Production of Polylactic Acid (PLA): A Review

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Abstract - **Poly(lactic acid) is the biodegradable aliphatic polyester produced in small quantity and in large quantities industrially and used very variously. Because of its good mechanical property and reconcilability with environment, it is one of the polymers most appropriate to replace non-biodegradable synthetic polymers based on crude oil. The objective of this project is to choose the best process for the production of Polylactic acid (PLA). The objectives of this research are to analyze the type of process for the production of Polylactic Acid (PLA), to differentiate 3 types of process in term of performances and properties of Polylactic Acid (PLA) and to recommend the suitable process for the production of Polylactic Acid (PLA). A polymer which is Polylactic acid (PLA) is used as a material of studies. Production of PLA will be undergoing 3 types of process such as direct condensation polymerization, azeotropic dehydration condensation and ring-opening polymerization. The ring-opening polymerization are the most used techniques rather than the other methods. This paper reviewed methods of making PLA by using the ring-opening polymerization and mainly mechanism of ring-opening polymerization as well as its chemical structure and properties, mechanical properties and thermal properties. A good type of isomers such as L-lactide isomer could achieved a higher molecular weight of PLA and also a good thermal properties of PLA such as high glass transition temperature as well as high crystallization temperature. Moreover, due to a high crystallization and glass transition temperature could achieved a good mechanical and chemical structure for the production of a high molecular PLA.**

Keywords - Poly(lactic acid), polymerization, ring-opening polymerization, mechanism, properties.

I. INTRODUCTION

Polylactic acid (PLA) is a one of a kind polymer that carries on from multiple points of view such as Polyethylene terephthalate (PET) which additionally plays out a ton like polypropylene (PP), a polyolefin. It also might be the polymer with the broadest scope of utilizations on account of its capacity to be stress solidified, thermally solidified, impact modified, filled, copolymerized and prepared in most polymer handling hardware. It can be produced into transparent films, strands or injection molded into blowmoldable preforms for containers, for example, PET. PLA likewise has fantastic organoleptic qualities and is superb for sustenance contact and related bundling applications.

PLA has been widely contemplated by numerous specialists and checked on in detail in a few recent productions (Hartmann, 1998). This section won't survey the greater part of the developing volume of data on PLA, yet will concentrate on the key components of innovation that will change this polymer from a strength material to an expansive volume ware plastic.

Polymers in view of lactic acid (PLA) are a most encouraging class of polymers produced using renewable assets. They are compostable and biocompatible, as well as processable with most standard handling gear. The properties of lactic acid based polymers shift to a vast degree which relying upon the proportion between, and the conveyance of the two stereoisomers or different comonomers (Sodergard, 2002). The polymers can be produced by various polymerization courses. PLA of high atomic weight is most ordinarily made by ring-opening polymerization (ROP) of the ring-framed dimer, dilactide (lactide; 3,6-dimethyl-1,4-dioxane-2,5-dione), which is made by depolymerization of the polycondensed lactic acid (LA; 2-hydroxypropanoic corrosive). This course is a two-stage response that more often than not includes extra sanitization steps and is thusly identified with noteworthy expenses.

It is regularly stated in the art that the planning of a high atomic weight PLA by an immediate lack of direct dehydration condensation reaction is not doable because of the balance which is not favoring a high sub-atomic weight polymer. PLA arranged from polycondensation which has low sub-atomic weight and poor mechanical properties and in this manner is not appropriate for some applications. The commercial interest for tackling this issue has expanded as a result of the need of savvy methodologies in the assembling of lactic acid based polymers with a high atomic weight.

The objectives of this research are to analyze the type of process for the production of Polylactic Acid (PLA), to differentiate 3 types of process in term of performances and properties of Polylactic Acid (PLA) and to recommend the suitable process for the production of Polylactic Acid (PLA).

A polymer which is Polylactic acid (PLA) is used as a material of studies. Production of PLA will be undergoing 3 types of process such as direct condensation polymerization, azeotropic dehydration condensation and ring-opening polymerization. The ring-opening polymerization are the most used techniques rather than the other methods.

The generally applied ROP process for polylactides involves three separate steps: polycondensation, lactide manufacturing, and ring-opening polymerization. All three chemical processes have basically been known for a long time. Carothers et al. (1932) did the first observations on the reversible formation of the ring-formed dimer of a-hydroxy acids and the self-condensation ability of LA was discovered even longer back in time (Pelouze, 1845). The results of these pioneering works have later been utilized in further scientific studies as well as in making and improving technically and economically feasible processes.

The three different processes deal with a number of critical steps. Some of these issues are intrinsically present in all the steps of the manufacturing process due to the nature of the lactic acid molecule, while other issues are generated in the separate process steps as a result of the process conditions. The most crucial parameters are summarized below along with a summary of the harmful effects that can be seen in the PLA:

i. Racemization: The racemization may have its origin in the optical purity of LA or be generated and pronounced in any of the process steps. An increased amount of the antipodal structure of the repeating unit will result in drastic changes in the crystallization behavior and eventually affect many other properties of the end products (Kolstad, 1996).

ii. Lactide Purity: The lactide can contain impurities such as acids or oligomers formed during the depolymerization or purification step. The presence of impurities in the lactide and the amount there of will affect polymerization rate, molecular weight, or both (Zhang, 1994).

iii. Residual Monomer Content: The presence of residual lactide in the polymer and the amount thereof will have harmful effects on the performance of the polymerduring processing and may also cause undesired property changes in the end products (Jacobsen, 2000).

ROP of L-lactide is by and large the most favored course to prepare high atomic weight polylactide because of the likelihood of a precise control of the science, and subsequently fluctuating the properties of the subsequent polymers in a more controlled way. This makes ROP appropriate for a huge scale prepare. Polymerizations of lactide have effectively been completed by utilizing melt polymerization, mass polymerization, arrangement polymerization, and suspension polymerization methods. Each of these strategies has its own particular focal points and impediments, however soften polymerization is for the most part considered the most straightforward and reproducible technique and will be talked about later in more detail (Nieuwenhuis, 1992).

A vast number of catalysts have been utilized in the ROP of lactide, of which the most studied are the carboxylates and alkoxides of Sn (Kricheldorf, 2002) and Al (Zhong, 2003). Of these, stannous 2-ethylhexanoate (tin octanoate) is the most intensively studied. The polymerization mechanism is suggested to involve a preinitiation step, in which stannous 2-ethylhexanoate is converted to a stannous alkoxide by reaction with a hydroxyl-bearing compound. Then, the polymerization proceeds on the tin–oxygen bond of the alkoxide ligand, whereas the carboxylate itself is inactive in the polymerization (Kowalski, 2000).

A review with emphasis on Sn- and Al-catalyzed ring-opening polymerization has been published by Stridsberg et al. (2002). Some kinetic studies were also included in the review. However, the highly active catalysts based on, for example, tin compounds are toxic (Tanzi, 1994), and efficient catalysts showing less toxicity based on Ca (Darensbourg, 2008), Fe (O'Keefe, 2002), Mg (Chamberlain, 2001), and Zn (Chen, 2006) therefore, have been developed for lactide and lactone polymerization.

Many of these, however, tend to cause racemization of PLA, especially when polymerizing at high temperatures. In addition to the aforementioned metals, Kricheldorf et al. (1999) used other salts prepared from cations and anions belonging to the human metabolism in the ROP. Zinc lactate was found to be the most efficient of the tested catalysts with regard to reactivity and obtaining high molecular weight PLA. Recently, however, a potassium-based catalyst been reported to be more efficient in the ROP of polylactide to high molecular weight (Lemmouchi, 2008). Other catalyst/ initiator systems of low-toxicity metals for ROP have been discussed in a study by Okada (2002).

Catalysts have been developed for the stereoselective ROP of lactides. Semi-crystalline PLAs were prepared from both meso-lactide (yielding syndiotactic PLA) and racemic lactide (yielding stereoblock isotactic PLA) using chiral aluminum catalysts containing bulky ligands (Ovitt, 1999). After annealing, a Tm of 152 ºC was obtained for the syndiotactic PLA and the racemic PLA was reported to have a Tm of 191 ºC. The high Tm for the latter PLA was believed to result from stereocomplex formation of synthesized stereoblock PLA. The work using aluminum catalysts in stereoselective polymerization has continued (Tang, 2004), and other metal complexes have been utilized as well (Russel, 2005).

Post-polymerization treatments for PLA prepared by ROP are much related to the processing and processability of the polymer. The processing of PLA is more demanding than that of commodity plastics due to the hygroscopic nature and the limited melt stability that can lead to hydrolytic degradation. The post-polymerization treatments can mainly be divided into those performed in the melt as a finishing process or those done as a subsequent and independent processing step. The processes performed in the melt that are described in the literature are mainly focusing on improving the melt stability and the process ability.

Catalyst deactivation is one important feature that has been applied to PLA. Deactivators used include phosphorous containing compounds (Higgins, 1954), antioxidants (Gruber, 2000), acrylic acid derivatives (Kolstad, 2001), and organic peroxides (Sodergard, 1999). The catalyst deactivation is generally performed in combination with a lactide removal process, which can be done by removing the low Mw material at low pressures and at a temperature sufficiently high for distillation (devolatilization) (Gruber, 1994). This process has been further developed by applying an inert gas flowin addition to the reduced pressure, which enables improved removal of the unreacted lactide (Ohara, 1998). The recovery of lactide has also been integrated in the polymerization process of new PLA as a means for improving the efficiency in the manufacturing chain (Ohara, 1998). Another way of reducing the lactide content for PLA is to apply solid-state polymerization of the residual lactide containing PLA below its Tm, which besides reducing the residual lactide content also increases the molecular weight of the polymer (Ohara, 1995).

Separate post-polymerization treatments of PLA have also been described in the literature. Drying of the polymer is generally done before processing to minimize the thermohydrolysis and molecular weight reduction during the melt processing. Suggested drying conditions for PLA are 60 ºC under vacuum and the use of hot dry air (http://www.natureworksllc.com, 2008). All the more as of late, the end-of-life choices of bio-based polymers have been brought into maintainability discourses. For PLA, this can be found as various proposed approaches on the best way to manage squander materials from the polymerization procedure, the assembling procedure of final results, or the finished result after its utilization.

II. METHODOLOGY

A. *Materials*

L-Lactic acid., 95% of tin octoate, 99.99% of Potassium tert-butoxide, 99.5% of Ethyl acetate, 99.5% of Acetone, 99.5% of 2-propanol, dry methanol and pure toluene.

B. *Instrument and apparatus*

Volumetric titration, nuclear Magnetic Resonance (NMR) magnets, proton Nuclear Magnetic Resonance (P-NMR), nuclear Magnetic Resonance (NMR), gas Chromotography with Flame-Ionization Detector (GC-FID), cyclodex-B column, oven, solvotrode, gel-Permeation Chromotography (GPC), refractor detector, thermogravimetric Analyzer (TGA) and differential Scanning Calorimetry (DSC).

C. *Ring-Opening Polymerization (ROP)*

Synthesis Process

Dehydration of lactic acid 80% is performed using a short path distillation (SPD) unit KDL5 from UIC GmbH at a pressure of 50 mbar and a temperature of 120 °C. Dehydrated lactic acid is oligomerized in batch at a pressure of 100 mbar. A temperature of 170 °C with 1% tin octoate as catalyst to yield a prepolymer with a degree of polymerization (DP) between 8 and 12. A reactive distillation is performed in the SPD unit at 250 °C and 5 mbar and 2% of tin octoate to form lactide. Raw lactide is purified by crystallization up to a purity of 99.9%. A batch polymerization of lactide is done in 2 hours at 170 °C and atmospheric pressure in a glass reactor with 0.04% tin octoate as catalyst.

Analysis of Process

The analysis of the process is used to determine the properties of a high molecular weight of Polylactic acid (PLA) such as thermal properties, chemical structure and chemical properties as well as mechanical properties.

Water content in lactic acid and lactide was measured by a volumetric titration using a titration solution. NMR analyses were performed using a nuclear magnetic resonance (NMR) magnets (300 MHz). The degree of polymerization (DP) of oligomers was evaluated by proton nuclear magnetic resonance (P-NMR) by dividing the integral of the peak corresponding to the CH3 of the repeating unit of the prepolymer ($\delta = 5.2$ ppm) by the integral of the peak corresponding to the CH3 of an end unit ($\delta = 4.2$ ppm or $\delta = 4.96$ ppm).

The purity of the products (lactic acid and lactide) was also checked by NMR. Enantiomeric purity was determined by gas chromatography with flame-ionization detector (GC-FID) equipped with a Cyclodex-B column (30 m × 0.25 mm × 0.25 µm). The oven was programmed to remain at 150 °C for 10 minutes, followed by a 50 °C/min ramp to 250 °C, where it remained for an additional 1 minute. The carrier gas was helium with a flow rate of 1.5 mL/min and a split flow of 1:20.

The residual acid content in lactide was quantified by a nonaqueous titration by potassium tert-butoxide in methanol with a Solvotrode. Molecular weights and polydispersity of PLA were determined by gel permeation chromatography (GPC) equipped with a differential refractometer detector and three columns in series, Phenogel Linear/Mixe 5µ, Phenogel 103Å 5µ and Phenogel 105Å 5µ. The detector and the columns are heated to 35 °C. The calibration curve is obtained with 6 standards of polystyrene. Thermal stability of PLA was evaluated by thermogravimetric analyzer (TGA) under a nitrogen atmosphere (100 mL/min). All analyses were run in an aluminium oxide pan 70 µL from 25 °C to 300 °C with a heating rate of 10 °C/min. Melting and glass transition temperature were measured by differential scanning calorimetry (DSC) under a nitrogen atmosphere (100 mL/min) in fully closed aluminum crucibles of 40 µL.

The analyses were carried out from 30–200 °C with a heating rate of 10 °C/min. Two runs of heating were made on each sample with a rapid cooling in-between to eliminate the thermal history of the polymer. Only the second scan was evaluated. The glass transition temperature was taken at the inflexion point of the heat capacity change, while the melting point at the maximum of the peak corresponding to the fusion.

III. RESULTS AND DISCUSSION

A. *Thermal properties of Polylactic acid (PLA)*

I. *Effect of different type of isomers towards PLA*

It has been reported by Achmad et al. (2009) that poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semi-crystalline polymers with melting points of about 180 °C, whereas the copolymer poly(DL-lactide) (PDLLA) is an amorphous material with a glass transition temperature of only 50 – 57 °C.

Table 3.1A (I): Effects of Isomers on the Thermal Properties of PLA (Ahmed and Varshney, 2010)

Isomer Type	M_n x 10^3	M_w / M_n	T_g (°C)	T_m (°C)	Δ H_m (J/g)	T_c (°C)	Δ H_c (J/g)
L	4.7	1.09	45.6	157.8	55.5	98.3	47.8
DL	4.3	1.90	44.7	-	-	-	-
L	7.0	1.09	67.9	159.9	58.8	108.3	48.3
DL	7.3	1.16	44.1	-	-	-	-
D	13.8	1.19	65.7	170.3	67.0	107.6	52.4
L	14.0	1.12	66.8	173.3	61.0	110.3	48.1
D	16.5	1.20	69.1	173.5	64.6	109.0	51.6
L	16.8	1.32	58.6	173.4	61.4	105.0	38.1

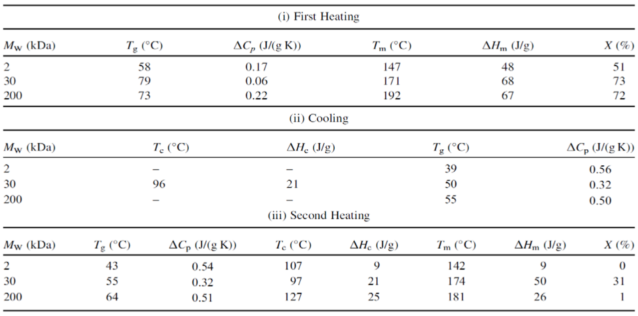
From Table 1, it can be seen that different lactide isomers can significantly affect the molecular number (Mn), glass transition temperature (Tg), melting temperature (Tm), enthalpy and crystallization temperature (Tc) of PLA. It can be observed that the Tg and Tm of PLA increases in relation to Mn regardless of whether the isomer type is L or D. Information about Tg is very important for polymers when the temperature is below its Tg large-scale molecular motion is not possible because the material is essentially frozen, whereas if the temperature is above its Tg molecular motion on the scale of its repeat unit (such as a single mer in a polymer) is able to take place, allowing it to be 'soft' or 'rubbery'. In other words, the Tg of a polymer is linked to its processability and service temperature. PLA with a low Tg is not suitable for containing hot water as the material would soften and be deformed.

II. *Effect of various temperature during a DSC Cycle towards PLA*

However, melting and crystallization of copolymers of PDLLA, which consist of polymerization of L-lactic and D-lactic acid, were not detectable even at high molecular weight. This can be explained by the formation of an atactic structure, which can affect the microstructure rearrangement upon cooling. At the same time, the molecular weight has minimal effects on the heat of crystallization ΔHc (0.3 J/g), as shown by comparing L isomers of Mn of 4.7 and 14.0, but the crystallization temperature increased by 12 °C.

This indicates that longer chain PLA requires higher kinetic energy to break down intermolecular bonds, while the free energy of crystallization of polylactide remains. This shows the limits of crystallization in PLA. Nevertheless, there were less obvious trends of poly-dispersity (Mw/Mn) influence on the thermal properties of PLA.

Table 3.1A (II): Glass Transition Temperature (Tg) and Change of Specific Heat at Tg (DCp), Melting Peak Temperature (Tm) and Enthalpy (DHm), and Crystallization Peak Temperature (Tc) and Enthalpy (DHc) for Different Molecular Weight of PLLA Samples During a DSC Cycle of Heating–Cooling–Heating Between 0 and 220 °C at ±10 °C/min



(i) First Heating

M_W (kDa)	T_g (°C)	ΔC_p (J/(g K))	T_m (°C)	ΔH_m (J/g)	X (%)
2	58	0.17	147	48	51
30	79	0.06	171	68	73
200	73	0.22	192	67	72

(ii) Cooling

M_W (kDa)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	ΔC_p (J/(g K))
2	–	–	39	0.56
30	96	21	50	0.32
200	–	–	55	0.50

(iii) Second Heating

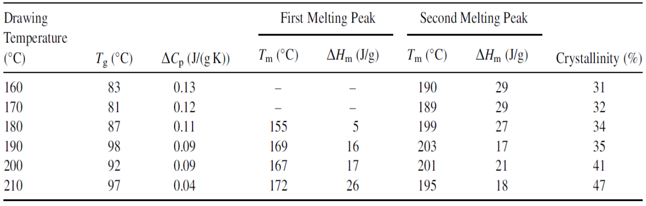
M_W (kDa)	T_g (°C)	ΔC_p (J/(g K))	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X (%)
2	43	0.54	107	9	142	9	0
30	55	0.32	97	21	174	50	31
200	64	0.51	127	25	181	26	1

While the first heating Tg values are higher than expected due to high crystallinity content (crystalline domains hinder the mobility of amorphous chains), as also confirmed from the low value of DCp at Tg, Tg measured during cooling proportionally depend on molecular weight.

It is also interesting to note that during cooling PLLA (30 kDa) developed some crystallinity, whereas in the other cases crystallization was inhibited by the high content of terminal groups that acted as defects in PLLA (2 kDa) and by the low mobility of the long PLLA (200 kDa) chains.

During the second heating, all the polymers evidenced glass transition, crystallization, and melting. Tg and Tm directly depend on molecular weight. The different Tg values measured during cooling and the following heating cycles of the amorphous PLLAs, that is, 39 versus 43 ºC for the 2 kDa PLLA and 55 versus 64 ºC for the 200 kDa PLLA, are due to a kinetic effect that depends on the molecular weight of the polymer. The lower Tc of PLLA (30 kDa) is attributable to its crystallinity before the second heating cycle that acted as a nucleating agent and promoted further crystallization, up to 53%, as determined from the melting enthalpy. In the case of PLLA (2 kDa) and PLLA (200 kDa), the lower DHm and crystallinity of about 10% and 28%, respectively, once again directly depend on the effect of short and long polymer chains.

Table 3.2A (II): Glass Transition Temperature (Tg) and Change of Specific Heat at Tg (DCp), Melting Peak Temperature (Tm) and Enthalpy (DHm), and Crystallinity of Solution-Spun Fibers After Drawing at Various Temperatures



Drawing Temperature (°C)	T_g (°C)	ΔC_p (J/(g K))	First Melting Peak		Second Melting Peak		Crystallinity (%)
			T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	
160	83	0.13	–	–	190	29	31
170	81	0.12	–	–	189	29	32
180	87	0.11	155	5	199	27	34
190	98	0.09	169	16	203	17	35
200	92	0.09	167	17	201	21	41
210	97	0.04	172	26	195	18	47

B. Chemical structure and properties of Polylactic acid (PLA)

I. Effect of different crystallization temperature towards PLA

The properties of PLA can be modified both through the variation of isomers (L/D ratio) as well as copolymerization with other monomers, such as glycolide and caprolactone. PLA can also be tailored by formulation involving the addition of plasticizers, other biopolymers and fillers. The biodegradability of PLA blends means that they are well suited for short-term packaging materials, and they also further expand PLA's applications in the biomedical field, where biocompatible characteristics are essential, such as implants, sutures and drug encapsulations.

The most important method for mass production of high molecular weight PLA is through the ring-opening polymerization approach. High-molecular-weight PLA is produced from the cyclic dilactate ester (commonly known as lactide), which commonly involves the action of stannous octoate as a catalyst. This mechanism does not generate additional water, hence, a higher molecular weight can be achieved. Polymerization of a racemic mixture of L- and D-lactides usually leads to the synthesis of PDLLA, which is amorphous. The utilization of stereospecific catalysts tends to produce stereochemically pure PLA with good crystallinity.

The degree of crystallinity and the physicomechanical properties are greatly determined by the ratio of D to L enantiomers, which is also partially related to the types of catalyst used. It has been reported that high-quality production of PLA yields a minimum amount of unreacted lactic acid monomer, which limits the tendency of lactic acid to leach out from the PLA when using as packaging. Furthermore, the amount of leached lactic acid is very much lower compared to the amount of lactic acid in common food ingredients (Mutsuga et al., 2008).

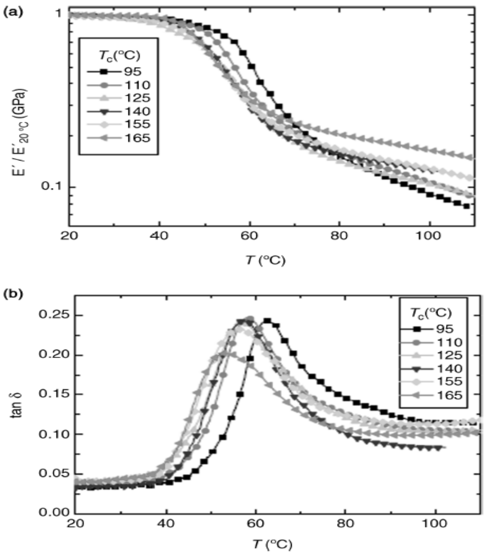


Figure 3.1B (I): Storage modulus (a) and loss factor (b) against temperature for PLLA fully crystallized at different crystallization temperatures (Tc), recorded at 1Hz and during a heating scan at 3 ºC/min.

II. Effect of glass transition temperature towards PLA

The glass transition of PLA has been widely investigated and reported. Pyda and Wunderlich (Puda et al., 2003) reported their studies on the glass transition of amorphous and semicrystalline PLA. The study was performed with adiabatic calorimetry, differential scanning calorimetry (DSC), and temperature-modulated DSC (TMDSC). The glass transition temperature from the reverse heat capacity and the enthalpy relaxation peaks from the non-reversing component of PLA both shifted to higher temperature with increasing extent of annealing. The relaxation times for aging decreased after cooling down to the glass transition temperature and then increased. The glass transition of the rigid amorphous phase of PLA has also been reported by Magon et al. (2007). The glass transition of the rigid amorphous phase was observed from changes of apparent heat capacity between the mobile glass transition temperature and the melting temperature. Because the heat capacity change of MAP at Tg depends on the fusion heat of semicrystalline PLA that has different thermal history, the RAF was selected to evaluate the nonlinearity of the change in heat capacity.

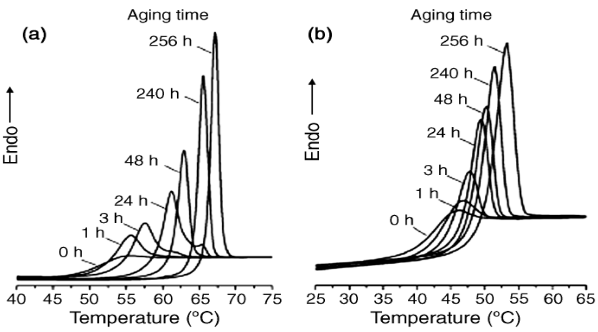


Figure 3.1B (II): DSC curves on heating at 10 ºC/min in the glass transition region for (a) PLLA and (b) PDLLA samples annealed at 40 ºC for the time (in hours) indicated on each curve.

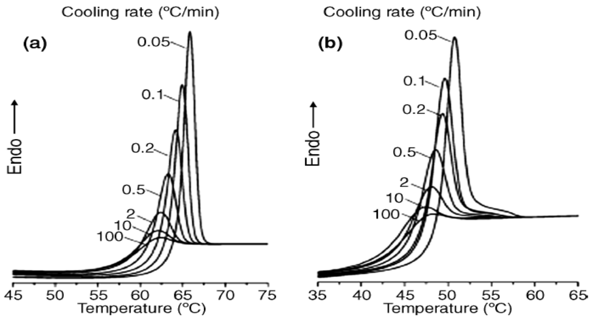


Figure 3.2B (II): DSC heating scan at 10 ºC/min in the glass transition region for (a) PLLA and (b) PDLLA samples cooled at the various rates (in ºC/min) indicated on each curve.

The properties of PLA are significantly influenced by the stereochemistry of its monomers. When PLA has high stereochemical purity, it tends to form a highly crystalline structure. Copolymerization of different lactide isomers can yield variety characteristics of PLA. The effect of isomerization in PLA can be detected by IR and NMR spectroscopic methods. Many studies have proven that PLA has a low solubility in a wide range of solvents/liquids, such as water, alcohol and paraffin. This indicates that PLA can be safely employed as a food packaging material without causing adverse health effects. In addition, PLA also possesses barrier properties that are just as effective as LDPE and PS. The 'green' aspect of PLA means that it represents a viable environmentally friendly substitute for petrochemical-based polymers.

The chemical structures of PLA, including chemical composition, interlocked structure, isomers, syndiotacticity, conformation, amorphous structure, semicrystal structure, frustrated structure, molecular weight, and so on, were reviewed in this chapter. The chemical structures play an important role in determining the properties of PLA. Further research is necessary to have a better understanding of some of PLA structures such as crystallization form, the frustrated structure model, and the structure of PLA copolymers or blends.

C. Mechanical properties of Polylactic acid (PLA)

I. Effect of different types of lactic acid/lactide toward PLA

Poly(lactic acid) (PLA) is a glossy, high modulus thermoplastic polymer with properties comparable to polystyrene (PS).

The polymers obtained from optically active monomers (L-lactide and D-lactide) are semicrystalline while the optically inactive monomers (racemic D,L-lactide and mesolactide) give amorphous materials (Sodegard et al., 2002).

Amorphous PDLLA is typically used for biomedical devices and in particular for slow drug release, while semicrystalline PLLA is selected for applications where higher mechanical and thermomechanical properties are required.

PLA is in general characterized by good mechanical properties, with elastic modulus of 3000–4000 MPa and tensile strength of 50–70 MPa. Therefore, it can in principle substitute conventional polymers in many applications, such as packaging, extruded and thermoformed containers, and so on.

However, the low elongation at break that is typical of this polymer limits some of its uses. PLA has a glass transition temperature of about 60–70 ºC, and it is brittle at room temperature, fracturing through a crazing mechanism. Efforts to improve the properties of PLA comprised copolymerization, blending with other biodegradable polymers, and plasticization.

Rubber modification through copolymerization has proven to be very effective in increasing the toughness of PLA. It is worth mentioning that the mechanical properties of PLA are not significantly influenced by its synthesis methods (Ajioka et al., 1995). Mechanical orientation is another method for improving the mechanical properties of PLA due to its morphological change from a-crystallites into b-crystallites upon drawing. This process converts the otherwise fragile polymer into a versatile and useful material for practical tools, packaging, and biomedical applications.

Table 4.1C (I): Mechanical Properties of PLLA Specimens with Different Molecular Weights (Perego *et al.*, 1996)

Sample	PLLA I		PLLA II		PLLA III	
Annealing at 105°C	No	Yes	No	Yes	No	Yes
Molecular weight (M_v, Da)	23,000	20,000	58,000	47,000	67,000	71,000
T_m (°C)	178	178	179	180	181	178
Crystallinity (%)	9	70	9	52	3	45
Tensile properties						
Yield strength (MPa)	–	–	68	68	70	70
Tensile strength (MPa)	59	47	58	59	59	66
Yield elongation (%)	–	–	2.3	2.2	2.2	2.0
Elongation at break (%)	1.5	1.3	5.0	3.5	7.0	4.0
Elastic modulus (MPa)	3550	4100	3750	4050	3750	4150
Flexural properties						
Flexural strength (MPa)	64	51	100	113	106	119
Maximum strain (%)	2.0	1.6	4.1	4.8	4.7	4.6
Elastic modulus (MPa)	3650	4200	3600	4150	3650	4150
Impact resistance						
Izod, notched (kJ/m^2)	1.9	3.2	2.5	7.0	2.6	6.6
Izod, unnotched (kJ/m^2)	13.5	18.0	18.5	34.0	19.5	35.0
Heat resistance						
HDT (°C)	57	66	–	–	55	61
Vicat penetration (°C)	60	157	59	163	59	165
Hardness						
Rockwell hardness (scale H)	85	84	83	84	88	88

Table 4.2C (I): Mechanical Properties of PDLLA Specimens with Different Molecular Weights (Perego *et al.*, 1996)

Sample	PDLLA I	PDLLA II	PDLLA III
Molecular weight (M_v, Da)	47,500	75,000	114,000
Tensile properties			
Yield strength (MPa)	49	53	53
Tensile strength (MPa)	40	44	44
Yield elongation (%)	1.7	1.4	1.5
Elongation at break (%)	7.5	4.8	5.4
Elastic modulus (MPa)	3650	4050	3900
Flexural properties			
Flexural strength (MPa)	84	86	88
Maximum strain (%)	4.8	4.1	4.2
Elastic modulus (MPa)	3500	3550	3600
Impact resistance			
Izod, notched (kJ/m^2)	1.8	1.7	1.8
Izod, unnotched (kJ/m^2)	13.5	14.0	15.0
Heat resistance			
HDT (°C)	51	50	50
Vicat penetration (°C)	52	53	52
Hardness			
Rockwell hardness (scale H)	78	72	76

Semicrystalline PLA has a tensile strength of approximately 50–70 MPa, tensile modulus of 3000–4000 MPa, elongation at break of 2–10%, flexural strength of 100 MPa, and flexural modulus of 4000–5000 MPa (Engelberg et al., 1991). PLA specimens obtained by a typical injection molding process are generally almost amorphous, because of the slow crystallization kinetics characterizing this material. In Tables 4.4 and 4.5, the results of physicochemical and mechanical characterization of, respectively, PLLA and PDLLA injection molded specimens with different molecular weights are presented (Perego et al., 1996).

From the analysis of the mechanical data reported in Tables 4 and 5, it is evident that in the selected range of molecular weights, the tensile and flexural properties of PDLLA and amorphous PLLA are quite different. Tensile strength for PLLA typically ranges from about 50 to 70 MPa while for PDLLA it ranges from 40 to 53 MPa. This different behavior is mainly related to the stereoregularity of the polymer chains, which are characterized, in the case of PLLA, by the presence of only S (-) chiral centers. It has been observed that after annealing at 105 °C PLLA samples showed a crystallinity ranging from 45% to 70%, as revealed by DSC analysis (100% crystallinity, 93 J/g).

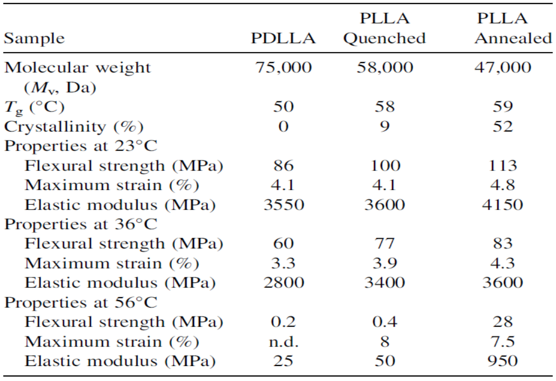
Tensile strength of these PLLA samples ranged from 47 to 70 MPa in the same range of molecular weights. The effect of molecular weight on tensile and flexural properties is more evident in annealed PLLA than nonannealed PLLA and PDLLA specimens, with an increase of tensile strength from 47 to 66 MPa in the range of molecular weight between 20,000 and 70,000 g/mol (viscosity-average molecular weight (Mv)). Above Mv 30,000–40,000, the tensile and flexural properties of amorphous PLLA increase more gradually, while for annealed PLLA the same behavior is reached at higher molecular weight, near Mv 50,000–60,000. In the case of PDLLA, the relationship between the increase in tensile and flexural properties with molecular weight becomes less pronounced when the molecular weight is higher than 45,000–50,000. A similar phenomenon is observed for amorphous PLLA.

II. *Effect of different temperature for polymerization of different lactic acid/lactide towards PLA*

As shown in Table 4.4C, the flexural properties of PDLLA, amorphous PLLA, and semicrystalline PLLA at 23, 36, and 56oC are quite different. At 36 °C, the flexural modulus decreased by 30%, 23%, and 26% as compared to the 23oC data for PDLLA, PLLA quenched, and PLLA annealed, respectively. However, increasing the temperature to 56 °C results in a marked drop of the flexural strength of PDLLA to 0.2 MPa. This result is expected due to glass transition at 50 °C together with the lack of crystallinity for the PDLLA polymer.

Similarly, the quenched amorphous PLLA shows a substantial reduction of flexural strength to 0.4 MPa at 56 °C. Only annealed semicrystalline PLLA maintains useful mechanical properties of 28 MPa flexural strength. Evidently, a small amount of crystallinity (9%) for the quenched PLLA is not sufficient to provide thermomechanical properties that are useful in practice. Therefore, solely PLLA that has been subjected to proper crystallization, by means of annealing, orientation, or nucleation, can offer useful properties for end-use applications where the temperature is greater than 50 °C.

Table 4.1C (II): Influence of Temperature on PLA Flexural Properties (Perego *et al.*, 1996)



Sample	PDLLA	PLLA Quenched	PLLA Annealed
Molecular weight (M_v, Da)	75,000	58,000	47,000
T_g (°C)	50	58	59
Crystallinity (%)	0	9	52
Properties at 23°C			
Flexural strength (MPa)	86	100	113
Maximum strain (%)	4.1	4.1	4.8
Elastic modulus (MPa)	3550	3600	4150
Properties at 36°C			
Flexural strength (MPa)	60	77	83
Maximum strain (%)	3.3	3.9	4.3
Elastic modulus (MPa)	2800	3400	3600
Properties at 56°C			
Flexural strength (MPa)	0.2	0.4	28
Maximum strain (%)	n.d.	8	7.5
Elastic modulus (MPa)	25	50	950

In general, annealing improves the thermomechanical properties. Therefore, extrusion or injection molding of PLA must be optimized. Proper crystallization of PLLA significantly improves the thermomechanical behavior, and this is an important requisite for applications at temperatures of 40–50 °C or higher. Biaxial orientation of PLLA film is an important method to increase tensile strength, elongation at break, and modulus of elasticity.

Here, the stereocomplex formed by equimolar amounts of PLLA and PDLA, particularly when subjected to biaxial orientation, exhibits very interesting thermomechanical properties, and it is therefore a promising material for new applications. Finally, the plasticization of PLA can have a strong effect on the mechanical behavior of this material, by increasing the elongation at break to about 300% with 20% by weight of a plasticizer such as tributyl citrate.

PLA has attracted the attention of industry for packaging and biomedical applications because of its biodegradability characteristics, in addition to its good mechanical and physicochemical properties. From a general point of view, PLA is a rigid, semicrystalline material, with tensile strength ranging from 50 to 70 MPa, modulus of elasticity of 3000–4000 MPa, and elongation at break of 2–5%. However, the toughness of PLA polymers can be successfully modified to meet specific applications by changing the formulation and manufacturing process. Thus, PLA is a versatile polymer that can be converted into several materials having useful properties for many different applications. The copolymerization of L-lactide with minor amounts of meso-lactide or D, L-lactide offers materials with lower brittleness and better film properties.

In general, annealing improves the thermomechanical properties. Therefore, extrusion or injection molding of PLA must be optimized. Proper crystallization of PLLA significantly improves the thermomechanical behavior, and this is an important requisite for applications at temperatures of 40–50 °C or higher. Biaxial orientation of PLLA film is an important method to increase tensile strength, elongation at break, and modulus of elasticity. Here, the stereocomplex formed by equimolar amounts of PLLA and PDLA, particularly when subjected to biaxial orientation, exhibits very interesting thermomechanical properties, and it is therefore a promising material for new applications. Finally, the plasticization of PLA can have a strong effect on the mechanical behavior of this material, by increasing the elongation at break to about 300% with 20% by weight of a plasticizer such as tributyl citrate.

IV. CONCLUSION

A good type of isomers such as L-lactide isomer could achieved a higher molecular weight of PLA and also a good thermal properties of PLA such as high glass transition temperature as well as high crystallization temperature. Moreover, due to a high crystallization and glass transition temperature could achieved a good mechanical and chemical structure for the production of a high molecular PLA.

The development of PLA applications in recent years mainly relates to environmental concerns and the adverse effects of using non-degradable petrochemical-based polymers. The use of PLA has grown well in the domestic market for general consumer goods and, importantly, in biodegradable packaging. The development of PLA is forecast to grow tremendously in the future, making the price of PLA as economical as commodity plastics, but with the added benefit of being kinder to the environment.

Thermal aspects are important in relation to their effect on the properties of PLA. The thermal properties and the crystallinity of PLA are inter-related. Importantly, the L and D stereochemistry has an effect on crystallization, which consequently affects the melting temperature and glass transition temperature of PLA. The properties of PLA are significantly influenced by the stereochemistry of its monomers. When PLA has high stereochemical purity, it tends to form a highly crystalline structure. The effect of isomerization in PLA can be detected by IR and NMR spectroscopic methods. The mechanical properties of pure PLA can be varied by changing the stereochemistry, crystallinity, molecular weight, etc. PLA with high stereochemical purity possesses the characteristic of high tensile strength and modulus, but lacks impact strength. In contrast, the copolymer of L-lactide and D-lactide remains in an amorphous state, which has poor mechanical properties. Researchers tend to utilize the copolymerization technique to modify the existing properties of PLA, in order to widen its applications.

PLA has been around for decades, but it is only in more recent years that the growth in its applications has expanded rapidly. PLA is a biodegradable polymer that possesses the potential to substitute existing petroleum-based commodity polymers, to help overcome the accumulation of plastic waste in landfills. In addition to its use in general and packaging products, it also has biomedical applications in surgery, due to its compatibility with living tissue. PLA is favored because it can be mass produced from agricultural sources, which are renewable, allowing society to reduce its dependency on petrochemicals. Continued research and development has made it possible to lower greenhouse emissions associated with the production process. In conclusion, PLA has got great potential and marketability as a biodegradable polymer for a sustainable future.

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