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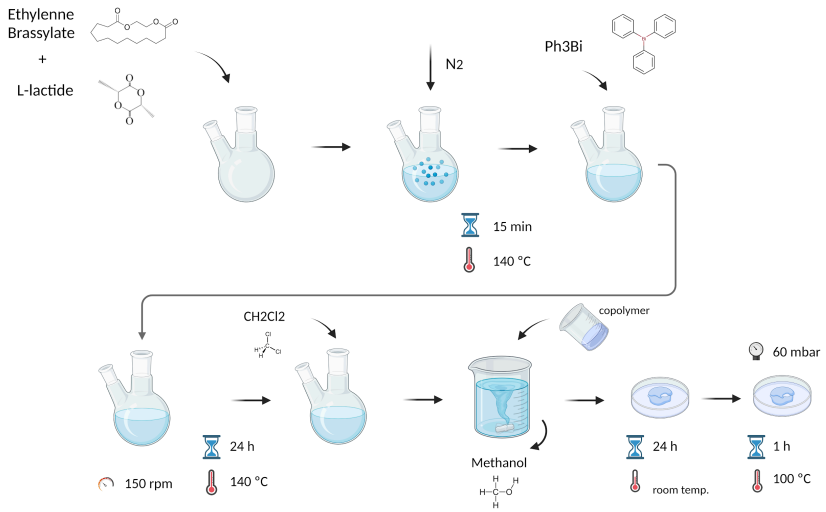
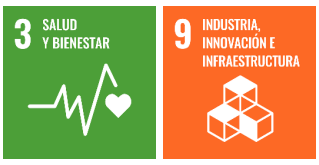
DEGREE IN INDUSTRIAL ORGANIZATION ENGINEERING

END OF DEGREE PROJECT

SYNTHESIS, CHARACTERIZATION AND PROCESSING OF LACTIDE AND ETHYLENE BRASSYLATE-BASED COPOLYMERS





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RESUMEN

En el presente trabajo de fin de grado (TFG), se realizó un estudio sobre copolímeros basados en L-lactida y brasilato de etileno, con el fin de modificar sus propiedades mecánicas a través de distintos tratamientos. En este estudio, se sintetizaron 3 copolímeros con distinto porcentaje en peso de brasilato de etileno, y posteriormente se procedió a su caracterización mediante calorimetría diferencial de barrido, resonancia magnética nuclear, cromatografía de permeación de gel y ensayos de tracción. A partir de estos, se obtuvo su peso molecular, su composición y sus transiciones térmicas. Una vez obtenidos los polímeros, estos se procesaron mediante moldeo por compresión, y las propiedades mecánicas de los filmes resultantes se determinaron mediante ensayos de tracción tanto a temperatura ambiente como a temperatura corporal. Ha sido un trabajo desarrollado en los laboratorios del Grupo de Ciencia e Ingeniería de Biomateriales Poliméricos (Grupo ZIBIO), grupo que cuenta con una gran experiencia en materiales poliméricos con amplios usos en el área biomédica.

Palabras clave: Copolímeros, L-lactida, Brasilato de Etileno, Termoplásticos

LABURPENA

Gradu amaierako lan honetan (TFG), L-laktida eta etileno-brasilatoan oinarritutako kopolimeroei buruzko ikerketa bat egin da, tratamendu ezberdinen bidez haien propietate mekanikoak aldatzeko. Ikerketa honetan, etileno-brasilatoaren pisu-portzentaje ezberdineko 3 kopolimero sintetizatu dira. Ondoren, haien karakterizazioa egin da ekorketako kalorimetria diferentziala, erresonantzia magnetiko nuklearra, gel-permeatze-kromatografia eta trakzio-probak erabiliz. Horietatik, haien pisu molekularra, konposizioa eta trantsizio termikoak lortu ziren. Polimeroak lortu ondoren, konpresio moldaketaren bidez bidez prozesatu ziren, eta ondoriozko filmen propietate mekanikoak tentsio-saiakuntzen bidez zehaztu ziren bai giro-tenperaturan, bai gorputz-tenperaturan. Biomaterial Polimerikoen Zientzia eta Ingeniaritza Taldeko (ZIBIO Taldea) laborategietan garatutako lana izan da. Ikerketa talde honek, esperientzia zabala baitu material polimerikoekin, arlo biomedikoan erabilera zabala dutenak.

Hitz gakoak: Kopolimeroak, L-laktida, Etileno Brasilatoa, Termoplastikoak

ABSTRACT

In this end of degree project (TFG) a study on copolymers based on L-lactide and ethylene brassylate was carried out, with the aim of modifying their mechanical properties through various treatments. In this study, 3 copolymers with different weight percentages of ethylene brassylate were synthesized and characterized using differential scanning calorimetry, nuclear magnetic resonance, gel permeation chromatography and tensile testing. From these analyses, the molecular weight, composition and thermal transitions were obtained. Once the polymers were synthesized, they were processed through compression molding, and the mechanical properties of the resulting films were determined by tensile tests at room temperature and body temperature. This work was developed in the laboratories of the Group of Science and Engineering of Polymer Biomaterials (ZIBIO Group), a group with extensive experience in polymeric materials with wide applications in the biomedical field.

Key words: Copolymers, L-lactide, Ethylene Brassylate, Thermoplastics

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ACRONYMS

CAD - Computer Aided Design

CDCl3 - Deuterated Chloroform

CH2Cl2 - Dichloromethane

DSC - Differential Scanning Calorimetry

EB - Ethylene Brassylate

ε - Engineering strain

FRP - Free Radical Polymerization

GPC - Gel Permeation Chromatography

LA - Lactide

MW - Molecular weight

NMR - Nuclear Magnetic Resonance

Ph3Bi - Triphenyl Bismuth

PLA - Polylactide

PLLA - Poly (L-lactide)

PLEB - L-lactide + Ethylene Brassylate

$\mathbf{T_a}$ - Room temperature

ROP - Ring Opening Polymerization

SDG - Sustainable Development Goal

σ - Engineering stress

$\mathbf{T_{cc}}$ - Cold crystallization temperature

$\mathbf{T_g}$ - Glass transition temperature

$\mathbf{T_m}$ - Melting temperature

WBS - Work Breakdown Structure

wt. % - Weight percent

1. Introduction

The aim of the present project is delimited by the theoretical framework that comprises industrial engineering, more precisely in the branch of knowledge related to advanced materials and innovation applied to industry. The main objective established for this research has to do with obtaining copolymers based on L-lactide and ethylene brassylate, whose mechanical properties can be manipulated and used to our advantage. Moreover, this project also involves analyzing thermal processes that can have an effect on the copolymer. For this purpose, the work has been structured in several tasks that will be explained throughout the document with thoroughness.

Summarizing, three (co)polymers will be synthesized (Pure PLLA, PLEB9010, PLEB8020) in order to proceed with their characterization. Afterwards, by using several techniques that include Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (RMN), a wide variety of features are going to be assessed.

Furthermore, for analyzing the mechanical properties of the (co)polymers, some polymeric films will be designed and produced through compression molding. Those films shall be subjected to tensile tests at different temperatures (room temperature-Ta and body temperature-37 ºC), in order to visualize the effect of polymer composition on the mechanical aspect.

This study will be developed in the laboratories of the Group of Science and Engineering of Polymeric Biomaterials (ZIBIO Group), in the Department of Mining-Metallurgy, Engineering and Materials Science, at the Bilbao School of Engineering. This research group is a consolidated research group (class A) from the Basque Government and focuses its research on biodegradable and biocompatible polymers for biomedical purposes.

Lasty, all the conclusions and possible development lines are explained at the end of the document, as well as all the guidelines necessary to fully understand the research and the aim of it.

2. Context

Polylactide, also known as PLA, is a widely used thermoplastic that can be obtained from natural resources, including corn and sugarcane. It is also recognised for being a great alternative to petroleum-based plastics [1]. Figure 1 illustrates the molecular structure of polylactide, highlighting its repeating unit.

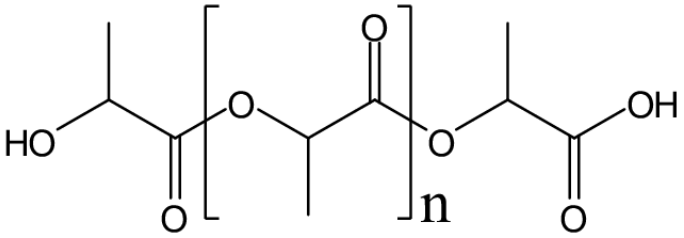

Figure 1. *Polylactide*

PLA was the most consumed bioplastic in the world in 2021 [1], even though it is not the easiest polymer to deal with. It has an incredibly large range of applications that include its use in 3D printing, by using it as a plastic filament. However, the use that really concerns us, has to do with its application in the biomedicine area for being biodegradable and cytocompatible [2] (material that does not produce any harmful reactions when in contact with living cells, approved by the U.S. Food and Drug Administration). Polylactide has an essential role in wounds, bone fixation implants or controlled drug release systems, among other uses [3].

Nevertheless, when analyzing the properties of PLA, some of them are noteworthy. It has a low melting point (150-160 ºC), low thermal expansion coefficient (126 - 145 μstrain/ºC) and it has a poor thermal stability, unless it undergoes an annealing process [3][4] (heating and cooling treatment that can modify the molecular structure of the polymer in order to increase its ductility, making it a more workable material). In addition, it has a Young's modulus of 3-3.3 GPa and an elongation at break below 10%, which makes it a really stiff and brittle material that cannot be used in treatments that try to reheal soft tissues.

One of the most common strategies to modify the chain structure of PLA and its composition, is to copolymerize it with macrolactones, such as epsilon-caprolactone or ethylene brassylate (EB). By doing so, we are able to obtain copolymers with completely renewed properties that can help in those treatments where a more elastomeric behavior is needed.

Figure 2 depicts the structure of L-lactide, the monomeric precursor of polylactide (PLA), which will be used in the synthesis process.

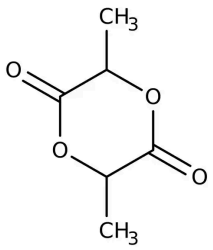

Figure 2. *L-lactide*

On the other hand, we have the previously mentioned macrolactone called ethylene brassylate (EB). Macrolactones are organic compounds found in natural products (e.g., fruit and dairy) that contribute in a significant way to its flavor and fragrance [5]. In fact, lactones have been of interest to a large number of fields, including biomedicine, as they have great potential to take part in a large amount of biological activities (antibiotics, antiviral agents, enzyme inhibitors, etc.).

EB is a 17 member ring lactone with two ester groups, and it has a sweet and floral taste [5]. When synthesized with lactide, EB can influence in a large variety of ways, as we can adjust the mechanical and thermal properties of the (co)polymer so that it can be used as a 'scaffold' when interacting with tissues [3]. The structure of ethylene brassylate is shown in Figure 3.

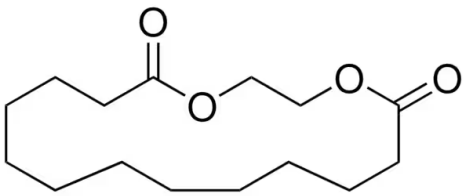

Figure 3. *Ethylene brassylate*

This research is just another way of showing the importance of copolymers in the field of polymer chemistry. By combining more than one monomer through polymerization, a range of opportunities opens up that would not be possible in its primitive version.

By tailoring and adjusting mechanical, thermal or physical characteristics of those copolymers, we end up having incredibly precise structures that cannot be obtained by using only monomers, and improve the path towards innovation in material and science technology [6].

3. Connection with Sustainable Development Goals

SDGs are a set of 17 global objectives that constitute a universal appeal to tackle poverty, protect the planet and improve the wellness of everyone around the globe. These goals provide a framework able to guide society towards a more sustainable, equal and fair future. By pooling international efforts, SDGs aim to create a more resilient world in 6 years, as established in the 2030 Agenda.

In relation to this research project, it addresses 2 out of the 17 Sustainable Development Goals (SDGs) related to innovation and health, aligning with the commitment of the University of the Basque Country (UPV/EHU) to the 2030 Agenda. Specifically, it contributes to the goal to "Ensure healthy living and promote well-being of all at all ages" (Figure 4).

Figure 4. *Good health and well-being*

The main goal of this research is closely related to the biomedical field. The use of polymers has had a serious impact in our society. Researchers have understood how to manipulate them in order to serve as a 'bracket' for tissues or to be incorporated in generic drugs, amongst other uses [6].

The biomedical use of collagen for being a natural and biocompatible has been going on for decades. However, experts such as chemists, physics or engineers have changed their perspectives on how to analyze issues. Because of this, a lot of doors have been opened towards the discovery of new biopolymers for having a good host response, useful mechanical properties and nontoxic degradation.

Polylactide is such a versatile polymer that it can be used as a cornerstone in a large number of areas. From tissue engineering benefits to designing resorbable membranes for surgical uses, PLA will have great importance in the near future, even though it is already starting to be. Therefore, any research done for understanding its properties and possible uses is always welcome. This aligns with the goal of "Building resilient infrastructure, promoting inclusive and sustainable industrialization, and fostering innovation" (Figure 5).

Figure 5. *Industries, innovation and infrastructure*

Biopolymers have a crucial role in promoting innovation, supporting sustainable industry practices and developing modern and improved infrastructures.

The ability of these materials for naturally breaking down into harmless pieces has had a great positive effect on reducing pollution and the use of other petroleum based polymers, which can really have detrimental effects on the world nowadays. The spirit of taking into account more sustainable and friendly perspectives when facing issues, involuntarily leads us to a more developed society with the willness of having a more responsible consumption that influences consumer choices and industry trends.

While Polylactide reaches everyone's ears, its role in waste management and circular economy becomes increasingly more important. Biopolymers contribute to the development of a circular economy where ecodesign is one of the main pillars that can tackle goals in recycling plastic waste. Therefore, many industry policies will have a turnaround when shaping them, as the positive effects that these materials have will eventually be reflected in our day to day lives.

4. Objectives and scope of the research

The aim of the project is to obtain copolymers based on L-lactide and ethylene brassylate with tunable mechanical properties, as well as evaluating the effect of temperature in order to increase ductility and observe its effect on mechanical attributes. To achieve this objective, the following phases need to be carried out:

- **Phase I:** Synthesize three copolymers based on L-lactide and ethylene brassylate (Pure PLLA, PLEB9010, PLEB8020)
- **Phase II:** Characterization of the three copolymers to determine their transition temperatures (DSC), molecular weight (GPC) and their composition (NMR).
- **Phase III:** Obtain polymeric films using compression molding.
- **Phase IV:** Analysis of mechanical properties through tensile tests at room temperature and at 37 ºC .

The scope of the work includes the analysis and interpretation of the studies conducted. It is expected to obtain results that may provide certain added value and can be of great assistance for future studies regarding PLA. Figure 6 illustrates the Work Breakdown Structure (WBS) of the project, outlining the detailed tasks and phases involved in achieving the objectives.

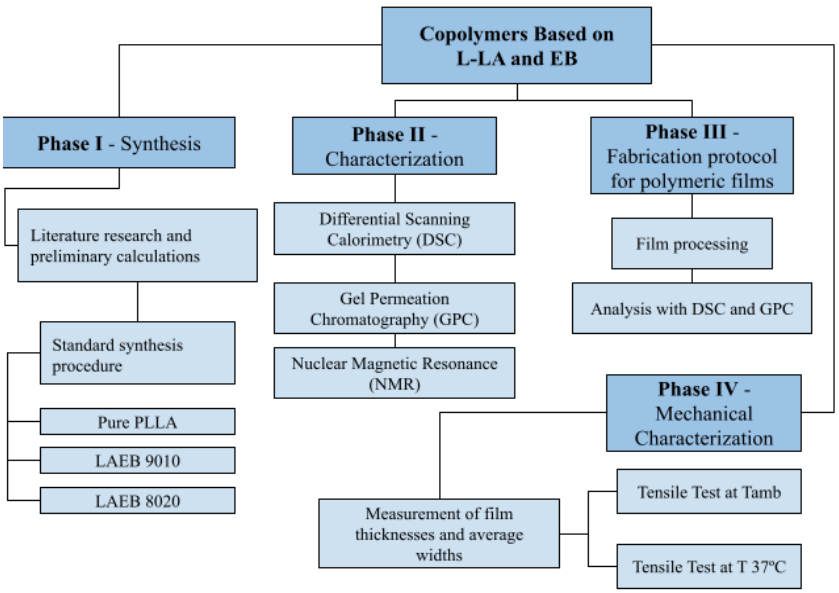

Figure 6. *WBS of the project*

5. Benefits of the research

There are several reasons why this research work may have an actual interest for certain scientific fields, especially for the biomedical one, but also for the analysis of different materials, whose properties have not been analyzed in detail before.

Up to now, copolymerization with ethylene brassylate (EB) has been scarcely studied. Also known as ethylene-tridecane-dioate, is a colorless liquid with a sweet taste that is frequently found in cosmetics, perfumes, cleaners or even detergents. It was not until 1999 when EB was synthesized using lipase enzymes (biological catalyst that facilitates the breakdown of lipids into smaller molecules). However, these synthesis had low polymerization rates and were only able to obtain low molecular weights.

Polymers derived from ethylene brassylate (i.e., poly(ethylene brassylate)) present similar mechanical properties to other compounds (e.g., epsilon-caprolactone or omega-pentadecalactone), but have a much lower cost. Therefore, it seems as a greater choice to be copolymerized with L-lactide at a first sight, as it may improve some of the issues that epsilon-caprolactone presents.

By polymerizing L-lactide with ethylene brassylate, we are able to go from a rigid polymer (PLA without being synthesized with lactones) to a more elastomeric one, compatible with soft tissues and that allows us to take advantage of its cytocompatibility.

Medical Advancements

The main reason for this research relies on biomedicine, where polymers play a crucial role in tissue engineering. Recent studies highlight the increasing importance of biomaterials in creating three dimensional prototypes that serve as cell anchor matrices. Advanced technologies such as nanotechnology and micromanufacturing have significantly contributed to the development of soft tissues for human applications [7].

Analyzing the mechanical properties of these polymers is essential due to the precision required in their application. The synthesis methods and the optimal composition are critical factors for improving their potential uses, which may include non-invasive techniques or implants. These advancements in polymer technology not only enhance medical treatments but also pave the way for innovative solutions in healthcare.

Technical benefits

Nanostructured scaffolds based on biopolymers offer precise emulation of the nanoscale environment, which is crucial for neuronal cell adhesion and integration. They also promote tissue regeneration in nerve injury treatments and neural testing [8].

Moreover, biopolymers in drug release systems ensure biocompatibility and controlled drug delivery, evolving from traditional methods to advanced technologies. This enables precise drug release profiles and supports sustainable medicine practices, enhancing therapeutic options for diverse medical needs [9].

Social benefits

Biopolymers offer life advancements by developing medical treatments for conditions like nerve injuries and neurological disorders. They enhance tissue regeneration and support more effective neural testing, potentially reducing healthcare costs and improving the quality of life of the patient.

Advanced technologies like 3D printing enable personalized medicine approaches, promoting equitable access to effective treatments. Additionally, biopolymers contribute to sustainable healthcare practices, aligning medical advancements with environmental responsibility.

Economic benefits

This research holds promise for future developments in the biomedical field that may have potential outcomes related with job creation and economic growth within related sectors.

As these technologies progress and become more widely adopted, they stand to not only enhance patient care, but also contribute positively to the economic landscape by encouraging innovation and efficiency in healthcare.

6. State of the art

Biodegradable polymers are eco-friendly materials that break down naturally through microbial or enzymatic action. These include aliphatic (organic compounds with straight or branched chain carbon atoms) and aliphatic/aromatic (include both chain-like and ring-like carbon structures) polyesters, designed to replace conventional plastics. They decompose into harmless byproducts, addressing environmental concerns and resource exhaustion [10]. In fact, in recent years they are becoming increasingly more important for being a 'friendly' alternative in comparison with non-degradable polymers and for contributing to tackle the carbon footprint issue.

Polymer science can be considered as a relatively new discipline which includes a very large number of areas. From the field of science it does comprise aspects from chemistry, physics and mechanical engineering, among others. This section aims to provide a brief review of all the fundamentals that encompass the project, which are necessary to understand everything analyzed about the copolymer.

6.1. Polymer synthesis

In recent years, it is apparent that all the possible monomers have already been polymerized and there is no need to keep racking our brains trying to find the way of commercializing new plastics on a large scale. However, there has been a considerable interest in finding new ways of reducing costs that producing polymers require by studying the use of new catalysts, and also in the production of better defined chain structures for obtaining controlled properties.

Polymers can be synthesized in various ways depending on the aim and the aspects required. In the following table 1, some of the synthesis mechanisms are assessed and the one that concerns us will be further developed [11][12][13].

Table 1. *Overview and Evaluation of Various Polymer Synthesis Mechanisms*

Mechanism	Brief explanation	Range of applications
Free Radical Polymerization (FRP)	Addition of free radical building blocks (repetitive units)	Plastics, adhesives, coatings, and elastomers
Photopolymerization	Photochemical reaction with a catalyst to obtain a polymer chain	Dental resins, 3D printing
Condensation Polymerization	Formation of polymers through the elimination of small molecules (e.g., water or methanol)	Polyesters, polyamides, and other high-performance polymers
Graft Copolymerization	Introduction of side chains attached to polymer's backbone	Modification of polymer properties
Ring Opening Polymerization (ROP)	Opening of cyclic monomers to initiate polymer chain formation	Biodegradable polymers (e.g., polylactide), drug delivery systems

Ring opening polymerization (ROP)

In the case of polylactide (PLA), the process where lactide monomers undergo polymerization in order to form repetitive polylactide units is known as ring opening polymerization. This technique is commonly used to synthesize biodegradable and biocompatible polymers, allowing the polymer to obtain controlled mechanical properties, better redefined chain structures and low polydispersity (narrow molecular weight distribution).

Polymerization starts with cyclic molecules with functional groups that are susceptible to nucleophilic or electrophilic attacks coming from positive or negative ions [14]. These ions will act as originators of the reactions and will promote the opening of the ring.

The chemical compound that favors polymerization by itself is known as an initiator. This initiator supplies the energy necessary to break down the monomers link and allows the formation of new polymeric chains. ROP with polylactide usually starts from a cyclic diester monomer (lactide) which is obtained from lactic acid. Afterwards, when lactide undergoes ring opening process, the initiator is able to react with reactive ends of lactide that have been exposed by splitting the cyclic ester ring (lactones have rings going from 3 to 20 membered rings). Polymerization continues by forming a growing polymer chain that is eventually consumed or finished deliberately. Once the process is completed, the result is a linear chain formed by lactide units that form PLA [15].

It is important to highlight that the catalyst or initiator does not become part of the final polymer. In fact, its only goal is to promote the formation of polymeric chains and enable the formation of the polymer. Figure 7 illustrates the ROP process of L-lactide. Depending on the catalyst, the monomer and the reaction conditions, a wide variety of polymers can be obtained through ROP (e.g., nylons, polycarbonates, polyesters,etc.).

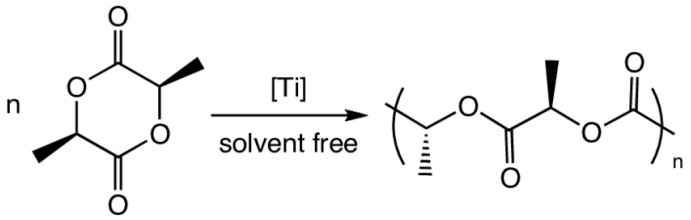

Figure 7. *ROP of L-lactide*

6.2. Crystalline structure of polymeric materials

Unlike metals or ceramic materials, polymers are not able to be completely crystalline. In fact, they are only able to achieve a certain degree of crystallinity and therefore they are known as 'semicrystalline'.

Crystallinity in a polymer is a complex process that involves the arrangement of long polymeric chains consisting of the packing of long molecular chains to produce an ordered atomic arrangement, giving rise to a crystal that can be classified into a crystalline system. However, only a small segment of the polymeric chain becomes part of the unit cell [16].

On the other hand, crystallinity in a polymer is able to provide high mechanical performance, better chemical and thermal resistance and higher density, while it suffers a loss of transparency. Figure 8 illustrates a lamella, which is a stack of polymer chains folded back on themselves. Lamellas are individual crystals within polymers, and within them, polymeric chains are arranged in a folded manner.

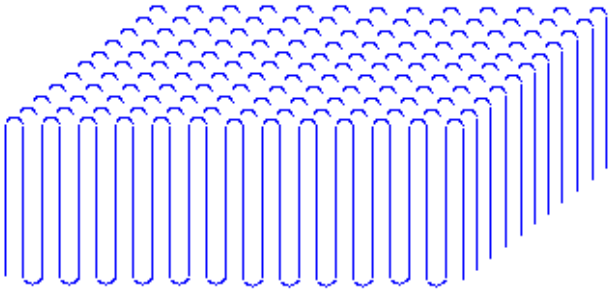

Figure 8. *Lamella - Stack of polymer chains folded back on themselves*

On the other hand, there are a large number of polymers that do not present a long-range order and can not be considered as semicrystalline. These polymers are considered to be amorphous. In the following figure (Figure 9), the difference between the two systems can be appreciated and how the degree of crystallinity affects the way the polymer is arranged [17].

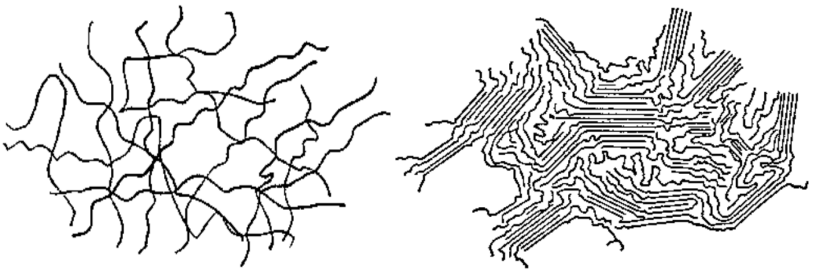

Figure 9. *Amorphous structure vs Semi Crystalline structure*

Polymers do present a wide variability in terms of mechanical and thermal properties that have a lot to do with the degree of crystallinity and the glass transition temperature, and are also favored by low cooling rates in order to give the polymer chains time to sort themselves out. Therefore, a high degree of crystallinity and crosslinking is directly related to a polymer with decent mechanical features.

In short, amorphous polymers are the ones that exhibit an irregular, short-range structure (e.g., polyethylene, branched polymers, etc.), and semicrystalline are the ones with an ordered, long-range structure that also present amorphous regions [17].

6.3. Mechanical properties

Mechanical properties refer to the characteristics that specify response from the material against various types of forces and loads. These properties are commonly determined throughout studies accomplished in laboratories, which are capable of mimicking with certainty natural conditions (e.g., temperature, humidity, surface conditions, etc.).

In the case of the Lactide:Ethylene Brassylate (LA:EB) copolymer, we are faced with a material composed of two building blocks with radically different mechanical properties. Because of this, it is necessary to carry out a study to determine its behavior under different stresses so that it can be used in controlled drug release systems or in bone fixation implants.

The most common test to obtain stress-strain curves is the tensile test. This method registers dimensional changes in the object while a known force is applied. For doing so, a load in the direction of the axis of the specimen is employed at a constant pace. The test lasts for the time it takes for the breakage to occur, obtaining an elongation-load curve.

For the case of specimens, these meticulously designed elements commonly follow preestablished standardized measures, in order to have a more controlled trial by imposing restrictions on the geometrical shape of the specimen. When relating test conditions for molding and extrusion, specimens adhere to the ISO 527-2 Standard, which ensures high comparability between results across different laboratories, companies, or international studies (see Figure 11 for the form and dimensions of the test tube following ISO 527-2 Norm) [19].

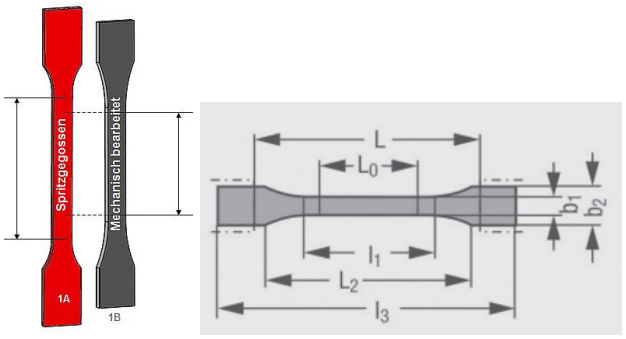

Figure 11. *Form and dimension of the specimen following ISO 527-2 Standard*

In a large number of materials, the relation between stress and strain in the elastic region has a linear behavior. For these materials, the elastic modulus can be determined using Hooke's law expressed as: **s = E * e** (s: stress, E: Young's modulus, e: unit elongation). However, there is also the case where the relation between stress and strain in the elastic region is not linear. For these cases, the tangent or secant modulus can be used as an alternative.

Tensile properties in polymers have a real interest when designing plastic parts and predicting their performance under stress, particularly when used in structural applications [20]. The following table 2 shows some of the most characteristic values that are recorded in these tests.

Table 2. *Key Parameters and Values Recorded in ISO 527 Tensile Testing for Characterizing Polymer Mechanical Properties [19]*

Characteristic value	Brief description
Tensile stress	Force referred to initial section of the test tube
Elastic modulus	Ability of a material to deform elastically under tension or compression.
Yield point	Transition from elastic to plastic behavior
Break point	Point when the material suffers fracture or breaks
Deformation	Measurement length variation
Poisson coefficient	Material's lateral contraction when subjected to longitudinal extension

On the other hand, in tensile tests plastic usually does not break down in an homogeneous way. In fact, stress tends to focus on a relatively small part of the sample, also known as 'necking' [22]. In this section, the cross-sectional area of the specimen is reduced due to traction which it is subjected to. Therefore, when measuring engineering stresses, this behavior is disregarded.

As the extensometer is not always able to measure by itself the breakage percentage, a term known as 'nominal deformation' is used. This term quantifies the amount of stretching or elongation a material undergoes under a tensile test. It is often expressed as a ratio and calculated by dividing the specimen length change by the original length.

6.4. Elastic and plastic regions

Elasticity refers to the ability to deform proportionally to an applied load and regain its original shape once the load is removed. Plasticity, on the other hand, describes the capacity of the material to deform permanently when subjected to a load exceeding its elastic limit, with these deformations persisting after the load is lifted [18].

The stress-strain curve provides insight into how a material will respond to an applied load. This curve reveals key characteristic values, including:

Elastic limit - Maximum stress an elastoplastic material can withstand without undergoing permanent deformations.

Yield strength (S_y) - The stress at which a material begins to deform permanently under tensile loading, marking the onset of plastic deformation.

Ultimate tensile strength (S_r)- Maximum stress a material can withstand while being stretched or pulled before breaking.

For small deformations, it is reasonable to assume that engineering strain **(e)** is similar to true strain **(ε)**. However, for large deformations, this relationship breaks down. In the case of being in the plastic regime, only true strain (ε) is used (see Figure 10).

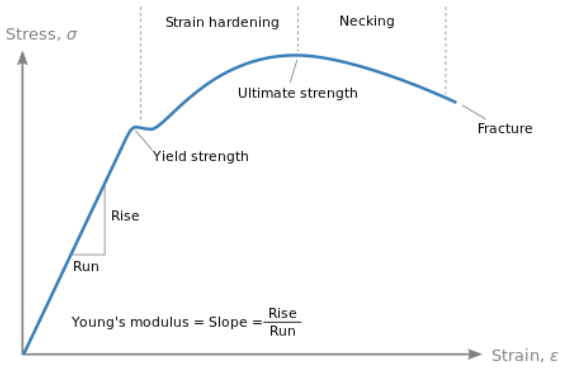

Figure 10. *Stress-Strain curve*

6.5. Glass transition (T_g) & melting temperatures (T_m)

As we know, polymers are formed by covalent bonds of repetitive units and can not be entirely cristalline (they can be either amorphous or semicrystalline). Amorphous polymers have a softening temperature where they present a vitreous, fragile behavior when they are found below it, and a viscoelastic one when being above. This is known as glass transition temperature (T_g) and refers to the point where the polymer experiences a change in its molecular arrangement and movement. T_g plays a crucial role in predicting thermal and mechanical properties of polymers, especially when aspects such as the brittleness or elastomeric behavior of the polymer are of vital importance for its understanding [21]. Glass transition temperature can be determined using a Differential Scanning Calorimetry (DSC).

In contrast, semicrystalline polymers can crystallize, and their polymeric chains exhibit a certain degree of uniformity. Therefore, not only do they have a glass transition temperature (T_g), but also a melting temperature (T_m). T_m represents the point where a crystalline material undergoes an abrupt volumetric change at a constant temperature, as secondary bonds that hold the chains together are surpassed (see figure 12).

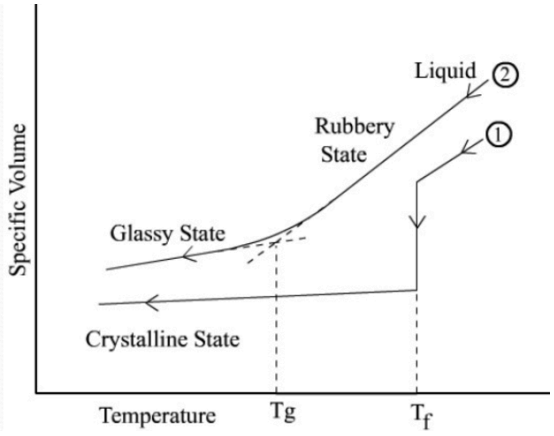

Figure 12. *Glass and melting temperatures of polymers*

7. Risk analysis

This section aims to identify the possible risks that may have an impact on the project and are likely to occur. In order to analyze those risks, a probability-impact matrix is going to be used for classifying the risks, the likelihood of them happening and the consequences that may lead to. Afterwards, a contingency plan will be designed and all the possible alternatives will be studied.

7.1. List of risks

- Laboratory incidents (1)
- Synthesis failure (2)
- Quality risks (3)
- Issue in processing samples (4)
- Delay due to stock shortage (5)

7.2. Detailed study

- Laboratory incidents (1)

It is not new that a lot of events can happen inside the experimental zone (e.g., power outages, incidents related with the use and deposition of reagents, fires, equipment with elevated employment risks, etc.).

Consequently, taking into account the low experience of the students in the laboratory security and all the possible risks that are related to handling damaging substances and equipment, the chances are **probable** to happen **(0.7).**

Besides, as the range of incidents that can be unleashed go from barely damaging issues which are very likely to happen (e.g., unintentional unset of a device) to real life risking ones which are less probable (e.g., causing a fire), the overall **impact** can be considered to be **high (0.4).**

- Synthesis failure (2)

Synthetic process of polymers involves a certain amount of risks that forces the student to perform the tests with extreme caution and without hesitation. The weighing of each substance and its preparation for synthesis do not pose a real risk. However, having to work with oils that exceed 140 ºC in order to carry out the process can present a real physical hazard.

Regarding all the incidents that may occur and all the safety measures that take part during the synthesis process, the **probability** of suffering an incident in this stage of the project is **unlikely (0.3).**

In terms of **impact**, accidentally putting your hand in burning oil or accidentally getting touched by a drop of methanol in the eye during the precipitation process can have fatal consequences. Thereby, this situations require to be classified as **very high (0.8)**

- Quality risks (3)

These risks arise from deviations during synthesis that can affect the strength, durability and functionality of the polymer. Impurities and inconsistent processing conditions may lead to unpredictable physical and chemical properties, compromising the integrity of the material. Managing these risks requires strict quality control measures and adherence to regulatory standards to ensure consistent product quality and performance.

As a result, the **impact** of wrong executions during synthesis can be listed as **low (0.1)**.

In terms of probability, however, the likelihood of this kind of incident regardless of experience level and considering statistical certainty, the **probability** is **very likely (0.9).**

- Issue in processing samples (4)

Even though samples have been developed following the established procedure, there is always a chance that, when analyzing them, the efficiency and results are not what is expected. These issues could have occurred due to several reasons which are not entirely in the student's hands (e.g., losing a lot of polymer during the synthetic process for not letting it stand for the right amount of time).

Making use of the matrix, the **probability** that these problems occur is **high (0.7)** and it can have serious impact in terms of time and money costs, due to the large amount of requirements that these processes involve. Therefore, the **impact** can be classified as **very high (0.8)**.

- Delay due to stock shortage (5)

The main materials used in this project include L-lactide, Ethylene Brassylate, Triphenyl Bismuth (catalyst). In theory, the laboratory is equipped with a sufficient amount of every substance used, and if that is not the case, those in charge of keeping an eye on the stock will incorporate the amount needed as soon as possible.

There is always the chance that, for any reason, the laboratory lacks a specific substance, but the odds are **very low (0.1).** In terms of **impact**, the risk can be considered as **low (0.1).**

Taking into account the perspective that the table shows on the hazards, it is clear that it is not exactly a study of low risk, as it contemplates situations of high danger and should be studied and carried out with the greatest possible caution (always with the help of a professional working in the laboratory or the supervisor in charge of the study).

Table 3 summarizes the Probability-Impact matrix of the project, highlighting potential risks and emphasizing by laboratory experts.

Table 3. *Probability-Impact matrix of the project*

PROBABILITY		IMPACT				
		Very Low (0. 05)	Low (0.1)	Moderate (0.2)	High (0.4)	Very High (0.8)
	Rarely (0.1)	Low 0.005	Low (5) 0,01	Low 0.02	Moderate 0.04	Moderate 0.08
	Unlikely (0.3)	Low 0.015	Low 0.03	Moderate 0.06	Moderate 0.12	High (2) 0.24
	Possible (0.5)	Low 0.025	Moderate 0.05	Moderate 0.1	High 0.2	High 0.4
	Probable (0.7)	Low 0.035	Moderate 0.07	Moderate 0.14	High (1) 0.28	High (4) 0.56
	Very likely (0.9)	Moderate 0.045	Moderate (3) 0.09	High 0.18	High 0.36	High 0.72

8. Contingency plan

Once the probability-impact matrix has been analyzed, this section considers the possible alternatives that could be implemented to minimize the risk presented in these cases.

- Laboratory incidents (1)

As the risks contemplated vary a lot from each other, both in seriousness and range, the measures to be adopted must be adapted to each case depending on the severity of the danger. Fortunately, ZIBIO Group has a 'workplace safety and risk' manual that considers most of the risks that may happen inside the laboratory.

It is the responsibility of the student to act with prudence and be aware of all the dangers that can occur within the site to know where everything is deposited. In case of doubt, it is key to always ask for help before leaving an object or chemical in any way.

- Synthesis failure (2)

In order to develop a study in the safest way, it is vital that the synthesis process is done with extreme caution and always with supervision. In addition, to avoid possible toxicity or problems caused by methanol in the precipitation process, work was conducted under an extraction hood, using gloves and protective goggles.

- Quality risks (3)

Polymer synthesis involves strict monitoring of parameters like temperature and reaction time to ensure consistency. Moreover, adherence to standardized procedures for handling monomers and catalysts are crucial to prevent contamination and to keep the reaction developing. Immediate response protocols will address any variance, with adjustments to reaction conditions or purification methods such as methanol precipitation. Equipment will be regularly calibrated and personnel trained to maintain quality standards will remain in charge of the project. Effective communication will facilitate quick resolution of any quality issues, ensuring that synthesized copolymers consistently meet specifications.

- Issue in processing samples (4)

The efficiency of (co)polymerization reaction is a factor that can seriously affect the result. In order to obtain a copolymer that retains almost all of its initial weight, all processes will be developed having carefully studied the exact amount of substance to be used, the temperature at which to carry them out and the settling time of the sample.

- Delay due to stock shortage (5)

In order to minimize the risk of running out of supplies, it is crucial to keep laboratory staff informed about material usage and give them notice when it is anticipated that existing stock will run out, facilitating the replenishment of materials.

9. Phase and task description

This section aims to give a brief description of all the phases and tasks performed throughout the research. It also includes the equipment and resources employed, task duration and work load. Afterwards, phases will be explained in detail and a Gantt diagram referred to the tasks will be presented.

Phase 0. Bibliographic research

In this stage, the basis for a research project is established. This phase involves gathering existing information from a wide variety of studies within the field that serve as an essential source of knowledge for developing future inquiries. Furthermore, getting deep into these works is crucial for formulating methodologies tailored to the specific needs of the study. Thus, bibliographic research serves as a cornerstone in guiding the trajectory, shaping new approaches and contextualizing the new study.

- ➔ **Equipment and resources:** Computer and relevant websites
- ➔ **Workload:** 40 h
- ➔ **Duration:** 6 months

Phase I. Synthesis (PLLA, PLEB9010, PLEB8020)

This phase describes the process by which the copolymer is synthesized from the monomers L-lactide and ethylene brassylate. It includes the amount of monomers employed for its development and the corresponding standardized process.

Task 1.1. Previous calculations

The values obtained for every copolymer in relation with the amount of catalyst used, and all the mass ratios referring to the Lactide and ethylene brassylate monomers.

- ➔ **Equipment and resources:** Computer
- ➔ **Workload:** 1 h
- ➔ **Duration:** 1 day

Task 1.2. Standard procedure

This task involves following a standardized procedure to synthesize a copolymer using ring-opening polymerization with L-lactide and ethylene brassylate monomers. The process includes preparing the reaction mixture in a flask submerged in an oil bath at 140 ºC, adding the catalyst and allowing the reaction to proceed for approximately 24 h. Different monomer ratios are tested, and the resulting copolymers are purified by precipitation and drying techniques. This process ensures reproducibility and consistency in copolymer synthesis.

- ➔ **Equipment and resources:** L-lactide, ethylene brassylate, Ph3Bi, Ohaus Pioneer Precision Balance, IKA C-MAG HS7 magnetic stirrer, dichloromethane, methanol, needles and syringes
- ➔ **Workload:** 10 h
- ➔ **Duration:** 5 weeks

Milestone 1: Synthesis completed and copolymers delivered for subsequent analysis.

Phase II. Characterization

The characterization process involved three main analytical techniques: Differential Scanning Calorimetry (DSC), Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR) spectroscopy. DSC was used to determine thermal properties including glass transition temperature (T_g) and melting temperature (T_m). GPC provided molecular weight information, while NMR spectroscopy confirmed the real composition of the copolymers.

Task 2.1. Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimeter (DSC) was used to analyze the glass transition temperature (T_g) and melting temperature (T_m) of the synthesized copolymers. DSC tests were conducted on both the copolymers and polymeric films obtained by compression molding to study their thermal behavior.

- ➔ **Equipment and resources:** DSC Q200 (TA Instruments)
- ➔ **Workload:** 6 h
- ➔ **Duration:** 3 weeks

Task 2.2. Gel Permeation Chromatography (GPC)

This task focused on employing Gel Permeation Chromatography (GPC) to measure the molecular weight (MW) of both the synthesized copolymers and the resulting polymeric films. Six samples (using chloroform as a solvent) underwent analysis on a Waters 1515 GPC device, with specific parameters set for flow rate, pressure and temperature.

- ➔ **Equipment and resources:** Waters 1515 GPC (Milford, United States)
- ➔ **Workload:** 3 h
- ➔ **Duration:** 1 day

Task 2.3. Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy was used to confirm the quantity of L-lactide and Ethylene Brassylate copolymerized during synthesis. NMR report is received once it is fulfilled.

- ➔ **Externally performed**
- ➔ **Workload:** 4 weeks

Milestone 2: Characterization completed

Phase III. Fabrication protocol for polymeric films

Films were processed using samples weighing around 4 g. Films obtained had an average thickness of 250 µm. Variations in processing were made for different copolymers and resulting films were analyzed for changes using DSC and GPC.

Task 3.1. Film Processing

The first task involved processing films using the Collin P200 E Press. Copolymer samples were chopped and placed inside metallic plaques, covered with Teflon sheets, and subjected to heating and pressure. Films were processed twice in order to prepare samples for two different tensile tests.

- ➔ **Equipment and resources:** Collin P200 E Press
- ➔ **Workload:** 9 h
- ➔ **Duration:** 4 weeks

Task 3.2. Analysis with DSC and GPC

The process required subjecting the obtained films to analysis using a Differential Scanning Calorimeter (DSC) and Gel Permeation Chromatography (GPC). These analyses aimed to assess any changes in temperature and molecular weight resulting from degradation caused by the press.

- ➔ **Equipment and resources:** DSC and GPC
- ➔ **Workload:** 8 h
- ➔ **Duration:** 2 weeks

Phase IV. Mechanical Characterization

Five specimens per polymer, adhering to ISO 527-2 standards, were prepared and marked for analyzing its mechanical properties. Tests were conducted at both room temperature and 37 ºC.

Task 4.1. Thicknesses and average widths of the 3 polymeric films

This task involved measuring the thicknesses and widths of three polymeric films at three different points within the necking zone using a micrometer with a resolution of 0.001 mm. These measurements were crucial for ensuring accurate input into the Bluehill software, used to conduct the tensile test.

- ➔ **Equipment and resources:** Micrometer
- ➔ **Workload:** 2 h
- ➔ **Duration:** 1 day

Task 4.2. Execution of tensile testing

Instron 5565 machine performed tensile tests on three copolymers to analyze Young's modulus, deformation and ultimate tensile strength. Specimens, following ISO 527-2 standards, were prepared with marked gripping zones, numbered and tested at both room temperature and 37 ºC.

- ➔ **Equipment and resources:** Instron 5565 testing device, Bluehill software
- ➔ **Workload:** 10 h
- ➔ **Duration:** 4 weeks

Milestone 3: Experimental work finished

Results and discussion

Throughout the duration of the project, a lot of effort has been dedicated to processing and analyzing the experimental results. This phase gained importance as the experimental part was coming to an end and remained as an ongoing endeavor.

- ➔ **Equipment and resources:** Computer, OriginPro License, Biorender
- ➔ **Workload:** 60 h
- ➔ **Duration:** 12 weeks

Milestone 4: Report finished

10. Procedure

10.1. Phase I - Synthesis (PLLA, PLEB9010, PLEB8020)

Equipment description

L-lactide monomer was supplied by Corbion (Netherlands), while ethylene brassylate comes from Sigma Aldrich (Spain). The catalyst employed, triphenyl bismuth (Ph3Bi), was provided by Gelest (United States). For the precipitation process, dichloromethane and methanol were supplied by Fisher Scientific (Spain). Furthermore, needles (Injeckt) and syringes (100 Sterican) were used to bubble nitrogen during the synthesis process.

IKA C-MAG HS7 magnetic stirrer has been used to immerse the flask containing the polymer mixture in an oil bath and bring it to a fixed temperature of 140 ºC. Ohaus Pioneer Precision Balance (OHAUS, Europe) has been used to measure and calibrate all compounds used in the synthesis of the copolymer.

Method

All three copolymers had undergone a ring opening polymerization synthesis. The method employed in our case includes a reaction through an oil bath at a fixed temperature (140 ºC) by immersing a round bottom flask to develop the synthesis. The flask had an ongoing nitrogen flow for 15 min, bubbling continuously and always in contact with the monomers. Afterwards, the catalyst (Ph3Bi) was added and the hot plate magnetic stirrer was kept at 150 rpm for approximately 24 h at 140 ºC.

Two different L:EB mass ratios were fed in the process, and for all three cases Ph3Bi catalyst weight (mg) used required previous calculations. The following table 4 shows comonomers/catalyst feed ratios, all with a 500:1 catalyst molar ratio and the quantity employed for each case.

MW: L-lactide 144.12 g/mol, Ethylene Brassylate 270.36 g/mol, Ph3Bi 440.3 g/mol

Table 4. *Weight percentages of L-lactide (LLA) and Ethylene Brassylate (EB), along with the catalyst-to-monomer (M/C) ratio and the corresponding amount of Ph3Bi catalyst in milligrams (mg) for three copolymer compositions.*

	L-lactide (wt %)	EB (wt %)	Ph3Bi (M/C)	Ph3Bi (mg)
Pure PLLA	100	0	500:1	61.1
PLEB 9010	90	10	500:1	58.1
PLEB 8020	80	20	500:1	55.4

The following images (Figure 13) provide a visual representation of how the monomers are pre-weighed and arranged in the flask, ensuring minimal loss of monomer. Then, the flask is submerged in the oil bath, covered, and brought to a fixed temperature of 140°C, where it will remain for nearly 24 h.

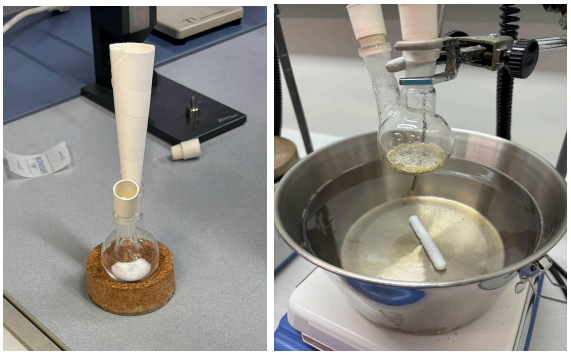

Figure 13. *Flask containing PLEB 8020 and submerged in oil bath*

Once the product is obtained, dichloromethane (CH2Cl2) is used to dissolve it, and then it is precipitated with methanol. This way, impurities generated by the use of the catalyst, as well as undissolved monomers are removed.

Finally, the polymer was left drying for 24 h at room temperature. Subsequently, it was placed in the oven at 100 °C and 60 mbar for 1 hour and phase I was concluded (see Figure 14). Once the three systems are obtained, phase II (characterization) initiates, where the three copolymers will be analyzed in depth.

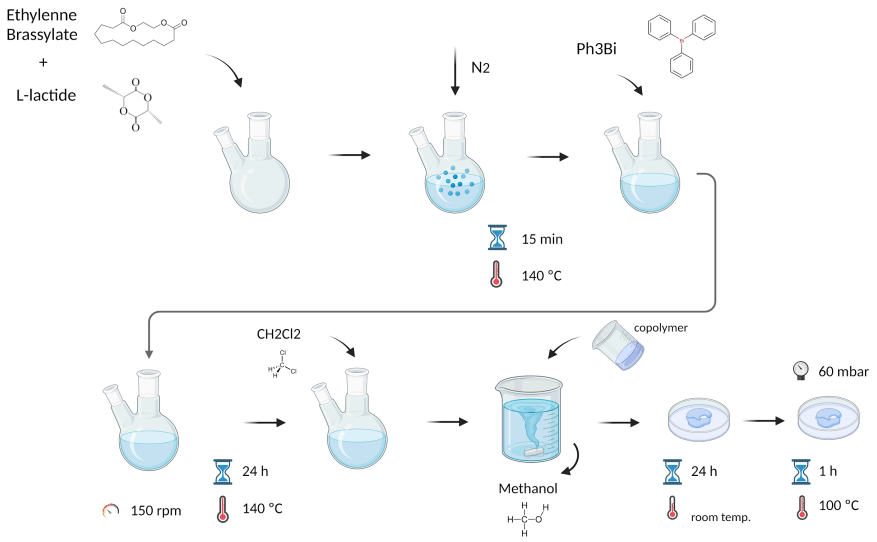

Figure 14. *Comprehensive Overview of the Synthesis Process (Biorender)*

10.2. Phase II - Characterization

10.2.1. Differential Scanning Calorimetry (DSC)

Equipment description

Thermal properties of the synthesized copolymers were analyzed by a Q200 Differential Scanning Calorimeter (TA Instruments, United States). Samples weighing around 5 mg were analyzed to study their thermal behavior, glass transition temperature (T_g), melting temperature (T_m), and melting enthalpy (ΔH_m). Samples were encapsulated in aluminum pans and two scans were performed. Scans were carried out from 20 to 210 ºC for all 3 samples (Pure PLLA, PLEB9010, PLEB8020).

Method

Differential Scanning Calorimeter (TA Instruments) was used for analyzing T_g and T_m of the synthesized copolymers. Samples weighing around 5 mg were encapsulated within aluminum pans (TA Instruments) with the help of dies.

Pan was introduced inside the lid and the system was designed so that two scans were performed, the first of which had the sole purpose of erasing the thermal history of the polymer and studying it from a 'virgin state' (for the entire process, a flow of 50 ml/min of nitrogen at 1 bar is used). First, it was equilibrated from -20 ºC, and a ramp from 20 ºC to 210 ºC at a rate of 20 ºC/min was designed, surpassing the melting temperature of the (co)polymer. Once the first scan was completed, an isotherm was applied for 2 min, and it was re-equilibrated at -20 ºC. Then, the second scan was carried out, where T_g, T_m, recrystallization temperature, and their respective enthalpies could be observed.

The results obtained were very consistent from the beginning, without the need to repeat the process for any of the three copolymers, allowing their analysis and evaluation to begin effectively.

Additionally, three DSC tests were conducted on the polymeric films obtained by compression molding to observe how degradation during the process could have affected the characteristic temperatures. On this occasion, only one scan was performed for each film from 20 ºC to 210 ºC, as a second scan was not necessary. However, the samples obtained from the plates were made with an average weight of 7 mg.

Unfortunately, two out of the three scans corresponding to PLEB9010 and PLEB8020 had to be repeated for two reasons. One of them was a failure in the data processing system that caused the data to be unexpectedly erased, and the other was due to an anomaly in the curve of the glass transition temperature (T_g), which required the scan to be repeated. Afterwards, the two new samples were obtained favorably without requiring significant additional effort.

10.2.2. Gel Permeation Chromatography (GPC)

Equipment description

Waters 1515 GPC (Milford, United States) device was used for analyzing molecular weight of the synthesized copolymers, containing two styragel columns (effective at achieving high-resolution separation of polymers in the mid-to-high molecular weight range). Samples had an average concentration of 10 mg/mL in chloroform (solvent).

Method

Molecular weight (MW) of the synthesized copolymers and polymeric films was determined with a Waters 1515 GPC device. Firstly, six samples were prepared using an average of 10.5 mg/mL in chloroform as a solvent. The following table 5 shows the exact amount used in each chromatography test.

Table 5. *Composition and Preparation Details of Samples for Molecular Weight Analysis using Waters 1515 GPC Device*

	PLLA	PLLA Processed	PLEB 9010	PLEB 9010 Processed	PLEB 8020	PLEB 8020 Processed
Polymer (mg)	10.2	11.3	10.4	10.8	9.8	10.6
Chloroform (mL)	1	1.1	1	1.1	1	1.1

Before starting the process, the device is set with a constant flow of 0.1 mL/min in chloroform. Once the samples are prepared, a flow of 1 mL/min is established, with a pressure of 300 psi (20.7 bar) and it is set at a constant temperature. Once equilibrated, the recirculation is stopped in order to perform the test. Approximately 400 µL are injected per sample into the system and a time of 30 min is allocated for each sample, resulting in an assay lasting over 3 h.

10.2.3. Nuclear Magnetic Resonance (NMR)

Method

Copolymer composition was studied through proton and carbon nuclear magnetic resonance ((^{1}H) NMR and (^{13}C) NMR Spectroscopy Testing). Spectra were obtained using Bruker Avance DPX 300 (Bruker, United States) operating at 300.16 MHz for proton (^{1}H) NMR and at 75.5 MHz for carbon-13 (^{13}C) NMR, respectively (see Table 6). Samples were contained in 5 mm sample tubes and were maintained at room temperature (NMR experiments were conducted on 0.7 mL solutions of deuterated chloroform (CDCl3)[23].

Table 6. *Experimental parameters for proton (^{1}H) and carbon-13 (^{13}C) NMR spectroscopy.*

Parameter	(^{1}H) NMR	(^{13}C) NMR
Sample	10 mg	40 mg
Acquisition time	3 s	3 s
Delay time	1 s	4 s
Pulse duration	8.5 microseconds	5.5 microseconds
Spectral width	5000 Hz	18800 Hz
Number of scans	32	> 25000
Sequence	-	Inverse gated decoupled

Nuclear Magnetic Resonance has been used primarily for ensuring the quantity of L-lactide and Ethylene Brassylate that has actually been copolymerized through the synthesis process. Even though the monomer proportions employed are indicated in Table 4, the synthesis process itself and numerous variables can significantly impact the copolymer obtained, potentially leading to discrepancies between the intended and actual proportions. Spectroscopy will provide information about the actual copolymers produced, where their mechanical properties will be greatly influenced by these results. It will determine both the molar and weight composition of the three samples sent for analysis.

10.3. Phase III - Fabrication Protocol for Polymeric Films

Equipment description

Collin P200 E Press was used to manufacture polymeric films from previously synthesized copolymers. This device is equipped with hydraulic cylinders that allow exact force adjustment. These cylinders ensure that the films are generated in the most precise way by uniformly applying pressure and leaving no inconsistencies. In order to get the polymer to its melting point, the press is provided with heating plates responsible for distributing heat evenly and allowing the polymer to deform.

Furthermore, the press incorporates advanced monitoring systems, so that all the parameters are supervised in real time processing. Once the films are obtained, the press is equipped with a cooling system that automatically activates after the heating process is finished. This system ensures that the materials cool down uniformly and in a controlled manner, helping to prevent unwanted deformations and maintain the structural integrity of the final products.

Method

Films were processed using Collin P200 E Press. Three samples from the previously synthesized copolymers weighing 4 g were chopped and placed inside 10 x 12 cm metallic plaques, and covered with two thin sheets of Teflon.

The first plate was inserted once the press was preheated at 200 ºC. Using a manual button to raise the bottom plate towards the top plate, both plates are brought closer together so that the polymer melts for 5 min with the press door open. Subsequently, the door is closed and 45 s are waited. The pressure is then increased until reaching 200 bar and another 45 s are timed. Once this time has elapsed, the heating is turned off, and the water flow is turned on without reducing the pressure.

The films related to PLEB9010 and PLEB8020 were obtained in the same way, with the only difference being the temperature at which the press was preheated, which was 190 ºC and 180 ºC respectively (the addition of brassylate decreased the melting point and such high temperatures were not necessary).

After pressing, three polymeric films of 10 x 12 cm with an average thickness of 250 µm were obtained. These three films were subsequently subjected to DSC and GPC treatments to analyze how their characteristic temperatures and molecular weights could have evolved due to degradation caused by the press (see Figure 15).

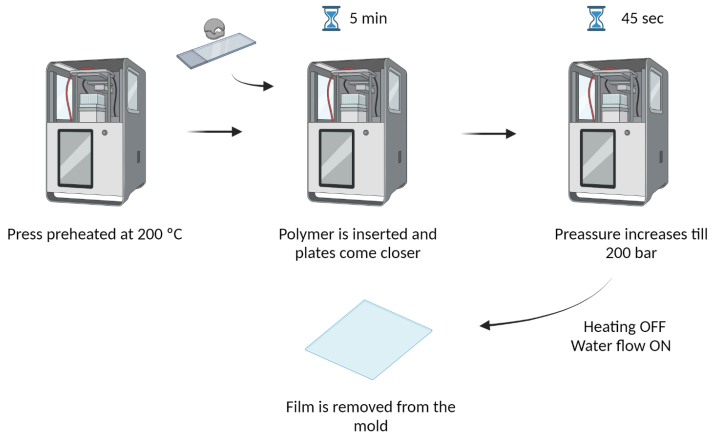

Figure 15. *Polymeric films obtained from compression molding (Biorender)*

10.4. Phase IV - Mechanical Testing: Tensile Strength Analysis

Equipment description

Tensile properties were studied with the Instron 5565 device (Instron, USA) under predetermined speed conditions. This machine is considered a universal testing equipment suitable for room temperature tests that allows strength and mechanical response under load analysis. The device utilizes a controlled gripping and traction system able to record deformations in the film at a constant force.

Bluehill software was used for monitoring the upper jaw and compiling all the necessary mechanical parameters for the analysis of the behavior of the (co)polymer. The test was conducted at room temperature and at body temperature (37 ºC) to see how temperature might affect the rigidity of the copolymer. Five determinations per film were done for analyzing mechanical properties.

Method

In order to study the Young's modulus, yield point, tensile strength and ultimate tensile strength, the Instron 5565 machine was employed to conduct the tensile test on the three copolymers.

The process of designing the specimens involved producing 5 samples per polymer, with approximate dimensions of 10x1 cm for subsequent analysis. Before the test, each sample underwent thickness and width measurements at three different points within the necking zone. The mean values were then calculated for each case, facilitating the input of adjusted measurements into the Bluehill software. The specimens were rectangular in shape and followed the ISO 527-2 standard for tensile testing.

In order to mark the gripping zone of the clamp and keep the zone visible, markings were made at both ends of the specimen, leaving a 5 cm necking zone visible. Each of them was also numbered to maintain proper order.

After the specimens were ready, the software was set up to input the necessary test parameters. The test was conducted at a speed of 10 mm/min, with a 5 cm separation between the grips as previously marked. The experiments were conducted at room temperature and at body temperature (37 ºC) using the average thickness and width values obtained earlier.

They were then placed between the grips, making sure to align the longitudinal axis of the specimen with the test axis. Afterwards, the grips were tightened to securely hold the specimen, avoiding any wrinkles or distortions and maintaining its straightness as much as possible (see Figure 16).

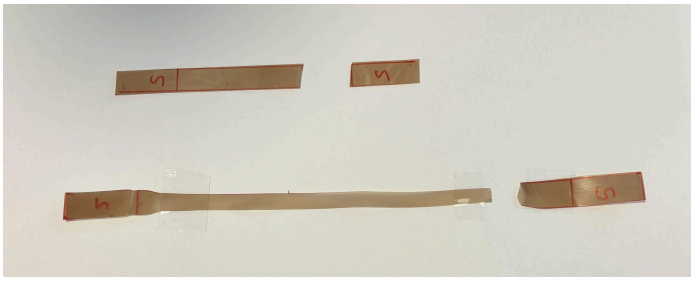

Figure 16. *Illustration of a specimen at Ta (above) and one at T 37 ºC (below)*

11. Gantt diagram

In the attached Gantt chart duration and phases will be visualized (Figure 17). This type of diagram allows a visual representation of phases, deadlines and tasks for better management. Horizontal bars are used to display the duration of each task and phase of the project, and milestones are indicated with a diamond shape.

This study aimed at analyzing mechanical properties and evaluating the effect of temperature on lactide and brassylate polymers lasted for 6 months (starting the last week of January and ending the second week of June).

Each phase has had a different duration due to various factors, but the study was carried out as efficiently as possible, with practically no failures during the process and only minor delays that did not cause any significant issues.

	Nombre
1	Bibliographic Research
2	Phase I - Synthesis
3	Task 1.1. Previous calculations
4	Task 1.2. Standard procedure
5	Synthesis completed
6	Phase II - Characterization
7	Task 2.1. Differential Scanning Calorimetry
8	Task 2.2. Gel Permeation Chromatography
9	Task 2.3. Nuclear Magnetic Resonance
10	Characterization completed
11	Phase III - Fabrication protocol for polymeric films
12	Task 3.1. Film Processing
13	Task 3.2. Analysis with DSC and GPC
14	Phase IV - Tensile Strength Analysis
15	Task 4.1. Thicknesses and average widths
16	Task 4.2. Execution of tensile testing
17	Experimental Work Finished
18	Results and Report Writting
19	Report Finished

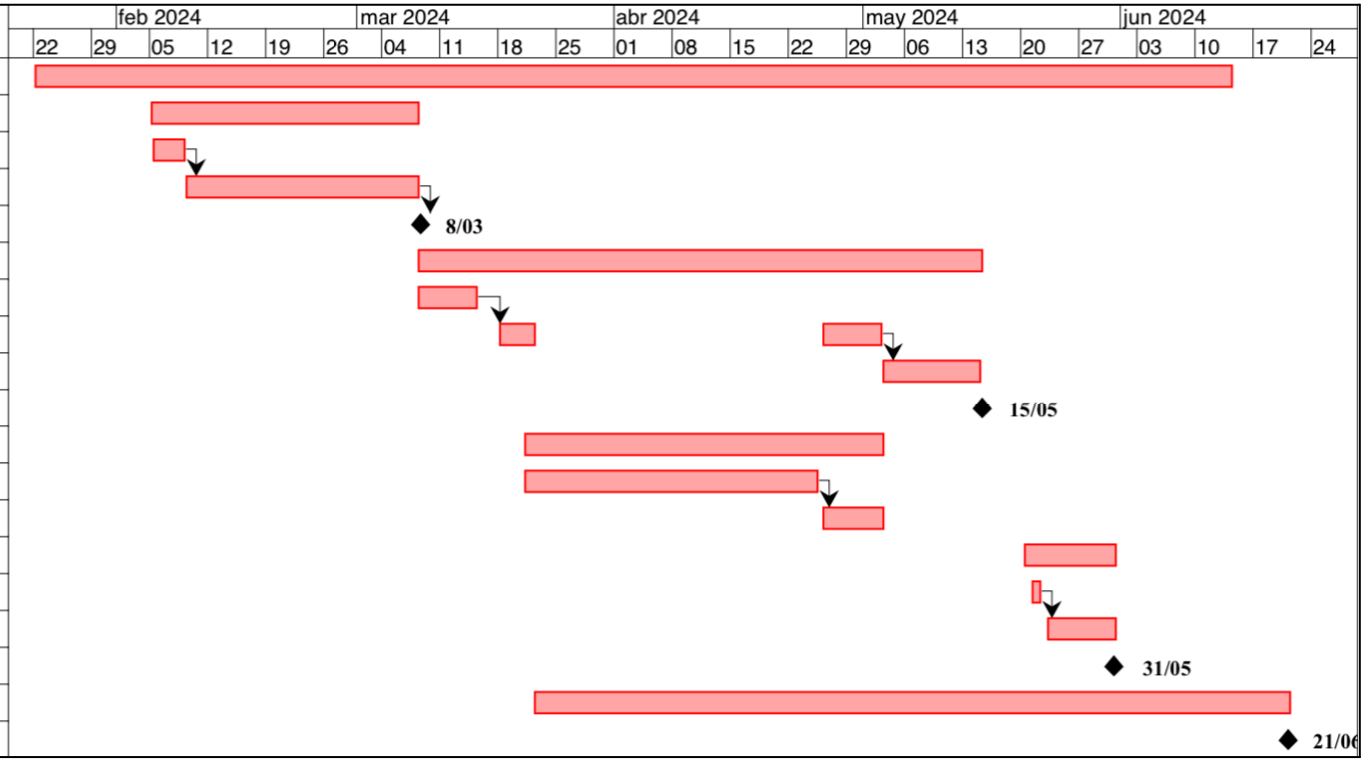

Figure 17. *Gantt Diagram*

12. Results Breakdown

The obtained results will be analyzed and discussed below. The results of Phases I and II, corresponding to the synthesis and characterization of the copolymers, as well as the mechanical properties obtained from the compression molding (Phases III and IV) will be examined.

12.1. Phases I and II (Synthesis and characterization)

Polymer yield

Each reaction was fed with a total of 10 g of (co)monomers, and then the amount recovered was determined to calculate the reaction yield.

First of all, polymerization reactions involve a great amount of factors that lead to imperfections, including inadequate reaction time or side reactions that result in incomplete reactions of monomers. Moreover, during purification with methanol, chain distribution leads to some chains not growing long enough to precipitate, contributing to lower yield rates. Washing and transporting the polymer from one flask to another also reduces the amount obtained, due to the adherence of the polymer to surfaces resulting in incomplete transfers.

Table 7 illustrates the yields achieved in all three cases, approximately around 80% each. This suggests a notably favorable yield and minimal weight loss throughout the process.

Table 7. *Analysis of Polymer Yield and Factors Affecting Yield in Copolymer Synthesis Using (Ph3Bi) Catalyst*

	Synthesized (Ph3Bi)		
	PLLA	**PLEB 9010**	**PLEB 8020**
Mass (g)	8.0	7.9	7.8
Yield (wt. %)	80%	79%	78%

Differential Scanning Calorimetry

Thermal properties of copolymers were analyzed through Differential Scanning Calorimetry. The subsequent Table 8 and Figure 18 consolidate all the values derived from the thermograms of the synthesized copolymers, while the accompanying graphs visually depict the scans conducted on the synthesized polymer samples (2nd scan) and processed polymer samples (1st scan).

Crystallinity degree (X_c) was determined from the equation below, where ΔH_m is the melting enthalpy, ΔH_c the cold crystallization enthalpy, χ is the weight fraction of L-lactide for every copolymer and ΔH^o_m is the melting enthalpy for 100% crystalline PLLA (ΔH^o_m = 142 J/g).

$$X_c = \frac{\Delta H_m - \Delta H_c}{\chi \cdot \Delta H_m^o} \qquad (1)$$

Table 8. *Thermal Properties of Synthesized and Processed Copolymers: Glass Transition Temperature (T_g), Cold Crystallization Temperature (T_{cc}), Melting Temperature (T_m), Melting Enthalpy (ΔH_m), and Crystallinity (X_c)*

			2nd Scan						Processed (1st Scan)					
Polymer	**LA (g)**	**EB (g)**	**T_g (ºC)**	**T_{cc} (ºC)**	**T_m (ºC)**	**ΔH_m (J/g)**	**ΔH_c (J/g)**	**X_c (%)**	**T_g (ºC)**	**T_{cc} (ºC)**	**T_m (ºC)**	**ΔH_m (J/g)**	**ΔH_c (J/g)**	**X_c (%)**
PLLA	10	0	56.3	105.4	172.1	57.9	49.4	6.0	54.7	94.5	165.5	34.3	30.6	2.6
L:EB	9	1	39.0	98.8	163.8	46.8	43.6	2.5	46.4	93.4	167	38.2	32.1	4.8
L:EB	8	2	32.3	83.2	157.8	40.1	36.4	3.3	48.8	84.9	165.4	43.3	36.9	5.6

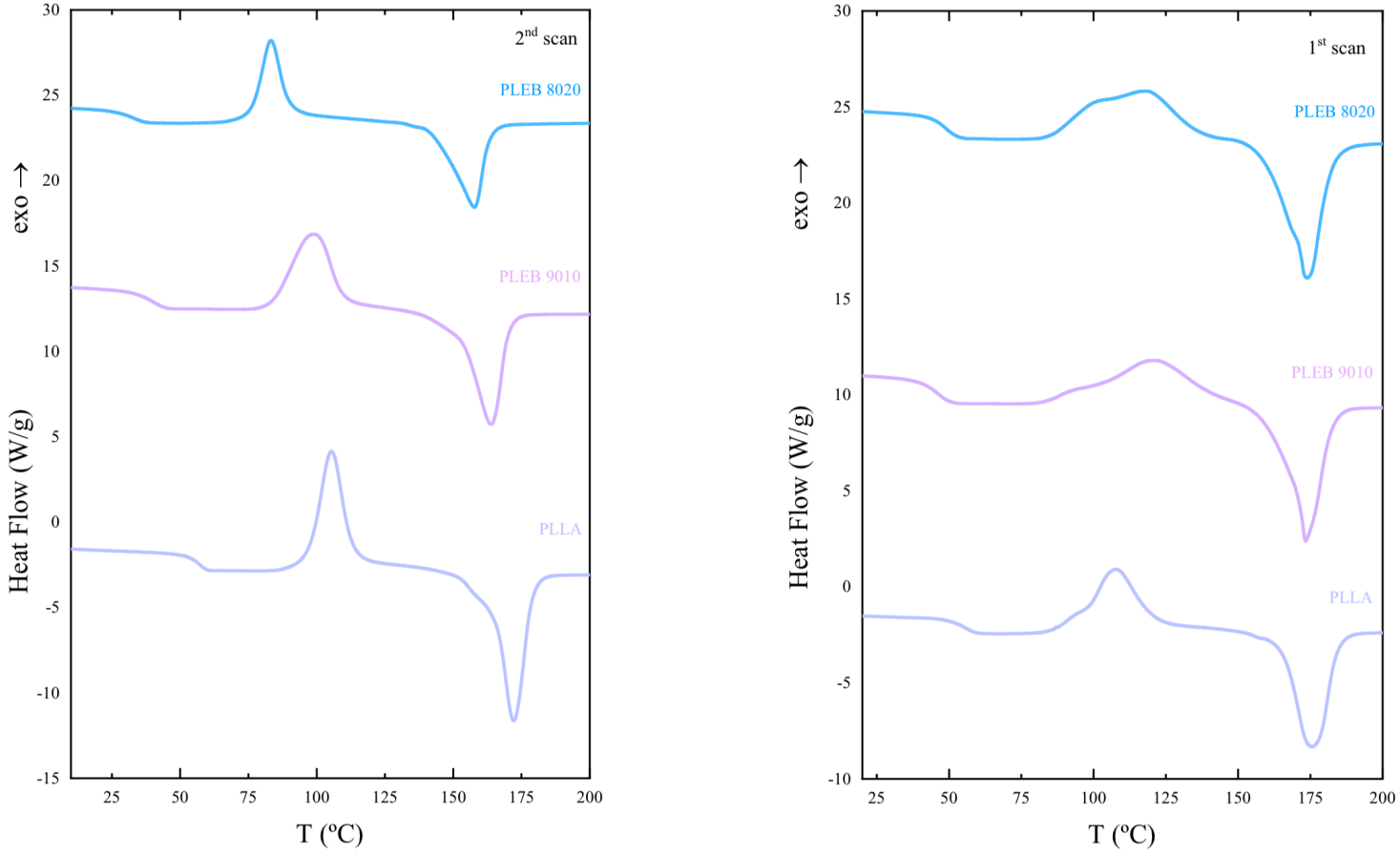

Figure 18. *Differential Scanning Calorimetry of Synthesized (left) and Processed (right) Copolymers*

Temperature and enthalpy values were obtained using TA Universal Analysis Software. Figure 18 shows the path followed by the (co)polymers where the three shifts in slope correspond to T_g, T_{cc}, and T_m, respectively. The exothermic peaks visualized in the middle of the graphs, represent the polymer chains rearranging themselves during heating, which is directly related to cold crystallization temperatures. Moreover, the noticeable valley at the end of the scan corresponds to melting temperature (T_m) of the copolymer, where it melts as it breaks down the crystalline structures providing a characteristic temperature of semi-crystalline polymers.

The graph associated with the synthesized copolymers (left) exhibits a proportional decrease in temperature values as ethylene brassylate is added to lactide. On the one hand, glass transition temperature (T_g) decreases 24 ºC by adding 2 g of EB. This suggests that the incorporation of EB into the polymer matrix disrupts its packing, leading to a reduction in the rigidity of the polymer chains. Cold crystallization and melting temperatures also suffer gradual reductions, which is also related to the consistent effect on polymer chain rearrangement.

These results suggest that the introduction of EB has an impact on the structural characteristics of the (co)polymer, potentially causing modifications in its crystalline configuration and molecular organization. Furthermore, the observed melting enthalpy (ΔH_m) as EB is incorporated into the copolymer shows how the energy requirement decreases for melting the polymer. These changes could lead to a reduction in the energy needed to interrupt the crystalline regions of the (co)polymer during the melting process.

On the other hand, the fluctuations observed in T_{cc} and T_m values compared to the synthesized copolymers could be attributed to the compression molding. This process can introduce different degrees of polymer chain alignment, which lead to variations in T_{cc} and T_m values among the copolymers. Similarly, fluctuations in melting enthalpy may arise due to differences in the degree of crystallinity, resulting in varying energy requirements for melting. Overall, these changes depict the sensitivity towards thermal properties of the (co)polymer to processing conditions.

Lastly, the data on crystallinity levels in the copolymers highlight a few differences between the ones synthesized and the ones processed through compression molding. Both synthesized copolymers and compression molded ones exhibit relatively modest levels of crystallinity, varying from 2.5% to 6%. In conclusion, these results remark how compression methods significantly affect both thermal and structural properties of copolymers.

Gel Permeation Chromatography

Table 9 shows the results obtained from the Gel Permeation Chromatography test:

Table 9. *Molecular Weight (MW) and Weight Loss Percentage in Synthesized and Processed Copolymers*

		MW (kg/mol)	MW Loss (%)
Synthesized (Ph3Bi)	PLLA	225	-
	PLEB 9010	215	-
	PLEB 8020	178	-
Processed (Film)	PLLA	75	66.5 %
	PLEB 9010	166	22.8 %
	PLEB 8020	138	22.5 %

In view of the results, certain conclusions can be drawn regarding the molecular weights obtained in the copolymers.

All six results exhibit molecular weights exceeding 70000 g/mol, so they can be considered polymers. Additionally, the three synthesized copolymers demonstrate weights above 170 kg/mol, suggesting a favorable synthesis and enabling subsequent processing. Ethylene brassylate (EB) seems to contribute to robust polymer stability at high temperatures and aids in facilitating smoother processing during manufacturing.

As anticipated, following compression molding, the copolymers undergo considerable degradation, leading to a reduction in their molecular weights. Specifically, PLLA stands out as the most affected one, experiencing a substantial weight loss of 66.5%. However, in the cases of the 90:10 and 80:20 ratios, the MW reduction is significantly lower, at 22% for both.

It is also worth noting the significant molecular weight observed in the 90:10 copolymer post-processing (166000 g/mol). This might be related to the reaction time used during synthesis. Initially, all were intended to undergo a 24 h period at 140 °C. However, an error in the hot plate resulted in inconsistent temperature maintenance throughout a substantial portion of the reaction, leaving the duration at that temperature uncertain. This suggests that the synthesis progresses relatively swiftly, and waiting for a full day may be counterproductive. Moreover, the 90:10 film displays a more translucent appearance and less brownish compared to the other two, which could also be related with the effective preservation of molecular weight.

Nuclear Magnetic Resonance

The results obtained from the spectroscopy shows the following values regarding the copolymers final composition (see Table 10):

Table 10. *Nuclear Magnetic Resonance (NMR) Analysis of Copolymer Composition*

	Initial		**NMR Spectroscopy**			
	L-LA (%)	**EB (%)**	**L-LA (mol %)**	**L-LA (wt. %)**	**EB (wt. %)**	**EB Loss (%)**
PLLA	100	0	100	100	-	-
LA:EB	90	10	97.0	95.4	4.6	46
LA:EB	80	20	95.8	92.4	7.6	38

Spectroscopy is clear evidence that not all of the ethylene brassylate used in the reaction was incorporated into the copolymer. Only 4.6% (in weight) managed to copolymerize in the case of 9010, and 7.6% (in weight) in the case of 8020, with assumed weight losses in EB of 46% and 38%, respectively. As a result, the samples used for the tensile tests will contain less ethylene brassylate than expected, which will significantly impact their properties.

The incomplete incorporation of EB into the copolymer can be attributed to several factors, including the inherent reactivity of the monomers, the kinetics of the copolymerization reaction or the efficiency of the catalyst system, among others. In these kinds of reactions, not all monomers have the same reactivity. Some of them may react more easily than others, leading to an uneven distribution of the monomers in the final polymer. Ethylene brassylate, for being a large macrolactone coming from organic compounds, may have hindrances that affect its ability to polymerize effectively with other monomers.

On the other hand, the weight losses of 46% and 38% in EB suggest that a significant portion of the ethylene brassylate does not take part in the copolymerization and might be lost due to side effects or degradation under the established reaction conditions. These losses indicate that the reaction conditions might not be fully optimized for the efficient incorporation of EB, possibly due to factors like temperature, reaction time, or the presence of impurities that could affect the copolymerization process.

Regarding the molar ratio of PH3Bi (500:1 Monomers/Catalyst) used for all of the reactions, the amount of catalyst employed has a crucial role in the synthesis process. Catalysts are essential in facilitating the copolymerization by increasing the reaction rate and lowering the activation energy. However, an excessive amount of catalyst might lead to unexpected behavior of sensitive monomers like ethylene brassylate.

Lastly, physical losses during the process due to volatilization, degradation or side reactions leading to unwanted products might have something to do with the observed weight losses of EB. These by-products that have not been copolymerized also affect the polymers yield rates, as all the catalyst impurities are removed with dichloromethane and fully eliminated with the heat treatment.

All things considered, the tensile tests performed to the polymeric films will analyze the effect of ethylene brassylate in different weight ratios from the initial ones (LA:EB 9010 → **LA:EB 9505**; LA:EB 8020 → **LA:EB 9208**).

12.2. Phases III and IV (Tensile Test in Polymeric Films)

Tensile Test

Instron 5565 device was employed for analyzing the mechanical attributes belonging to three different copolymers with different % of EB added to the polymer matrix. In order to carry out a more detailed study of the obtained results, some aspects related to the process and preservation of the films are needed.

Polymeric samples analyzed at **ambient temperature (T_a)** were maintained at room temperature in the laboratory for a month without any intermediate handling. On the other hand, the films tested at **body temperature (T_{37})** were processed using the same method. However, after molding, they were stored in a freezer for approximately a month to maintain the samples in their original condition until the day of testing. In this case, the testing was performed using an oven capable of performing the tensile test at the selected temperature.

The assays lasted for no more than a minute per sample in the case of T_a, and approximately 15 min per sample for T_{37}. From the beginning, this highlights the aging process experienced by films exposed to outdoor conditions, leading to increased fragility observed during the tensile test (refer to Table 11). Additionally, testing at 37 ºC is instrumental in mitigating this fragility.

Table 11. *Average Mechanical Properties Calculated for 15 Samples Studied at Ambient Temperature (T_a) and 15 Samples at Body Temperature (T_{37}), with Standard Deviation*

	L-LA	EB	Young's Modulus - E (MPa)	S_y (MPa)	S_r (MPa)	Elongation at Break - e (%)
Ta	100	0	2833.2±253.3	-	25.3±8.9	1.0±0.3
T37	100	0	1950.3±243.7	27.98±5.2	13.1±5.4	148.6±4.8
Ta	90	10	2699.6±143.6	46.05±3.4	34.2±12.9	2.8±0.3
T37	90	10	2167.8±183.0	30.08±5.5	21.5±0.8	268.6±8.2
Ta	80	20	2541.7±201.4	49.18±6.5	45.5±9.2	2.9±0.4
T37	80	20	1986.4±104.9	26.14±5.1	13.3±7.8	248.0±75.7

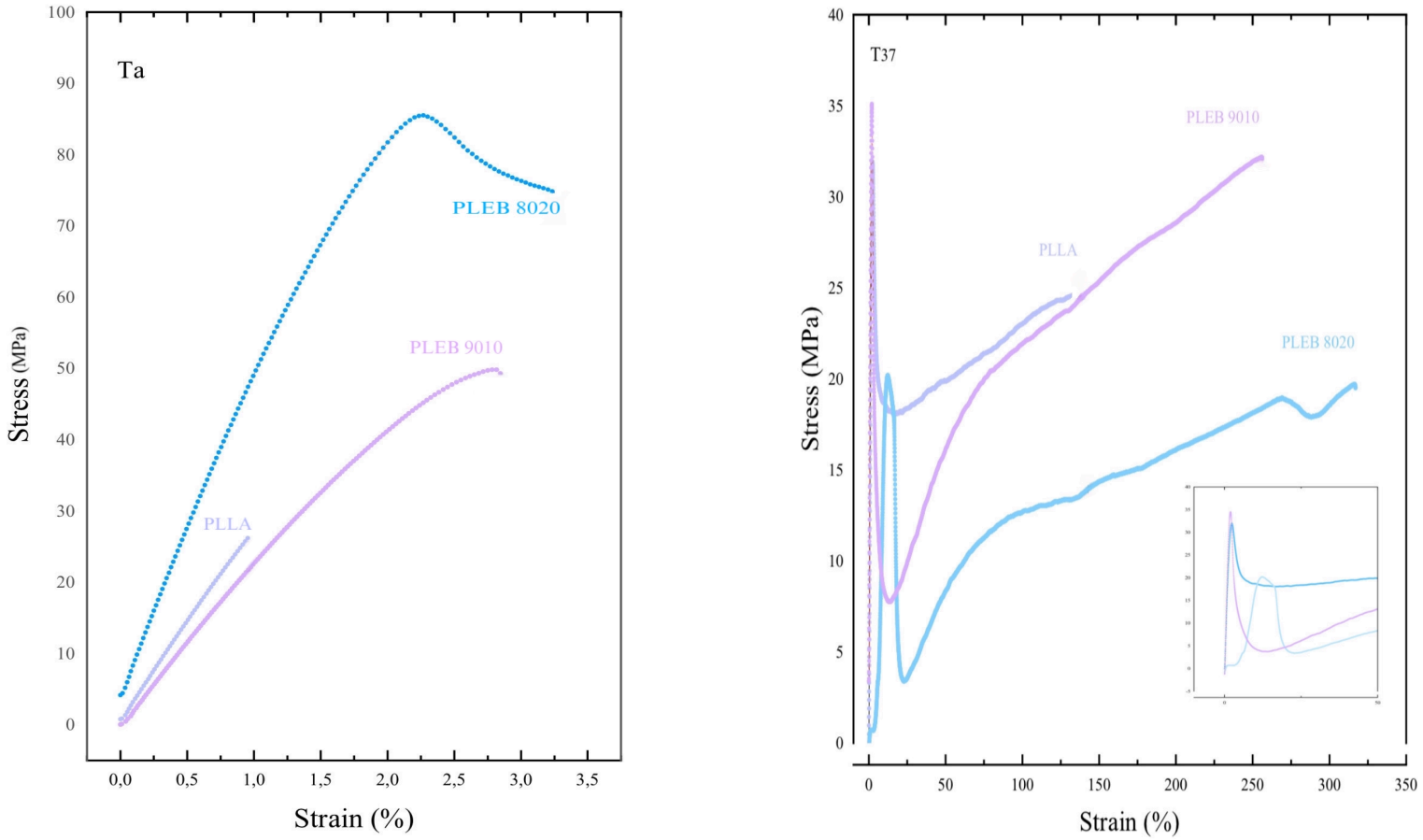

Figure 19. *Mechanical Properties of LA:EB copolymers at Ta (Left) and T37 (Right)*

Right from the beginning it is clear that, regardless of the ethylene brassylate content, the deformation observed is notably higher in the test conducted at 37 ºC. The rise in temperature, combined with the polymer preservation method aimed at preventing aging, makes it easier for the specimen to deform and highlights more clearly the impact of ethylene brassylate on the polymer, even when tested with lower than expected percentages.

The mechanical properties outlined in the table offer information about the behavior of copolymers with varying percentages of EB. Firstly, the variations in Young's Modulus (E) across different EB compositions and testing temperatures highlight the significant influence of EB content on the stiffness of the films (the lower the Young's Modulus, the more flexible and less rigid the material becomes). This suggests that the addition of EB alters the structural integrity of the material, impacting its ability to withstand deformation.

Furthermore, the differences in yield strength (S_y) and ultimate tensile strength (S_r) between Ta and T37 samples with similar EB compositions suggest that testing temperature plays a crucial role in determining the strength characteristics of the material. The decrease in both S_y and S_r values for the body temperature samples indicates that elevated temperatures contribute to a reduction in the overall strength, operating close to the glass transition temperature (T_g).

Finally, regarding the elongation at the breaking (e), the variation between the values obtained in the Ta test is practically negligible (0.97% to 2.98%), with all three polymers exhibiting total brittleness that does not allow for a clear appreciation of the effect of ethylene brassylate in the film. This is likely due to the state in which the films have been preserved and the testing temperature, which has caused the copolymer to age and to hold a fragility that does not align with the expected results. Fortunately, the tests conducted at body temperature clearly reveal the effect of adding ethylene brassylate to the polymer, where progressive deformation is observed as the amount of ethylene brassylate increases, reaching its maximum peak in one of the samples with a deformation of 305% for PLEB 8020.

13. Expense Evaluation

This section is solely dedicated to analyzing the project cost broken down by sections. In general terms, there have not been significant unforeseen events that required a major expense in the study, and it has been conducted in the most economical manner.

13.1. Personnel expenditure

For the study, the collaboration of several individuals was required, including the supervisor of the project and laboratory staff. The supervisor, due to professional commitments, had to leave halfway through the study and could not continue the work in person. Consequently, significant collaboration was needed from various laboratory personnel who greatly assisted in the final stages of the project which required supervision to complete.

In order to analyze the cost, it is necessary to estimate the number of hours invested in carrying out the project. On the part of the faculty, 30 h of work supervision have been required, whereas on the laboratory staff, a total of 10 h were needed.

13.2. Amortizations

In this section, all the machinery and utensils used during the study are included, as well as the Origin Pro software for data analysis and processing.

13.3. Materials

This part includes all the monomers and reagents used for the synthesis and obtaining of copolymers, including all the chemicals necessary for the operation of certain devices.

13.4. Outsourcing

Exclusively includes the nuclear magnetic resonance (NMR) performed on the polymers.

13.5. Indirect Costs

Indirect costs have been estimated at 10% of direct costs. In this way, expenses related to cleaning, electricity, water, and maintenance costs are covered.

13.6. Unexpected costs

To prevent potential harmful deviations in the budget, contingency expenses have been estimated at 7% of the total.

13.7. Cost breakdown

The following table displays the total costs accumulated from the study, which have been essential for its effective completion.

Table 12. *Cost Breakdown of Project Expenses*

Item	Cost per unit	Service Life	Usage time	Quantity	Cost
Personnel Expenditure					**970 €**
Student	-	-	150 h	-	0 €
Tutor	25 €/h	-	30 h	-	750 €
Lab Staff	22 €/h	-	10 h	-	220 €
Amortizations					**12,9 €**
Collin P200 E	10.000 €	15 years	6 h	-	0,5 €
Ohaus Scale	1.000 €	10 years	20 h	-	0,23 €
Hot Plate Stirrer	750 €	10 years	80 h	-	0,17 €
DSC Q200	40.000 €	10 years	4 h	-	1,8 €
GPC	30.000 €	15 years	3 h	-	0,7 €
Instron 5565	100.000 €	20 years	10 h	-	5,7 €
Computer	1250 €	8 years	100 h	-	1,8 €
Origin Pro License	850 €	1 year	20 h	-	2 €
Materials					**541,47 €**
L-lactide	1,7 €/g	-	-	30 g	51 €
EB	0,11 €/mL	-	-	10 mL	1,1 €
Ph3Bi	3,7 €/g	-	-	175 mg	0,65 €
Methanol	5,00 €/L	-	-	1 L	5 €
Dichloromethane	0,013 €/mL	-	-	1,2 L	15,6 €
Nitrogen	5,9 €/L	-	-	70 L	413 €
Aluminium Pan	2,7 €/u	-	-	20 u	54 €
Needle	0,18 €/u	-	-	1 u	0,18 €
Syringe	0,067 €/u	-	-	2 u	0,134 €
Petri Dish	0,8 €/u	-	-	1 u	0,8 €

Outsourcing					**60 €**
NMR	20 €/sample	-	-	3 samples	60 €
Direct Costs					**1584,37 €**
Indirect Costs (10%)					**158,43 €**
SUBTOTAL					**1742,81 €**
Unexpected Costs (7%)					**122 €**
TOTAL					**1864,8 €**

14. Conclusions

The present TFG describes the synthesis, characterization and processing of copolymers based on L-lactide and ethylene brassylate. The main objective was to advance in the biomedical field by improving the mechanical properties of PLA adding different percentages of EB. With that purpose, three (co)polymers ranging from 0% to 20% in EB composition were synthesized and studied in a six month period.

The characterization performed through DSC, GPC and NMR revealed that incorporating EB reduces rigidity and increases flexibility, as evidenced by lower glass transition and melting temperatures. However, NMR showed a lower EB content in the final copolymers, affecting their expected performance. These results emphasize the necessity for optimized reaction conditions to improve EB incorporation and highlight how both composition and processing phases influence the characteristics of the copolymers.

Moreover, the mechanical properties obtained demonstrated how EB has a notorious effect by softening the copolymer and providing a more plastic behavior at body temperature, making their properties similar to soft tissues and turning them into an attractive option for tissue engineering or pharmaceutical applications.

This study provides extensive information on the thermal and mechanical properties of an emerging copolymer, emphasizing its potential in biomaterials due to its thermoplastic nature, cytocompatibility and bioresorbable capacity. Its ease of processing and similarity to human soft tissues make it ideal for medical applications, eliminating the need for additional interventions as it degrades safely in the body. This research offers a solid foundation for future studies in tissue engineering and drug delivery systems, paving the way for advanced medical devices.

In summary, the study highlights the exceptional capabilities of this copolymer and sets the groundwork for future innovations in biomedicine.

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16. Appendix I

This following figure shows additional data regarding the Gantt diagram, including information about starting time and finish dates, duration and milestones.

Bibliographic Research	22/01/24 9:00	14/06/24 17:00
Phase I - Synthesis	5/02/24 9:00	8/03/24 17:00
Task 1.1. Previous calculations	5/02/24 10:00	9/02/24 10:00
Task 1.2. Standard procedure	9/02/24 9:00	8/03/24 15:00
Synthesis completed	8/03/24 9:00	8/03/24 17:00
Phase II - Characterization	8/03/24 12:00	15/05/24 17:00
Task 2.1. Differential Scanning Calorimetry	8/03/24 13:00	15/03/24 17:00
Task 2.2. Gel Permeation Chromatography	18/03/24 8:00	3/05/24 13:00
Task 2.3. Nuclear Magnetic Resonance	3/05/24 13:00	15/05/24 9:00
Characterization completed	15/05/24 8:00	15/05/24 17:00
Phase III - Fabrication protocol for polymeric films	21/03/24 8:00	3/05/24 17:00
Task 3.1. Film Processing	21/03/24 8:00	25/04/24 17:00
Task 3.2. Analysis with DSC and GPC	26/04/24 8:00	3/05/24 17:00
Phase IV - Tensile Strength Analysis	20/05/24 14:00	31/05/24 17:00
Task 4.1. Thicknesses and average widths	21/05/24 8:00	22/05/24 17:00
Task 4.2. Execution of tensile testing	23/05/24 8:00	31/05/24 17:00
Experimental Work Finished	31/05/24 8:00	31/05/24 17:00
Results and Report Writting	22/03/24 9:00	21/06/24 17:00
Report Finished	21/06/24 8:00	21/06/24 8:00

Figure 20. *Project timeline (Gantt)*

The diagram below illustrates the thicknesses and average widths of the 3 polymeric films, measured at three different points within the necking zone using a micrometer with a resolution of 0.001mm. These measurements were then used in the Bluehill software to conduct the tensile test.

Table 13. *Average thickness and width of polymeric films*

	µm				mm			
PLLA	thickness 1	thickness 2	thickness 3	**average**	width 1	width 2	width 3	**average**
1	267	270	257	**265**	10,521	10,401	10,423	**10,45**
2	308	315	308	**310**	9,892	9,951	10,106	**9,98**
3	298	307	302	**302**	10,152	10,197	10,155	**10,17**
4	300	307	312	**306**	10,439	10,304	10,311	**10,35**
5	290	277	265	**277**	10,136	9,901	9,871	**9,97**
LAEB 9010								
1	330	310	282	**307**	9,42	9,329	9,7	**9,48**
2	297	320	340	**319**	10,05	10,341	10,359	**10,25**
3	322	314	295	**310**	10,317	10,475	10,411	**10,40**
4	323	310	288	**307**	9,978	9,793	9,848	**9,87**
5	321	311	289	**307**	10,414	10,434	10,121	**10,32**
LAEB 8020								
1	314	325	327	**322**	10,568	10,561	10,762	**10,63**
2	256	262	263	**260**	9,641	9,694	9,659	**9,66**
3	301	293	282	**292**	10,304	10,298	10,135	**10,25**
4	278	274	271	**274**	10,532	10,358	10,222	**10,37**
5	316	319	299	**311**	10,127	10,037	10,12	**10,09**