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POLYLACTIC ACID (PLA) FOR FOOD PACKAGING APPLICATIONS – A SHORT OVERVIEW

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Abstract

Polylactic acid (PLA) is one of the most versatile biopolymers, being available in large quantities produced by industrial fabrication in a wide range of grades. PLA is aliphatic polyester of lactic acid (2-hydroxypropanoic). Lactic acid can be obtained from the microbial fermentation of carbohydrate or chemical synthesis from the petrochemical. There are many ways to obtain PLA from lactic acid. The main methods are: direct condensation of lactic acid, azeotropic dehydration polymerization, and ring opening polymerization. PLA it is a relatively cheap polymer and has some remarkable properties, being suitable for different applications such as automotive, packaging, consumer goods, building and construction, consumer electronics, sportswear, biomedical. Nowadays, biopolymers such as starch, protein, cellulose, chitosan, PLA, and their derivatives are used in food packaging. These biopolymers are used as edible film or coating on the food with the aim of reducing the loss of moisture, prevention of oxidation, decreasing the migration of lipids, and so on. According to the latest market data, global bioplastics production capacity is set to increase from around 2.05 million tons in 2017 to approximately 2.44 million tons in 2022. Innovative biopolymers such as PLA and PHAs (polyhydroxyalkanoates) are the main drivers of this growth in the field of bio-based, biodegradable plastics. The development of packaging materials based on PLA polymers is expected to grow in the future with major focuses on enhancing food safety and quality and concurrently exploring alternatives to synthetic polymers made from petrochemicals that are less environment friendly.

Keywords: PLA, lactic acid, food packaging, biopolymers.

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1. INTRODUCTION

Polylactic acid (PLA) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources (corn starch, cassava roots, chips, sugarcane) under fermentation conditions.

PLA is the first melt-processable natural-based fiber (Dugan, 2000; Avinc *et al.*, 2009; Sin, 2012) (Fig. 1).

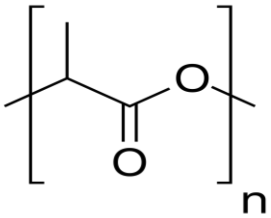

Fig.1 Structure of PLA

PLA has average molecular weight and is sensitive to water solubility. Its main characteristics are presented in Table 1.

PLA was first reported in 1932 by a group of chemists from DuPont led by W. Carothers which showed the dimerization of polycondensated lactic acid into lactide and the Ring Open Polymerization of lactide (Carothers *et al.*, 1932).

A very important aspect is that the use of renewable raw materials is not itself a guarantee for a low environmental impact. Several other factors like production processes, technical performance as well as weight of the final product and its disposal have to be carefully considered during all product life (Siracusa *et al.*, 2016).

2. SYNTHESIS of PLA

The basic constitutional unit of PLA is lactic acid. Lactic acid (2-hidroxypropionic acid) is an α-hydroxy acid having an asymmetric carbon atom and existing either as L(+) or D(-) stereoisomer, as presented in Figure 2.

Table 1 Characteristics of PLA

Characteristics	Unit	PLA
Glass transition temperature (Tg)	°C	62.1 ± 0.7
Melting temperature (Tm)	°C	195 – 245
Enthalpy	J/g	93 – 148
Density	g/cm^3	1.36
Solubility	-	dichloromethane, acetonitrile, chloroform
Degradation	-	Hydrolysis
Molecular weight (Mw)	kDa	66
O_2 permeability	$cm^3 \cdot ml/m^2$	550
CO_2 permeability	$cm^3 \cdot ml/m^2$	3000
Water vapor transmission	$g \cdot \mu m/kPa \cdot m^2 \cdot d$	161 – 237
Tensile modulus (E)	GPa	3500
Tensile strength (σ)	MPa	48 – 53
Elongation at break	%	7
Percent of elongation	%	12
Transmission	(230-250 nm)	95%
Thermal conductivity	(190 °C)	0.195

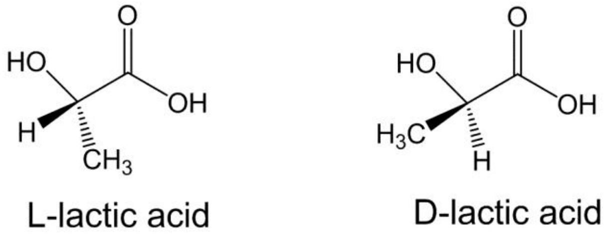

Fig.2 Stereoisomers of lactic acid

The L-isomer of lactic acid is produced in human and other mammal body, whereas both the D- and L-enantiomers are produced in bacterial systems. Lactic acid can also be chemically obtained from renewable resources such as ethanol or acetaldehyde, but, the large majority is obtained by bacterial fermentation of simple sugars using homofermentative strains of the genus Lactobacilli (Holten *et al.*, 1971; Auras *et al.*, 2004). Processing conditions are generally batch fermentation at a pH of 5.4-6.4, temperature of around 40 °C and low oxygen concentration. Lactic acid produced is neutralized with $Ca(OH)_2$ or $CaCO_3$. Strains such as *L. amylophilus*, *L. bavaricus*, *L. casei*, *L. maltaromicus* and *L. salivarius* produce exclusively L-lactic acid, while strains such as *L. delbrueckii*, *L. jensenii* and *L. acidophilus* produce mixtures of both l- and D-lactic acid. Main carbon sources are represented by glucose and maltose from corn, sugar beet, etc. (Hartman, 1998; Domenek *et al.*, 2016).

The synthesis of PLA is a complex, multistep process starting from the production of lactic acid and ending with its polymerization (Hartmann, 1998; Garlotta, 2001; Sodergard *et al.*, 2002; Auras *et al.*, 2004, Mehta *et al.*, 2005). As an intermediate step is the formation of lactide. Usually, synthesis of PLA can follow three main routes, as presented in Figure 3.

The first route is represented by direct condensation polymerization. It is the least expensive route, its yields low molecular mass polymers with mechanical properties which are insufficient for most applications. Chain coupling agents can be added in order to increase molecular weight but a purification step is required to remove unreacted coupling agents and prepolymers (Garlotta, 2001; Hyon *et al.*, 1997).

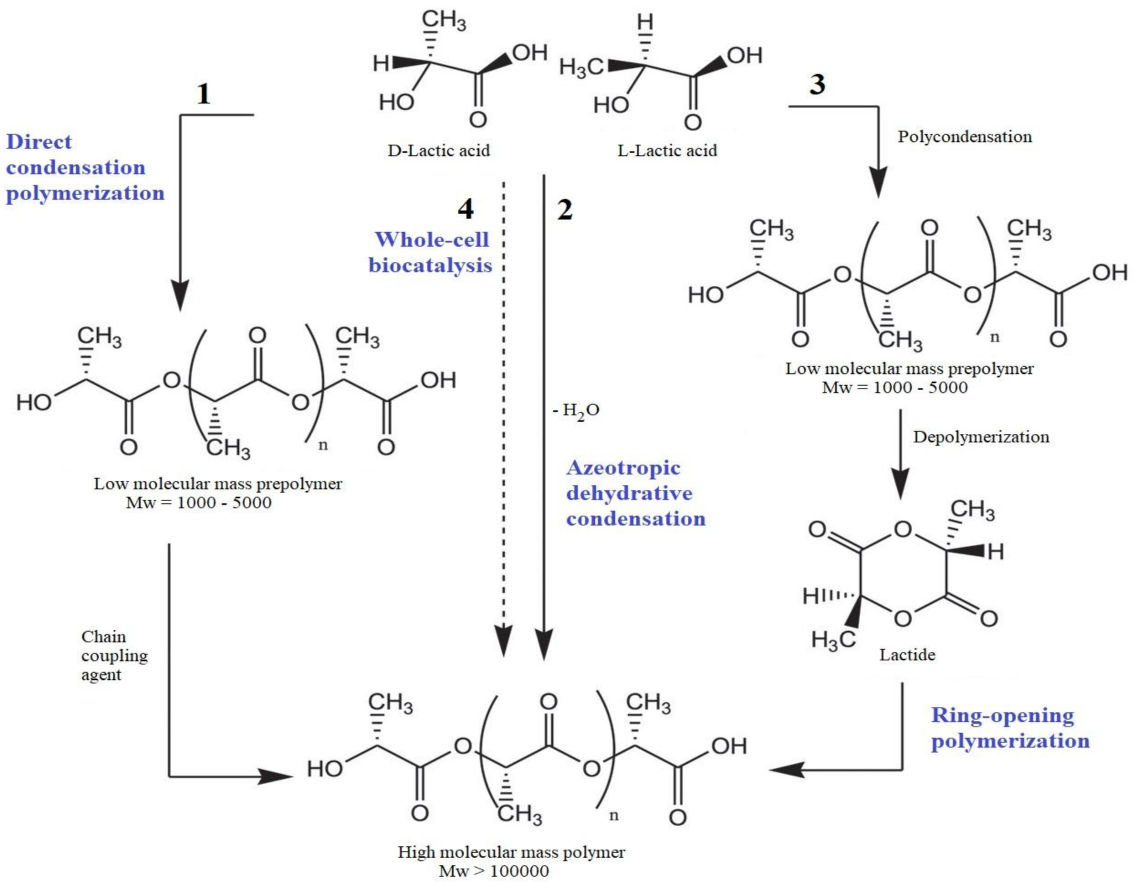

Fig. 3 Synthesis routes of PLA (Domenek et al., 2016)

The second route is represented by azeotropic dehydration and condensation polymerization. This route yields directly high molecular mass polymers. It was patented by Mitsui Toatsu Chemicals (Enomoto *et al.*, 1994; Kashima *et al.*, 1995). The procedure consists in the removal of condensation water via reduced pressure distillation of lactic acid for 2-3 hours at 130 °C and the purification of polycondensated PLA to reduce the residual catalyst content to ppm range (Garlotta *et al.*, 2001; Auras *et al.*, 2004; Averous, 2008).

The third route is also the most employed route to obtain high molecular mass polymers. It is called ring-opening polymerization (ROP) of lactide and was patented by Cargill (Gruber et al., 1992 and 1994). This route requires several steps: direct polycondensation reaction which produces low molecular mass prepolymers, followed by depolymerization in order to obtain lactides (Hitunen, 1997). ROP can be carried out in solution, in the melt, in the bulk or in suspension, involving a mechanism that can be ionic (anionic or cationic), coordination-insertion or free-radical polymerization (Sodergard *et al.*, 2002).

There is a fourth route, whole-cell synthesis of lactate containing polyesters, research being at the beginning (Taguchi *et al.*, 2008; Piotrowska *et al.*, 2015).

3. PLA as FOOD PACKAGING MATERIALS

PLA polymers are Generally Recognized as Safe (GRAS) which permits them to be used in direct food contact with aqueous, acidic and fatty foods under 60 °C and aqueous and acidic drinks served at less than 90 °C. Lactic acid is listed in Amendment 4 of the Monomers Directive 96/11/EC as an approved monomer for food contact applications. PLA is a very versatile polymer, suitable for a wide range of applications in flexible, rigid or foaming packaging (Chen, 2010; Chen *et al.*, 2012; Yokesahachart *et al.*, 2011).

The processability of PLA can be greatly improved when small amounts of lactite enantiomers of opposite configuration are randomly copolymerized with the monomer. For example, the addition of small amounts of D (-) lactide to L (+) lactide yields poly-D-lactic acid (PDLA) which has a noticeably lower melting point. However, PDLA resins are rather stiff and brittle (low impact resistance). These limitations can be overcome by blending PLA with low molecular weight plasticizers such as sorbitol or glycerol. PLAs are also often blended with other resins to lower cost and to increase its biodegradability (starch) or to further enhance its performance and processing properties. Most commercial high-purity grades are semicrystalline, have high transmittance (> 90 %), and high yield and tensile strength (about twice of HDPE). These resins can be easily converted into films and sheets via standard forming methods. In fact, many commercial grades are specifically designed for thermoforming or extrusion/injection molding.

There are several papers related to the use of PLA and PLA polymers for food packaging applications. PLA is used for packaging materials for short shelf-life products such as containers, drinking cups, salad cups, overwrap and lamination films, blisters, etc.

Fig.4 PLA cup and bowl (Grujic et al., 2017)

Table 2 Top producers of PLA polymers

Company	***Country***	***Characteristics***
NatureWorks (Joint venture between Cargill (USA) and PHH (Thailand).	USA	The products versatility means fiber, film, and rigid parts can be integrated into packaging systems like form-fill-seal yogurt containers or coffee capsules that desire performance attributes such as compostability. Provides excellent gloss, transparency and clarity and has exceptional flavor and aroma barrier properties. Better rigidity means thermoformed packaging can be down gauged to use less material. Foam trays are naturally light weight and safe for use with meats, produce, dairy and eggs. Films have excellent shrink, folding, and twist properties.
Total Corbion PLA Joint venture between Total (France) and Corbion (Netherlands).	Netherlands	Luminy is a range of specially developed high-performance PLA polymer resins, which are compliant with the most relevant regulations and requirements related to bioplastics.
Futerro 50:50 partnership between Galactic and Total Petrochemicals	Belgium	Futerro PLA grades have been successfully used in various transformation techniques, such as cast film, blown film, injection, thermoforming, blown molding, etc. Despite being a biopolymer, Futerro PLA perfectly complements polymers already available on the market, such as polyolefins, polystyrene, cellulose and polyester, used in a good number of applications.

New applications include thermoformed containers used for fresh fruits and vegetables in retail markets (Auras *et al.*, 2004; Cabedo *et al.*, 2006; Raithatha, 2009; Casey, 2010; Sanjay *et al.*, 2011; Juneja *et al.*, 2012; Molinaro *et al.*, 2013; Ayana *et al.*, 2014; Youngjae *et al.*, 2014; Tawakkal *et al.*, 2014; Arrieta *et al.*, 2015). Some examples of PLA based packaging materials are presented in Figure 4 and the most important producers of PLA in the world are presented in Table 2.

4. CONCLUSIONS

PLA is a high versatile biodegradable polymer that can be processed using conventional industrial equipment. The raw material is based on agricultural feedstock, having a positive impact on the global agricultural economy. During the last years, researchers made huge efforts into design of the macromolecular structure of PLA and the creation of nanocomposites. This will put forward the use of renewable resources in the plastic sector.

5. ACKNOWLEDGMENTS

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