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Applications of Poly(lactic Acid) in Commodities and Specialties

Mario Malinconico, Erwin T.H. Vink, and Andrea Cain

Abstract The use of oil-derived polymers has been of great benefit to mankind, but it is evident that it causes considerable damage to the ecosystem. Public concern about the environmental impact of wastes is growing day by day and waste management methods are limited as are petroleum resources, so it is very important to find substitutes, particularly in those applications where a relatively short lifetime can be forecast, such as packaging and agriculture. This has led to research work to find new biodegradable polymers as an alternative to conventional non-degradable ones. Among bio-based totally biodegradable polymers, poly(lactic acid) (PLA) has been studied for use in different fields because of its compostability and renewability. In this chapter, information on the present situation and trends regarding the applications of PLA is offered. The use of life cycle assessment principles helps to quantify the environmental benefits of PLA polymers. Most recent developments with PLA in the field of packaging show how this plastic material is moving from commodity to specialty applications, facing competition from polyolefins, particularly as barrier polymers for shelf-life enhancement.

Keywords Applications • Commodities • Environmental characteristics • Poly(lactic acid) • Specialties

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M. Malinconico (✉)
Istituto per i Polimeri, Compositi e Biomateriali, Consiglio Nazionale delle Ricerche, Via Campi Flegrei, 34, 80078 Pozzuoli, NA, Italy
e-mail: mario.malinconico@ipcb.cnr.it

E.T.H. Vink and A. Cain
NatureWorks B.V., P.O. Box 5528, 1410EA Naarden, The Netherlands

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1 Characteristics of Poly(lactic Acid)

1.1 General Considerations on PLA Properties

The polymerization of lactic acid leads to a family of poly(lactic acid) (PLA) polymers that, together with other natural polymers, enables biodegradable and bioresorbable polymers to be obtained. Among biodegradable plastics, PLA is one of the most promising to replace conventional plastics because of its excellent physical and mechanical properties and because it can be processed using existing plants with only minor adjustments. PLA is also a highly versatile material that can be adapted with various formulations to meet most product specifications [1]. When blended with other natural polymers it enables materials with better water resistance properties to be developed [2]. Products made in PLA are totally compostable in existing installations. With the proper equipment PLA can also be reverted to monomer (via hydrolysis) and again to polymer. PLA is a stable, odorless polymer. It is clear and shiny, similar to polystyrene (used to make cups, batteries and toys), and is resistant to moisture and grease. It has flavor and odor barrier characteristics similar to polyethylene terephthalate plastics, and can be used for non-alcoholic beverages and for other non-food products. The tensile strength and modulus of elasticity of PLA are also comparable to those of polyethylene. However, it is more hydrophilic than polyethylene, which has a lower density. It is stable in ultraviolet light, resulting in fabrics that do not fade. Its flammability is low [3].

PLA can be formulated to be rigid or flexible and can be copolymerized with other materials. It can be made with various mechanical characteristics depending on the manufacturing process followed.

1.2 Properties of PLA

In addition to its ability to biodegrade, PLA has properties that compare favorably with plastics commonly used, for example, for packaging. This is an important factor because it allows PLA to replace petrochemical polymers without redesigning products or investing heavily in new processing equipment [1].

PLA may be formulated to be both rigid and flexible and copolymerized with other monomers; it can also be prepared using appropriate specific manufacturing processes such as injection molding, sheet extrusion, blow molding, thermoforming, film formation, and spinning, using most conventional techniques and equipment. PLA is classified as generally recognized as safe by the US Food and Drug Administration [4].

The hydroxy acid precursor of PLA, lactic acid, with an asymmetric carbon atom, has four stereoisomeric forms: L, D, meso, and racemic mixture. It is made from corn, sugar beet, wheat, and other starchy grains from amorphous to crystalline by manipulation of mixtures of isomer D (−) and L (+).

The physical, mechanical, biological and, physiological properties of PLA depend on the composition of the polymer, its molecular weight, and its crystallinity. The crystallinity can be adjusted from a value of 0–40% in the form of linear or branched homopolymers and copolymers such as random or block [5].

As an example, in biomedical applications a crystalline form (mostly composed of L-lactide) of high molecular weight (>100,000 Da) ensures long resorption (approximately 1–2 years), and different formulations and the addition of side chains enable the resorption rate to be controlled. Using 100% L-PLA, a material with high melting point and high crystallinity is obtained. If a mixture of D and L is used, an amorphous polymer with a glass transition temperature of 60°C is obtained. With a mixture of 90% D and 10% L, a copolymer material which can be polymerized in an oriented manner with temperatures above its glass transition temperature is obtained. The processing temperature is between 60 and 125°C and depends on the proportion of D- or L-lactic acid in the polymer. However, the PLA can be plasticized with monomeric or alternatively oligomeric lactic acid and this allows a decrease in the glass transition temperature [6].

Södergard [7] indicates that the PLA has mechanical properties in the same range as those of petrochemical polymers, except for low elongation. However, this property can be tuned during the polymerization (copolymerization) or post-modifications (for example by plasticizers). Table 1 shows a comparison of some mechanical properties of plastics of petrochemical origin with those of PLA. One of the limitations of PLA, compared with other plastic packaging, is the low distortion temperature (HDT); this can be a problem in applications where the packing material is exposed to heating peaks during filling, transport, or storage, and can eventually deform [7]. This limitation can be partly solved by blending PLA with other compatible polyesters, such as polybutylene succinate [8].

PLA can be as hard as acrylic, soft as polyethylene or polystyrene, or rigid as flexible elastomer. It can also be formulated to provide a variety of resistances. PLA resins can be subjected to sterilization with gamma rays and are stable when exposed to ultraviolet rays. PLA formulations may impart properties of interest such as softness, scratch resistance, and wear resistance [10].

Table 1 Comparison of typical biodegradable polymer properties [9]

	T_g (°C)	T_m (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
LDPE	−100	98–115	8–20	300–500	100–1,000
PCL	−60	59–64	4–28	390–470	700–1,000
Starch	–	110–115	35–80	600–850	580–820
PBAT	−30	110–115	34–40	–	500–800
PTMAT	−30	108–110	22	100	700
PS	70–115	100	34–50	2,300–3,300	1.2–2.5
Cellulose	–	–	55–120	3,000–5,000	18–55
PLA	40–70	130–180	48–53	3,500	30–240
PHB	0	140–180	25–40	3,500	5–8
PHA	−30 to 10	70–170	18–24	700–1,800	3–25
PHB-PHV	0–30	100–190	25–30	600–1,000	7–15
PVA	58–85	180–230	28–46	380–530	–
Cellulose acetate	–	115	10	460	13–15
PET	73–80	245–265	48–72	200–4,100	30–300
PGA	35–40	225–230	890	7,000–8,400	30
PEA	−20	125–190	25	180–220	400

PET polyethylene terephthalate, *PGA* poly(glutamic acid), *PEA* poly(ester amide)

1.3 Biodegradation of PLA

With PLA, microorganisms (fungi and bacteria) can colonize the polymer surface and are capable of secreting enzymes that break the polymer into small fragments. Colonization depends on factors such as surface tension, porosity, surface texture, and accessibility to the polymer chains. The hydrophilic groups of enzymes (–COOH, –OH, –NH) attack the ester groups of the polymer chains by hydrolysis followed by oxidation reactions, thus reducing the polymer molecular weight to fragments less than 500 g/mol, which can be digested by microorganisms. In living tissue, PLA is completely depolymerized by chemical hydrolysis. Polymer degradation begins by a loss of molecular weight (no mass loss) and is terminated by a loss of mass, decomposition of the polymer in monomers, and phagocytosis by macrophages [11]. The fact that it is an enzymatic process, reabsorption of the polymer leads to a weak reaction of the tissue, which is limited to a foreign body reaction. After solubilization, lactic acid is degraded via lactates and pyruvate, and is then removed as carbon dioxide (CO_2), essentially via a respiratory process [12]. Current research focuses on lowering production costs of precursor (through the use of agro-industrial wastes as fermentation substrates, in the search for strongly producing microorganisms and the application of new technologies for extraction processes), on improving the physical and mechanical properties of the polymer, on improving methods for assessing the microbial stability of packaging based on PLA, and on studies of laws and norms for food contact packaging [13].

2 Environmental Characteristics of PLA

2.1 *General Considerations on PLA Environmental Characteristics*

Many recent reports indicate that PLA appears to be a useful and environmental friendly product. It is biodegradable, so PLA objects, having completed their life cycle, can be efficiently composted in an industrial composting plant. It also comes from renewable resources, so the raw material is always available. A major point of criticism of the polymer occurs during its biological disruption. PLA degradation under anaerobic conditions releases CO_2 and methane, substances involved in the greenhouse effect. Actually, the net balance is zero CO_2 because the CO_2 released into the atmosphere is the same CO_2 that was absorbed during photosynthesis of the plant [14]. Another criticism is that fossil fuels are still needed to produce PLA. Although fossil fuels are not used in the polymer itself, they are necessary in the processes of collecting the crop and in the chemical production. PLA producers recognize that fossil fuels are used to produce plastic, but indicate that their manufacture requires 20–50% less fossil resources than plastics derived from oil. They also make use of abundant fossil resources such as coal and natural gas and ongoing research on the use of biomass [15].

Lactic acid, and therefore PLA, may also be derived from corn, beet, and other crops, allowing its production to adapt to the specific climates of each region. Importantly, PLA manufacturing technology is new, just 10 years old, compared with almost 100 years manufacture of petrochemical plastics, during which technology has been improving. A frequently reported criticism of the use of crops for production of lactic acid rather than food is less relevant than claimed. Actually, it is estimated that less than 0.02% of arable land is used for the production of bioplastics, including PLA. However, such criticism is pushing research toward the exploitation of different sources for lactic acid production, such as cellulosic biomass, organic waste, and algal biomass, so-called third generation biorefinery.

Finally, PLA needs to be composted to degrade correctly and is usually mixed with organic waste which is then used as fertilizer.

2.2 *Carbon Footprint of PLA INGEO: A Case Study*

Figure 1 illustrates the major flows in the global carbon cycle.

In the atmosphere, carbon is present primarily as CO_2, which is fixed as biomass during photosynthesis. This process has been going on for hundreds of millions of years and has led to the vast resources of oil, gas, and coal that our society relies on at present. From the beginning of the industrial revolution, these resources have been used at an increasing rate to produce materials, chemicals, and fuels. As a result, much of the carbon stored millions of years ago is now being released into the atmosphere in

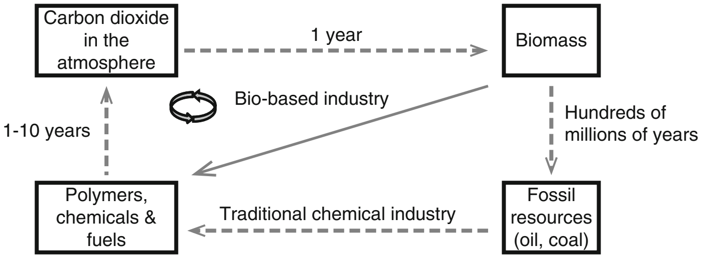

Fig. 1 Global carbon cycles. The fossil carbon cycle vs the biological carbon cycle

a very short period of time, geologically speaking. The result is that there is a net translocation of vast quantities of carbon from the earth into the atmosphere, leading to the above-mentioned increase in CO_2 level, which recently passed 400 ppm and continues to rise [16]. The increasing levels of CO_2 and other greenhouse gases such as methane and nitrous oxide trap more of the sun's heat, thereby raising the average temperature of the atmosphere – including both land and ocean – and leading to global climate change. This process will dramatically affect life on this planet. The use of fossil resources can, from a carbon point of view, be considered as a simple, linear process. The biobased industry offers an alternative and more sustainable route in terms of material carbon, with biobased resources utilized in a more circular process. The carbon harnessed during photosynthesis is used to produce biomaterials and, depending on the application, is released back into the atmosphere within a period of 1–10 years. Each year, plants repeatedly harness this CO_2 to produce biomass, closing the material carbon loop. The key value proposition of biobased materials such as PLA is their intrinsic zero material carbon footprint, assuming that after use the carbon in the polymer flows back to the atmosphere by composting or incineration. In other words, the fundamental intrinsic material carbon footprint value proposition for PLA is CO_2 removal from the environment and incorporation into the polymer molecule in harmony with nature's biological carbon cycles. Specifically, the value for PLA is 1.83 kg of CO_2/kg PLA. Plastics made from fossil resources cannot be credited with any CO_2 removal [17]. With each fossil-based item used and incinerated at the end of its useful lifecycle, the material carbon released to the atmosphere increases by an amount equivalent to the quantity of fossil carbon present in the product, whereas the material carbon released in the case of the biobased product remains zero as the biobased carbon is again taken up from the atmosphere for the next product cycle. Recycling of fossil-based materials has been considered as a long-term solution, but from a material carbon point of view it is just a minimal delay in the process of translocating fossil carbon from the earth into the atmosphere.

In 2003, NatureWorks published the first cradle-(corn production)-to-polymer factory-to-exit gate life cycle inventory data, also often referred to as an ecoprofile, for Ingeo polylactide production [18], with updated ecoprofiles presented in 2007 and 2010 [19, 20].

The data provided in the underlying 2014 report are specific to the corn feedstock currently in use by NatureWorks [21], and are only valid for Ingeo and not for polylactide production in general. The ecoprofile data for polylactides produced elsewhere are different because of the use of different feedstocks (i.e., sugarcane, sugar beet) and local production practices, different logistics, different technologies for processing sugars for fermentation, different fermentation and polymerization technologies, and different data for electricity and fuels used at all stages. For these reasons, the specific nomenclature “Ingeo” is used below to delineate clearly wherever NatureWorks’ polylactide biopolymer is being referenced.

Up-to-date life cycle inventory data are needed by research institutes, universities, retailers, brand owners, and authorities to provide better insights into the environmental performance of the products they use and to investigate and make meaningful comparisons between products. It should be noted, however, that the production and use of PLA and products made from PLA are still in their infancy compared with traditional petroleum-based polymers and products. Therefore, there is significant potential for further reduction in the environmental footprint of PLA and products made from it over their complete life cycles. This chapter reports on the life cycle performance/impacts of the 2014 Ingeo polylactide manufacturing system from cradle-to-polymer factory exit gate for a 150,000-ton production facility.

The study was conducted according to the requirements of ISO14040 and 14044. The simplified process flow diagram for the production of Ingeo is given in Fig. 3. The production system is divided into five steps:

Corn production and transport of corn to the corn wet mill
Corn processing and the conversion of the corn starch into dextrose
Conversion of dextrose into lactic acid
Conversion of lactic acid into lactide
Polymerization of lactide into Ingeo polymer pellets

The primary inputs to these five steps are listed on the right and left sides of the flow diagram. In the final ecoprofile, all primary inputs are traced back to the extraction of the raw materials from the earth. All the processes included in the calculation of the Ingeo ecoprofile are given within the black lined box in Fig. 2.

The box surrounding all the processes represents the system boundary; the ecoprofile is the inventory of all the flows (inputs and outputs) passing this system boundary, including the raw materials from the earth, CO_2, water, and the emissions to air, water, and soil. Here only aggregated data are provided to protect the proprietary information of Cargill and NatureWorks.

The life cycle of Ingeo starts with corn production; all free energy consumed by the corn plant comes from solar energy captured by photosynthesis. The basic stoichiometric equation for photosynthesis is

$$\mathrm{nH_2O + nCO_2 \overset{light}{\rightarrow} (CH_2O)n + nO_2}$$

In this equation, $(CH_2O)n$ represents simple sugars that are the basic building blocks for all substances present in the corn plant, such as starch, sugar, and cellulose. Therefore, all the carbon, hydrogen, and oxygen found in the starch

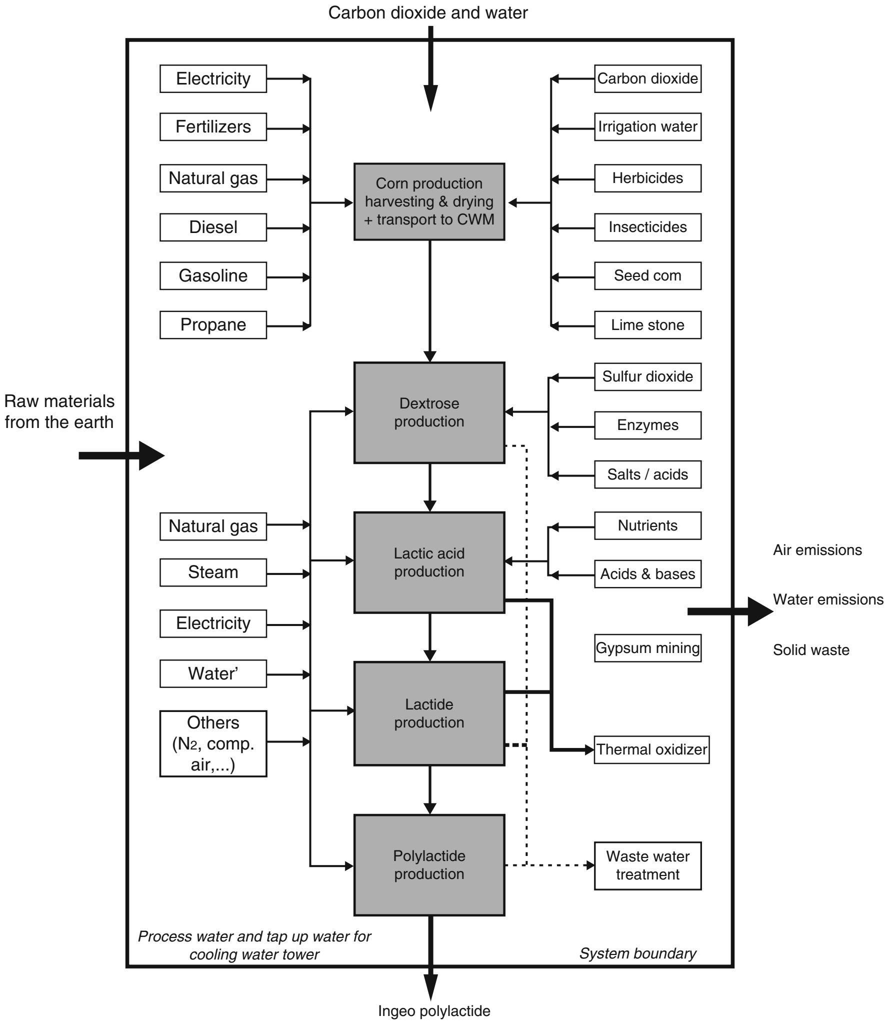

Fig. 2 Flow diagram for the manufacture of Ingeo PLA biopolymers

molecule and the final Ingeo polymer originates from water and CO_2. The data include all the relevant inputs for corn production, including production of corn seed, fertilizers, limestone, electricity, and fuels (natural gas, diesel, propane, and gasoline) used on the farm. the atmospheric CO_2 used through photosynthesis, the irrigation water applied to the corn field, and the production of the herbicides and insecticides used to protect the corn. On the output side, emissions including dinitrogen oxide, nitrogen oxides, nitrates, and phosphates are taken into account. The production of the farm equipment (tractors and harvest combines) employed was investigated, but their contributions are negligible.

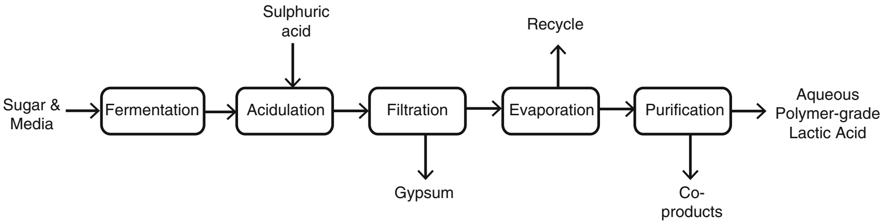

Fig. 3 Lactic acid production process

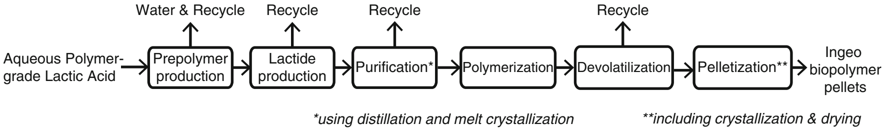

Fig. 4 NatureWorks' lactide formation and polylactide polymerization process

Lactic acid is produced by fermentation of the dextrose sugar. The process, illustrated in Fig. 3, combines dextrose and other media, adds a microbial inoculum, and produces crude lactic acid.

Figures 4 and 5 illustrate the process and the steps, respectively, of the polymerization process.

Figure 6a presents the latest available data for the primary energy of non-renewable resources in MJ Higher Heating Value (HHV)/kg polymer for a selection of polymers produced in the US and EU and Fig. 6b provides the global warming potential expressed as CO_2 equiv/kg polymer for the same polymers. These are net GWP (global warming potential) values from cradle-to-polymer factory-to-exit gate. For Ingeo, the uptake of CO_2 from the atmosphere is included, as this takes place during corn production, a process within the system boundary.

3 Applications of PLA

3.1 World Request for Poly(lactic acid)

Global demand for poly(lactic acid) and lactate esters for 2015 was 200,000 tons, a sector dominated by the food, beverage, and personal care industries (https://www.gminsights.com/industry-analysis/lactic-acid-and-polylactic-acid-market). PURAC BIOCHEM (Netherlands) is the worldwide leader in biotechnological production of lactic acid. A survey of lactic acid producers (the precursor of PLA) revealed that production capacity could even rise to roughly 950,000 tons/year to meet concrete requests.

At 30 sites worldwide, 25 companies developed a production capacity of more than 180,000 tons/year of PLA in 2012.

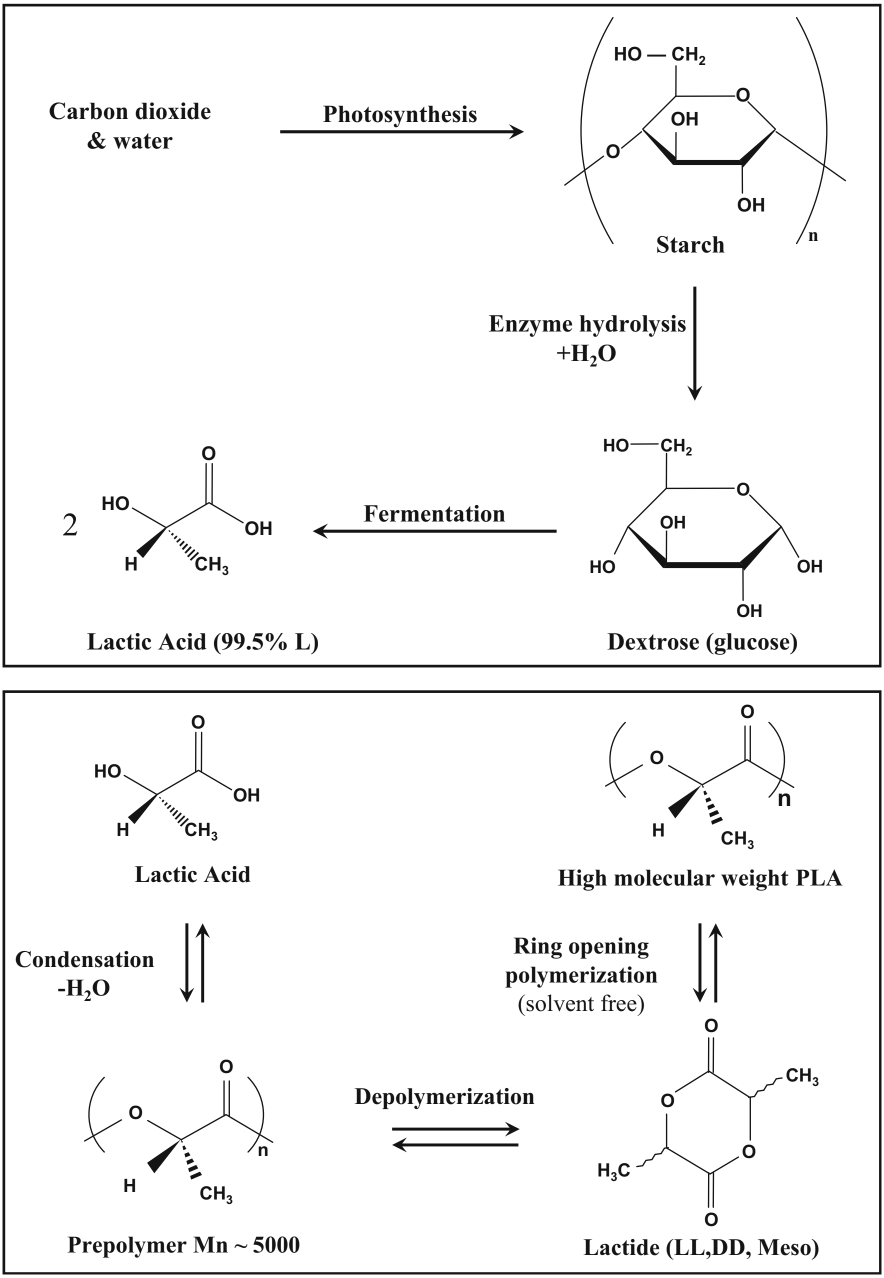

Fig. 5 Steps to Ingeo production

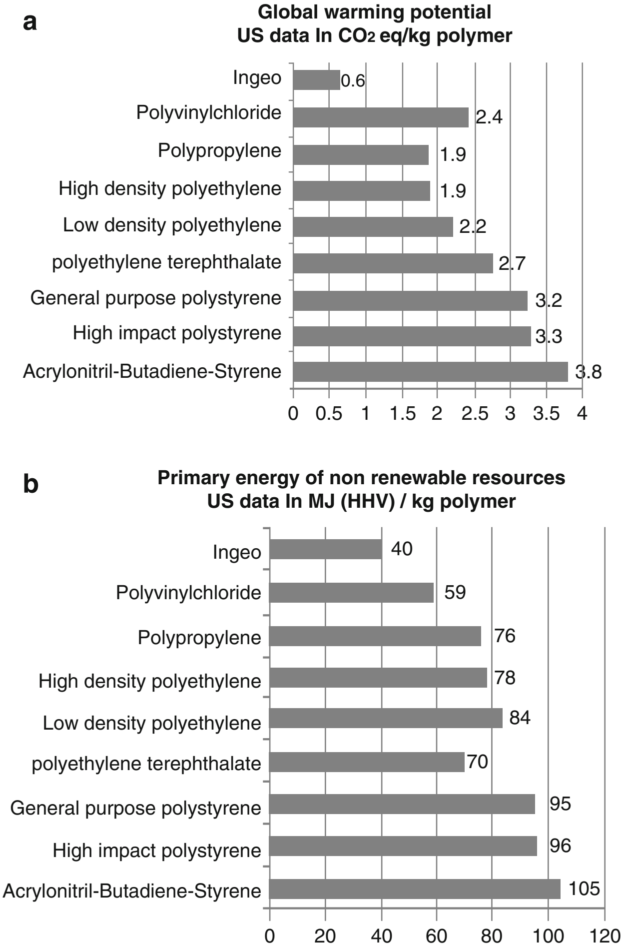

Fig. 6 (**a**) Primary energy of non-renewable resources. (**b**) GWP-cradle-to-polymer factory-gate

The largest producer, NatureWorks, had a capacity of 140,000 tons/year in 2011. The other producers have current capacity of between 1,500 and 10,000 tons/year. According to their own forecasts, existing PLA producers are planning to expand considerably their capacity of over 50,000 tons/year by that time. Current (2015) world production of PLA is 200,000 tons/year and it is used in the food, chemical, and pharmaceutical industries. In 2004 the NEC Corporation developed a plant-based plastic PLA with high fire resistance and no toxic halogens or phosphorus derivatives, and in the same year the Japanese company Sanyo® introduced a compact disc made of PLA, incorporating plastic packaging foams formed from mixtures of starch with PLA, protecting from damp and against shock and vibration during transport.

3.2 Textile Industry

PLA polymers also have many potential applications in fiber technology. They present very attractive features for many traditional uses. PLA polymers are more hydrophilic than polyethylene terephthalate, have a lower density, and exhibit high bending and stretching strengths [22].

The degree and temperature of shrinkage of PLA materials are readily controllable. These polymers tend to be stable to UV light, resulting in fabrics with little discoloration. It is a fire retardant and low smoke material.

Its applications include clothing, upholstery of certain furniture, diapers, feminine hygiene products, and fabrics resistant to UV radiation for outdoor uses [23].

3.3 Medical and Pharmaceutical Industry

The selection criteria for PLAs depend on the applications, so higher mechanical strength is obtained by selection of the amorphous (DL-PLA) or long-term biodegradability by selection of the semi-crystalline form (L-PLA). Copolymers of L/DL-PLA are used to preserve the mechanical properties and speed of biodegradability [24].

In the field of surgery, L-PLA finds great applications as material for absorbable sutures (ophthalmological surgery, conjunctival, thoracoabdominal, neurological anastomosis), and in orthopedic surgery (resorbable implants, screws, pins, plates, staples), reconstructive surgery, and craniofacial and maxillofacial surgery involving bone and soft tissues [13, 24, 25].

PLA is used in the creation of matrices for guided tissue regeneration as skin, cartilage, bone, cardiovascular structures, intestine, and urinary tissue among others [26].

It is also used to microencapsulate and nanoencapsulate slow release drugs such as insulin, cisplatin, taxol, somatostatin, anti-inflammatory drugs, ganciclovir, angiogenesis inhibitors, etc. The drug is absorbed in the center of a matrix of PLA polymer microspheres, which is capable of protecting the drug or organism. As the matrix is hydrolyzed, the drug is released. It is also used in the application of cancer chemotherapy or contraception [27, 28].

The following are the worldwide applications:

Biodegradable scaffolds for tissue engineering
Reconstructive and bioabsorbable implants
Equipment and instrumentation for surgeons
Implants for fracture fixation
Treating facial lipoatrophy
Absorbable internal fixation plates face fractures, orthognathic and craniofacial surgery
Preparation of biodegradable microspheres
Bioresorbable fixation devices in orbital reconstructions
Intravitreal administration of antivirals

3.4 Agriculture

The main effect of crop mulching is to promote soil warming, thereby allowing root development of the plant, and mulching is also often complemented by a tunnel microclimate [29]. The use of mulching for horticultural crops can advance harvesting, reduce water consumption, avoid the use of herbicides, and enhance the quality of production, fostering integrated and organic production.

Traditional mulching materials are linear low density polyethylenes, opaque or transparent, depending on the crop cycle in which it is used and the effect it is intended to have. These plastic materials have mechanical properties and exceptional optics, often being directly responsible for the success of planting. Other purposes are reducing soil evapotranspiration, combatting weed flora, reducing the loss of minerals, and, by black coloration, stopping the growth of infesting plants. The problems arising from their use, on the other hand, arise because of their excellent mechanical properties, which gives them a long life. End-of-life management, although illegal, often involves soil burial or incineration or superficial abandonment with climate agents such as wind taking the residues to various locations and ecosystems, in all cases leading to soil contamination [30–33]. This, together with their great development that has allowed them to be used anywhere, their repeated use, their small thicknesses and poor agricultural practices, has prompted the search for alternatives in those places where they cannot be recovered after use [34, 35].

The alternative of biodegradable mulching could be the solution to the problem, provided that the degradation of the mulching material occurs in a fast and reliable way [36–38]. For those mulching materials whose base polymer is composed of or derived from PLA, there are two factors, among others, related to soil condition which have a direct influence on degradation processes, the degree of humidity and the microbiota existing in the areas where the pieces of mulched films are buried, that assure complete degradation of the residual films prior to the beginning of the next crop [39, 40]. The activity of the bacterial flora is responsible for the disappearance of the sheets of films when feeding them, and their presence and multiplication is possible provided there is some degree of moisture in the soil.

3.5 Packaging

The most successful application of PLA is in containers and food packaging. However, the higher affinity to water and, consequently, the higher potential for fungal growth in biodegradable materials compared to non-biodegradable oil-derived polymers may be a negative characteristic for use in some food sectors [41, 42]. Therefore bio-packages are more suitable for foods with high breathing and short storage life such as vegetables, and for the packaging of some bakery products.

In the food industry, PLA has been the subject of a detailed study by the FDA in which it was found that the migration of lactic acid, lactide, and lactoyllactic acid was limited and it was therefore concluded that PLA is a substance recognized as safe and can be used as a packaging material for food [7].

Materials consisting of 10% PLA plus 90% copolyester, 10% PLA plus 90% copolyamide, 10% PLA plus 90% starch, and 10% PLA plus 90% polycaprolactone have been used as packing material for yogurt, butter, margarine, and cheese spread. These materials have fulfilled functions such as mechanical protection and a barrier to moisture, light, grease, and gases. They have also been used as "windows" in packaging for dry goods such as bread, which play a role as a moisture barrier, and in the preparation of coated paper PLA containers for packaging beverages, also playing a role as a moisture barrier [43].

Södergard [7] says that the most promising application of PLA in packaging materials is for products that must remain cold and have limited lifetimes, such as dairy products. However, in a study conducted at the Technical University of Denmark, where the convenience of using biobased packaging materials for foods was assessed, they concluded that the high fungal growth on materials obtained from biodegradable bases is a negative factor for use in foods and claim that biopackagings are more suitable for foods with high breathing and short storage life such as vegetables, and for the packaging of some bakery products [43].

4 The Future of PLA-Based Materials

Although the values of global installed capacity for the production of biodegradable plastics do not reach 1% of the total world demand for plastic resins, progress is vigorous in the packaging market. The growth and acceptance of biodegradable resins is related to the high price of oil, consumer awareness of environment protection, technological achievements in the new generation of biodegradable resins, and governmental laws. Some companies predict market growth in Europe at a rate of 20% annually, and the Association of Biodegradable Polymers (IBAW) estimates that, with existing quality and price, a possible potential for about 10% of the plastics market share, which in Europe is 40 million tons/year is forecastable.

It appears that in the food industry, in food packaging, packaging for toys, candy wrappers and flowers, in making boxes, milk cartons, soda bottles, oil bottles, home curtains, sheets, pillows, tablecloths, upholstery, and textile fibers, products of PLA will increase significantly in the coming years.

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