheated to 190°C in a second heat.

DSC analysis was executed on neat PDLLA, amorphous, pretreated at 80 °C under vacuum for 1 hour and on neat PLLA, crystalline, pretreated at 95 °C overnight.

In figures 26 and 27 the graphs obtained from the DSC analysis of the PDLLA and PLLA, respectively, are shown. In these graphs the heat flux is reported as a function of sample temperature, which is measured throughout the process.

Peaks are represented according to the exo-endo convention whereby exothermic peaks correspond to a positive variation with respect to the baseline and endothermic peaks to a negative variation.

- **PDLLA**

From the figure 26, relative to PDLLA, is possible to observe that the first heating DSC curve shows two endothermic events.

The first small broad peak at 58 °C corresponds to the glass transition temperature T_g (reported in table 11). The second event on this first heat is caused by melting and corresponds to a temperature of 126 °C.

The reversibility of thermal events was evaluated from the second heating cycle. Moreover, it is possible to evaluate the crystallinity degree (X_c) of films according to the following equation:

$$x_c = \frac{\Delta H_m}{\Delta H_{litt}}$$

Where, ΔH_m is the measured melting temperature while ΔH_{litt} , corresponds to that of literature defined for the totally crystalline material.

All the parameters obtained are reported in table 11.

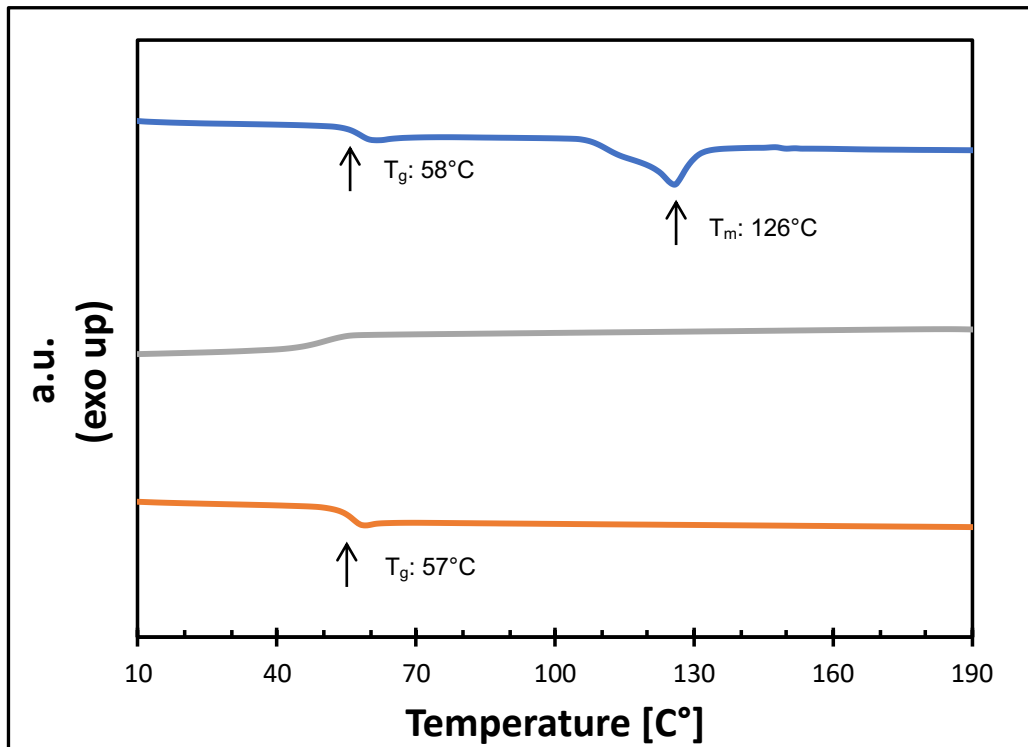


Figure (26). DSC curve of PDLLA.

— First heat
— Second heat
— Cooling

Table (11). PDLLA: a) Thermal treatment executed; b) crystallinity degree; c) data obtained from DSC analysis

a.

Thermal treatment
1h at heat 80 °C under vacuum

b.

X_c (%) *
7

*Determined by the melting enthalpy of PLA crystal (213.0 J/g) and the melting enthalpy of the first heat of PDLLA

c.

	First heat	Second heat
T_g (C°)	58	57
T_m (C°)	126	-
ΔH_m (J/g)	16	-
T_c (C°)	-	-
ΔH_c (J/g)	-	-

- **PLLA**

Figure 27 shows the results of DSC analysis in PLLA. First of all, from the first heat, it is possible to observe, even if not very clearly, the peak relative to the T_g that corresponds to 67°C while, the second peak is referred to the melting temperature that was appeared at 171°C . As shown, the presence of crystalline regions in PLLA caused, compared to that in PDLLA, an increase in T_g .

Comparing the first and the second heat, no significant changes in the glass transition temperature T_g and the melting temperatures were observed

On the second melting scan a cold crystallization around 113°C is detected.

Compared to the previous case, the crystallinity degree is increased up to 19%.

All the parameters obtained are reported in table 12

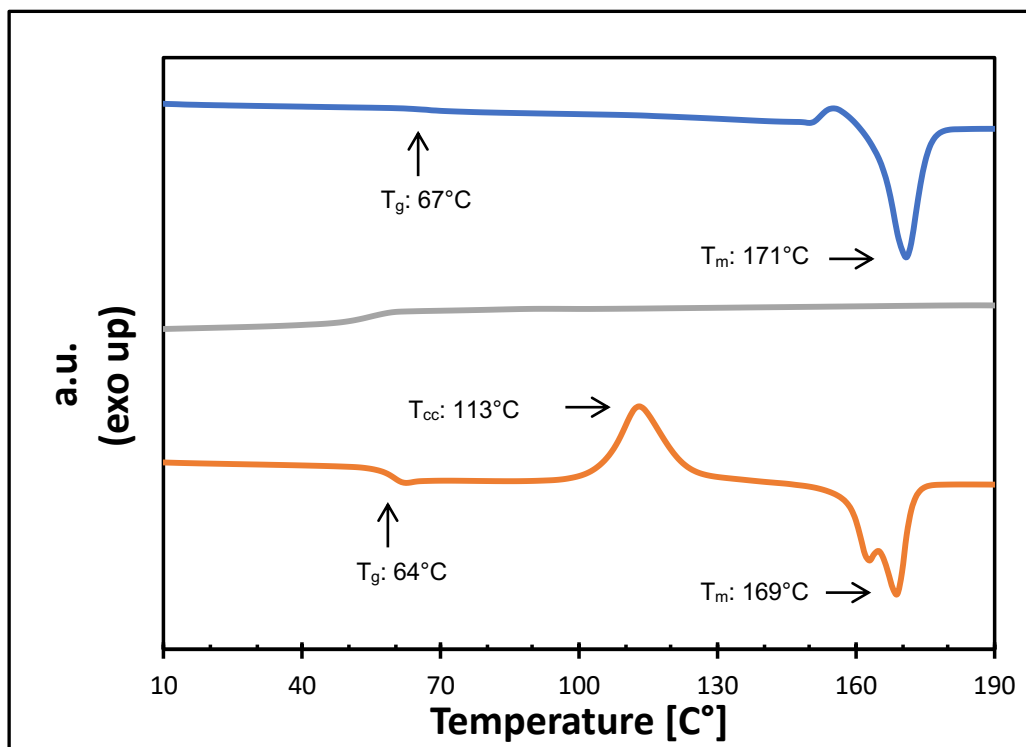


Figure (27). DSC curve of PLLA.

- First heat
- Second heat
- Cooling

Table (12). PLLA: a) Thermal treatment executed; b) crystallinity degree; c) data obtained from DSC analysis.

Thermal treatment	
Heat 95 °C overnight	

X_c (%)	
19	

	First heat	Second heat
T _g (C°)	67	64
T _m (C°)	171	169
ΔH_m (J/g)	41	39
T _c (C°)	-	113
ΔH_c (J/g)	-	32

*Determined by the melting enthalpy of PLA crystal (213.0 J/g) and the melting enthalpy of the first heat of PLLA

5.4.2 Evaluation of a possible enantiomeric excess of absorbed liquid:

HPLC

High performance liquid chromatography or commonly known as HPLC is an analytical technique used to separate, identify or quantify each component in a mixture. In particular, in this study it has been used with the aim to verify if the use of neat crystalline PLA, (PLLA), a chiral substrate, may lead to an enantioenrichment of the terpenes L-linalool in order to use such membrane in enantioselective processes in order to separate chiral compounds into their individual enantiomers.

The analysis has been carried out as follow. Once equilibrium was reached, absorbed liquid was extracted with methanol (MeOH), non-solvent for PLA, with the use of a Soxhlet extractor whose functioning is explained in the paragraph 4.3.3.

When the extract is obtained, the analysis with high performance liquid chromatography has been done, however it did not lead to the expected results.

Chapter 6. Results

The results obtained, at the end of the adsorption test, thus at the achievement of equilibrium, were plotted in graphs in which on the x-axis we can find the time while on the y-axis we can find M_t/M_∞ , where M_t denotes the total amount of diffusive substance that entered the sheet at time t while, M_∞ the corresponding amount after infinite time.

In this way it was possible to evaluate the diffusivity of the chosen terpenes in the polymer films, according to a model suitable for regressing the data of mass sorption kinetics [31], and the solubility which corresponds to the total amount of liquid absorbed per gram of polymer (Figure 25).

In the paragraphs 6.1 and 6.2 it is possible to find the absorption kinetics (Figure 28-35) related to each substance tested on both PLLA and PDLLA. More details on the solubility and diffusivity results obtained, are given in section 6.3 and 6.4 respectively.

6.1 Absorption kinetics of terpenes on poly (L-lactic acid) (PLLA)

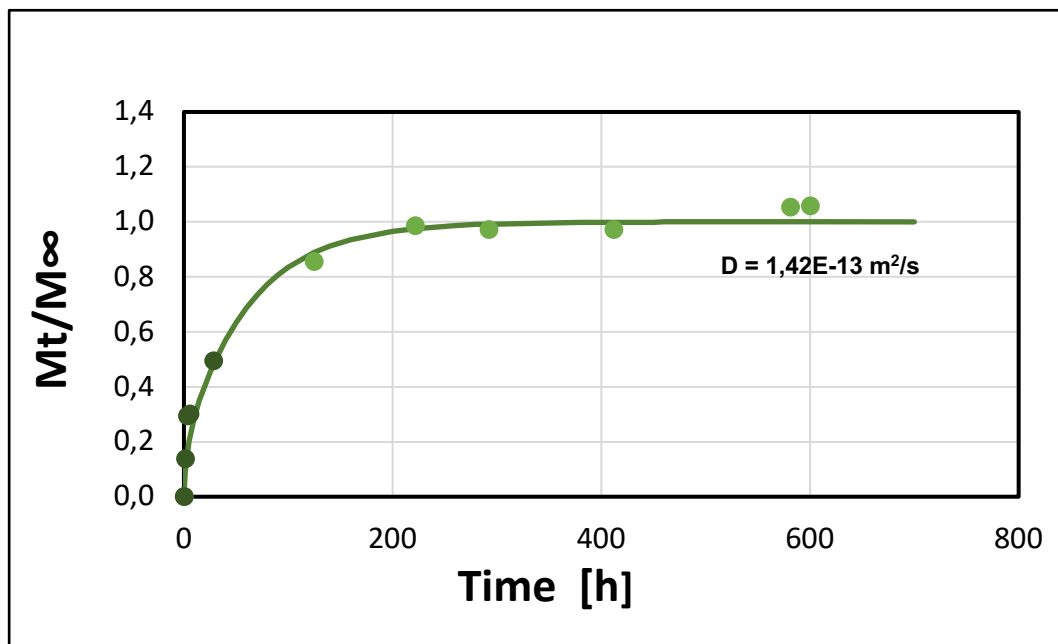


Figure (28). Absorption kinetics of α -Pinene on PLLA.

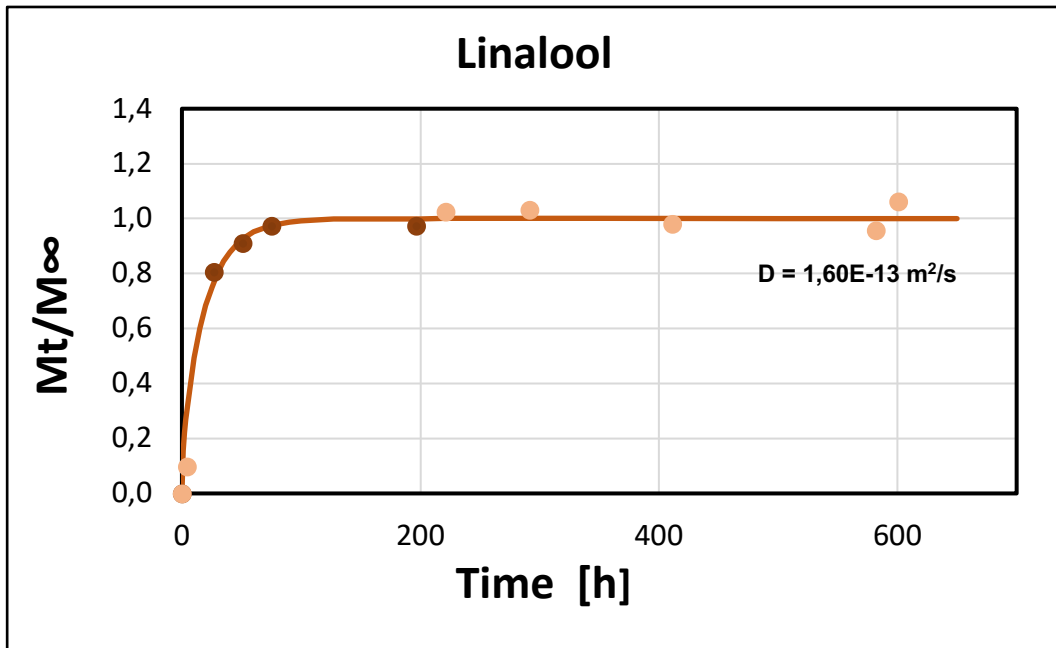


Figure (29). Absorption kinetics of Linalool on PLLA treated at (95°C).

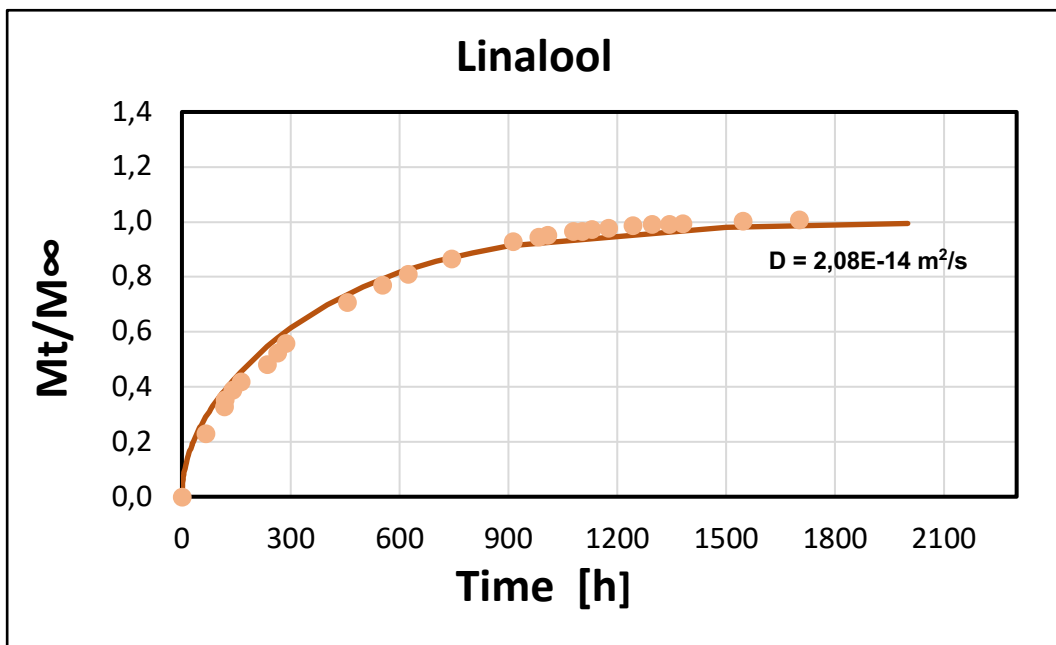


Figure (30). Absorption kinetics of Linalool on PLLA treated at 80°C.

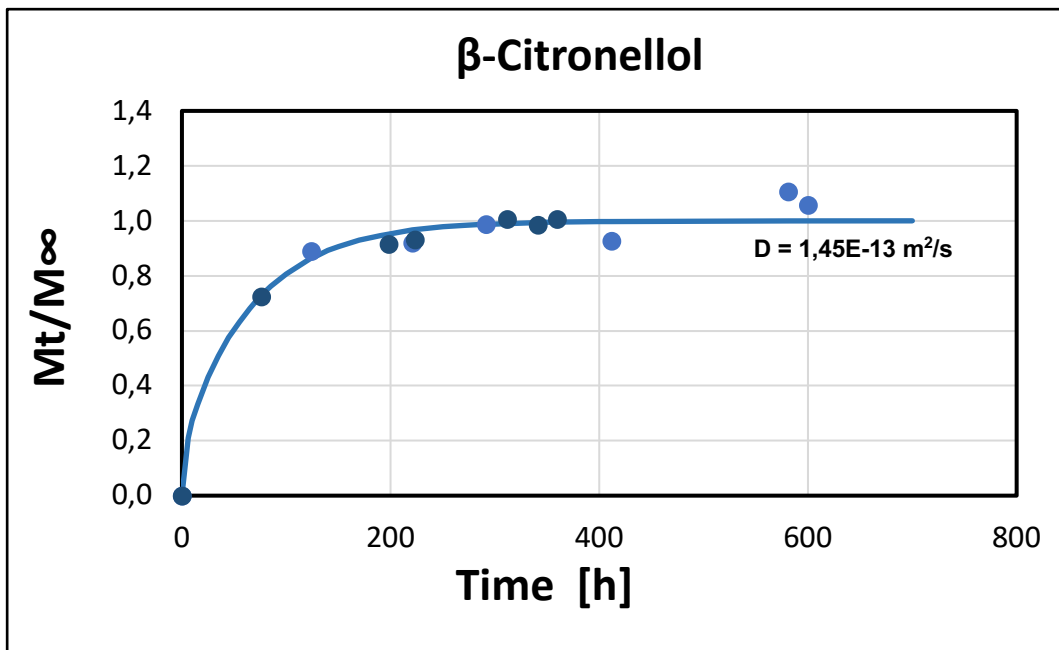


Figure (31). Absorption kinetics of β -Citronellol on PLLA.

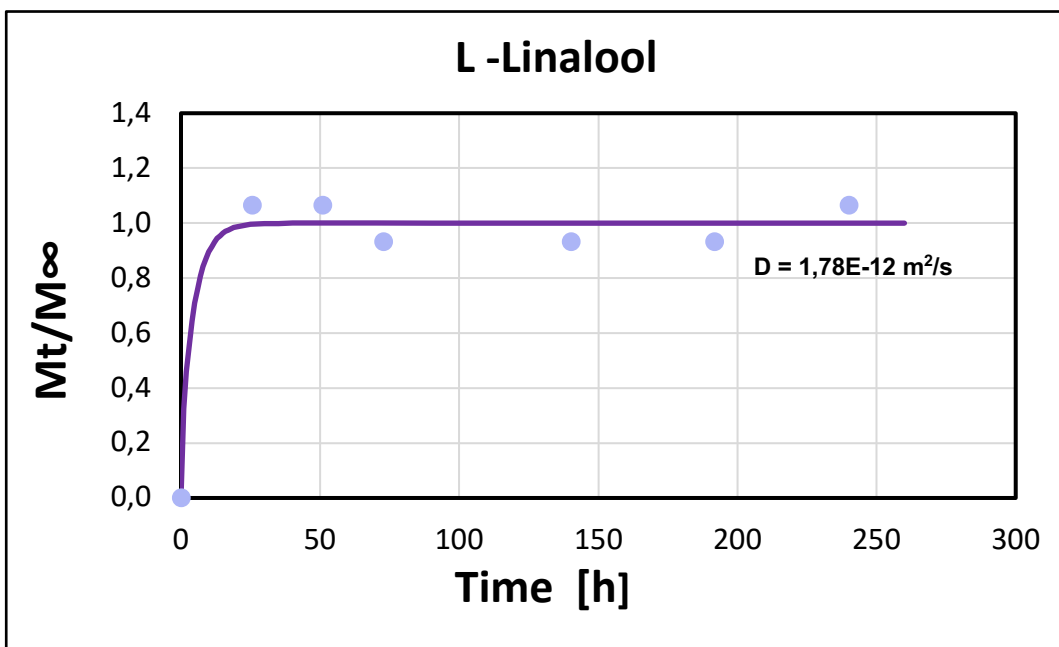


Figure (32). Absorption kinetics of L-Linalool on PLLA.

6.2 Absorption of terpenes on poly (D, L-lactic acid) (PDLLA)

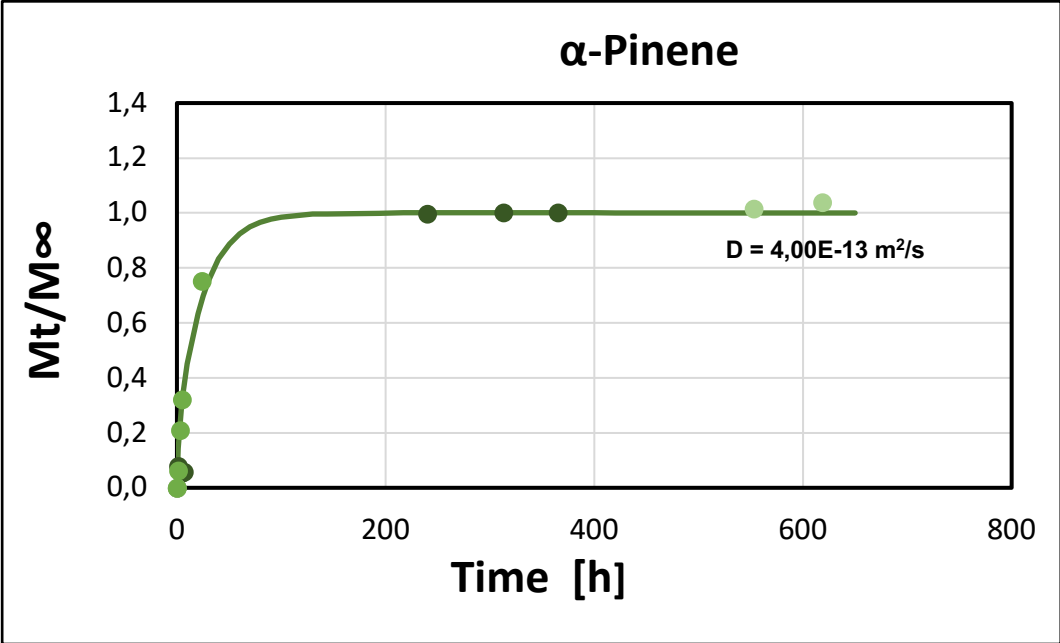


Figure (33). Absorption kinetics of α-Pinene on PDLLA.

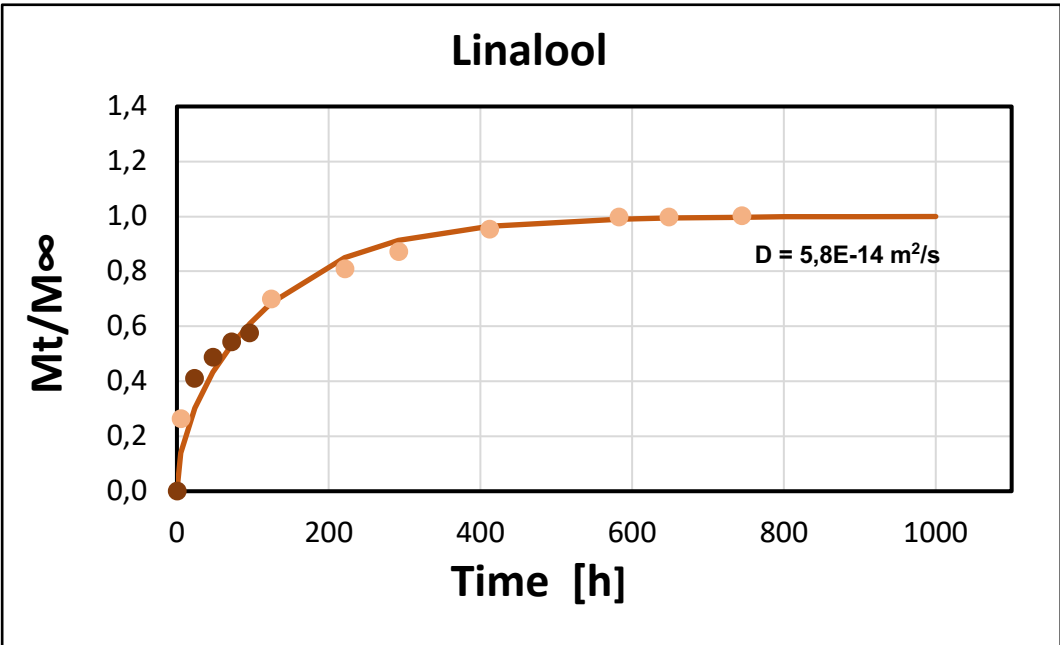


Figure (34). Absorption kinetics of Linalool on PDLLA.

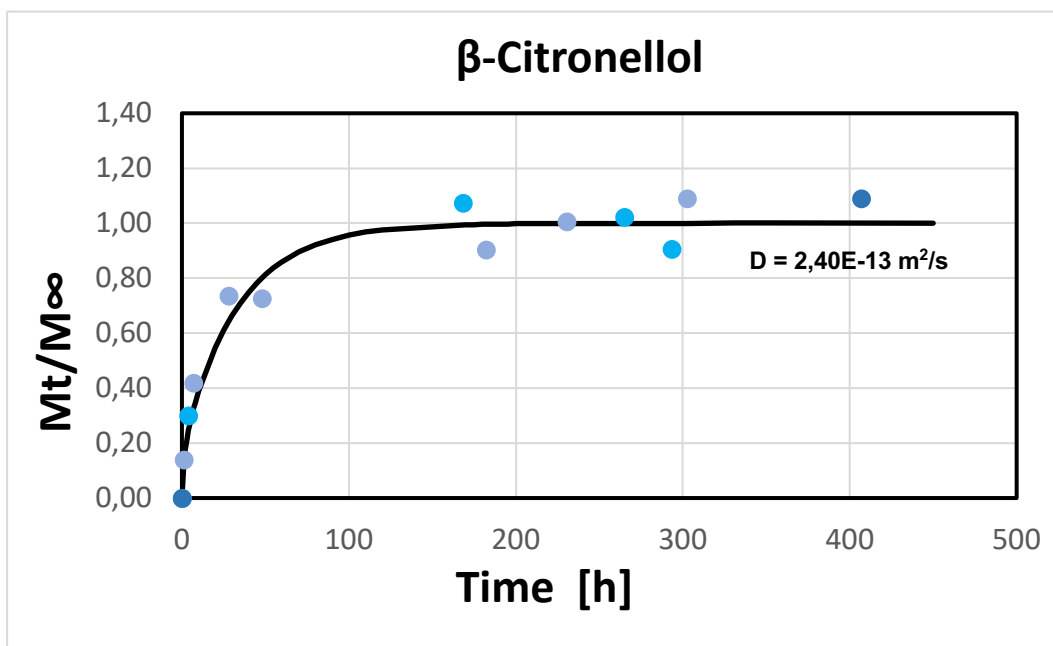


Figure (35). Absorption kinetics of β -Citronellol on PDLLA.

6.3 Solubility

Sorption experiments were performed with the following substances, α -Pinene, Linalool, β -Citronellol and L-Linalool having a molecular structure quite different, but they all belong to the class of terpenes.

Solubility can be calculated at the end of the absorption test when the equilibrium is reached, and no weight increase is detected. As shown in figure (27) solubility corresponds to the total amount of absorbed liquids per gram of polymer.

6.3.1 PDLLA

Solubility values for the tested substances in PDLLA are shown in Figure 36. It is interesting to note that, among tested terpenes, linalool is the one characterized by the highest solubility.

Compared to α -pinene, linalool and citronellol have a similar structure, consequently one might expect similar solubility values. As can be seen from the figure, this is not the case. β -citronellol is a primary alcohol while linalool,

whose solubility is higher, is tertiary one. Therefore, such behavior can be explained in terms of energetic interactions which, at similar molecular weight, are more favorable to the dissolution of the tertiary structure. [32].

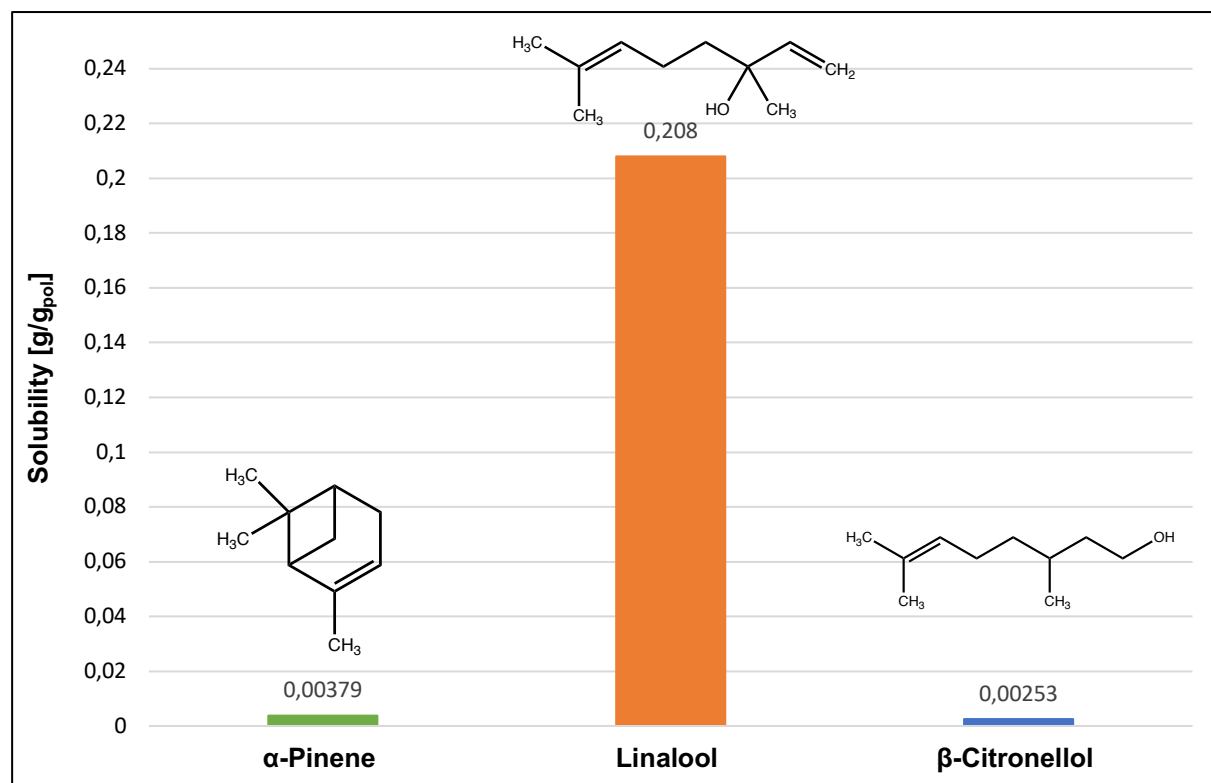


Figure (36). Solubility values for the tested substances in PDLLA.

6.3.2. PLLA

Even in this case, as in the previous one, linalool is the terpene which, among those examined, presents the highest solubility.

The difference in solubility between linalool and citronellol, both used with PLLA films treated at 95 °C overnight, is attributable, as in the previous case, to energy interactions more favorable to the dissolution of the tertiary structure (linalool).

In addition, with regard to linalool, the experiment was conducted even using PLLA films treated at 80 °C for one hour under vacuum. From the figure 37, it is possible to notice that there is a great difference in solubility between these films, which can be just attributed to the two different heat treatments performed. This is because longer times allowed PLLA to crystallize in a better way and consequently, presenting a more compact structure than PLLA treated at 80 °C

for one hour, the penetration by the terpene, linalool, was more difficult, resulting in a lower solubility.

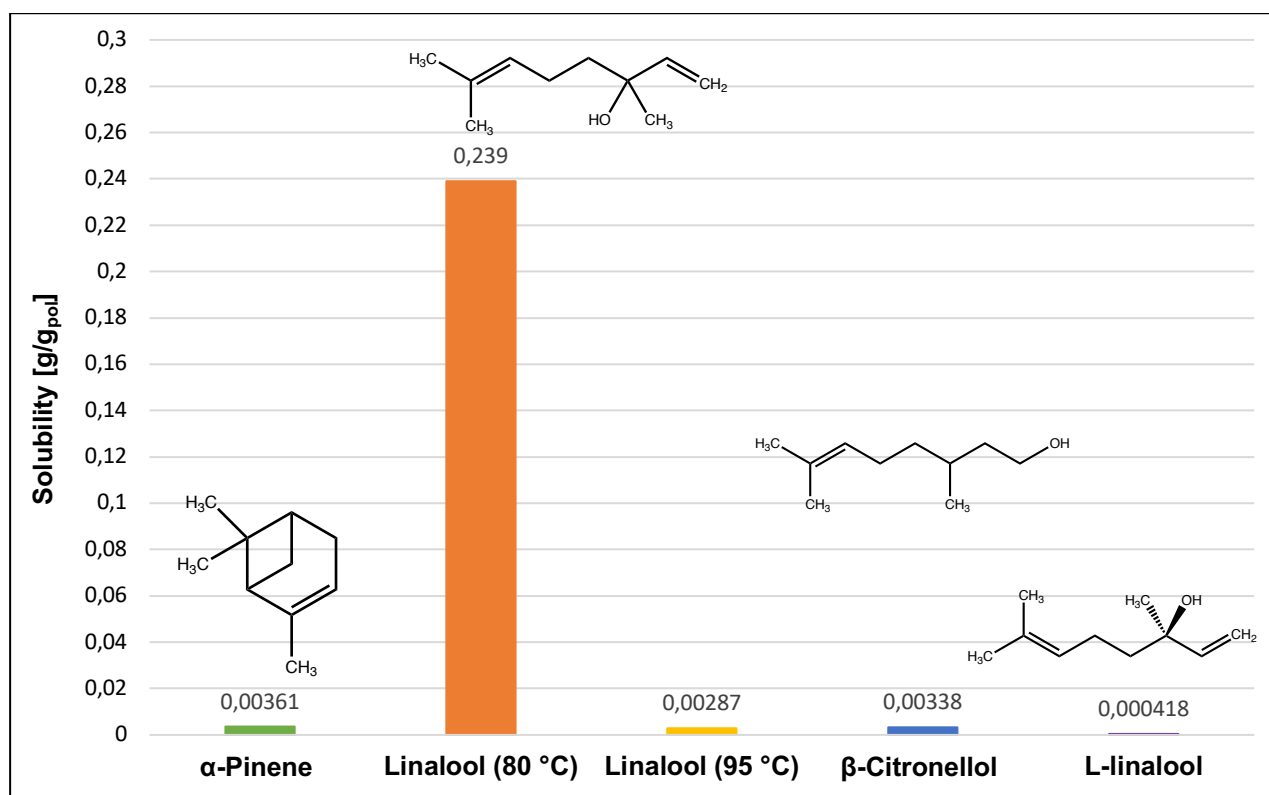


Figure (37). Solubility values for the tested substances in PLLA.

6.4 Diffusivity

6.4.1 PDLLA

Diffusivity of terpenes in PDLLA is reported in Figure 38.

It is possible to observe that, for the three substances tested on PDLLA, quite different diffusivity values were obtained. The diffusivity decreases following this order $D(\alpha\text{-pinene}) > D(\beta\text{-Citronellol}) > D(\text{Linalool})$.

The highest value is shown by pinene. The latter has a lower molecular weight (136.23 g/mol) compared to the other two tested terpenes, which present rather similar values, linalool (154.25 g/mol) and citronellol (156.27 g/mol). Consequently, this could be the reason why, when it comes to amorphous structures, easy to penetrate, alpha pinene has a higher diffusivity.

If we consider citronellol, a primary alcohol, and linalool, a tertiary alcohol, we can see that the first one has a higher diffusivity value. The long alkyl chain of these alcohols makes thermodynamic interactions with the polymer more favorable and therefore it can be deduced that thermodynamic factors, in this case, do not have a relevant role.

Since diffusivity is inversely proportional to solubility according to equation (10), it can be deduced that, as previously occurred in the case of solubility in PDLLA film (6.3.1. paragraph), this behavior can be explained in terms of energy interactions that, at similar molecular weight, are more favorable to the dissolution of the alcohol with tertiary structure (linalool) rather than to the dissolution of the substance presenting a primary structure (β -citronellol).

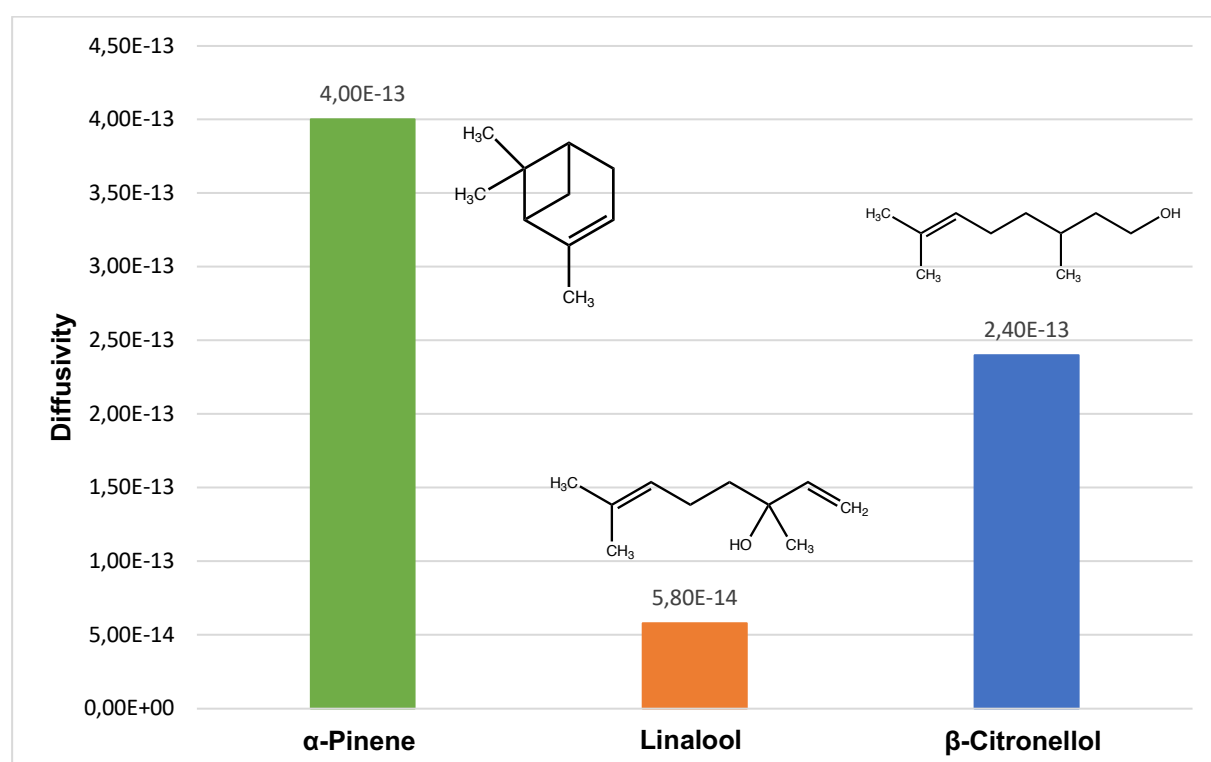


Figure (38). Diffusivity values of terpenes in PDLLA.

6.4.2 PLLA

As shown in Figure 39, α -pinene, linalool (PLLA treated at 95 °C) and citronellol present very similar diffusivity values and this can be attributed to the similar size. The lowest diffusivity value is presented by linalool in PLLA treated at 80 °C. This behavior can again be attributed to the different type of heat treatment

used in the PLLA. This is because longer times allowed PLLA to crystallize in a better way, presenting, consequently, a more compact structure than PLLA treated at 80 °C for one hour. The structure of the latter has more amorphous parts and therefore more space in which linalool can penetrate. However, this required longer times in order to reach equilibrium thus resulting in a low diffusion coefficient.

From Figure 41, it is evident that L-linalool has the highest diffusivity value. An enantiomer which has strong interaction with chiral recognition sites may diffuse slowly through the membrane [34], therefore, it can be said that in this case the interaction between L-linalool and PLLA (PLA from L-lactide form) is weak.

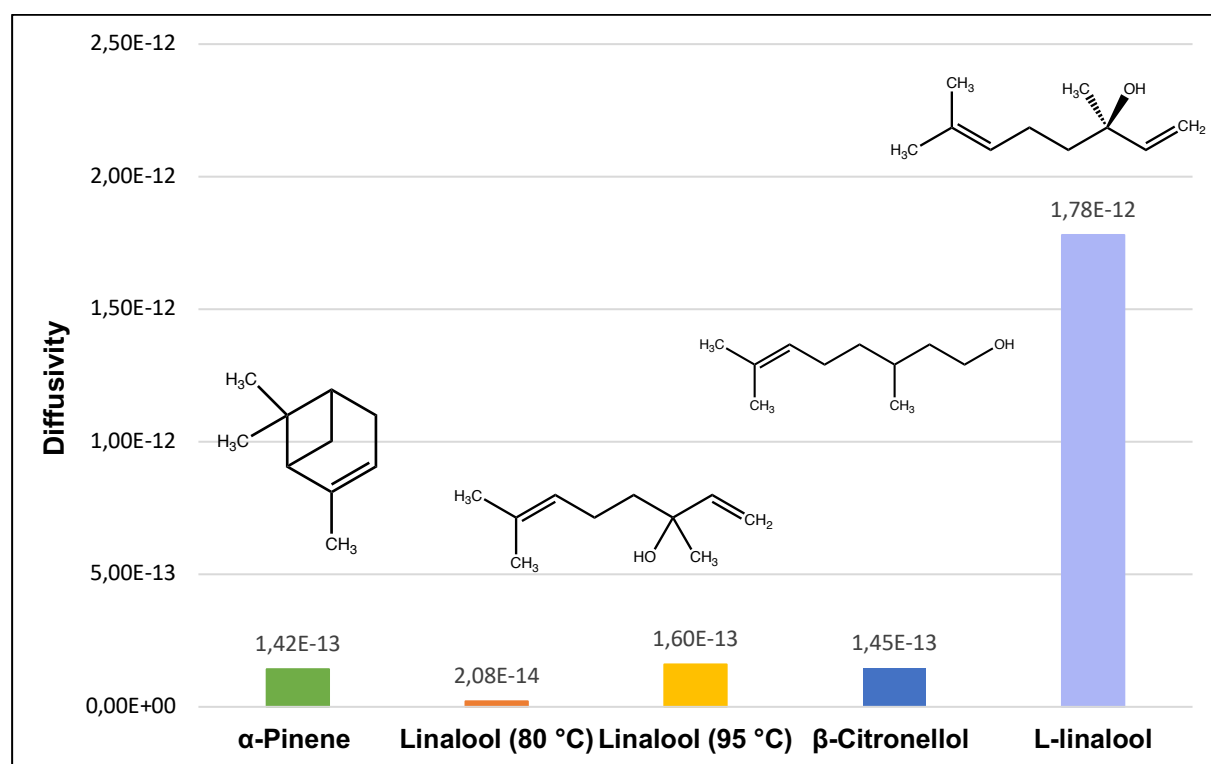


Figure (39). Diffusivity values of terpenes in PLLA.

6.5 Comparison between PLLA and PDLLA

In the following tables, 13 and 14, are shown the values of solubility and diffusivity of the chosen terpenes, α -Pinene, β -Citronellol, Linalool, L-Linalool in two different grades of polylactic acid (PLA), Amorphous (PDLLA) and Crystalline (PLLA).

We can see that for both PDLLA and PLLA, the substance that is more absorbed, resulting in higher solubility, is linalool. This may be due to a number of factors such as the structure of the molecule, cyclic or linear, the energy interactions, more favorable to the dissolution of a structure rather than another, a lower molecular weight compared to some of the terpenes tested, or due to a substantial chemical affinity between the penetrant and the polymer matrix.

As for the diffusivity, it is L-linalool, one of the two enantiomers of linalool, to present the highest value, thus demonstrating that there is no affinity between the latter and PLLA, poly (L-lactic acid).

Table (13) sorption terpenes in PDLLA: solubility and diffusivity results obtained.

	Terpenes absorbed (g)	Diffusivity (m²/s)	Solubility (g/g_{pol})
α-Pinene	0,0194	4,00E-13	3,79E-3
β-Citronellool	0,0117	2,40E-13	2,53E-3
Linalool	0,9733	5,8E-14	0,208

Table (14) Sorption of terpenes in PLLA: solubility and diffusivity results obtained.

	Terpenes absorbed (g)	Diffusivity	Solubility
α-Pinene	0,0173	1,42E-13	3,61E-3
β-Citronellool	0,0171	1,45E-13	3,38E-3
Linalool	0,0143	1,60E-13	2,87E-3
L-Linalolo	0,0008	1,78E-12	4,18E-4
Linalool*	1,1643	2,08E-14	0,239

* Absorption test of Linalool on PLLA treated at 80°C.

Chapter 7. Conclusion

The solubility and diffusivity of a series of terpenes such as Linalool, α -Pinene, β -Citronellol and L-Linalool has been measured in two different grades of polylactic acid (PLA), Amorphous (PDLLA) and Crystalline (PLLA).

First of all, since two different types of PLA were used, heat treatments, performed on the specimens, have been optimized in order to ensure the reproducibility of the measurements. PDLLA was treated under vacuum for one hour at a temperature of 80°C, while PLLA was treated overnight at a temperature of 95°C.

After that, by the use of gravimetric methods, the absorption kinetics of various terpenes, in the two different types of PLA, was determined. In this way it was possible to evaluate solubility and diffusivity values.

Diffusivity and solubility parameters are very important in order to evaluate, respectively, how fast the penetrant can penetrate in the polymer, and how similar polymer and penetrant are, hence, to express the penetration and dispersion of a compound within the polymer matrix.

Considering the solubility, the highest value, for both PDLLA and PLLA, is shown by linalool while, α -Pinene, β -Citronellol and L-Linalool have lower solubility values.

As for diffusivity, it is L-linalool, one of the two enantiomers of linalool, to present the highest value, thus showing that there is no affinity between it and PLLA, poly (L-lactic acid). However, it can be seen that there is a difference in solubility and diffusivity results obtained using L-linalool and its raceme with PLLA.

From the above considerations, it can be stated that the analyses performed on L-linalool and pure crystalline PLA (PLLA), in order to use the latter as a membrane in enantioselective processes to separate chiral compounds into their individual enantiomers have provided results that, however, cannot be considered definitive and need further investigation. In this regard, future developments may involve more precise tests with different optically active penetrants; tests of direct permeation, not just absorption; study of absorption

and permeation in PDLA and a more detailed evaluation of the effect of crystal and crystallinity on solubility and transport

In all cases, in general, very low solubility and diffusion coefficients were obtained, thus showing the excellent barrier properties of PLA towards the tested terpenes.

Therefore, it can be concluded that PLA has excellent advantages in the field of food packaging where it is used for food preservation, as a simple container and, increasingly, as a means to reduce the rate of quality decay of the product, protecting it from microbiological and chemical contamination.

PLA is derived from renewable resources, it is biodegradable, recyclable, compostable and therefore can help to reduce our society's dependence on fossil fuels.

Bibliography

- [1] S. Singh, A. Rajeshkannan, S. Feroz, A.K. Jeevanantham, *Effect of Normalizing on the Tensile Strength, Shrinkage and Surface Roughness of PLA Plastic*, IConAMMA, ELSEVIER, 2018.
- [2] S. Saeidlou, M.A. Huneault, H. Li, C.B. Park, *Poly (lactic acid) crystallization*, Prog. Polym. Sci. 37 (2012).
- [3] J.M. Raquez, Y. Habibi, M. Murariu, P. Dubois, *Poly(lactide (PLA)–based nanocomposites*, Prog. Polym. Sci. 38 (2013).
- [4] Lin Xiao, Bo Wang, Guang Yang, Mario Gauthier, *Poly (Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications, Biomedical Science, Engineering and Technology*, 2012.
- [5] R. M. Rasal, A. V. Janorkar, D. E. Hirt, *Poly (lactic acid) modifications*, United States, ELSEVIER, 2009.
- [6] R. Auras, B. Harte, S. Selke, *An Overview of Polylactides as Packaging Materials, Macromolecular bioscience*, 2004.
- [7] Auras R., Harte B., Selke S., *An overview of polylactides as packaging materials*, Macromol. Biosci., 2004.
- [8] Shady Farah, Daniel G. Anderson, Robert Langer, *Physical and mechanical properties of PLA, and their functions in widespread applications — A comprehensive review*, USA, 2016.
- [9] D. Garlotta, J. Polym. Environ. 9 (2002).
- [10] Yunzi Hu, Walid A. Daoud, Kevin Ka Leung Cheuk, and Carol Sze Ki Lin, *Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly(Lactic Acid)*, Marek Kowalczyk , 2016
- [11] Astrid J.R. Lasprilla, Guillermo A.R. Martinez, Betânia H. Lunelli, André L. Jardini, Rubens Maciel Filho, *Poly-lactic acid synthesis for application in biomedical devices*, Campinas. ELSEVIER.2011.
- [12] Shady Farah, Daniel G. Anderson, Robert Langer, *Physical and mechanical properties of PLA, and their functions in widespread applications — A comprehensive review*, ELSEVIER, 2016.

- [13] Guravtar Singh Mann, Lakhwinder Pal Singh, Parmod Kumar, Sunpreet Singh, Chander Prakash, *On briefing the surface modifications of polylactic acid: A scope for betterment of biomedical structures*, Journal of Thermoplastic Composite Materials, 2019
- [14] E. Breitmaier, *Terpenes: Flavors, Fragrances, Pharmaca, Pheromones*, Wiley- VCH, Weinheim, 2006.
- [15] Martin, V. J. J., Pitera, D. J., Withers, S. T., Newmann, J. D. et al., *Engineering the mevalonate pathway in Escherichia coli for production of terpenoids*. Nat. Biotechnol. 2003,
- [16] B. Salehi, S. Upadhyay, I. E. Orhan, A. K. Jugran, S. L.D. Jayaweera, D. A. Dias, F. Sharopov, Y. Taheri, N. Martins, N. Baghalpour, W. C. Cho, J. Sharifi-Rad, *Therapeutic Potential of α - and β -Pinene: A Miracle Gift of Nature*, MDPI, 2019.
- [17] M. E. Mohamed, Y. S. Abduldaium, N. S. Younis, *Ameliorative Effect of Linalool in Cisplatin-Induced Nephrotoxicity: The Role of HMGB1/TLR4/NF- κ B and Nrf2/HO1 Pathways*, MDPI, 2020.
- [18] S. Nikfar, A.F. Behboudi, *Limonene*, Elviesier, 2014.
- [19] U. Sonchaeng, F. Iñiguez -Franco, R. Auras, S. Selke, M. Rubino, Loong-Tak Lim, *Poly(lactic acid) mass transfer properties*, ELSEVIER, 2018
- [20] V. Stannett, H. Yasuda, *The measurement of gas and vapor permeation and diffusion in polyme*, In: Schmitz JV, editor, New York: Johh Wiley & Sons; 1965
- [21] Meares P., *Transient permeation of organic vapors through polymer membranes*, J Appl Polym Sci 1965.
- [22] Crank J., *The mathematic of Diffusion*, Brunel university uxbridge, 2006.
- [23] C. Schick, *Differential scanning calorimetry (DSC) of semicrystalline polymers*, Springer-Verlag, 2009.
- [24] J. D. Menczel, R. Bruce Pime, *Thermal analysis of polymer*, John Wiley & Sons publication)
- [25] I. M. Kalogeras, *Glass-Transition Phenomena in Polymer Blends*, National and Kapodistrian University of Athens, 2016.

- [26] R. J. Hamilton, P. A Sewell, *Introduction to high performance liquid chromatography*, CHAPMAN AND HALL, 1982.
- [27] *What is HPLC (High Performance Liquid Chromatography)?*, SHIMADZU, https://www.shimadzu.com/an/service-support/technical-support/analysis-basics/basic/what_is_hplc.html.
- [28] M. R, Bansal V*, Pal O.P., S. P.K., *High performance liquid chromatography: a short review*, JGPT, 2010.
- [29] A. Zyglar, M. Slominska, and J. Namiesnik, *Soxhlet Extraction and New Developments Such as Soxtec*, ELSEVIER, 2012.
- [30] M. D. Luque De Castro, L. E. Garcia Ayuso, *Soxhlet Extraction*, Academic Press, 2000.
- [31] *Ingeo™ Biopolymer 3100HP Technical Data Sheet*, NatureWorks, <https://www.natureworkslc.com>.
- [32] G. Cocchi, M. G. De Angelis, F. Doghieri, *Solubility and diffusivity of liquids for food and pharmaceutical applications in crosslinked polydimethylsiloxane (PDMS) films: I. Experimental data on pure organic components and vegetable oil*, ELSEVIER, 2015.
- [33] K. Singh, P. G. Ingole, H. C. Bajaj, H. Gupta, *Preparation, characterization and application of β -cyclodextrin-glutaraldehyde crosslinked membrane for the enantiomeric separation of amino acids*, ELSEVIER, 2012.