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Triethyl citrate-based oligomeric plasticizers for poly(lactic acid)

Tesi di laurea sperimentale

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Table of contents

1.	INTRODUCTION.....	1
1.1.	PLA BASED MATERIALS	2
1.2.	PLA SYNTHESIS	3
1.3.	PLA SYNTHESIS VIA RING OPENING POLYMERIZATION	5
1.4.	PLA PROCESSING.....	7
1.5.	PLA PROPERTIES.....	9
1.6.	CRYSTALLINITY	11
1.7.	GLASS TRANSITION	15
1.8.	MIGRATION.....	18
1.9.	PLA PLASTICIZERS, STATE OF THE ART	19
2.	AIM.....	26
3.	RESULTS AND DISCUSSION.....	28
3.1.	SYNTHESIS OF THE PLASTICIZERS.....	28
3.2.	SCREENING OF REACTION CONDITIONS	29
3.3.	PRELIMINARY CHARACTERIZATION OF THE OLIGOMERS	32
3.4.	NON-ISOTHERMAL CHARACTERIZATION OF THE OLIGOMERS.....	38
3.5.	BLENDS PREPARATION.....	45
3.6.	NON-ISOTHERMAL CHARACTERIZATION OF THE BLENDS	47
3.7.	THIN FILM PREPARATION.....	51
3.8.	PHYSICAL AGING	55
4.	EXPERIMENTAL	60
4.1.	OLIGOMERS SYNTHESIS, MATERIALS AND PROCEDURE.....	60
4.2.	BLENDS PREPARATION.....	61
4.3.	THERMAL ANALYSIS	62
5.	CONCLUSIONS.....	63
6.	REFERENCES.....	65

1. INTRODUCTION

Our society has achieved enormous advances in quality of life due to an extensive discovery and availability of plastics derived from petroleum. However, as with any technology, unanticipated negative secondary effects are produced as well. The persistence of plastics in the environment, shortage of landfill space, concerns over emissions resulting from incineration, and hazards to human health as well as hazards to animals and plants caused by materials have encouraged efforts to find more environment friendly alternative materials. The depletion of petroleum resources coupled with increase in environmental regulations have added to this effort of finding new materials and products that are compatible with the environment and independent of fossil fuels.

Although steps have been taken to educate people about the environmental impact caused by the exploitation of plastics, these materials continue to represent the largest proportion of domestic waste. Conventional plastic waste takes a very long time to be broken down into harmless substances compared with common organic materials.

Due to the better degradability of biomass over conventional plastics, polymer biomass blends were the first step in providing alternatives to help reducing plastic waste problems. Generally, abundant biomass such as lignocellulosics and starches are blended with synthetic polymers, these polymer compounds are partially degradable by microorganisms. However, after the biomass portion has been consumed, the leftover polymer skeleton will still cause harmful effects to the environment.

These days, the focus is on completely biodegradable polymeric materials. These polymers are naturally degradable when disposed in the environment. The carbon footprint of production of these polymers is monitored to ensure sustainable environmental protection. Bio-based polymers may be obtained from renewable resources and are gaining much importance over petroleum-based biodegradable polymers in recent years. Some of the examples for biopolymers include cellulosic biopolymers derived from renewable cellulose, starch plastics, corn-derived plastics, and bacterial polyesters.

1.1. PLA BASED MATERIALS

Poly lactide or poly(lactic acid) (PLA) is the front runner in the emerging bioplastics market with the best availability and the most attractive cost. Poly(lactic acid) (PLA) belongs to the family of aliphatic polyesters commonly made from α -hydroxyacids which include polyglycolic acid and polymandelic acid, and it is bio based, resorbable, and biodegradable under industrial composting conditions. End uses of PLA are in rigid packaging, flexible film packaging, cold drink cups, cutlery, apparel and staple fibres, bottles, injection moulded products, extrusion coating, biomedical implants and so on.

Compared to conventional, petroleum-derived plastics, PLA has many advantages. After its decomposition the net CO₂ atmospheric emission balance is neutral because PLA is produced from vegetal organisms (mainly corn starch and sugarcane) which use CO₂ as nutrient. This makes PLA environmentally sustainable not only during the polymer synthesis but also during the material recycling making the whole PLA life cycle “*bio-friendly*”.

The basic monomer of PLA is lactic acid (LA), also named 2-hydroxy propionic acid. Lactic acid is chiral, consisting of two optical isomers. One is known as L-(+)-lactic acid and the other, its mirror image, is D-(-)-lactic acid. The optical purity of lactic acid is a crucial parameter for PLA production. As the optical purity of LA is lowered, the tendency to crystallize of the corresponding PLA decreases until reaching a threshold composition of 92% beyond which the crystallization is not observed anymore [1].

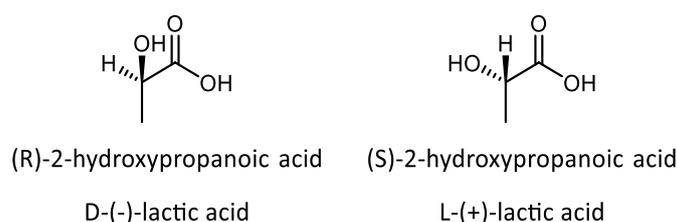


Figure 1: Optical isomers of lactic acid, L-(+)-lactic acid and D-(-)-lactic acid

The separation of the two enantiomers is very difficult to perform on an industrial scale so it is necessary to choose an appropriate method to selectively produce only one of the two forms [2].

LA can be produced via bacterial fermentation or via direct chemical synthesis [3], with 90% of the global LA production covered by bacterial fermentation. As a starting material for

industrial fermentative production of lactic acid almost any carbohydrate source containing C5/C6 sugars can be used. Pure sucrose, glucose from starch, raw sugar beet juice are frequently applied [4].

The product of the fermentation reaction is a mixture of 99.5% of the L-isomer and 0.5% of the D-isomer [5]. Other advantages of the bacterial fermentation route are low cost of substrates, low production temperature, and low energy consumption [6].

1.2. PLA SYNTHESIS

The two main routes to produce PLA from lactic acid are: direct polycondensation of lactic acid [7] and *ring-opening polymerization* using a cyclic dimer intermediate, the lactide [8].

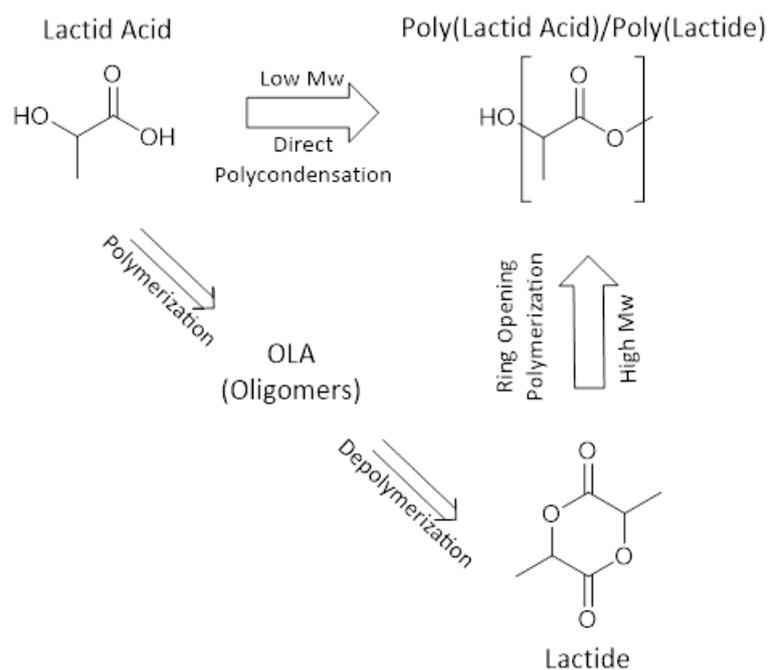


Figure 2: Routes to produce PLA. Direct polycondensation of lactic acid and ring-opening polymerization through lactide intermediate.

Direct polycondensation of lactic acid is the least-expensive route since it proceeds in one step. However, only low-molecular-weight PLAs can be obtained, mainly due to the viscous polymer melt, the presence of water, impurities, and the “back-biting” equilibrium reaction that forms the six-member lactide ring during polymerization.

Most commercial routes utilize the more efficient conversion of the cyclic dimer of lactic acid—to PLA via ring opening polymerization (ROP) catalysed by a Sn(II)-based catalyst rather than polycondensation.

The cyclic dimer of lactic acid (3,6-dimethyl-1,4-dioxane-2,5-dione) is commonly called lactide. Due to the two asymmetric carbon atoms in the molecule, lactide exists in three different forms. In addition to the three diastereomeric structures mentioned above, also a racemate of D-lactide and L-lactide exists: rac-lactide or DL-lactide.

The stereoregularity of the final polymer depends on the purity of the lactide [9] Depending on the diastereoisomer used for the polymerization 3 different homopolymers can be obtained: poly-L-lactic acid (PLLA, from the L-lactide, poly-D-lactic acid (PDLA, from the D-lactide) and poly-D,L-lactic acid (PDLLA, from the meso-lactide). The two enantiopure forms have similar physical and chemical properties while the PDLLA has a significantly lower glass transition temperature and can't crystallize due to the lower chain order.

The different amounts of one of the lactide isomers, depends on the lactic acid feedstock, as well as on the temperature and catalyst used during dimerization.

The fraction with high L-lactide levels can be used to produce semi-crystalline polymers whereas the other produces more amorphous materials. Applications of the meso-lactide by-product include its use as chemical intermediates in various surfactants, coatings, and copolymers [10].

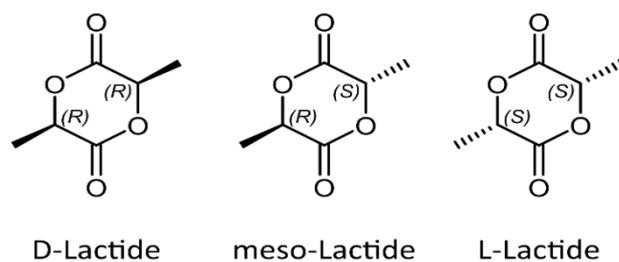


Figure 3: Stereoisomers of lactide. D-lactide, meso-lactide and L-lactide.

By considering the different L/D stereoisomeric ratio a different nomenclature is typically used. PLLA refers to a Poly(lactide) containing only L-lactide, PDLA refers to a Poly(lactide)

containing only D-lactide. When both the isomers are present (as it happens in many commercial grades) the term PLA should be used.

1.3. PLA SYNTHESIS VIA RING OPENING POLYMERIZATION

Polymerization is thermodynamically favoured, during ROP the lactide molecules undergo a transformation from cyclic to linear configuration which releases the tension caused by the ring. After the cleavage of the lactide ring atoms are free to rearrange in a more stable, less-energetic configuration with less steric hindrance.

Many catalysts have been studied for this reaction such as zirconium (II), titanium (IV), calcium (II) and aluminium (III) carboxylates [11], [12]. The best performance however has been achieved using tin (II) ethyl-hexanoate ($\text{Sn}(\text{Oct})_2$) as its use brings the following benefits:

- Allows the achievement of high molecular weight
- It's soluble in the melt polymer, allowing a solvent-less bulk polymerization
- It has higher activity compared to other catalysts resulting in higher reaction speed
- It causes low racemization ($\leq 1\%$)

All the previously mentioned catalysts are Lewis acids capable of coordinating the carbonylic oxygen of the lactide, coordination with a metal lowers the required activation energy for the cleavage of the ester bond.

The ROP reaction reaches equilibrium with a monomer conversion around 95%-97% [13], the unreacted monomer must be removed before commercialization of the product. However, it has been found that the equilibrium between polymer and monomer is established again upon heating the polymer above melting temperature.

The ROP reaction is a chain-growth polymerization with a *coordination-insertion* mechanism. As shown in the picture below an alcoholic initiator is used to coordinate to the tin atom in place of the carboxylate bonds activating the catalyst (a). Subsequently a lactide molecule coordinates to the metal (b) and the alcohol insertion take place through a nucleophilic

attack on the carbonylic carbon (c) followed by the cleavage of an ester bond and the monomer ring opening (d). The reaction propagates following the same mechanism (e).

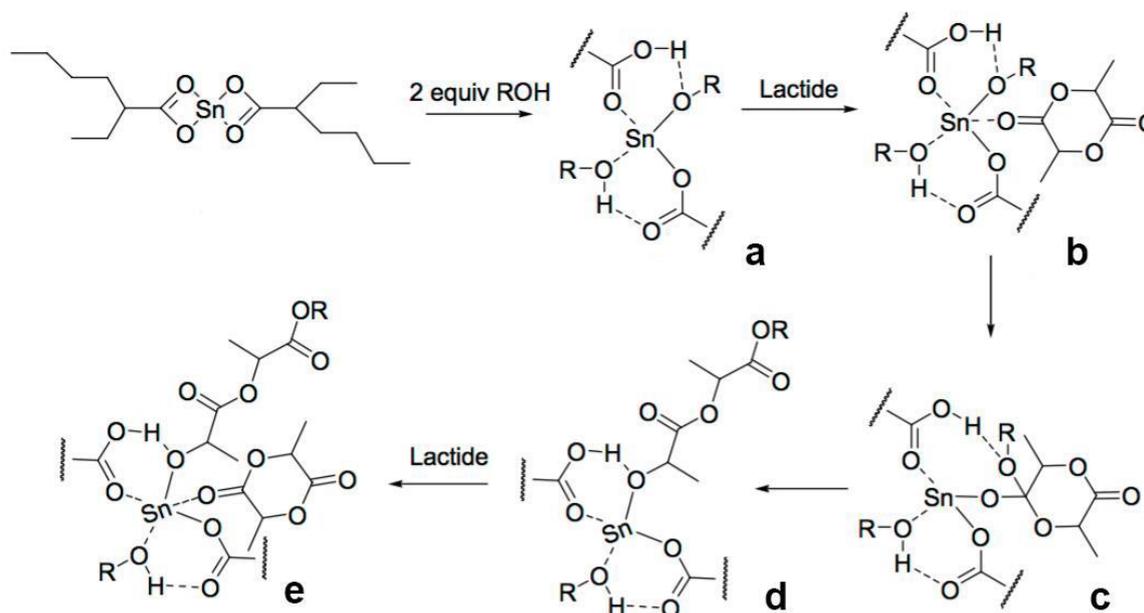


Figure 4: Coordination-insertion mechanism of tin (II) octanoate catalysis. Coordination of octanoate ligands (a) Coordination of lactide to the metal centre (b) Insertion of the alcohol (c) Ring-opening of Lactide (d) Chain propagation (e).

The growing polymer chain remain bonded to the tin atom during the whole reaction and the monomer insertion always occur from the same side of the catalyst, this leads to products with very high stereoregularity when using enantiopure monomers as starting materials.

Molecular modelling suggests that two molecules of an alcohol (ROH) exchange with the octanoate ligands followed by the coordination of lactide to the metal centre. The insertion of the alcohol followed by ring-opening generates a linear chain that subsequently starts propagation [14].

The reaction rate is increased with the increasing concentration of alcohol (typically added to the reaction mixture), since alcohol shifts the equilibrium towards the tin(II) alkoxides until finally the whole amount of $\text{Sn}(\text{Oct})_2$ is converted into these propagating species. Also hindered amines, such as 2,6-di-tert-butylpyridine or bis(dimethylamino)naphthalene, increase the rates of polymerization, being able to complex protons during coordination [15].

Although tin (II) octanoate has been approved by FDA for polymers used in coatings that contact food [16], metal free catalysts have been proposed, mainly based on chiral organic

molecules. Such organocatalysts are attracting an increasing attention, mainly due to their lower toxicity if compared to metallic counterparts. However, the high temperature required by these polymerizations and the difficulty of synthesizing stereoregular PLA chains at such high temperature without any racemization, transesterification reactions and macrocyclizations is currently hindering their scale up from laboratory use to large scale production [10].

1.4. PLA PROCESSING

One of the key factors behind the increasing interest on PLA, in comparison with other bioplastic, consists in its suitability to be processed by the techniques employed with other commercial polymers, such as polystyrene (PS) and polyethylene terephthalate (PET), with well-established manufacturing techniques [17].

Typically, the main technique for conversion of high Mw PLA into end products (such as consumer goods, packaging, and other applications) is melt processing. It consists in heating the material above its melting temperature, forming the molten polymer into desired shapes, and finally cooling to stabilize its final dimensions. Extrusion is the most important technique for continuously melt processing of PLA. The plasticizing extruder can be part of the forming machine systems for injection moulding, blow moulding, film blowing and melt spinning.

Some of the examples of melt processed PLA are injection moulded disposable cutlery, thermoformed containers and cups, injection stretch blown bottles, extruded cast and oriented films, and melt-spun fibers for nonwovens, textiles and carpets [18].

Like most of other aliphatic biopolyesters, PLA is a hygroscopic material [19], very sensitive to high relative humidity and temperature. Hydrolytic degradation takes place when PLA is exposed to moisture: the ester groups of the main chain of the polymer are cleaved, resulting in a decrease of molecular weight and the release of soluble oligomers and monomers. The hydrolysis of PLA starts by the diffusion of water molecules into the amorphous regions, which in turn initiates the cleavage of the ester bonds. The products of the hydrolysis self-catalyse the reaction. Then, degradation continues in the boundary layer of the crystalline domains [20].

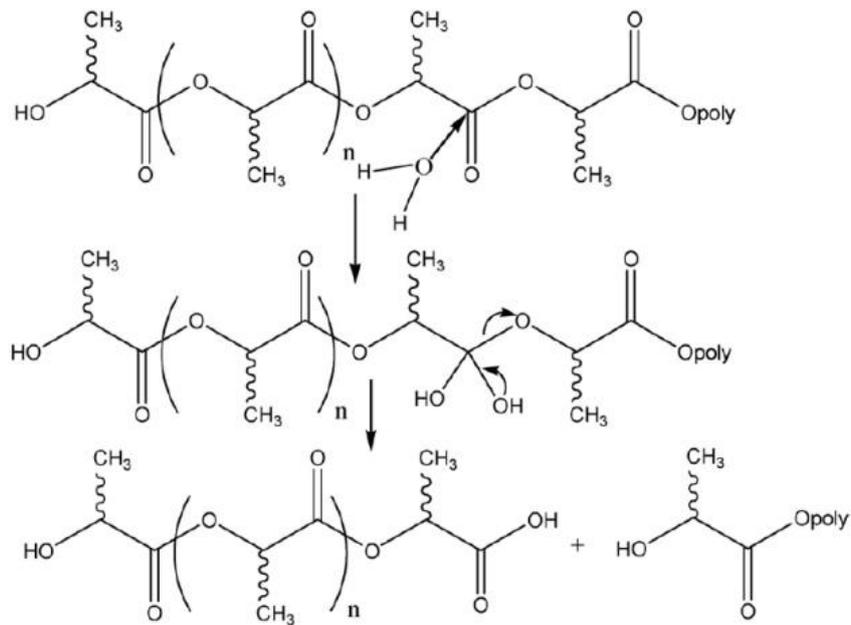


Figure 5: PLA hydrolytic degradation mechanism

In order to avoid hydrolysis, PLA should be dried to a water content less than 100 ppm (0.01%, w/w) before being processed while during industrial production it is mostly dried to values below 250 ppm water (0.025%, w/w) [21].

High temperature processing of PLA can also cause thermal degradation that it is mainly due to intramolecular transesterification reactions leading to cyclic oligomers of lactic acid and lactide. Simultaneously, there is a recombination of the cyclic oligomers with linear polyesters through insertion reactions, while molecules with longer chains lengths are favoured. Thermal degradation can be caused also by intermolecular transesterification. In this case two ester molecules exchange their radicals, leading to a variation on the distribution of molecular weights. It can be minimized by the addition of suitable stabilizers such as benzoyl peroxide and 1,4-dianthraquinone.

At the same time PLA should never be processed at temperatures above 240°C, since it can be degraded by pyrolytic elimination, which leads to the formation of an acid moiety and a molecule with acrylic end groups, or by radical degradation, which can be assumed to start with either an alkyl-oxygen or an acyl-oxygen homolyses [21].

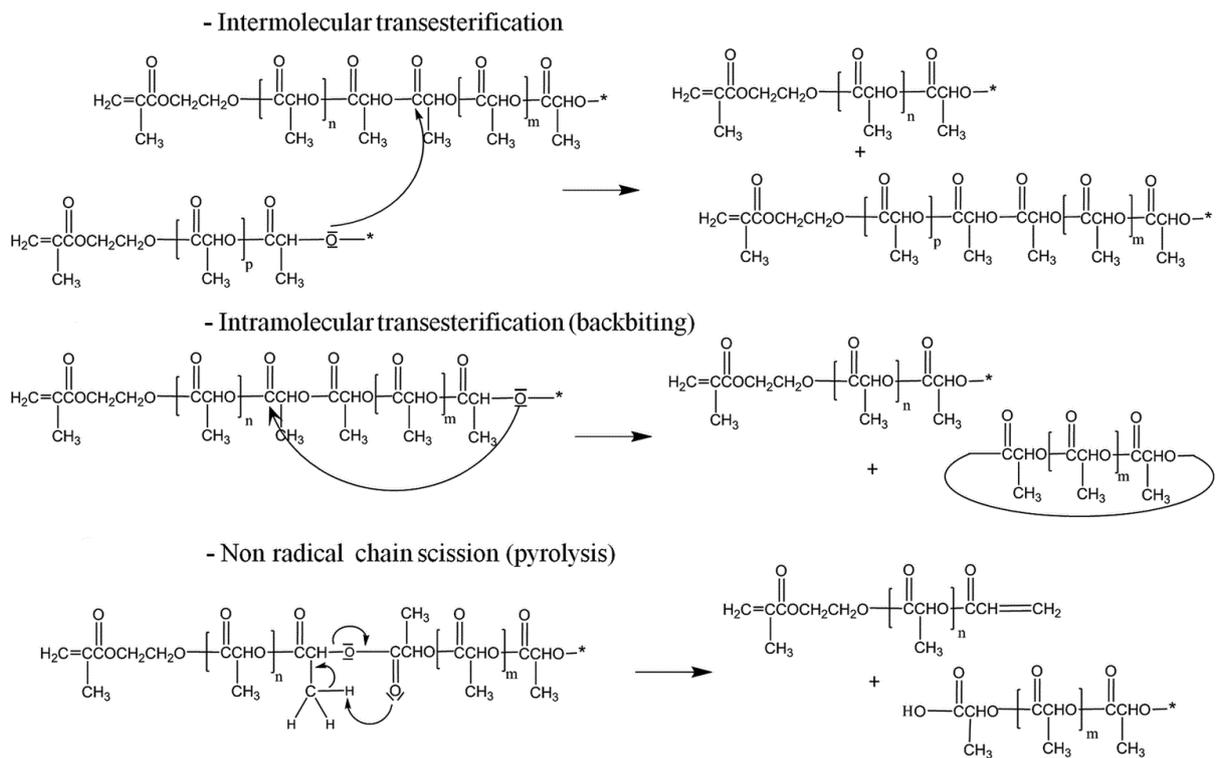


Figure 6: Scheme of possible PLA degradation routes

Another typical problem that can occur during any step preceding or following the polymerization, or during polymerization itself, is racemization of lactoyl moieties. It typically occurs at temperatures exceeding 200°C, depending on the type of the catalyst used, leading to a reduction of the tendency to crystallize of the formed polymer [22]. Racemization must be taken especially under control if a crystalline material is desired, since, as reported in the previous paragraphs, only stereoregular PLAs are able to crystallize.

1.5. PLA PROPERTIES

The physical properties of PLA, including melting temperature, crystallization behaviours, and mechanical properties strongly depend on its molecular weight and on its stereochemical composition, which determinate the price and application of commercially available PLA grades.

As general indication it can be pointed out that, by comparison with commodity polymers such as PE, PP, PS and PET, the mechanical properties of semi-crystalline PLA are attractive,

particularly its Young's modulus, making it an excellent substitute for commodity polymers. Mechanically, un-oriented PLA is quite brittle, but possesses good strength and stiffness. Oriented PLA provides better performance than oriented polystyrene (PS), comparable to PET. Tensile and flexural moduli of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and PS, but the Izod impact strength and elongation at break values are smaller than those for these polymers [23].

POLYMER	Tensile modulus (Gpa)	Stress at break (Mpa)	Elongation at break (%)	Izod impact strength (J/m)	T _g (°C)
Polypropylene (PP)	1,4	35	200	80	-15
Polystyrene (PS)	2,5	65	75	85	100
Poly(ethylene terephthalate) (PET)	3,0	54	125	70	70
Polyethylene (PE)	0,2-1,0	15-30	300-500	150-600	-120
Poly(vinyl chloride) (PVC)	2,6	50	30	43	80
Nylon-6,6	2,0	70	150	110	50
Polycarbonate (PC)	2,5	65	100	800	145
Poly(lactic acid)	1-3	70	5-15	15	60
Poly(vinyl acetate) (PVA)	0,6	35	10-20	160	30

Table 1: Mechanical properties of common polymeric materials

Despite its interesting mechanical properties, many properties of PLA still need to be improved in order to make it a viable alternative to petroleum-based thermoplastics.

For instance, in food products where high barrier protection is important, replacement of PET by PLA packaging may not be feasible, since the barrier properties of PLA are not on par with PET [24]. At the same time, PLA biodegradability may in some cases result in unpredicted performance if the polymer is exposed to uncontrollable abusive temperature and humidity conditions.

Furthermore, PLA has a slow crystallization rate if compared with many other thermoplastics, resulting in longer processing time if semi-crystalline samples are desired. Even at high L-LA

content, PLA crystallization is typically too slow to develop significant crystallinity unless the crystallization is induced by strain such as in processes used to produce biaxially oriented films or bottles. In processes such as injection moulding, where the orientation is limited, and the cooling rate is high, it is much more challenging to develop significant crystallinity and thus formulation or process changes are required. Moreover, PLA high viscosity is a problem for the mixing of polymerization batches, as the viscosity increases along with the conversion, but also for injection moulding processes.

Probably the most important limiting factor for the use of PLA is its glass transition temperature which is higher than room temperature. This makes PLA brittle and the production of thin films without the relevant addition of plasticizer is therefore impossible.

1.6. CRYSTALLINITY

Many polymer characteristics such as mechanical resistance, degradability and physical properties depend on its *degree of crystallinity* which is defined as the fractional amount of polymer that is crystalline and it is either expressed in terms of the mass fraction or the volume fraction.

Polymer crystallization is a complex process that follows the folding of the macromolecular chains forming highly ordered regions called *lamellae* which themselves form aggregates called *spherulites*. Chain packing occurs due to Van der Waals interactions that bring nearby atoms close together with an exothermic process which releases energy.

Fundamental requirements for the crystallization are: structural and configurational regularity; however it is not possible to obtain completely defect-free macromolecular chains as the end-chain groups act as defects themselves. This is the main reason why totally crystalline polymer cannot exist, the crystallinity degree is usually between 10% and 80% and completely amorphous polymers (0% crystalline) frequently occur.

Polymer crystallization can happen both in the bulk and solution, the latter technique however is not industrially relevant not only due to higher costs but also due to the lower *atom efficiency* of the process which is caused by the use of a solvent.

Bulk crystallization can happen both during the cooling of the polymer melt from a temperature T_c and during the heating of the solid polymer up to a temperature T_{cc} (Cold Crystallization Temperature). The two processes are not the same and they lead to different amounts of crystalline domains with different crystallization kinetics. Usually PLA does not crystallize from the melt state, while crystallization during heating is always present. This happens because ordered microstructures already present in the solid polymer act as *crystallization nuclei*.

Crystallization speed usually grows along with the *supercooling*, defined as the difference between the melting temperature and the crystallization temperature ($\Delta T = T_m - T_c$). The crystallization process can be divided into two separate stages: nuclei formation (primary crystallization) and nuclei growth (secondary crystallization). Nucleation can happen by spontaneous formation of small polymer chain aggregates, this is referred to as *homogeneous* crystallization. It can also be sped up by the presence of *external moieties*, this process is called *heterogeneous* crystallization. Crystal growth happens with an additional process during which whole polymer chains or chain segments are added to the external surface of the crystal nuclei.

The global crystallization speed is defined as the sum of the two crystallization process speeds; however primary and secondary crystallization depend on factors such as temperature and molecular weight in a different ratio and often the global crystallization process is limited by the kinetics of one of the two stages. Nucleation is generally hindered close to the melting temperature due to the creation of a solid-liquid equilibrium which leads to the swift re-melting of the newly formed crystallization nuclei while the speed of the spherulitic growth process reaches its maximum in these conditions thanks to the higher chain mobility promoted by the high temperature.

Molecular weight also has an influence on primary and secondary crystallization speeds: longer polymer chains (higher M_w) have a higher probability of forming stable crystal nuclei but the diffusive processes which lead to the formation of the lamellae are slowed down.

These opposite effects on the crystallization kinetics mean that the maximum crystallization speed is reached within a narrow temperature range that is favourable for both processes (nuclei formation and growth). The fastest way to determine crystallization speed is to

evaluate the inverse of the *half crystallization time* taken at different temperatures ($\tau_{50\%}$): the resulting Gaussian curve which trend is determined by the decrease in the crystallization speed due to the viscous motions in the vicinity of the glass transition temperature and the reduction of the “*thermodynamic push*” when approaching the melting temperature.

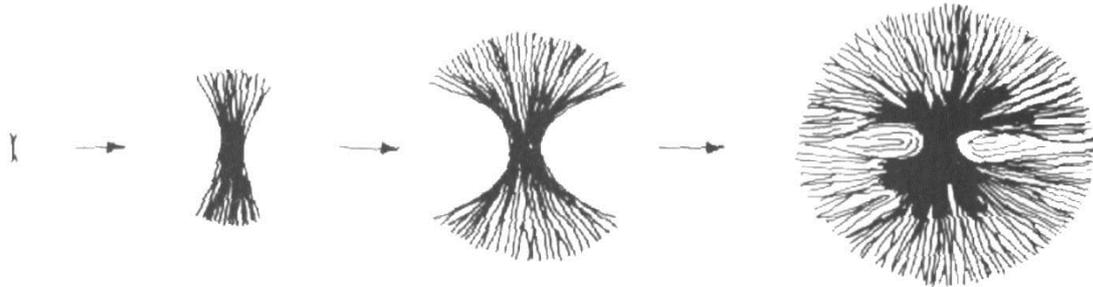


Figure 7: Development of a spherulite from the nucleus

The spherulites’ dimensions and the extension of the crystalline domains depend on the speed of formation, thus on the degree of supercooling. If ΔT is large the process is controlled by diffusion processes, this situation leads to the formation of a huge number of small crystals because of the fast primary crystallization compared to a slow secondary crystallization. On the contrary, if ΔT is small secondary crystallization will prevail leading to the formation of a smaller number of bigger crystals.

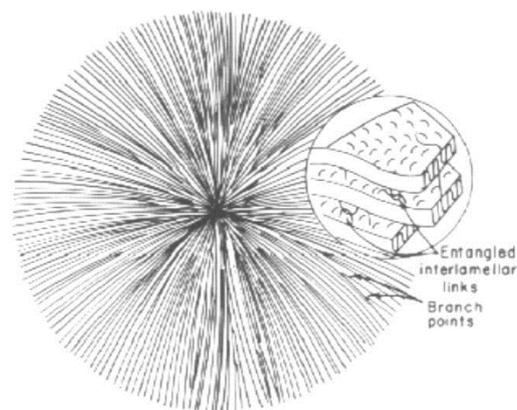


Figure 8: Scheme of a spherulitic structure

While crystallization implies the formation of ordered structures, fusion can be seen as the opposite process, this implies that the *latent heat of fusion* is directly proportional to the crystalline degree of the polymer:

$$\text{degree of crystallinity (\%)}: 100 * (\Delta H_m / \Delta H_m^\circ)$$

Where ΔH_m is the melting enthalpy of the analysed sample and ΔH_m° is the standard melting enthalpy for an ideal perfect crystal, found in literature (for PLA the most commonly found value is 93.6 J/g) [25].

PLA is polymorphic, therefore, depending on crystallization temperature, different crystalline structures may be obtained [26]. Crystallization above 120°C, from melt or solution, results in the most common and stable PLA polymorph, the α -form [27]. This structure consists of two antiparallel 10_3 helical chain segments, packed in an orthorhombic unit cell, with 3.3 monomers per turn and a monomer repeat unit of 27.8 nm [28]; other conformation are known such as α' , γ and β [29], [30].

Recent studies demonstrate that the α' -form crystal is preferentially formed only at crystallization temperatures below 100°C, while at crystallization temperature between 100 and 120°C α' -form coexist with α -form.

The existence of the two different crystal morphologies gives rise to a peculiar thermal behaviour. As previously stated the crystallization behaviour of polymers can be investigated by using differential scanning calorimetry (DSC). In PLA crystallized at temperatures corresponding to α' -form crystal formation, a small exotherm appears immediately before the single melting peak, due to the transformation of the more disordered α' -form to the ordered α -form crystals. On the other hand, when PLA is crystallized at a temperature of coexistence of the two crystals forms, a double melting behaviour appears. However, double melting can also be due to reorganization during the heating scan [31], [32].

Commercially available PLA has a slow crystallization speed because is synthesized from an enantiomeric mixture of lactic acid with a diastereomeric L/D ratio of 98/2, it follows that the obtained polymer has the same enantiomeric composition. Bearing in mind that the D form is regarded as a chain defect, commercially available PLA is not capable of crystallizing at a sufficiently high speed as those required by common extrusion and injection industrial

procedures. Therefore, the majority of PLA-based materials are completely amorphous or show very low degree of crystallinity.

To accelerate the formation of crystalline domains two main strategies can be pursued:

- Resolve the enantiomeric lactic acid mixture until L-form concentration exceeding 99% are reached. This method however is exceedingly expensive if compared to the added value of the final material.
- Add a plasticizer. The addition of a plasticizer enhances macromolecular mobility which in turn speed up the spherulitic growth. Common, low-molecular weight plasticizer though, are affected by *migration* issues due to the incompatibility of the plasticizer with the polymeric matrix, this worsen the performance of the material during the product life cycle [33]. Moreover, low molecular weight plasticizers are often harmful when released into the environment and non-biodegradable, invalidating the “green” properties of PLA.

1.7. GLASS TRANSITION

All thermoplastic polymeric materials have a glass transition temperature (T_g) which is the temperature at which the movements of the chemical groups bonded to the polymer backbone become possible. Below T_g thermoplastic materials are hard and brittle as the only allowed movements are the vibration and rotation of single atoms, above T_g they become rubbery and flexible.

This transition is caused by the increase in the kinetic energy of atoms and molecules when the temperature rises. Above T_g the system has enough energy to activate the collective movements of portions of the polymer backbone, for this reason T_g is influenced by the energetic parameters which determine the rotational barriers around the chain bonds. For example, the presence of lateral functional groups along the backbone, due to the higher steric hindrance, cause a substantial increase in the glass transition temperature. The

presence of crystalline domains has a similar effect as crystalline regions dispersed in the amorphous phase stiffen the whole structure and limits the possible chain movements.

The polymer molecular weight has an effect on the T_g as well: depending on the length of the polymer chains the influence of terminal groups on the properties of the polymer change. Terminal groups have a lower activation energy compared to the central portions of the polymer chain, this means that these groups will have higher mobility at lower temperature. If the chain is shorter the impact of the terminal groups on the overall polymer properties is proportionally higher resulting in a lower T_g [34]. However, after reaching a certain weight the T_g remains constant and is not affected by a further increase of the Mw.

The glass transition is a *second order phase transition*, this means that during its occurrence the heat capacity of the material is always a finite quantity. Unlike melting which is a first order transition, if energy is continuously provided to the material the temperature will continue to rise *during* the transition itself. Because of this it would be more appropriate to use a range of temperature between which the transition begins and end, for practical reason a single temperature value is often used.

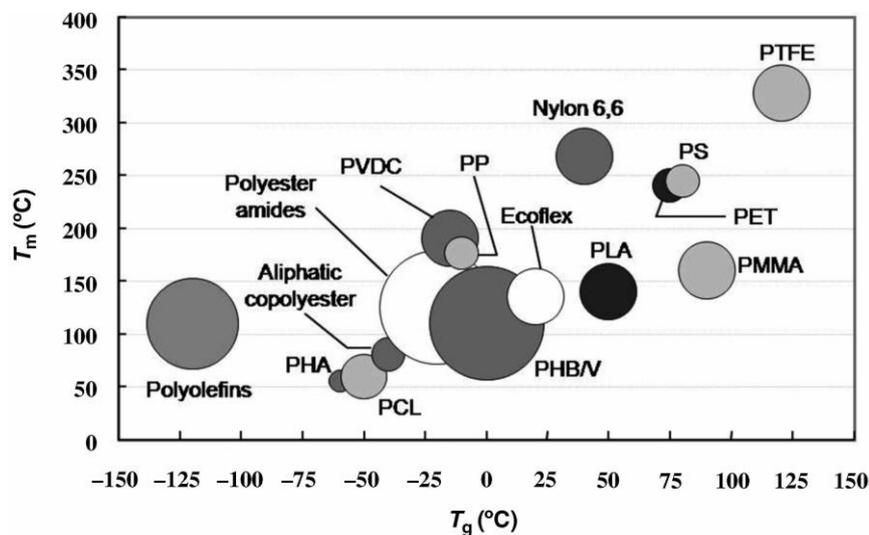


Figure 9: Comparison of glass transition and melting temperatures of PLA with other thermoplastics

The glass transition occurs in the reverse direction if the temperature is instead lowered from above to below T_g , with the material then undergoing “vitrification”, this reverse transition upon cooling can be described as going from viscous to glassy behaviour.

The glass transition temperature can be determined by DSC curves where it's detected as a change in the base line of the heat flux as a function of temperature. It is important to note that, as discussed later in greater detail, the observed value of T_g can be significantly affected by kinetic factors. T_g is, therefore, dependent on the measurement rate. For example, the T_g measured by differential scanning calorimetry can be increased significantly by increasing the heating rate or by decreasing the cooling rate during a calorimetric scan. Furthermore, the glass transition does not occur at a single sharply defined temperature but instead over a range of temperatures [35]. There is often confusion in the literature about which point in that range (its onset, midpoint, or end) to use as the value of T_g , during our research we have chosen the onset point of the heat flux slope during the transition and always used the same heating and cooling ramps to obtain comparable results between different specimens.

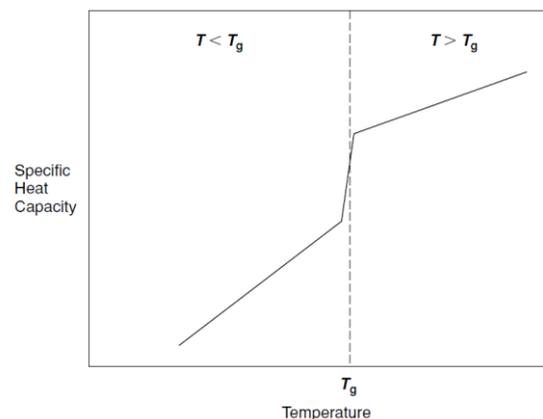


Figure 10: Schematic illustration of temperature dependences of specific heat capacities of amorphous polymers.

Many other physical properties change whether the polymer is in the rubbery or in the glassy state: specific volume, tensile modulus and refractive index. Mechanical properties greatly change depending on the polymer state: a glassy material possesses high tensile modulus but low mechanical resistance and low elongation at break, on the other hand a rubbery polymer has a lower modulus and a much higher elongation at break.

The reported glass transition temperature of PLA is around 60°C [36] this limits the use of PLA for application where a flexible material is required at room temperature; in this case one of the most used strategy to reduce the T_g value is to use a *plasticizer*.

A plasticizer is usually a low molecular weight compound added to the polymeric matrix to increase the mobility of the polymeric chains and the conformational freedom of the

molecules. In order to be feasible for industrial application the plasticizers must satisfy some basic requirements: they have to be non-toxic, cheap and, most of all, compatible with the polymeric matrix. The plasticizer has to be miscible with the polymer to guarantee miscibility with the matrix but also needs to remain linked to the polymeric structure avoiding *migration* which would lead to the formation of regions with different composition within the bulk of the material.

Moreover, extrusion casting of PLA film for packaging and many other applications is relatively difficult compared to other polymers. In fact, there is no tolerance for PLA film tearing or cracking when subjected to forces during package manufacturing [37]. It therefore becomes important to modify these properties in such a way that PLA is able to compete with other more flexible commodity polymers such as polyethylene, polypropylene, PET, or PVC.

1.8. MIGRATION

This phenomenon is critical for polymers used in the food industry; thanks to its excellent bio compatibility and biodegradability PLA is one of the best candidates to replace common petroleum-derived polymers for food-packaging applications. The term *migration* is generally used to describe the transfer of substances from polymeric packaging (like polymerization residuals, additives, and decomposition products) to food. Plasticizers, stabilizers, and other substances are now integrated in the plastic articles that will be in contact with food. These compounds have low molecular weight with a potential to diffuse through the polymeric matrix when used in contact with food.

Diffusion of chemical substances from polymers is a very complex process, and is dependent on several parameters, such as their concentration in packaging film and food, nature of the foods, temperature, and the time period over which duration of contact occurs. During the process of diffusion, these compounds enter into another matrix (such as film or food), which changes their concentration in both the packaging and food.

The migration process can be divided into 4 major steps: diffusion of chemical compounds through the polymers, desorption of the diffused molecules from the polymer surface,

sorption of the compounds at the plastic-food interface, and desorption of the compounds in the food [38].

The likelihood of monomer and oligomer migration increases when a plastic is exposed to high temperatures during thermal processing or when food is stored for extended periods. Transfer of chemical compounds from plastics into food has raised concerns about the potentially adverse effects of food products on human health. Migration would also cause the blended material to regain the brittleness of neat PLA over time.

Preventing the mass transfer from the polymer matrix by surface modification is a way to contrast the migration phenomena. Unfortunately, surface coating, surface crosslinking or the use of multi-layered tubing, also often reduces migration at the cost of other properties such as flexibility, thermal stability, surface characteristics, and appearance [39].

There is thus a large demand for finding alternative plasticizers. A way to obtain safe plasticized PLA grades is to substitute common low-molecular weight plasticizers with compatible and nontoxic polymeric ones.

Increasing the molecular weight of the plasticizer could be a way to prevent (or at least to reduce) the migration of the plasticizing compound. In this way solubility could be maintained through the polar interactions, whereas the higher molecular weight would decrease the tendency for migration. However, increasing the molecular weight too much would eventually decrease the solubility causing phase separation and the formation of a two-phase system, an optimization of the molecular weight is therefore needed [40], [41].

1.9. PLA PLASTICIZERS, STATE OF THE ART

There are several means for improving the flexibility of PLA by modifying its physical properties, such as through copolymerization. An example of a suitable comonomer is ϵ -caprolactone, which can result in soft copolymers [42], [43]. Also blending with biomaterials, such as thermoplastic starch, is a feasible method to prepare PLA-based materials that can be successfully used for film manufacturing [44].

However, an interesting and practical route to modify the mechanical properties of PLA consists in introducing biodegradable plasticizers in the material composition. In general, plasticizers improve the ductile characteristics of PLA.

The introduction of plasticizers in the formulation of semi-crystalline polymers such as PLA can in principle reduce not only the T_g of the amorphous phase but also the T_m of the crystalline domains. Even though the T_m of PLA can be in part reduced without significantly affecting its thermomechanical properties from a practical point of view, it is quite important to also avoid depressing excessively the melting point. Therefore, the choice of a suitable plasticizer for PLA has to take this aspect into consideration, with the aim of plasticizing this polymer without affecting its heat resistance and without modifying its compostability.

In general, the T_g values of polymers can be predicted with Fox's law:

$$T_g = T_g^\infty - \frac{K}{M_n}$$

where T_g^∞ is the glass transition temperature for infinite molecular weight, K is a constant that depends on the free volume and M_n is the number-average molecular weight of the polymer [45]. An increase in the molecular weight decreases the efficiency of the plasticizer and can lead to phase separation [46].

A second aspect to be considered is the drop of tensile strength, which should be minimized as much as possible. It is also worth mentioning here the need to select PLA plasticizers that are stable during material aging, to avoid unfavourable property changes during the intended material life.

A plasticizer may also have contrasting effects on the crystallization behaviour. On one hand, T_g depression upon plasticizer addition shifts the crystallization temperature window to lower temperatures and thus facilitates the movement of chains from the amorphous phase into the existing crystal surface. Theoretically, the higher the plasticizer content, the higher is the chain mobility of PLA, which leads to faster cold crystallization. On the other hand, as previously stated, plasticization may also cause melting point depression, with a consequent overall crystallization rate decrease due to the reduced degree of undercooling [47].

It is evident how plasticization of PLA affects quite significantly the mechanical properties of this material; however, the choice of a plasticizer and its concentration requires great attention to avoid losing desired physicochemical characteristics.

Many compounds have been evaluated as plasticizers for PLA, here we report a quick summary of the most relevant ones.

It is well known that *lactide monomer* itself is an effective plasticizing agent for PLA, but it has the disadvantage of rapid migration due to its small molecular weight. The plasticization of PLA with lactide therefore results, besides accelerate aging, in a stiff polymer with a sludgy surface [48],[49].

Oligomeric lactic acid is also highly compatible and it causes a sharp depression in the T_g value along with a great increase in the elongation at break, however these advantages are accompanied by drawbacks such as melting point depression and elastic modulus decrease [44].

Polyethylene glycol (PEG) is the most investigated plasticizer for PLA. The addition of PEG reduces the T_g by approximately 2°C per % plasticizer, depending on its molecular weight, while it does not affect melting point significantly [46], [50]. However, if used in high concentration (i.e., 30 wt%) in blends with PLA, it could undergo phase separation at ambient temperature, due to epitaxial crystallization of PEG on the edge of the PLA spherulites.[46]

Polypropylene glycol (PPG) is another oligomeric plasticizer, with effects similar to PEG on PLA T_g . However, PPG is less miscible than PEG with PLA, and phase separation occurs at only 12.5% of PPG [46]. On the other hand, it is known that PEG tends to crystallize with time, whereas PPG does not crystallize. It is rather difficult to disentangle the various elements in the effect of PPG on PLA because it is not clear whether enhanced spherulite formation (thanks to the plasticization effect) is desirable or not; indeed it is undesirable because it leads to local “pools” of the plasticizer, excluded from the crystals, but it is desirable because the pools act as stress absorbers and enhance elongation to break [46].



Figure 11: PEG (left) and PPG (right) structure

Triphenyl phosphate and dioctyl phthalate are commonly used to enhance PLA crystallization [51]. In particular, in the case of triphenyl phosphate, the plasticizer used at 10, 20 and 30% reduces significantly the T_g of PLA by 14, 26 and 39°C, respectively, and increases the spherulite growth rate of two or three time fold if used in high concentration (i.e., 20 and 30 wt%) [52]. Unfortunately, these compounds are toxic and non-biodegradable so are not suitable for a “green” application.

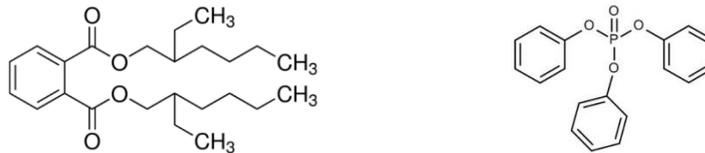


Figure 12: Dioctyl phthalate (left) and triphenyl phosphate (right) structures

Dipropylene glycol dibenzoate would be predicted to be a satisfactory plasticizer, however the non-green credentials of these aromatic plasticizers seem to have excluded them, along with phthalates, from consideration within the PLA marketplace [53].

Adipates are another family of PLA plasticizers, however, this group of plasticizers lead to a T_g decrease with plasticizer concentration only up to concentration of 10% probably due to limited miscibility with PLA. Accordingly, only modest crystallization enhancements were found [54], [55].

Even though it cannot be used as a conventional plasticizer because of its high volatility, *carbon dioxide* has shown outstanding plasticization and crystallization enhancement effects on PLA, due his highly solubility. On a weight-basis, CO₂ is much more effective in reducing T_g than the plasticizers above mentioned, however the use of this technology is restricted to only few applications, as in the extrusion foaming process where CO₂ can be used as a physical blowing agent for PLA.[56], [57]

Malonate esters, such as DBM (see Figure 13), have also been tested as plasticizers for PLA. These compounds lowered T_g of PLA from an initial value of 60°C to 30°C with 15 wt% and to a T_g of 5°C with plasticizer at 25 wt%. However, at a concentration of 20–25 wt%, phase separation occurs because of saturation of the amorphous phase of PLA. Aging a blend containing 15 wt% DBM for 4 months at ambient temperature also leads to phase separation

and to the migration of the plasticizer to the film surface. Malonate oligomers, prepared by reacting DBM with acid chlorides, lead to more stable materials in aging tests [58], [59].

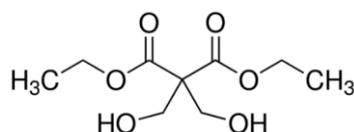


Figure 13: Diethyl bis(hydroxymethyl)malonate (DBM) structure

Among the low molecular weight plasticizers for PLA, *citrate esters* are the most investigated ones. The intrinsic advantage of these plasticizers is their bio-based and biodegradable nature, which are on par with neat PLA. Citrate plasticizers are nontoxic and approved for many food packaging and medical applications. These materials are as effective as PEG for reducing the glass transition temperature but induce a higher melting point reduction.

Labrecque et al. demonstrated good miscibility of PLA with different citrate esters at up to 20–30% by weight of plasticizer concentration, depending on the type of citrate employed [60]. Tensile strength and elongation at break of PLA plasticized with citrate esters are reported in literature and show a marked positive effect of the plasticizer at concentrations between 10% and 30%. As expected, all of the plasticizers decrease the tensile strength of PLA significantly (by about 50%) even at 10% concentration, and the worsening is larger at higher concentrations. On the other hand, elongation at break does not show any significant change at the lower percentages but significantly increases at higher concentrations in all cases [60]. The boiling point of these plasticizers is close to the processing temperature of PLA, leading to probable partial evaporation of the plasticizer during extrusion.

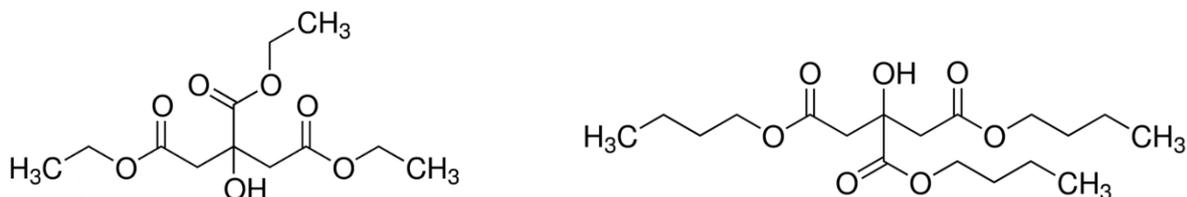


Figure 14: Triethyl citrate (left) and tributyl citrate (right) structures

A significant problem with the citrates is their tendency to bleed out of the PLA due to their low compatibility with the PLA matrix. Ljungberg and Wesslen [61] investigated the

plasticization of PLA with tributyl citrate (TBC) oligomers. They showed that at lower molecular weight of TBC the migration from the bulk of PLA to the film surface is higher. To overcome this migration issue, they increased the molecular weight of TBC. TBC trimers and heptamers prepared by transesterification were added at 10, 15, and 20 wt% to the PLA matrix. Low molecular weight molecules were more effective as plasticizers. Phase separation occurred in TBC trimer at 10 and 15 wt%. For 20 wt% TBC trimer in the PLA matrix, migration was observed. High molecular weight plasticizer molecules reached saturation at a lower weight percentage. Moreover an enhanced crystallinity was obtained as a result of the increased molecular mobility of the PLA chains. It was also found that the crystallization temperature decreased with an increasing amount of plasticizer since mobility of the PLA chains was facilitated as a consequence of the lowered T_g [44].

An interesting approach to solving this issue is shown in a patent where a plasticizer that seems to give the right thermomechanical properties without significant bleeding due to migration is prepared [52]. The patent shows an OLA (oligomeric lactic acid)-capped, short-chain polyethylene glycol (PEG) used as plasticizer. As noted above, PEG is also a fairly good plasticizer therefore the use of glycol/esters as plasticizers seem reasonable. Unfortunately, being a quite rigid polymer, it is not really a practical plasticizer so it had to be blended with triacetin. Although the mix seems to give good plasticization, the study does not report whether the triacetin bleeds out.

It is also reported that a lower molecular weight of the polymer resulted in an increased crystallization rate as well as a higher global crystallinity because of increased chain mobility. A large amount of crystallinity in PLA results in having a high modulus and strength, but also a brittle nature and a lack in toughness. These drawbacks are especially disadvantageous in the film extrusion industry.

The compatibility within the polymeric matrix and plasticizer affects physical properties such as T_g , T_m , crystallinity, and morphology. Consequently, these properties determine the macroscopic properties of the material, e.g. processability, rigidity, impact and tensile strength, barrier properties, and degradation. The plasticizer must be compatible with the polymer in order to be evenly distributed in its matrix and thus fully exploit its potential.

The reduction of the glass transition temperature of PLA arising from the presence of the plasticizer led to a system where the PLA chains had enough mobility to rearrange. Therefore, upon aging, cold crystallization occurred, having the effect that the amorphous domains in PLA were reduced in size. This resulted in a reduction of the critical amount of plasticizer and further on to phase separation. There seems to exist a competition between the efficiency of a plasticizer and the kinetics of the aging or cold crystallization in PLA. The more the material is plasticized, the larger the increase in mobility and the faster the cold crystallization process is. It is therefore imperative to find an optimum where the PLA is sufficiently flexible for the desired application without the cold crystallization taking place too fast.

2. AIM

We already reported how neat oligomeric lactic acid (OLA) has a plasticizing effect on the PLA matrix resulting in a lower T_g and an increased elongation at break [44]. Being made of the same repeating unit as the matrix, the compatibility of OLAs in the PLA matrix is very high with no expected phase separation for the percentages used.

We have also seen how citrate esters such as tributyl citrate (TBC) and triethyl citrate (TEC) are very effective in reducing the T_g of PLA when used in quantities below 25% w/w while retaining the “green” properties of PLA as they are bio-based and biodegradable. Unfortunately, these compounds have a boiling point close to the processing temperature of PLA and have a tendency to migrate out of the polymeric matrix due to their low compatibility with PLA.

Finally, we also reported the use of an oligomeric lactic acid-capped, short-chain polyethylene glycol (PEG) used as plasticizer in a tentative to reduce the bleeding of the additive from the matrix thanks to its increased molecular weight [62].

A natural follow-up was to engineer a novel type of bio-based, bio-degradable citrate ester-capped oligomeric plasticizer.

The backbone of this molecule is constituted by an oligomeric PLA chain to which a triethyl citrate “head” was attached. This compound was expected to retain the very good plasticizing capabilities shown by low molecular weight citrate esters thanks to the high free-volume associated with the citrate moiety along with a decrease in the migration deriving from the good compatibility of the OLAs with the PLA matrix.

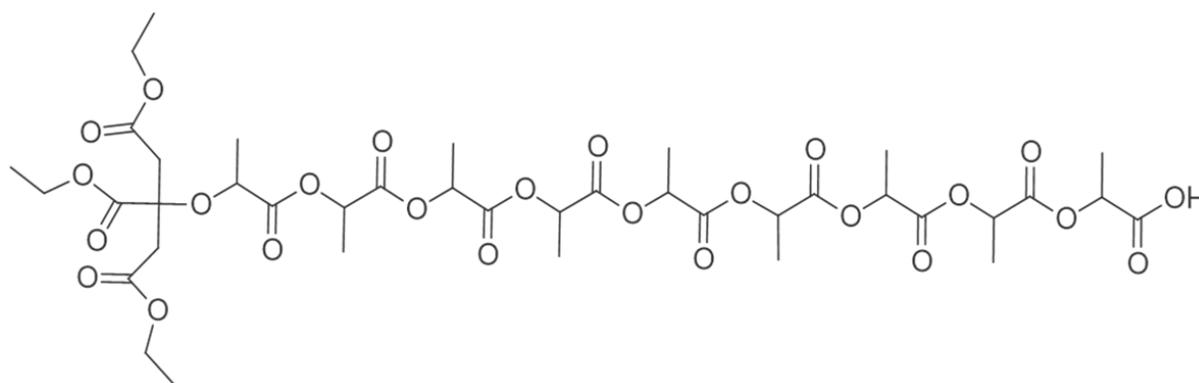


Figure 15: TEC-capped oligomeric PLA plasticizer

Poly(lactic acid) is a polymeric material which is receiving more and more attention in recent years due to its “green” characteristics. PLA is a bio-based, bio-degradable and bio-compatible material. Nevertheless, some of its properties limit its use as a substitute of common petroleum-derived plastics. The main drawbacks of PLA are its brittleness at room temperature and the slow crystallization rate.

The addition of a suitable plasticizer to the PLA matrix can solve both these issues. In order not to lose the *green* properties of PLA the plasticizer must be: bio-based, bio-degradable and bio-compatible, used in the smallest amount possible and must not show any migration from the bulk to the surface of the finished product.

In this research the efficacy of triethyl citrate-based plasticizers has been evaluated; TEC is a biodegradable, naturally derived molecule. Based on our assumptions, joining an oligomeric PLA chain to a TEC molecule would result in an effective plasticizer with almost total compatibility with the PLA matrix, thus drastically reducing migration issues. These compounds would also greatly increase the mobility of the PLA chains with a resulting increase in the crystallization rate.

Moreover, the total amount of actual plasticizer (the TEC *head* attached to the oligomers) in the polymeric mixture is negligible even when the plasticizer is used in fairly high concentrations (up to 30%).

3. RESULTS AND DISCUSSION

3.1. SYNTHESIS OF THE PLASTICIZERS

As previously stated, the underlying principle for our novel type of plasticizers is to combine two already available compounds to obtain a new additive for PLA with enhanced properties. Triethyl citrate (TEC) is a plasticizing agent, enhancing polymeric chain mobility, thus lowering the overall T_g and speeding up the crystallization rate [61], [63]. The low molecular weight of TEC, however, causes migration issues leading to a progressive deterioration of the material properties. Oligomeric lactic acid (“OLA”) is not as effective as TEC in lowering the T_g but, thanks to its almost complete compatibility with the PLA matrix, is virtually not affected by migration issues [64]. Ideally, chemically linking TEC and OLAs into a single compound would also merge their desired properties without the drawbacks, resulting in a *novel type of bio-based and bio-degradable plasticizer for PLA*.

The synthesized plasticizers will be from now on referred to as “TEC-g-PLA” (TEC-grafted-PLA). The synthesis of these compounds occurs by a Ring Opening Polymerization (ROP) catalysed by $\text{Sn}(\text{Oct})_2$ (see Figure 16). Usually 1 or 2 equivalents of a suitable alcoholic initiator is used to activate the catalyst, 1-octanol is reported to be the best choice [65]. In our synthesis there is no need for an external initiator as one of the three alcoholic groups of the TEC is used as initiator for the ROP. It follows that the OLA chain will grow grafted to the TEC molecule, with no risk of obtaining non-grafted OLA chains.

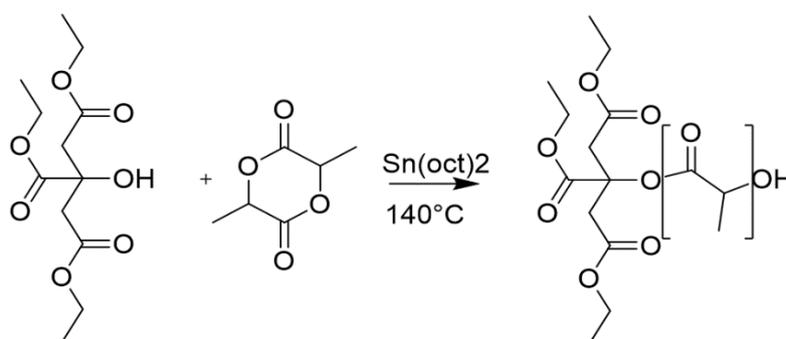


Figure 16: ROP reaction scheme for the synthesis of TEC-g-PLA

The presence of TEC molecules is useful for other reasons too. Bulk polymerization in the melt state is a technique frequently troubled by mixing problems. As the viscosity of the melt

polymers is usually high, a homogeneous mixing is not easily achievable. The addition of liquid triethyl citrate to the reaction melt lowers its overall viscosity making it easier to stir and obtain a homogeneous mixture.

One of the aims of our research was to investigate the effect of different reaction conditions on the final properties of the TEC-g-PLA product. In order to do so, we selected some starting “standard” conditions which were determined by previous work in our research group along with literature most used ones [61].

The reactions were all conducted in small scale, 2-3 grams batches, using standard round bottom flasks and always under inert nitrogen atmosphere (more detailed information about the synthesis procedure can be found in the “experimental section”).

“Base” reaction conditions are:

- Polymerization temperature 140°C
- Reaction time 6 hours
- 1 to 10 TEC-Lactide ratio
- 1 to 100 Sn(Oct)₂-Lactide ratio

3.2. SCREENING OF REACTION CONDITIONS

Altering these values led to variations in the final product characteristics but the synthetic procedure was always practically the same. Changing one of the parameters while keeping the others stable allowed us to observe the effect of such single alteration on the final properties. Following this method, we were able to *tune* the reaction conditions to obtain a final product with the desired characteristics.

Normalizing all the used chemicals amount to the amount of cyclic lactide used for each reaction meant for a more immediate and simple visualization of the different conditions applied.

The screening of the TEC-g-PLA synthesis was divided into many “sub-screenings”, each focusing on altering just one of the reaction conditions. Catalyst amount, TEC amount, temperature and reaction time were changed to observe their effect on the final products.

Moreover, we also investigated the effect on the enantiomeric purity of the starting material by repeating many of the batches with both the enantiopure (“L-Lactide”) and the racemic lactides.



Figure 17: enantiopure L-lactide (left) and racemic lactide (right) structures

Firstly, a screening of the catalyst amount was carried out, varying the ratio of Sn(Oct)₂ from a large excess (0,4 equivalents) to a much smaller amount (0,001 equivalents) for 1 lactide equivalent. After a preliminary set of synthesis (samples ML1 to ML5), some of the reactions were repeated using the racemic lactide. In the table below the conditions used for the synthesis of all the samples prepared during the screening of the Sn(Oct)₂ amount are listed. Please note that after the preliminary synthesis (sample ML1-5) the amount of TEC used was reduced from 0,40 to 0,10, as higher molecular weights (for samples ML31-35) and higher T_{cc} and T_m (for samples ML41-45) were achieved using this TEC/lactide ratio.

Sample name	Lactide (eq.)	TEC (eq.)	Sn(Oct) ₂ (eq.)	Time (min)	Temp. (°C)	
ML1	1	0,40	0,40	360	140	ENANTIOPURE lactide
ML2	1	0,40	0,20	360	140	
ML3	1	0,40	0,10	360	140	
ML4	1	0,40	0,04	360	140	
ML5	1	0,40	0,02	360	140	
ML31	1	0,10	0,02	360	140	RACEMIC lactide
ML32	1	0,10	0,01	360	140	
ML33	1	0,10	0,005	360	140	
ML34	1	0,10	0,002	360	140	
ML35	1	0,10	0,001	360	140	
ML41	1	0,10	0,02	360	140	ENANTIOPURE lactide
ML42	1	0,10	0,01	360	140	
ML43	1	0,10	0,005	360	140	
ML44	1	0,10	0,002	360	140	
ML45	1	0,10	0,001	360	140	

Table 2: reaction parameters for the screening of Sn(Oct)₂ quantities

The effect of different quantities of TEC on the final properties was investigated in the second *screening* in which the amount of TEC was varied from a large excess (ca. 1,5 equivalents) to a much smaller amount (around 0.05 equivalents). In the table below the conditions used for the synthesis of all the samples prepared during the screening of the TEC amount are listed.

Sample name	Lactide (eq.)	TEC (eq.)	Sn(Oct) ₂ (eq.)	Time (min)	Temp. (°C)	
ML6	1	1,47	0,1	360	140	ENANTIOPURE lactide
ML7	1	0,73	0,1	360	140	
ML7bis	1	0,37	0,1	360	140	
ML8	1	0,15	0,1	360	140	
ML9	1	0,07	0,1	360	140	
ML10	1	0,04	0,1	360	140	

Table 3: reaction parameters for the screening of TEC quantities

To analyse the effect of the reaction time on the product properties we carried out two sets of screenings, one for the enantiopure lactide and one for the racemic lactide. For each reaction the same lactide, catalyst and TEC amounts were used (chosen after analysing the samples produced in the previous screenings), the temperature has been kept constant at 140°C. In the table below the conditions used for the synthesis of all the samples prepared during the screening of the reaction times are listed.

Sample name	Lactide (eq.)	TEC (eq.)	Sn(Oct) ₂ (eq.)	Time (min)	Temp. (°C)	
ML36	1	0,1	0,005	60	140	RACEMIC lactide
ML37	1	0,1	0,005	180	140	
ML38	1	0,1	0,005	360	140	
ML39	1	0,1	0,005	540	140	
ML40	1	0,1	0,005	720	140	
ML46	1	0,1	0,005	60	140	ENANTIOPURE lactide
ML47	1	0,1	0,005	180	140	
ML48	1	0,1	0,005	360	140	
ML49	1	0,1	0,005	540	140	
ML50	1	0,1	0,005	720	140	

Table 4: reaction parameters for the screening of reaction times

Finally, to further investigate the effect of TEC on the final properties some of the batches were prepared without the addition of the citrate to obtain plain OLAs that were later compared with the TEC-g-PLAs. These samples were prepared via another screening of the reaction times by using similar conditions to the ones just described for the screening of reaction times of TEC-containing oligomers, the only difference was the temperature which was kept constant at 120°C instead of 140°C. In the table below the conditions used for the synthesis of all the oligomeric PLA samples prepared during the screening of the reaction times are listed.

Sample name	Lactide (eq.)	TEC (eq.)	Sn(Oct)2 (eq.)	Time (min)	Temp. (°C)	
ML11	1	0	0,1	60	120	ENANTIOPURE lactide
ML12	1	0	0,1	120	120	
ML13	1	0	0,1	180	120	
ML14	1	0	0,1	240	120	
ML15	1	0	0,1	300	120	
ML16	1	0	0,1	360	120	
ML17	1	0	0,1	420	120	

Table 5: Reaction parameters for the screening of reaction times during the synthesis of OLAs

3.3. PRELIMINARY CHARACTERIZATION OF THE OLIGOMERS

The molecular weight of the oligomers, the amount of TEC contained in each oligomeric sample, the lactide and TEC conversions have been determined using NMR spectroscopy (¹H-NMR). All these calculations were made assuming that every oligomer have a TEC molecule attached to the polymeric chain according to the ROP mechanism (for the TEC-less OLAs a different method was used). These measurements are affected by an experimental error due to the manual integration of the signals via NMR analysis software but, assuming the same error was repeated for each integration, we can assume the results are still valid for relative comparisons between the samples.

The crude of each reaction containing the TEC-g-PLA product and the unreacted lactide, TEC, Sn(Oct)₂ and other impurities has been purified by treatment with methanol. All compounds

except the oligomeric product are soluble in MeOH so the pure TEC-g-PLA could be isolated via simple vacuum filtration utilizing a Buchner filter. The spectra used for the calculation of the molecular weights are those of the purified samples.

A fraction of the crude mixture of each reaction was preserved and its NMR spectrum has been recorded to obtain information about the triethyl citrate and lactide *conversion*. The quadruplet signal at 5.05 ppm is attributed to the unreacted lactide while the more complex signal resembling a quadruplet around 5.15 ppm is attributed to the reacted lactide, namely OLA's repeating unit. By integrating the unreacted lactide signal and giving a value of 1 to its area, the area resulting from the integration of the repeating unit gives us a value that we can easily rearrange to a more "friendly" form indicating the conversion of the lactide at the end of the reaction (see equation 1).

$$\text{Lactide conversion (\%)} = \left(1 - \frac{1}{(1 + \text{reacted lactide peak area})}\right) \times 100 \quad (\text{eq.1})$$

From the crude spectra the conversion of the TEC can also be evaluated following a procedure similar to the one we just described for the lactide conversion. This time we integrated the quadruple signal between 4.25 and 4.3 ppm and gave its area a value of 6, accounting for the 6 methylenic protons of triethyl citrate. The faint signal between 4.35 and 4.40 ppm, belonging to the reacted TEC, was integrated relative to the previous, the resulting value could again easily be rearranged to give a percentage conversion of the TEC used in the reaction (see eq. 2).

$$\text{TEC conversion (\%)} = \left(\frac{\text{unreacted TEC peak area}}{(6 + \text{reacted TEC peak area})}\right) \times 100 \quad (\text{eq. 2})$$

The lactide conversion have all resulted very high (between 95 and 99%) for all the samples. Such result was expected because an excess of catalyst was used even for the samples containing the smaller amount of Sn(Oct)₂.

The conversion of TEC was quite low (between 10 and 25%) for most of the samples, this result is again explained by the use of an excess amount of TEC. The excessive amounts of both catalyst and TEC were used to guarantee the minimum required reagents quantities for the reactions. An optimisation of the reaction conditions would be required before scaling up the procedures to bigger batches.

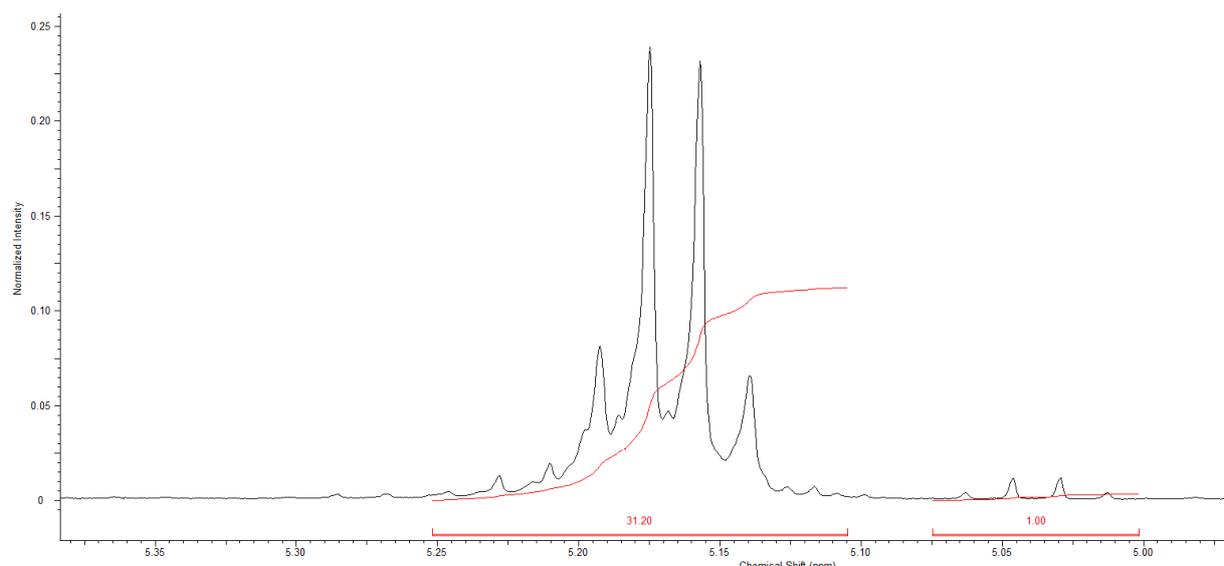


Figure 18: NMR spectra of a reaction crude, zoom on the lactic acid area

To determine the molecular weight of the oligomeric products the area of certain signals along the NMR spectra of the purified samples have been used. For instance, the multiplet in the region between 4.35 and 4.40 ppm belongs to the TEC (to its methylenic hydrogen atoms). After integrating this signal, a value of 6 was given to it, accounting for the 6 protons which generate it. The integrated area of the signal between 5.10 and 5.25 ppm is proportional to the oligomeric chain length. Having integrated the previous signal imposing 6 as the area value, integrating the area of the peaks between 5.10 and 5.25 directly gives the total *number of repeating units* in the oligomer chain as result. It is sufficient to multiply this value by the molecular weight of the single repeating unit (72 g/mol for PLA) to obtain the molecular weight of the oligomer.

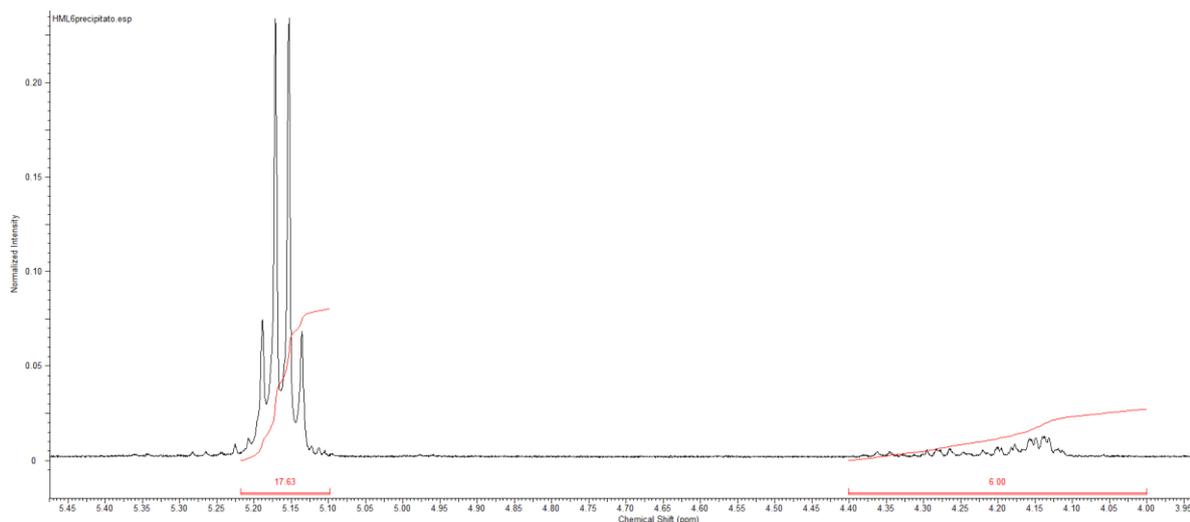


Figure 19: portion of the NMR spectra of a purified oligomeric product

By comparing the conversion data for TEC-g-PLAs and OLAs without the TEC “head” a difference in the trends of lactide conversion over time has been found (see graph below). It is clear how the TEC-g-PLA and PLA oligomers show different reaction kinetics.

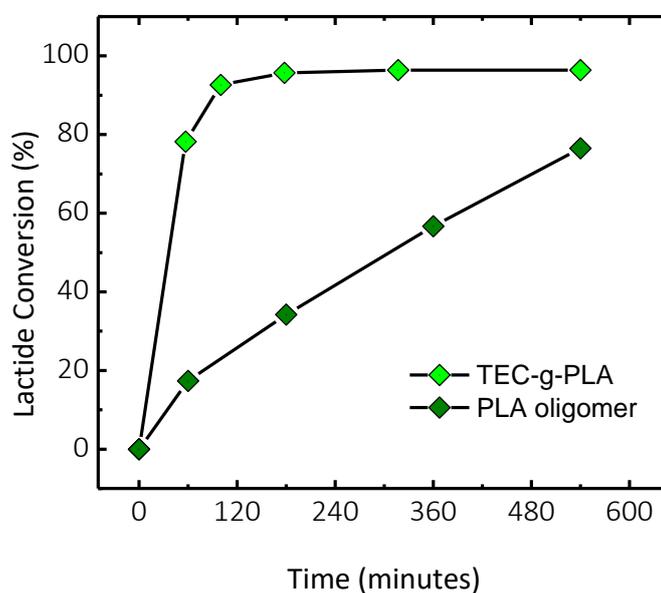


Figure 20: Lactide conversion over reaction time, comparison between TEC-g-PLA and pure OLA samples

The different kinetics could be explained by the presence (or absence) of TEC during synthesis. As previously stated one of the OH groups of the TEC molecule works as initiator for the reaction, activating the catalyst and removing the need of an external alcoholic

initiator. During the synthesis of the non-modified PLA oligomers no TEC was used and no alcoholic initiator was added. This limits the efficiency of the catalyst and highlights even more the benefits of the TEC-capped oligomers, already during synthesis. OLAs also show a linear *increase* of M_n over time while TEC-g-PLA show a linear *decrease* of M_n over time due to the excess TEC amount which promotes trans-esterification reactions (Figure 5). The TEC-g-PLA reaches almost complete conversion in around 180 minutes and this trend has been confirmed by further analysis. The presence of TEC in the formulation of this plasticizer is desirable as it also shortens the time required by each batch to reach full conversion.

The presence of TEC is beneficial also to the final molecular weight of the product. By comparing TEC-g-PLAs and OLAs prepared using the same reaction conditions it has been always found that samples containing TEC have a much higher M_n compared to the OLAs prepared with the same reaction times (see graph below). This could be explained using the assumptions made for the previous graph: the faster-reacting TEC-g-PLAs chains are less affected by transesterification reactions leading to cyclic oligomers of lactic acid and lactide.

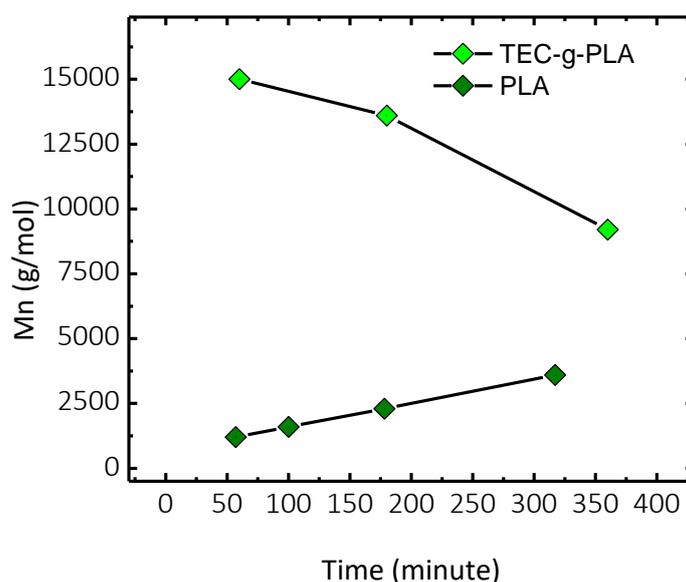


Figure 21: Molecular weight over reaction time, comparison between TEC-g-PLA and pure OLA samples

Molecular weights for the samples prepared range from 2000 to 15000 g/mol with most of the samples weighing between 4000 and 10000 g/mol. Many interesting trends have been found when comparing data from different reactions. For instance, it has been found that reactions containing *higher* amounts of TEC resulted in oligomeric products with *lower*

molecular weight (see image below). This can be ascribed to the polymerization reaction mechanism. As previously stated, the synthesis of the oligomers proceeds via ROP to obtain TEC-capped lactic acid oligomers. Every OLA chain grows attached to the TEC alcoholic group, the TEC is by all means the chain initiator. If the initial amount of TEC is increased the total number of chains will be increased, the result is many *short* oligomeric chains thus a TEC-g-PLA with lower molecular weight. If the amount of TEC in the reaction batch is reduced the total number of chains will be lower but their molecular weight will be higher.

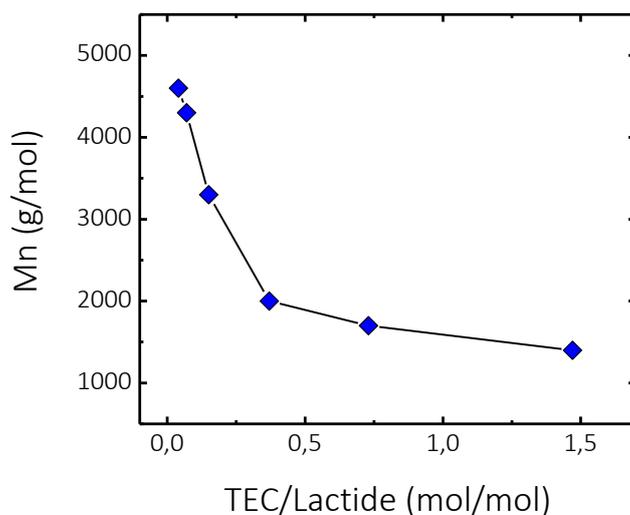


Figure 22: relation between TEC/lactide amount and Mn of the final oligomeric product

Another interesting trend has been found when comparing the molecular weight of the products to the amount of catalyst used during their synthesis (see the graph below).

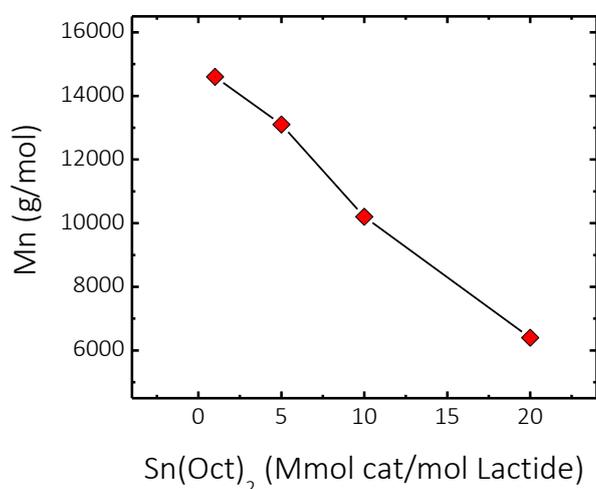


Figure 23: Relationship between catalyst amount used and resulting oligomeric product molecular weight

From Figure 23 it is clear how using *lower* amounts of catalyst leads to *higher* molecular weight products. The explanation for this trend is fairly similar to the previous one: the ROP reaction proceeds via a coordination-insertion mechanism with the polymer chain growing from the alcoholic moiety of the TEC while being *coordinated* to the catalytic centre. If more $\text{Sn}(\text{Oct})_2$ is used the total number of chains will be higher but the final weight of those chains will be lower.

Both for the TEC and the $\text{Sn}(\text{Oct})_2$ a certain minimum amount of the compounds is obviously needed for the reaction to take place. As previously stated, an excess of both components has been used during this set of reactions, so the trend could be also explained by this assumption and would be expected to diverge when approaching the minimum amounts required by the reaction.

Repeating the polymer synthesis slightly varying the reaction parameters and comparing the resulting molecular weight of the products enabled us to tune the reaction depending on the oligomer we want. In other words, by determining the relationship between reagents amount, reaction time and temperature we could predict with reasonable certainty the molecular weight of the final oligomeric product given the initial reaction conditions.

To obtain a low-molecular weight TEC-g-PLA ($M_n \approx 3000$ g/mol) it is necessary to use *high TEC amount* (≥ 0.5 equivalents) and *high catalyst amount* (≥ 0.05 equivalents) along with a *long reaction time* (6 or more hours).

To obtain a high-molecular weight TEC-g-PLA ($M_n \approx 10000$ g/mol) it is necessary to use *low TEC amount* (≤ 0.5 equivalents) and *low catalyst amount* (≤ 0.05 equivalents) along with a *short reaction time* (1-3 hours).

3.4. NON-ISOTHERMAL CHARACTERIZATION OF THE OLIGOMERS

Differential scanning calorimetry (DSC) has been used to evaluate the thermal properties of the samples. Using DSC analysis we can measure the glass transition temperature (T_g), the

melting temperature (T_g), the cold-crystallization temperature (T_{cc}) and the enthalpies associated with these physical transitions.

For every oligomeric samples the same analysis method has been used:

- 1: Equilibrate at 30°C
- 2: Ramp 10°C/min to 180°C
- 3: Isothermal for 2.00 min
- 4: Ramp 10°C/min to 0°C
- 5: Isothermal for 1.00 min
- 6: Ramp 10°C/min to 180°C

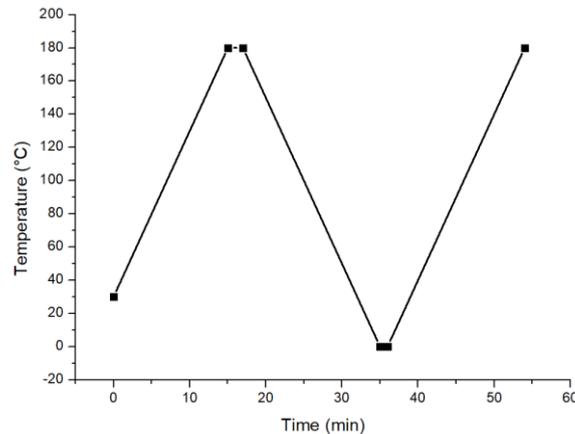


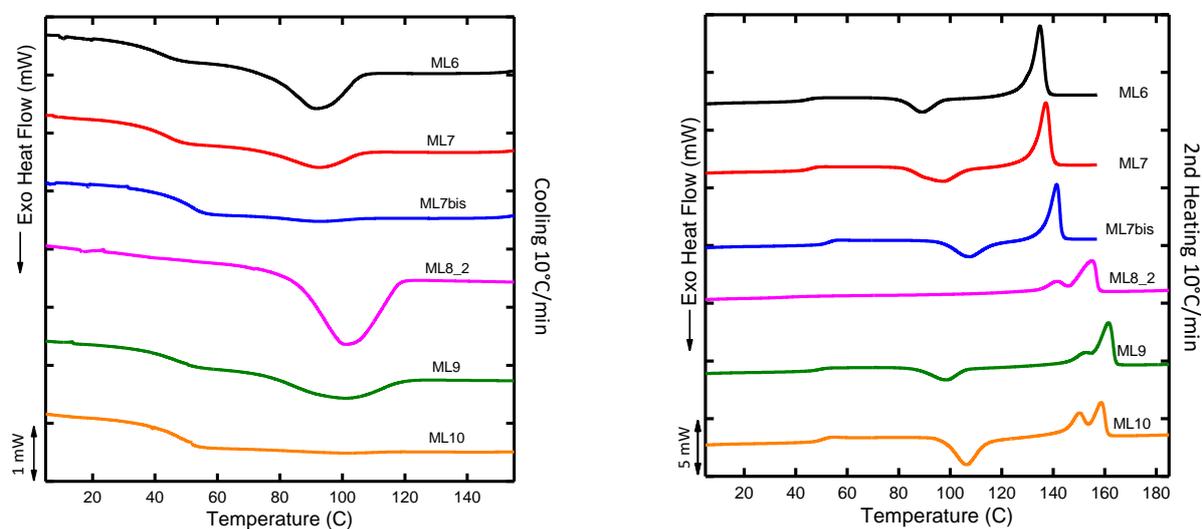
Figure 24: DSC method for the analysis of the oligomers

The first heating cycle purpose is to reset the *thermal history* of the sample while the rest of the thermal method is where the actual DSC data come from. Both crystallization from the melt state during cooling and during heating (*cold crystallization*) are visible with DSC measurements, they are both visualized as exothermic peaks in the heat flux.

As mentioned before, the glass transition is visualized as a change in the slope of the heat flux, the temperature correspondent to the inflection point of the slope is taken as T_g . The melting process, being a first-order transition, is visualized as an endothermic peak. The maximum value of the peak is taken as melting temperature and the area of the peak is the melting enthalpy. When the melting peak is split because of the crystalline polymorphism of PLA (see Introduction), the maximum temperature of the highest peak is usually taken as T_m . While the glass transition is always present in polymers, the melting process takes place only if there is a crystalline portion as it only affects those regions of the material.

As mentioned in the introduction, the control of PLA crystallization kinetics is not a trivial issue, since it depends on the relative amount of the two stereoisomeric forms in which lactide exists (i.e., L or D lactide). Only if one of the two forms is present in enough amount (at least more than 96–97%), PLA is able to develop significant crystallinity. The presence of low amounts of isomer co-units (L or D) in the PLA chains during structure formation leads to a reduction in the maximum achievable crystallinity and to the slowing of the crystallization

process [66]. The samples prepared using the *racemic* lactide showed no crystallization at all, confirming this assumption. These samples were completely amorphous and have been used as a reference to assess the influence of the plasticizer's crystallinity on the properties of the plasticized PLA materials. From the curves registered during the cooling process it is evident that not every oligomer could crystallize in the provided experimental conditions. As expected the glass transition temperature of the prepared polymers is influenced by the molecular weight. Oligomers always have a *lower* T_g when compared to polymers of the same repeating unit, this property of oligomers is useful when they are used as plasticizers as the overall glass transition temperature is lowered when the high- T_g polymeric matrix is mixed with the low- T_g oligomeric plasticizer.



Sample	COOLING		SECOND HEATING					Mn (g/mol)
	Tc (°C)	ΔHc (J/g)	Tg (°C)	Tcc (°C)	ΔHcc (J/g)	Tm (°C)	ΔHm (J/g)	
ML6	91,8	13,2	44	89	16,4	134,9	44,9	1400
ML7	92,3	7,0	45	97	23,6	137,8	41,9	1700
ML7bis	91,9	1,5	53	107	21,6	141,3	32,5	2000
ML8_2	100,6	33,5	36	-	-	(140,9) 155,2	38,5	3300
ML9	99,9	14,8	50	99	19,4	(151,8) 161,6	43,0	4300
ML10	-	-	51	106	33,5	(150,2) 158,8	38,7	4600

Figure 25: Cooling (left), 2nd heating (right) and numerical data from DSC measurements of 5 enantiopure TEC-g-PLA samples

Establishing a direct correlation between the oligomer molecular weight and the T_g has not been very successful due to the inaccuracies in the molecular weight calculations from NMR spectra. No direct correlation between T_g and M_n has been found within the range of molecular weights analysed.

It is also worth noting that the molecular weight range of the oligomers was so small (around 10000 g/mol) that any difference in T_g could be very well lie within the experimental error. Nevertheless, DSC measurements have been carried out for every oligomeric sample produced and the results show that almost every oligomeric sample of TEC-g-PLA has a T_g between 35 and 50 degrees, as expected these values are lower than neat high-molecular weight PLA (60°- 65°C). Some of the samples were not able to crystallize from the melt state during cooling, this usually happened for the heaviest oligomers which contain lower percentages of TEC over their total weight. Because of this the viscosity of these samples is higher, resulting in diminished chain mobility which in turn slows down the spherulitic growth process. Molecular weight has opposite effects on the nucleation and crystal growth. There is a range of molecular weights where the sum of nucleation and crystal growth speeds is sufficiently high to allow crystallization of the oligomer in the given experimental conditions.

Figure 25 shows the DSC curves for five samples prepared during the screening of TEC amounts. It can be clearly seen how some of the curves have different trends even if they are all quite similar. The glass transition is not always visible because of the small scale used but the T_g is easily detectable for all sample using data analysis software. Looking at the melting phase transition we can see how heavier oligomers have higher melting temperatures, this is in agreement with the literature data [67], [68]. This trend is confirmed also when all the samples that were able to crystallize (all the oligomers prepared using enantiopure lactide) are compared (see Figure 26).

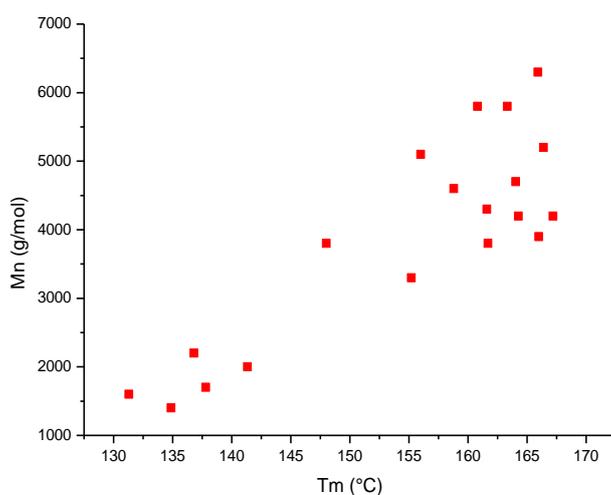


Figure 26: melting temperature vs molecular weight for semi-crystalline TEC-g-PLA samples

TEC-g-PLAs from ENANTIOPURE LACTIDE

Sample	T _c (°C)	ΔH _c (J/g)	T _g (°C)	T _{cc} (°C)	ΔH _{cc} (J/g)	T _m (°C)	ΔH _m (J/g)	M _n (g/mol)	
ML2	110	4,90	42	94	30,3	(138,9) 154,3	40,3	3100	↓ DECREASING CATALYST AMOUNT
ML3	90	29,8	37	83	2,45	131,3	39,1	1600	
ML4	96	33,5	56	100	2,32	(132,7)149,3	39,0	4300	
ML5	117	54,4	43	-	-	148,0	57,7	3800	
ML41	107	44,1	32	-	-	(151,1) 161,7	47,9	3800	
ML42	116	47,2	46	-	-	(159,0) 167,2	47,9	4200	
ML43	111	43,8	41	-	-	(156,8) 166,4	50,8	5200	
ML44	113	51,9	45	-	-	(150,9) 156,0	59,0	5100	
ML45	113	46,6	44	-	-	157,7 (160,8)	55,5	5800	
ML6	92	13,2	44	89	16,4	134,9	44,9	1400	↓ DECREASING TEC AMOUNT
ML7	92	7,0	45	97	23,6	137,8	41,9	1700	
ML7bis	92	1,5	53	107	21,6	141,3	32,5	2000	
ML8	101	33,5	36	-	-	(140,9) 155,2	38,5	3300	
ML8_2	101	33,5	36	-	-	(140,9) 155,2	38,5	3300	
ML9	100	14,8	50	99	19,3	(151,8) 161,6	43,0	4300	
ML10	-	-	51	106	33,5	(150,2) 158,8	38,6	4600	
ML46	114	50,9	36	-	-	(156,20) 163,32	54,5	5800	↑ INCREASING REACTION TIME
ML47	114	50,6	46	-	-	(158,93) 165,93	54,1	6300	
ML48	117	55,8	45	-	-	(157,62) 164,04	59,0	4700	
ML50	117	53,1	46	-	-	(161,00) (166,00)	58,3	3900	
ML51	117	54,5	36	-	-	(158,34) 164,26	56,3	4200	

Table 6: DSC data for oligomeric samples produced using ENANTIOPURE lactide

TEC-g-PLAs from RACEMIC LACTIDE

Sample	T _c (°C)	ΔH _c (J/g)	T _g (°C)	T _{cc} (°C)	ΔH _{cc} (J/g)	T _m (°C)	ΔH _m (J/g)	M _n (g/mol)	
ML31	-	-	36	-	-	-	-	6400	↓ DECREASING CATALYST AMOUNT
ML32	-	-	43	-	-	-	-	8100	
ML33	-	-	25	-	-	-	-	9200	
ML34	-	-	35	-	-	-	-	10200	
ML35	-	-	27	-	-	-	-	14600	
ML36	-	-	36	-	-	-	-	15000	↓ INCREASING REACTION TIME
ML37	-	-	50	-	-	-	-	13600	
ML38	-	-	47	-	-	-	-	9200	
ML39	-	-	46	-	-	-	-	8100	

Table 7: DSC data for oligomeric samples produced using RACEMIC lactide

NON-modified Lactic Acid Oligomers from ENANTIOPURE LACTIDE

Sample	T _c (°C)	ΔH _c (J/g)	T _g (°C)	T _{cc} (°C)	ΔH _{cc} (J/g)	T _m (°C)	ΔH _m (J/g)	M _n (g/mol)	
ML11	101	0,470	56	124	25,5	146,2	27,7	1500	↓ INCREASING REACTION TIME
ML12	103	0,640	53	102	39,6	(151,9) 159,2	38,1	1700	
ML13	103	0,420	54	105	37,6	(153,1) 160,0	40,3	1800	
ML14	96	2,80	51	96	33,7	(149,7) 157,6	38,4	1700	
ML15	100	0,370	52	102	39,5	(152,0) 158,5	39,7	1700	
ML16	88	6,10	49	93	32,6	(147,62) 156,83	41,7	1500	
ML17	94	0,650	54	102	43,3	(152,9) 160,1	38,7	1800	

Table 8: DSC data for oligomeric samples produced using ENANTIOPURE lactide and NO TEC (OLAs)

When comparing DSC data for a low molecular weight TEC-g-PLA, a high molecular weight TEC-g-PLA and a low molecular weight OLA, clear differences in the DSC curves are noticeable both for the cooling and the 2nd heating processes.

We chose sample ML3 as LMw TEC-g-PLA, sample ML42 as HMw TEC-g-PLA and sample ML13 as LMw OLA. These samples are representative of others with similar molecular weight and/or synthesis conditions.

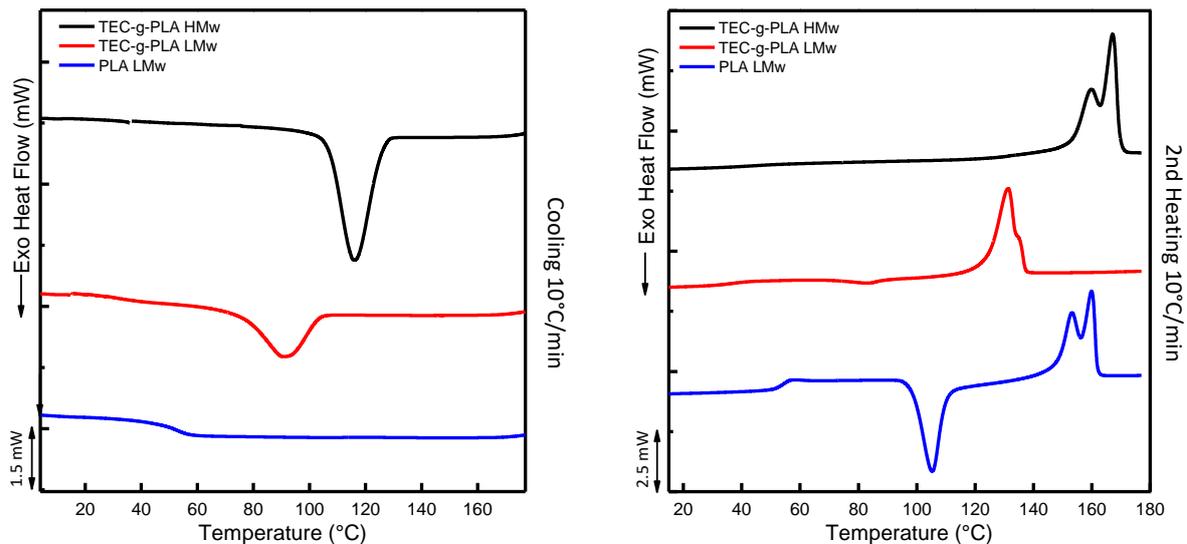


Figure 27: DSC curves for cooling (left) and second heating (right) of high a low molecular weight TEC-g-PLA and an oligomeric PLA sample

During cooling the high molecular weight plasticizer undergoes crystallization around 120°C while the low molecular weight TEC-g-PLA does so around 90°C. The enthalpies for the two transitions are different, the first (HMw) being much higher than the latter (LMw). No crystallization during cooling is noticeable for the lactic acid oligomer. The glass transition temperatures are not always clearly visible due to the *shape* of the graphs. The unmodified PLA oligomer has the highest T_g (54°C) followed by the TEC-g-PLA HMw (46°C) and the TEC-g-PLA LMw (37°C).

The melting temperatures for TEC-g-PLA HMw and PLA LMw are very similar, respectively 167 and 160°C while the TEC-g-PLA LMw has a lower T_m of 131°C. Comparing the melting enthalpies for the three samples enables us to assess the crystallinity of the materials (ΔH_m° for a perfect PLA crystal is 93.6 J/g, see *Crystallinity* in the Introduction). TEC-g-PLA LMw and PLA LMw have very similar melting enthalpies (respectively 40,1 and 39,3 J/mol) resulting in a degree of crystallinity of 42

and 43%. The TEC-g-PLA HMw has higher melting enthalpy (47.9 J/mol) which corresponds to a crystallinity degree of 50.

When comparing DSC curves for TEC-g-PLA and unmodified PLA oligomers produced using enantiopure lactide with the curves for TEC-g-PLA produced using *racemic* lactide it is evident how the stereoregularity of the polymeric chain is crucial for the development of crystalline regions in the material. The T_g transition is present for all samples but no crystallization during cooling or heating is visible for the plasticizer produced using the racemic lactide while the melting peak (indicating the presence of a crystalline phase) is visible for both the samples prepared using enantiopure lactide. The cooling curve for enantiopure TEC-g-PLA also shows the evidence of a cold crystallization phase transition around 120°C. (see Figure 28).

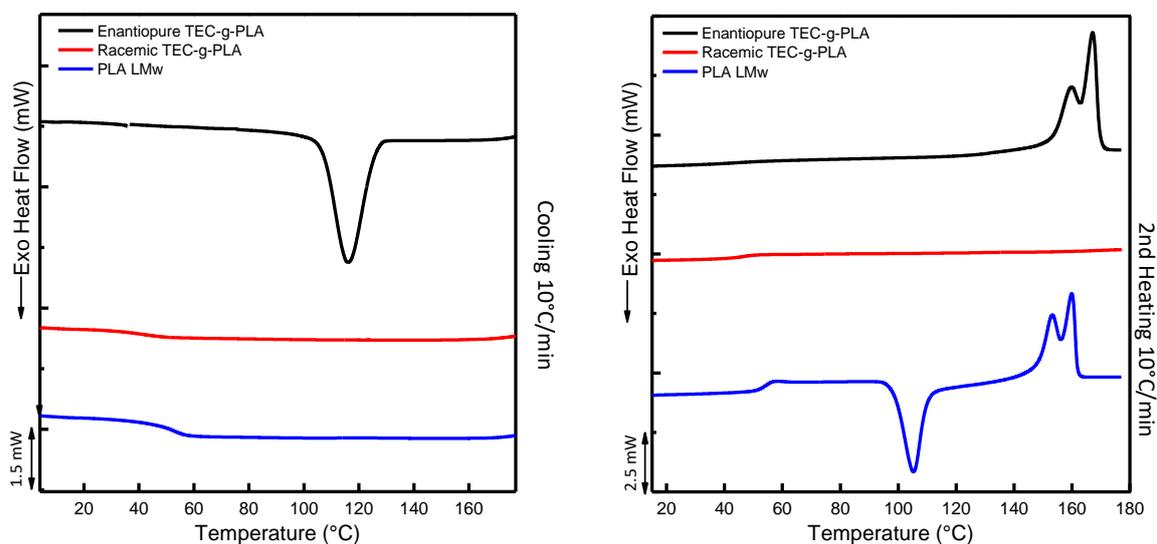


Figure 28: comparison between racemic and enantiopure oligomers, DSC curves for cooling (left) and second heating (right).

3.5. BLENDS PREPARATION

After successfully preparing many different samples while screening the effect of different reaction conditions on the final products, we moved on by choosing one TEC-g-PLA and one non-modified PLA oligomer to be used for the blending with a commercial high-molecular weight PLA matrix. The PLA oligomer has been used as reference to assess the effect of the TEC on the formulation of the plasticizer. To obtain plasticized blends that were as representative as possible of the TEC-capped plasticizer performance we chose a sample

possessing thermal properties that were average between all the prepared products. Sample ML2 was chosen for this purpose, with a molecular weight of 3100 g/mol and a T_g of 42°C. This plasticizer is capable of crystallizing both during cooling from the melt state ($T_c= 110^\circ\text{C}$, $\Delta H_c= 4,90 \text{ J/g}$) and during heating ($T_{cc}= 94^\circ\text{C}$, $\Delta H_{cc}= 30,3 \text{ J/g}$); its melting temperature is 154°C.

In order to have enough material for the preparation of the blends the synthesis of ML2 (which from now on will be referred to as “TEC-g-PLA”) was repeated scaling up the quantities used for the screening synthesis fifteen-fold. The ratio of the reagents used was 1 equivalent of enantiopure lactide, 0,4 equivalents of TEC and 0,2 equivalents of catalyst. Each scaled up reaction batch produced roughly 4 grams of purified product.

For the non-modified PLA oligomer (which from now on will be referred to as “PLA LMw”) we used a sample previously produced in abundant quantities. This PLA LMw have a M_w of 3200 g/mol and a T_g of 55°C. Having been synthesized using enantiopure lactide this oligomer too is capable of crystallizing both during cooling from the melt state ($T_c= 118^\circ\text{C}$, $\Delta H_c= 1,40 \text{ J/g}$) and during heating ($T_{cc}= 115^\circ\text{C}$, $\Delta H_{cc}= 39,3 \text{ J/g}$); its melting temperature is 168°C.

Blends containing 10%, 20% and 30% (w/w) of plasticizer dispersed in a high molecular PLA matrix were prepared along with a non-plasticized PLA sample to be used as reference. The blends were prepared via solvent casting in Petri dishes using chloroform as solvent. The required amounts of plasticizer and PLA were dissolved in the solvent which was later eliminated by drying in a vacuum oven until constant weight was achieved.

BLEND COMPOSITION	TEC (w/w %)
PLA	-
PLA/PLA LM _w 90/10	-
PLA/PLA LM _w 80/20	-
PLA/PLA LM _w 70/30	-
PLA/TEC-g_PLA 90/10	0,9
PLA/TEC-g_PLA 80/20	1,8
PLA/TEC-g_PLA 70/30	2,7

Table 9: Blends composition and TEC amount contained in each one

Looking at the blend weight/weight compositions and the amount of TEC out of the total weight of the blend it is evident how, even for the blends with the highest plasticizer amount the total weight of *non-lactic acid material* is just under 3%. As explained in the introduction, having a low amount of plasticizer in the material helps limiting the unwanted phase separation phenomena.

3.6. NON-ISOTHERMAL CHARACTERIZATION OF THE BLENDS

Preliminary thermogravimetric analysis

Before proceeding with the Differential Scanning Calorimetry analysis, a *Thermogravimetric Analysis (TGA)* was performed on the casted blends. A thermogravimetric analyser continuously measures mass while the temperature of a sample is changed over time. A typical TGA graph shows the mass over temperature curve along with the derivative of the same curve. Using TGA the thermal degradation phenomena of the sample can be studied, indeed every loss of weight resulting from thermal decomposition upon heating is reported as a percentage of the total initial weight. Another information provided by TGA is the *temperature of maximum degradation ($T_{deg\ max}$)*, this is the temperature at which the decomposition rate reaches its maximum. For a polymeric material, if the analysis is conducted under nitrogen, the weight loss is caused by the cleavage of the covalent bonds of the polymer backbone chain, as a result monomers and oligomers as well as other low molecular weight substances are produced. These compounds have a much inferior boiling temperature, so they leave the sample as gases. The degradation phenomena often begin at temperatures much lower than the $T_{deg\ max}$, the temperature at which the first weight loss is detected is called T_{onset} or simply T_{deg} .

The T_{onset} is a crucial property for polymeric materials as it marks a limit of temperature that must not be overcome during the processing. Most of the industrial methods used to produce polymeric materials (i.e. extrusion, injection moulding, blow moulding) involve high temperatures stages to achieve a sufficient fluidity of the polymer to be shaped into moulds. The polymeric material must be able to withstand the processing temperatures without

losing any of its original properties. The addition of chemical compounds, such as plasticizers into a homogeneous matrix lowers the overall temperature of maximum degradation of the material because the physicochemical stability of the plasticized material is lower. The TGA analysis is useful also during the preliminary study of a newly prepared material, the $T_{deg\ max}$ must be known before submitting the sample to DSC analysis. The maximum temperature reached during the DSC heating must be at least 50°C lower than the $T_{deg\ max}$ and in any case lower than the T_{onset} .

We also used this technique to check for the presence of remaining solvent after the drying of the casted blends. Knowing the boiling temperature of the solvent used we looked specifically for weight losses around that temperature and kept further drying the samples until any boiling solvent-caused weight loss was inferior to 1% of the total mass. A TGA analysis of a plasticized PLA sample containing residual amounts of $CHCl_3$ is shown Figure 29. At 65°C the sample starts to lose weight, this is visualized as a downwards slope in the weight curve and as a “bump” in the derivative, the total weight lost during this decomposition is 7,0%. The $T_{deg\ max}$ for the sample is 270°C but the sample starts losing weight around 204°C so this temperature is the upper limit temperature for the DSC analysis.

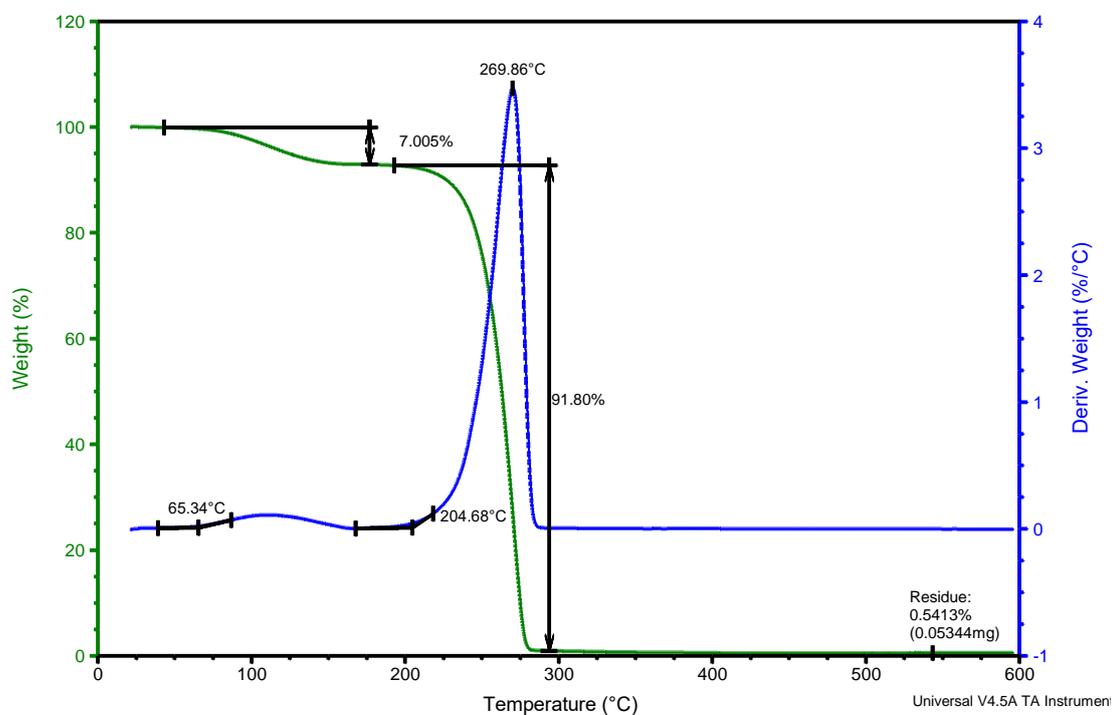


Figure 29: TGA analysis of a plasticized PLA casted sample containing a residual amount of solvent

During the thermal decomposition of this sample 92% of the initial mass is lost leaving just 0,5% of residual as solid at the end of the analysis. Chloroform was used as solvent for the casting of the sample, CHCl_3 has a boiling temperature of 62°C so the lower temperature weight loss must derive from traces amount of solvent present in the material which will then need further drying in the vacuum oven until no weight loss around this temperature must be detected.

All the TGAs that have been performed on the samples prepared during this research showed a similar shape in the weight loss curves and were interpreted in the same way. The heating ramp used for all the TGA analysis is a $10\text{ C}^\circ/\text{min}$ from 30°C to 600°C under nitrogen atmosphere.

In Figure 30 the temperature of maximum degradation for the samples plasticized with TEC-g-PLA and PLA LMw are compared along with those of neat PLA and neat TEC-g-PLA and PLA LMw as reference. As expected the presence of the plasticizer lowers the $T_{\text{deg max}}$ and there is a direct relationship between the amount of plasticizer added to the material and the resulting $T_{\text{deg max}}$ decrease. As previously stated, (see section 1.4) the degradation of PLA mainly happens via transesterification reactions, above 240°C pyrolytic elimination can also happens via a radical scission mechanism [21].

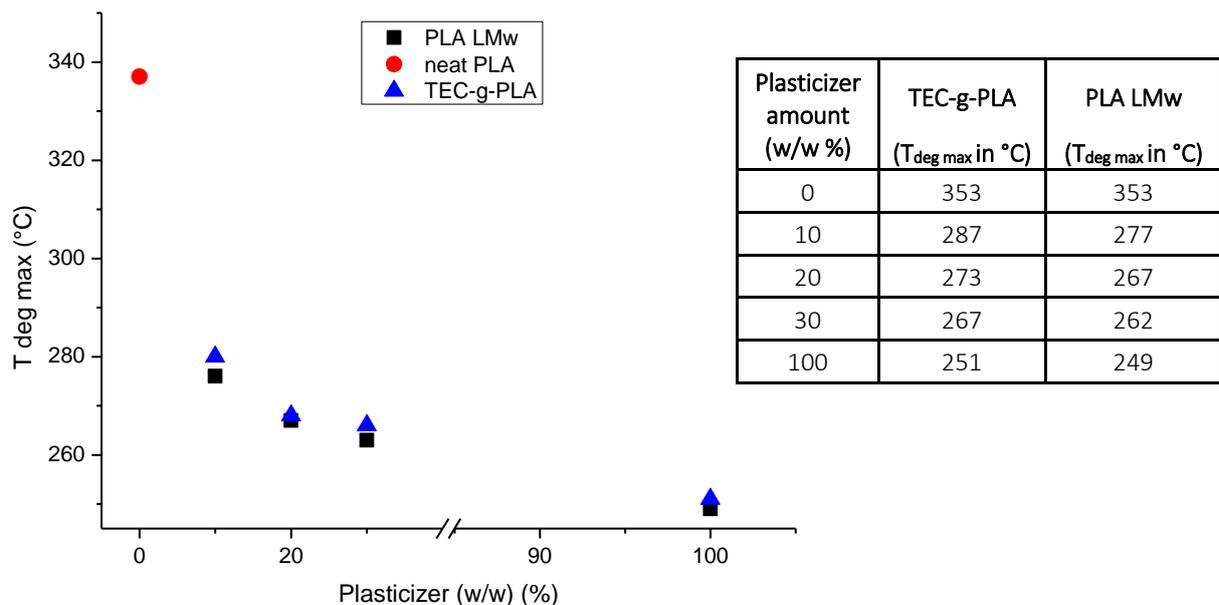


Figure 30: TGA analysis, $T_{\text{deg max}}$ for plasticized samples, neat PLA and pure plasticizers.

Both these phenomena contribute to the lowering of the $T_{deg\ max}$ of the materials. Plasticized samples showed temperatures of maximum degradation 60 to 80° inferior to the neat PLA, samples plasticized with TEC-g-PLA have a slightly higher $T_{deg\ max}$ than those that used PLA LMw. Even if much lower than those of neat PLA the $T_{deg\ max}$ detected were fairly good when thinking to industrial application where temperature exceeding 200°C are rarely reached.

Differential scanning calorimetry

The casted blends were analysed with DSC to check the thermal properties such as the effect of the plasticizer on the T_g of the material. This time the method used for the DSC analysis was a bit more complex, involving an additional heating-cooling cycle. As usual the first heating ramp is used to erase the thermal history of the sample, after the first controlled-rate heating a fast cooling (*quench*) was added. The last heating cooling-heating cycle was carried out at a controlled rate. After checking the temperature of maximum degradation with TGA the highest temperature reached during heating was raised to 200°C and the minimum temperature reached during cooling was lowered to -80°C.

- 1: Equilibrate at -80°C
- 2: Ramp 10.00°C/min to 200°C
- 3: Fast cooling (quench) to -80°C
- 4: Ramp 10°C/min to 200°C
- 5: Ramp 10°C/min to -80°C
- 6: Ramp 10°C/min to 200°C

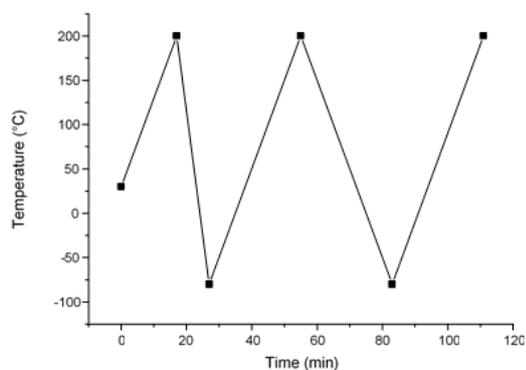


Figure 31: DSC method used for the blended samples

The quenching after the first heating prevented the sample from crystallizing during cooling, thus resulting in a completely amorphous material. The amorphous blend is a good starting material for the last heating cycle of the DSC analysis as all the eventual crystallinity detected would have developed during heating (via a cold-crystallization process from the solid state) and would not depend on the original blend crystallinity. This allowed us to make

assumptions regarding the effect of TEC on the final crystallinity of the material by comparing results of DSC analysis performed on PLA plasticized using TEC-g-PLA and PLA LMw.

Focusing on the T_g values it is clear the effect of plasticizers on the PLA matrix properties: adding a plasticizer to the polymeric matrix lowers its T_g (see Figure 32). As expected higher amounts of plasticizers lead to bigger decrease in the T_g of the material with the TEC-g-PLA being more effective than the uncapped-PLA oligomer when used in the same quantity. This was a preliminary confirmation of the beneficial effect of TEC on the plasticizing capability of the oligomeric PLA compounds.

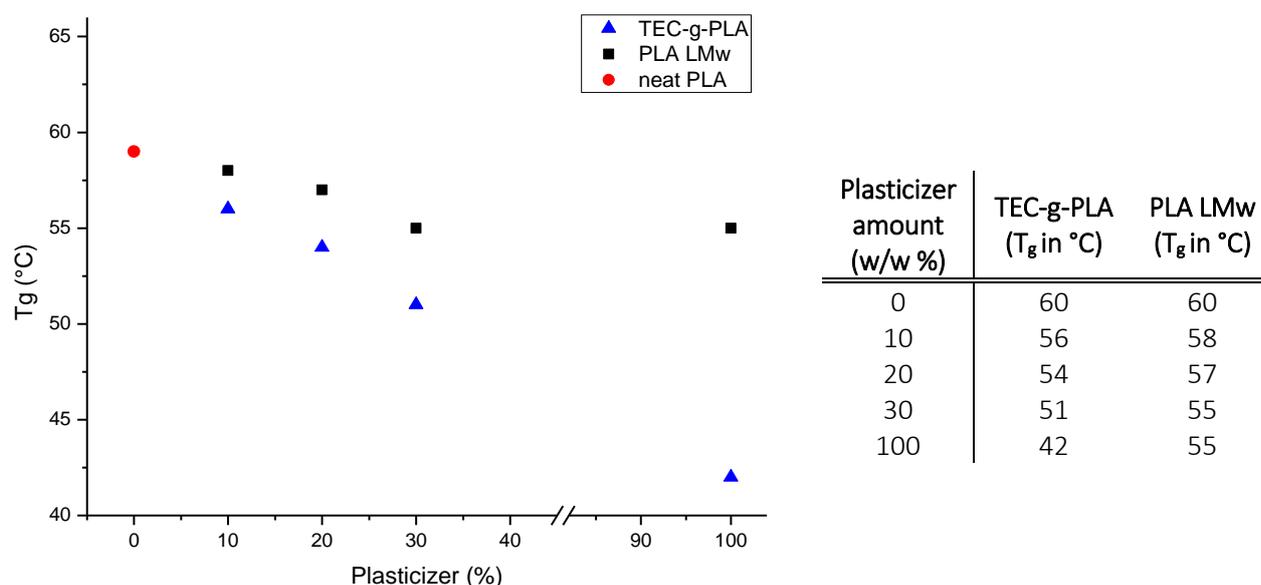


Figure 32: DSC analysis on the casted blends, T_g comparison

3.7. THIN FILM PREPARATION

The casted samples were reduced into thin films before further analysis using a heated hydraulic press to simulate a real-world application of the material, TGA and DSC analysis were conducted on the filmed samples.

To transform the casted samples into thin films 25 bar of pressure at 200°C were applied to the material for 2 minutes, the thin films produced under these conditions have a thickness of 0.4mm.



Figure 33: From left to right: vacuum dried casted blend, hydraulic press, thin film

Before proceeding to the DSC analysis, the thin films degradation temperatures were investigated to check if the filming procedure lowered the $T_{\text{deg max}}$.

Results showed that the $T_{\text{deg max}}$ were exactly the same for the casted samples and the thin films of the same composition. Also, the *onset temperatures* (the temperature at which the material starts to lose its weight) were identical.

No change to the DSC heating-cooling cycles used for the analysis of the casted samples was needed.

Data from the DSC analysis of the thin film samples showed that the pressing procedure slightly lowered the T_g of each sample (see Table 10). This phenomenon has been detected for all samples, regardless of the composition, the average T_g decrease is 1-3°C. The T_g reduction may be caused by a partial degradation of the polymer during the heated pressing. As previously reported (see section 3.6) the oligomers have a lower $T_{\text{deg max}}$ compared to the polymers, it follows that materials with higher oligomeric plasticizer content will have an overall lower $T_{\text{deg max}}$.

Sample	Plasticizer amount (% w/w)	Solvent casted T_g (°C)	Thin film T_g (°C)
PLA/TEC-g-PLA	30	51	47
"	20	54	53
"	10	56	54
PLA/PLA LMw	30	55	54
"	20	57	56
"	10	58	57
PLA	0	60	60

Table 10: Glass transition temperatures, comparison between solvent casted and thin film samples.

The previously described analysis method for the DSC included a first heating ramp to erase the thermal history of the material, followed by a fast cooling (quench), followed by a slow heating–slow cooling cycle. Such procedure should eliminate every eventual thermal effect caused by the heated pressing.

Nevertheless, the plasticizer effect on the T_g of the finished material was investigated and the performance of the TEC-capped novel oligomeric compound were promising. All plasticized thin film samples showed a reduction in the T_g respect to the neat PLA, samples plasticized using TEC-g-PLA showed bigger T_g reduction compared to samples prepared using analogue quantities of PLA LMw. When 30% of TEC-g-PLA is added into the PLA matrix the T_g is decreased by approximately 13 degrees (see Figure 34).

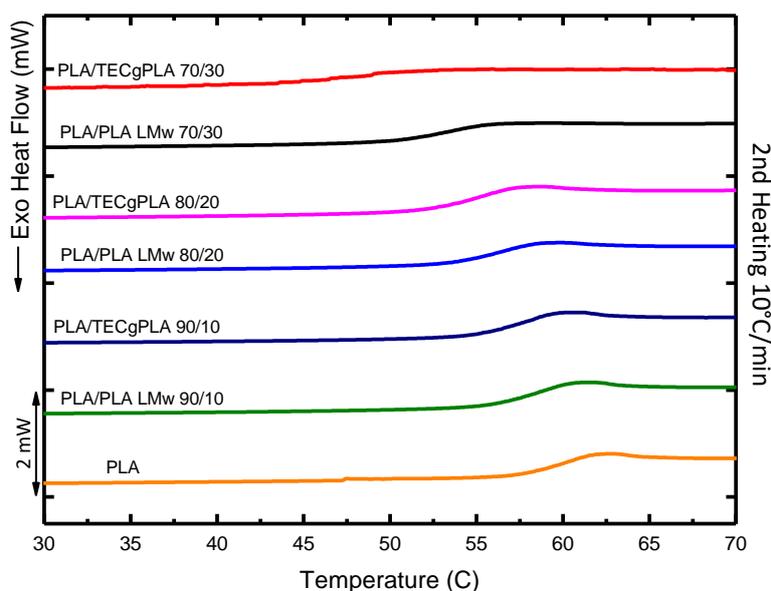


Figure 34: DSC heating curve of thin film samples, zoom in the T_g area

To investigate the effect of the plasticizers on the material crystallization we can compare melting and cold crystallization enthalpies for each sample. The enthalpies were calculated by integration of the DSC curves and normalization over the samples' weight. By subtracting the cold crystallization enthalpy from the melting enthalpy, we obtain the enthalpy relative to the crystallization during cooling. Indeed, this crystallization transition during cooling often covers a wide range of temperatures and is not very energetic thus, the resulting "dip" in the heat flow curve is stretched and it is hard to integrate, using the $\Delta H_m - \Delta H_{cc}$ method we avoid

this issue. From now on " ΔH_c " will be used in place of " $\Delta H_m - \Delta H_{cc}$ " for a simpler interpretation of the data.

Comparing the data from samples using TEC-g-PLA and PLA LMw we can see how for *both* sets of materials during the heating ramp following the fast cooling (quench), the difference between the melting enthalpy and the cold crystallization enthalpy is negligible. This means that as expected during the fast cooling polymeric chains couldn't rearrange in a crystalline phase. The ΔH_c values for the last heating cycle, which was preceded by a slow cooling (10 °C/min-controlled rate) show different trends (see Figure 35).

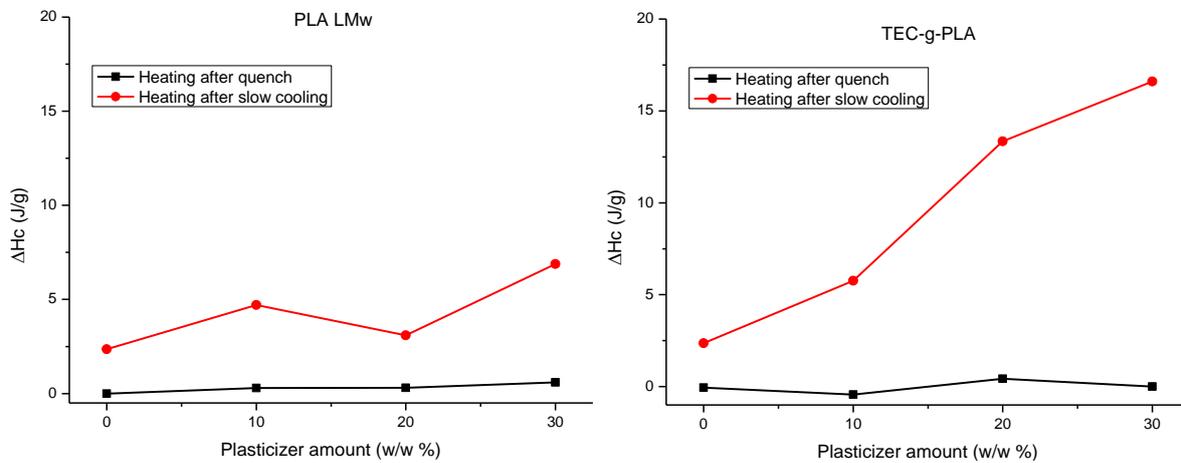


Figure 35: ΔH_c , comparison between samples plasticized with PLA LMw and TEC-g-PLA

Samples plasticized using TEC-g-PLA were able to crystallize from the melt during cooling much more than the sample obtained using the same amounts of PLA LMw. ΔH_c values for samples plasticized using PLA LMw are more or less constant, averaging around 4 J/g and do not show any immediate correlation to the amount of plasticizer used. ΔH_c values for samples plasticized with TEC-g-PLA are higher than the relative PLA LMw and are directly proportional to the amount of plasticizer used.

The presence of TEC in the formulation of the oligomeric plasticizer increased the mobility of the polymeric chains, this increases the crystallization rate of the polymeric material. Upon cooling the samples within the same conditions, TEC-g-PLA-containing samples were able to crystallize during cooling from the melt state showing crystallization enthalpies up to 3 times bigger than PLA LMw-containing materials.

This was the first direct evidence that the addition of TEC to the formulation of the oligomeric plasticizer helped increasing the crystallization rate of PLA.

The presence of TEC also lowers the cold crystallization temperature more than the same quantity of PLA LMw does, but this could also be an indirect consequence of the decrease in the T_g values. Crystallization during heating can take place in the temperature range between the glass transition and melting temperatures, if the T_g is lowered the T_c value is “brought down” along with it. The melting temperatures are virtually not affected by the presence of the plasticizers, as a result the cold crystallization temperature range gets bigger, this helps the material in reaching a higher total crystallinity. The widening of the cold crystallization window is more pronounced for samples plasticized using TEC-g-PLA (see Table 11).

Sample	Plasticizer amount (% w/w)	T_g (°C)	T_{cc} (°C)	T_m (°C)	$T_m - T_{cc}$ (°C)
PLA/TEC-g-PLA	30	47	94	156	62
"	20	53	100	160	60
"	10	54	103	161	58
PLA/PLA LMw	30	55	105	161	56
"	20	56	106	162	56
"	10	57	105	162	57
PLA	0	59	109	162	53

Table 11: DSC data for thin films samples, cold crystallization temperature range (last column on the right)

3.8. PHYSICAL AGING

When PLA is quenched from the melt and vitrifies, and a non-equilibrium glassy state is reached. Even in the glass, short-range mobility produces molecular rearrangements that drive the thermodynamic variables closer to their equilibrium values. The mobility of the polymer chains, that is, the ability to eliminate the excess free volume, is directly related to temperature.

The rapid development of brittleness during physical aging can be attributed to the reduction of free volume caused by the rapid relaxation toward the equilibrium amorphous state [69].

Literature data shows that the extent of aging increases with decreasing molecular weight, this was attributed to the increased chain terminals that possess higher motional freedom than the internal chain segments [70]. Since aging below T_g is mainly related to the amorphous phase of the polymer, increasing the crystallinity of the polymer (e.g., by reducing the D-isomer composition or the use of nucleating agents) will reduce the aging effect. Furthermore, the crystallites formed also act like physical cross-links to retard the polymer chain mobility.

The plasticizer has a tendency to migrate upon aging, which leads to increase in the crystallinity. High molecular weight plasticizers tend to show phase separation from the PLA matrix. The higher the plasticizer content, the higher is the chain mobility of PLA, which leads to faster cold crystallization. It was also observed that aging leads to the development of spherulites in the PLA [71], [72].

To investigate physical aging samples that have been kept in storage at room temperature for many days were analysed by DSC. The same materials were then “annealed” in an oven at 90° for 12 hours and the DSC analysis done again. The purpose of this annealing procedure was to erase any physical aging effect and develop the maximum possible crystallinity in the material for the future mechanical analysis.

The annealing temperature chosen is an average of the cold crystallization temperature for the different blends. Heating the materials at such temperature provided the necessary energy for the rearrangements of the polymeric chains in a crystalline fashion.

The DSC curves of the non-annealed samples showed that the materials suffered physical aging since the presence of an endothermic peak at temperatures very close to the T_g (see Figure 36). This gives an indication of the relaxation of materials stored at temperatures below T_g , the area of such peak corresponds to the relaxation enthalpy (ΔH_r).

The driving force for the relaxation process is the difference between storage temperature and T_g , samples with lower T_g (higher plasticizer content) have a weaker driving force. In reality the added chain mobility provided by the higher plasticizer amount has a greater impact on the ΔH_r which was found to be higher for samples with lower T_g . Samples plasticized with PLA LMw showed similar behaviour to those that used TEC-g-PLA (see Figure 37).

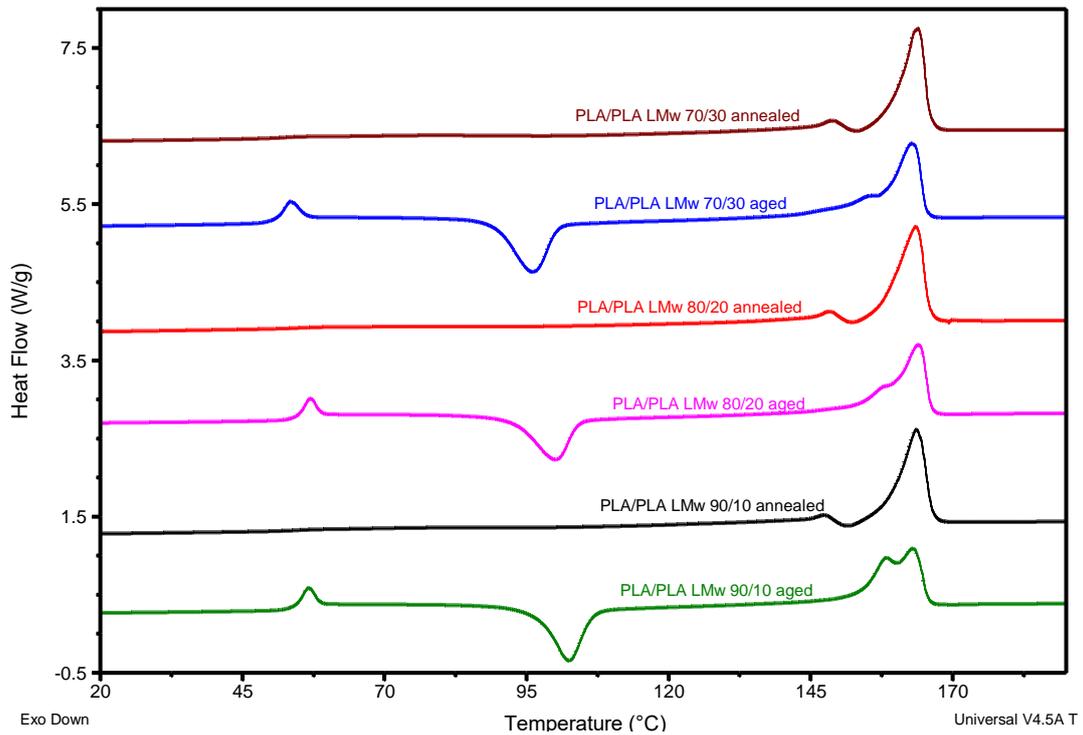


Figure 36: DSC analysis, comparison between 1st heating cycles of annealed and aged samples of PLA/PLA LMw blend

For almost every sample a small increase in T_g values after annealing was observed due to the reduction in free volume and consequently in the mobility of macromolecular segments (see Table 12). The presence of the relaxation endotherms makes an accurate determination of T_g difficult when using conventional DSC. This T_g increase after annealing is small (1 to 2°C) and samples containing 30% w/w of plasticizer showed no increase at all. This may be due to the already increased chain mobility caused by the higher plasticizer amount.

After annealing, T_{cc} shifted to higher values, the more plasticizer is contained in the material, the higher the T_{cc} increase. Samples plasticized with TEC-g-PLA showed bigger increases in the T_{cc} compared to the ones where PLA LMw was used.

A double melting peak was observed during the whole ageing study, with no significant changes in melting temperatures. As previously mentioned, this double melting peak could correspond to α' and α homocrystal forms with different thermodynamic stabilities [70].

After heating the shape of the melting peak changed, the double peak is transformed into a tall single peak shifted to higher temperature and a much smaller peak at lower temperatures. This peculiar behaviour has been detected for all samples, regardless of the composition and it's caused by the rearrangement of the polymeric chains during annealing to a more stable configuration (α homocrystal) which has higher melting temperature.

In order to determine the possible crystallinity of materials during ageing, the total enthalpy ($\Delta H_m - \Delta H_{cc}$) was calculated by assuming that continuous transitions were occurring in the interval between 75°C and 170°C [73].

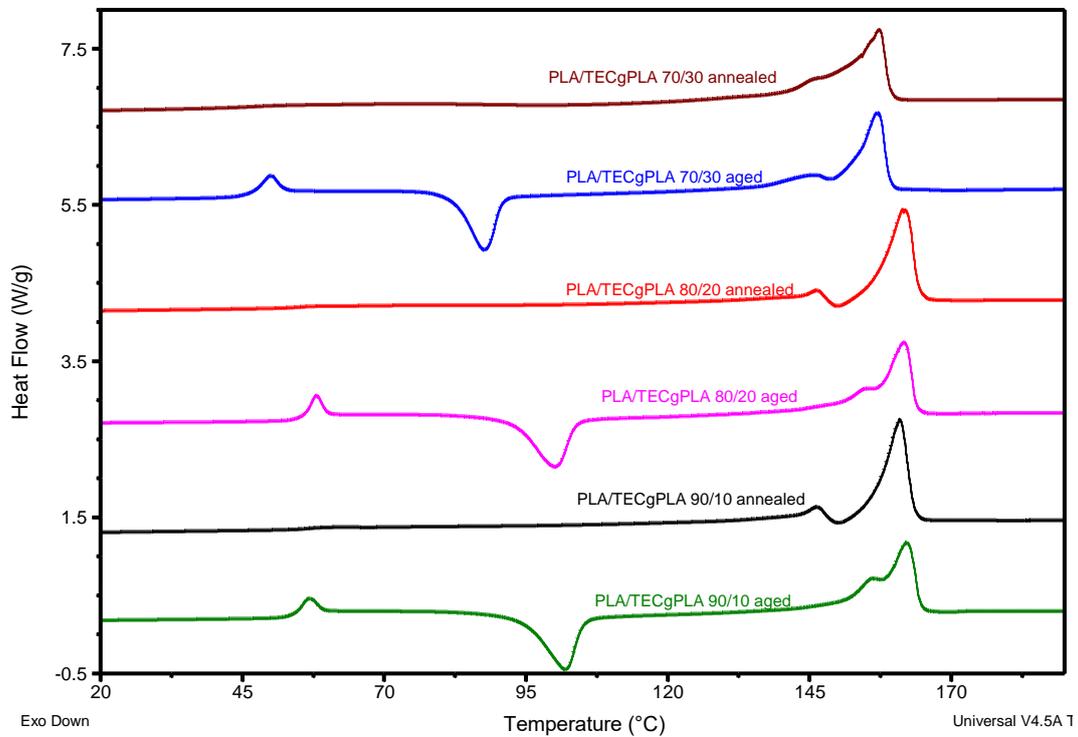


Figure 37: DSC analysis, comparison between 1st heating cycles of annealed and aged samples of PLA/TEC-g-PLA blends

Sample	ΔH_r (J/g)	T_g (°C)	T_{cc} (°C)	Tcc increase after annealing (%)	T_m (°C)	$\Delta H_m - \Delta H_{cc}$ (J/g)
PLA/TEC-g-PLA 70/30 aged	5,51	47	88		(146) 156	10,1
PLA/TEC-g-PLA 80/20 aged	4,85	53	100		(154) 160	3,93
PLA/TEC-g-PLA 90/10 aged	4,26	54	102		154 (161)	2,90
PLA/PLA LMw 70/30 aged	5,84	55	96		157 (162)	4,47
PLA/PLA LMw 80/20 aged	4,67	56	100		156 (161)	4,20
PLA/PLA LMw 90/10 aged	4,59	57	105		162	4,15
neat PLA aged	3,09	59	109		159	1,87
PLA/TEC-g-PLA 70/30 annealed	0	47	94	6,8	(148) 156	47,9
PLA/TEC-g-PLA 80/20 annealed	0	55	104	4,0	(155) 161	41,7
PLA/TEC-g-PLA 90/10 annealed	0	55	104	2,0	161	45,5
PLA/PLA LMw 70/30 annealed	0	55	101	5,2	156 (162)	43,8
PLA/PLA LMw 80/20 annealed	0	55	103	3,0	156 (162)	46,0
PLA/PLA LMw 90/10 annealed	0	58	106	1,0	159 (163)	39,6
neat PLA annealed	0	59	110	0,9	159	36,7

Table 12: Ageing tests, DSC data for annealed and non-annealed samples

The ΔH_{tot} values determined during the first heating scan for the aged samples plasticized with TEC-g-PLA are non-zero, meaning that crystallinity has developed during annealing. Samples containing more plasticizer have higher total enthalpy values thus, higher crystallinity. While samples containing TEC-g-PLA showed an increase of the total enthalpy directly proportional to the amount of plasticizer used, the same relationship was not found for samples containing PLA LMw which showed similar ΔH_{tot} values for different plasticizer contents.

The annealed samples have much higher and similar ΔH_{tot} values for all materials. This means that the materials reached the maximum possible crystallinity during the annealing procedures and are no longer affected by cold-crystallization phenomena.

4. EXPERIMENTAL

4.1. OLIGOMERS SYNTHESIS, MATERIALS AND PROCEDURE

The following compounds have been used for the synthesis of the oligomeric plasticizers, they were all bought from Sigma-Aldrich and used as received: L-Lactide CAS number 4511-42-6, rac-Lactide CAS number 95-96-5, Triethyl citrate (TEC) CAS number 77-93-0, Tin ethyl hexanoate CAS number 301-10-0.

As previously described in the Results and Discussion chapter, many different lactide, TEC and catalyst ratios were used during the synthesis screenings. Nevertheless, here we describe the typical synthetic procedure which were always the same for all the samples prepared. The numbers in *italic* are the quantities that have been slightly changed during the screenings, we have reported the average values.

In a 250ml three-neck flask 1 g of L-Lactide was weighted and, under nitrogen atmosphere, 0.5 mL of TEC and 0.5 ml of catalyst were added using an Eppendorf pipette. The temperature was kept constant at 140°C using an oil bath, stirring was provided by a magnetic stirrer previously inserted into the flask. The reaction was carried out for 3 to 6 hours (up to 12 during the screening of reaction times). The flask was then lifted out of the oil bath to cool down until room temperature was reached.

Dichloromethane (DCM) was added to the reaction flask until the solid was completely dissolved, if too much DCM was added the obtained solution was concentrated using a rotatory evaporator (the more concentrated the solubilized crude is, the better the following purification procedure outcome will be). The dissolved reaction crude was precipitated in methanol and then filtered under vacuum using a Buchner filter to remove any trace of unreacted lactide and catalyst (both soluble in methanol), a 1:10 ratio between solvent and non-solvent was used. The precipitation procedure was repeated up to 3 times to achieve the best possible yield and purity, the filtrated product was finally dried at room temperature in a Petri dish.

We observed yields around 60% for the purified, TEC-containing product and around 80% for the non-modified PLA oligomers.

A list of every oligomeric sample prepared along with the reaction conditions and reagents ratios used can be found in the Results and Discussion section.

After choosing one of the TEC-capped plasticizer and one non-modified oligomers prepared during the screenings the synthesis of the two compounds were repeated in bigger batches, to obtain enough material for the following blending. The batches were scaled up five-fold keeping the same ratio between the reagents, unfortunately the yields for the scaled-up batches were much inferior compared to the screening ones leading to a total of less than 10 grams per batch of final purified product.

Spectroscopic analysis of the oligomers

The synthesized oligomers were analysed by ¹H-NMR experiments. ¹H-NMR spectra have been recorded with a spectrometer Varian “Mercury 400” operating at 400 MHz on samples dissolved in CDCl₃ at the 1.0 wt%. Chemical shifts (δ) for ¹H are given in ppm relative to the known signal of the internal reference (TMS). For a full description of the NMR data elaboration please see the “Results and Discussion” section.

4.2. BLENDS PREPARATION

Poly(L-lactide) (PLA Lacea H.100-E, $M_w = 84$ kDa, PDI = 1.7) was provided by Mitsui Fine Chemicals. Before processing it was dried overnight under vacuum at 60 °C to avoid degradation reactions induced by moisture.

The blends were prepared by solvent casting, PLA and plasticizer oligomers were dissolved in chloroform at the concentration of 1 g/dL and stirred at room temperature for 3 hours. The solutions were casted in Petri dishes (diameter = 5 cm) obtaining thick films that were dried for 24 hours at room temperature and for another 24 hours at 60 °C under vacuum in order to remove any solvent residue. The dried casted blends were then reduced into thin films using a hydraulic press with an integrated heating and cooling apparatus, applying 25 bar of pressure at 200°C for 2 minutes, the thin films produced under these conditions have a thickness of 0.4 mm. For the complete list of the prepared blends see Table 9 in section 3.5.

4.3. THERMAL ANALYSIS

All the blends and neat plasticizers used for the blending were analysed by Thermogravimetric Analysis (TGA). All the synthesized oligomers and blends were also analysed by and Differential Scanning Calorimetry (DSC).

The thermal stability of the blends, both solvent casted and thin films, was studied by TGA using a thermobalance from TA Instruments, model TGAQ500. All measurements were performed under nitrogen atmosphere and using sample masses of approximately 5 mg. All the samples were heated from 30 to 600 °C at a rate of 10 °C/min.

The thermal behaviour of the oligomers was studied by DSC using a TA Instruments Q2000 DSC equipped with the Liquid Nitrogen Cooling System (LNCS) accessory. All measurements were performed under nitrogen atmosphere and using sample masses of approximately 5 mg.

In non-isothermal analyses, the oligomers were heated from 25 °C to 180 °C at the rate of 10 °C/min and held at 180 °C for 2 minutes to erase the thermal history. Then they were cooled at 10 °C/min until 0 °C and finally heated at 10 °C/min to 200 °C.

The analyses were conducted with slightly different methods: the maximum temperature reached during heating was sometimes lowered to 160°C or raised to 200°, the heating rate was always kept constant at 10°C/min (see “Results and Discussion” for a detailed description of the DSC analysis method).

The thermal behaviour of the blends, both solvent casted and thin films, was studied by DSC as well, using a TA Instruments Q2000 DSC equipped with the Liquid Nitrogen Cooling System (LNCS) accessory. All measurements were performed under nitrogen atmosphere and using sample masses of approximately 5 mg. The analyses were conducted with different methods as a function of the experiments.

The blends were heated from -80 °C to 200 °C at the rate of 10 °C/min and then cooled as fast as the machine could to simulate a quench. This was done by not setting a cooling rate in the analysis method, the resulting effective cooling rate was approximately 50°C/min. The blends were then heated from -80 °C to 200 °C at the rate of 10 °C/min and then cooled back to -80°C at 10°C/min; finally the samples were heated up to 200°C at 10 °C/min.

5. CONCLUSIONS

During this research a novel type of bio-based, biodegradable, TEC-containing oligomeric plasticizer have been prepared. More than 50 different TEC-g-PLA samples have been synthesized and characterized via DSC and TGA. The effect of different reagent ratios and reaction conditions (in terms of temperature and time) on the final product have been investigated.

By tuning the reaction parameters, a “tailor-made” oligomeric plasticizer can be obtained: to obtain a low-molecular weight TEC-g-PLA ($M_n \approx 3000$ g/mol) it is necessary to use *high TEC amount* (≥ 0.5 equivalents) and *high catalyst amount* (≥ 0.05 equivalents) along with a *long reaction time* (6+ hours). On the other hand, to obtain a high-molecular weight TEC-g-PLA ($M_n \approx 10000$ g/mol) it is necessary to use *low TEC amount* (≤ 0.5 equivalents) and *low catalyst amount* (≤ 0.05 equivalents) along with a *short reaction time* (1-3 hours).

The *green* properties of lactic acid are retained in the final TEC-capped product since the plasticizer is biodegradable, biocompatible and produced from renewable sources. Moreover, the synthesis of the compound doesn't involve any solvent, except for the latter purification procedure.

The TEC-g-PLA plasticizers have higher molecular weight, lower glass transition and cold crystallization temperatures compared to the non-modified oligomeric PLAs. TEC-g-PLAs also have higher specific melting enthalpies, deriving from higher crystallinity values and are able to crystallize during cooling while OLAs cannot.

TEC-g-PLAs samples prepared using racemic lactide reached higher molecular weights compared to the ones prepared using enantiopure lactide in the same reaction conditions but weren't able to crystallize, in agreement with literature data.

Upon blending with a PLA matrix, the TEC-g-PLAs plasticizer showed a T_g reduction proportional to the amount of plasticizer used. The same proportionality was found for the non-modified oligomeric PLA too but smaller T_g decreases were observed. The degradation temperature of the plasticized materials also decreases with increasing plasticizer amount, but the decrease is smaller for sample plasticized using TEC-g-PLA.

The addition of 30% w/w of TEC-g-PLA to the PLA matrix lowered the T_g by 10°C, the total amount of non-lactic acid derived molecules in this sample was just 2,7% w/w, such a low percentage, along with the compatibilizing effect of the oligomeric PLA chain, is expected to reduce the phase separation phenomena typically associated with polymeric mixtures.

While neat PLA can't crystallize from the melt, the addition of TEC-g-PLAs to a PLA matrix allows the material to crystallize during cooling, with a crystallization enthalpy again proportional to the amount of plasticizer added to the matrix. Non-modified OLAs have a similar effect on the PLA matrix but the crystallization enthalpies are smaller, indicating a better performance of the TEC-g-PLAs in increasing the crystallization capabilities of the polymeric matrix.

Annealing the plasticized materials deletes any ageing effect and increases the cold crystallization temperature thus widening the temperature range in which crystallization during heating can take place. The T_{cc} increase is bigger for samples plasticized with TEC-g-PLAs compared to the ones that used OLAs. The maximum crystallinity for the plasticized materials can also be reached following the annealing procedures.

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