



# Poly(lactic acid)—Mass production, processing, industrial applications, and end of life☆



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## ABSTRACT

Global awareness of material sustainability has increased the demand for bio-based polymers like poly(lactic acid) (PLA), which are seen as a desirable alternative to fossil-based polymers because they have less environmental impact. PLA is an aliphatic polyester, primarily produced by industrial polycondensation of lactic acid and/or ring-opening polymerization of lactide. Melt processing is the main technique used for mass production of PLA products for the medical, textile, plasticulture, and packaging industries. To fulfill additional desirable product properties and extend product use, PLA has been blended with other resins or compounded with different fillers such as fibers, and micro- and nanoparticles. This paper presents a review of the current status of PLA mass production, processing techniques and current applications, and also covers the methods to tailor PLA properties, the main PLA degradation reactions, PLA products' end-of-life scenarios and the environmental footprint of this unique polymer.

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**Abbreviations:** AATCC, American Association of Textile Chemists and Colorists; ABS, Acrylonitrile butadiene styrene; AD, Anaerobic digestion; APR, Association of Postconsumer Plastic Recyclers; CFA, Chemical foaming agent; CNT, Carbon nanotube; CWM, Corn wet mill; DFS, Direct fuel substitution; DMR, Direct measurement respirometer;  $\delta_p$ , Solubility parameter;  $E_{act}$ , Average energy of activation; EFP, Environmental footprint; EGMA, Poly(ethylene-glycidyl methacrylate); EPA, Environmental Protection Agency; ESR, Electron spin resonance; EVOH, Ethylene vinyl alcohol; GHG, Greenhouse gas; GWP, Global warming potential; HA, Hydroxyapatite; HDPE, High density poly(ethylene); HDT, Heat deflection temperature; HHV, Higher heating values; HRC, Hydrogen release compound; IC, Industrial composting; IR, Infrared; ISBM, Injection stretch blow molding; LA, Lactic acid; LCA, Life cycle assessment; LDPE, Low density poly(ethylene); LF, Landfilling; LLDPE, Linear low density poly(ethylene); MCC, Microcrystalline cellulose; MD, Machine direction; MFR, Melt flow rate; MMT, Montmorillonite; MR, Mechanical recycling; MSW, Municipal solid waste; MSWI, Municipal solid waste incineration; MWCNT, Multiwall carbon nanotube;  $M_w$ , Weight average molecular weight;  $M_n$ , Number average molecular weight;  $m_s$ , Sound velocity;  $m_{sh}$ , Sound velocity of propagation of transverse waves; NAPCOR, National Association for PET Container Resources;  $\eta$ , Intrinsic viscosity; OI, Oxygen index; PA, Polyamide; PAE, Polyamide elastomer; PBAT, Poly(butylene adipate-co-terephthalate); PBS, Polybutylene succinate; PBSA, Poly(butylene succinate-co-adipate); PBSL, Poly(butylene succinate-co-L-lactate); PC, Polycarbonate; PCDI, Polycarbodiimide; PCL, Poly( $\epsilon$ -caprolactone); PCR, Post-consumer recycled; PDLA, Poly(D-lactic acid); PDLLA, Poly(D,L-lactic acid); PE, Polyethylene; PEG, Poly(ethylene glycol); PENNR, Primary energy from nonrenewable resources; PEO, Poly(ethylene oxide); PET, Poly(ethylene terephthalate); PEVA, Poly(ethylene-co-vinyl acetate); PFA, Physical foaming agent; PGA, Polyglycolic acid; PGS, Poly(glycerol sebacate); PHAS, Poly(hydroxyalkanoates); PHB, Polyhydroxybutyrate; PHBHxx, Poly[(3-hydroxybutyrate)-co-(3-hydroxyhexanoate)]; PHBV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PIP, Poly(cis-1,4-isoprene); PLA, Poly(lactic acid); PLLA, Poly(L-lactic acid); PP, Poly(propylene); PPC, Poly(propylene carbonate); PS, Polystyrene; PTAT, Poly(tetramethylene adipate-co-terephthalate); PTFE, Polytetrafluoroethylene; PTT, Poly(trimethylene terephthalate); PU, Poly(ether)urethane; PVC, Polyvinyl chloride; PVOH, Polyvinyl alcohol; RH, Relative humidity; RIC, Resin identification code; ROP, Ring-opening polymerization; SCORIM, Shear-controlled orientation in injection molding; SF, Silk fibroin; SIC, Solvent induced crystallization; SPC, Soy protein concentrate; SPI, Soy protein isolate; TKGM, Thermoplastic konjac glucomannan; TNPP, Tris(nonylphenyl) phosphite; TPO, Thermoplastic polyolefin elastomer;  $T_{d,0}$ , Initial decomposition temperature;  $T_{d,1/2}$ , Half decomposition temperature;  $T_g$ , Glass transition temperature;  $T_m$ , Melting temperature;  $T_{mc}$ , Melt crystallization temperature; US, United States; UV, Ultraviolet; Vc, Molar volume of semicrystalline polymer; Vg, Molar volume of glassy amorphous;  $V_w$ , Van der Waals volume;  $\Delta H_m$ , Enthalpy.

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## 1. Introduction

Poly(lactic acid) (PLA) is a biodegradable and bio-based aliphatic polyester derived from renewable sources such as corn sugar, potato, and sugar cane. PLA has played a central role in replacing fossil-based polymers for certain applications [1,2]. As a compostable polymer, PLA is considered a promising alternative to reduce the municipal solid waste (MSW) disposal problem by offering additional end-of-life scenarios [3]. High weight average molecular weight ( $M_w$ ) PLA is generally

produced by polycondensation and/or ring-opening polymerization (ROP) [4]. NatureWorks LLC is the major producer of PLA, with a capacity of 150,000 metric ton year in its US manufacturing facility (in Blair, Nebraska) [2,5]. Due to great market penetration, worldwide attention, and the rise of PLA production [6], the number of published research studies and reports about PLA have exponentially increased in the last 25 years, as shown in Fig. 1.

The use of PLA was initially limited to medical applications due to its high cost and low availability, but high  $M_w$  PLA now can be processed by injection molding, sheet and film extrusion, blow molding, foaming, fiber spinning, and thermoforming. Also, PLA provides comparable optical, mechanical, thermal, and barrier properties when compared with commercially available commodity polymers such as polypropylene (PP), poly(ethylene terephthalate) (PET), and polystyrene (PS), expanding its commercial range of applications [2,5]. In the medical field, PLA is extensively used because of its biocompatibility with the human body, including for applications such as medical implants, surgical sutures and medical devices [8–12]. In addition, PLA has been used

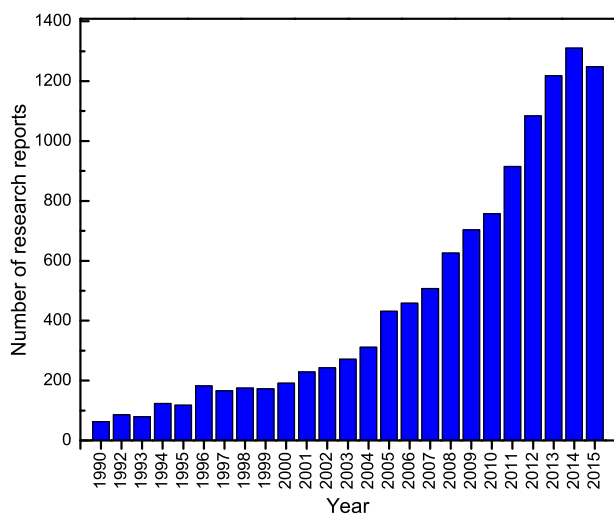


Fig. 1. Number of research reports published since 1990 based on the Web of Science search using keywords “PLA”, “PLLA”, “PDLA”, “polylactic acid”, “poly(lactide)”, and “poly(lactic acid)” [7].

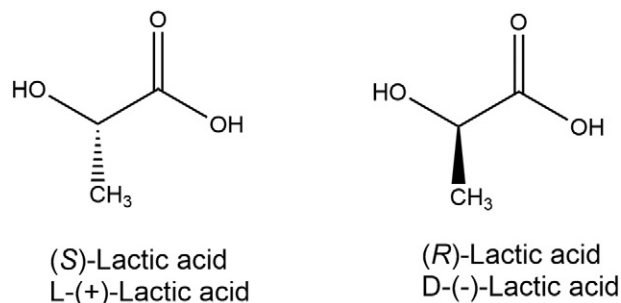


Fig. 2. Chemical structure of L(+) and D(−) lactic acid.

for applications such as fibers, textiles, plasticulture, serviceware, packaging containers (i.e., food packaging for short-life products), and environmental remediation films [13]. PLA is considered as a Generally Recognized as Safe (GRAS) material by the US Food and Drug Administration (FDA). However, PLA has also some limitations (e.g., poor toughness), so research efforts are centered on obtaining PLA products with particular desired properties by blending PLA with other biodegradable and non-biodegradable resins, and/or by compounding PLA with fillers such as fibers or micro- and nanoparticles.

This critical review focuses on the status of PLA polymer regarding its mass production, the main processing techniques, and methods that have been used to extend PLA applications on the basis of its intrinsic properties. Furthermore, this review provides a panorama of the current main applications categorized according to PLA commercial usage, and an overview of different environments to which PLA products can be exposed during their lifetime that lead to their degradation, including hydrolysis in non-medical applications. Finally, the end-of-life

scenarios of PLA products as well as the cradle-to-grave and cradle-to-cradle environmental footprint (EFP) are discussed.

## 2. PLA resin production

Lactic acid (LA), also named 2-hydroxy propionic acid, is the basic monomer of PLA. The monomer exists as two stereo isomers, L-LA and D-LA. Fig. 2 shows the different chemical structures of these two isomers [2].

The two main methods to produce LA are by bacterial fermentation of carbohydrates or by chemical synthesis [14]. Bacterial fermentation is the preferred industrial process used by NatureWorks LLC and Corbion®, the two major producers of PLA. Chemical synthesis has many limitations, including limited production capacity, inability to produce only the desired L-LA isomer, and high manufacturing costs [15].

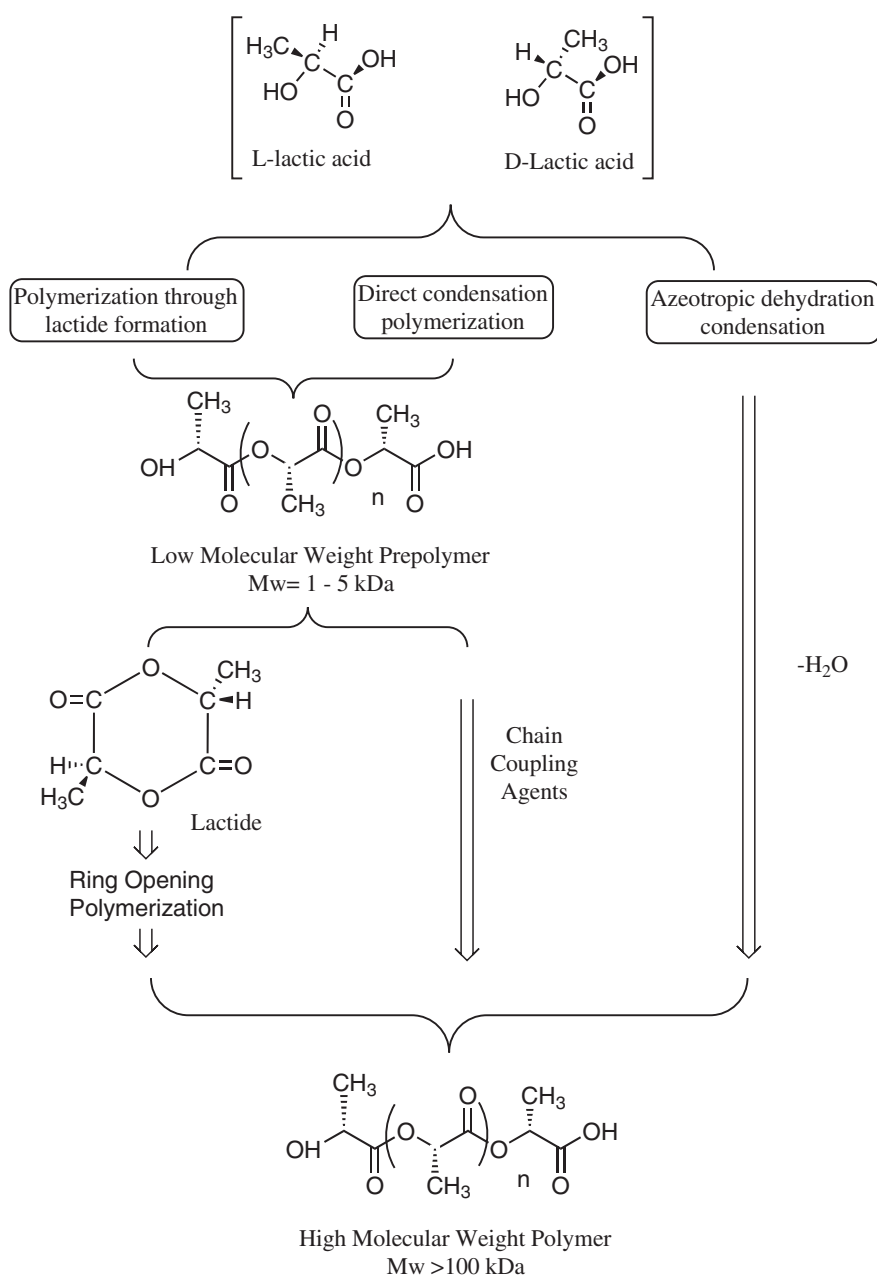


Fig. 3. The manufacturing processes to produce high molecular weight PLA, adapted from Hartmann [17].

The bacterial fermentation processes to produce LA can be classified as homofermentative or heterofermentative methods, depending on the bacteria used. In the heterofermentative method, 1 mole of hexose produces less than 1.8 moles of LA, along with significant levels of other metabolites such as acetic acid, ethanol, glycerol, mannitol, and carbon dioxide. However, in the homofermentative method, 1 mole of hexose can produce an average of 1.8 moles of LA, with minor levels of other metabolites, which means every 100 g of glucose could yield more than 90 g of LA. The homofermentative method is more frequently used by industry due to its greater production yields and lower levels of by-products in comparison with the heterofermentative method [16].

In the homofermentative method, species of the *Lactobacillus* genus, such as *Lactobacillus delbrueckii*, *L. amylophilus*, *L. bulgaricus* and *L. leichmannii*, are used under conditions of a pH range from 5.4 to 6.4, a temperature range from 38 to 42 °C, and a low oxygen concentration. The nutrients used to feed the bacteria can be simple sugars, such as glucose and maltose from corn or potato or other sources such as vitamin-B, amino acids, and nucleotides provided by rich corn steep liquor. In general, batch production processes can yield 1 to 4.5 g L<sup>-1</sup> h<sup>-1</sup> of LA, whereas continuous processes can achieve 3 to 9.0 g L<sup>-1</sup> h<sup>-1</sup> of LA. On a larger scale, cell recycle reactors can produce up to 76 g L<sup>-1</sup> h<sup>-1</sup> [16,17]. After the initial production process, the LA must be purified by distillation if it will be used for pharmaceutical and food derivative purposes. NatureWorks LLC is currently using a lower pH process to produce LA, which reduces the amount of calcium hydroxide and sulfuric acid by-products, resulting in the lower production of calcium sulfate (gypsum) [5]. Corbion®, through a proprietary technology, produces LA in a gypsum-free process, which uses second generation feedstocks (i.e., plant-based materials such as corn stover, bagasse, wheat straw, and wood chips) [18,19].

LA can be used to produce the PLA of variable molecular weights; however, usually only the high  $M_w$  PLA has major commercial value in the fiber, textile, plasticulture, and packaging industries. Fig. 3 shows the three main methods available to produce high  $M_w$  PLA from LA: (1) direct condensation polymerization; (2) direct polycondensation in an azeotropic solution; and (3) polymerization through lactide formation [17].

The direct condensation polymerization process involves three main steps: 1) free water removal, 2) oligomer polycondensation, and 3) melt polycondensation of high  $M_w$  PLA. A detailed description of this process can be found in Hartmann [17]. Direct condensation polymerization is generally considered the least expensive process to produce high  $M_w$

PLA. However, the necessity to use chain coupling agents and adjuvants to obtain a solvent-free PLA increases the costs of the products and the complexity of the process [14,17,20,21].

Direct polycondensation in an azeotropic solution is the method applied by Mitsui Toatsu Chemicals, Inc. to produce high  $M_w$  PLA [22]. In the process, no chain extenders or adjuvants are used. The PLA is produced by a direct condensation while the condensation water is continuously removed by the azeotropic distillation. The process includes reduction of the distillation pressure of LA for 2–3 h at 130 °C, and the majority of the condensation water is removed. Catalyst is added along with diphenyl ester. A tube packed with 3-Å molecular sieves is attached to the reaction vessel, and the solvent is returned to the vessel via the molecular sieves for an additional 30–40 h at 130 °C. Finally, the polymer is isolated as is or it is dissolved and precipitated for further purification. The effect of difference catalysts on the azeotropic dehydration of LA in diphenyl ether and additional details of the technique is reported elsewhere [17,22].

NatureWorks LLC, the major producer of high  $M_w$  PLA based on the original Cargill-Dow patented process [23], combines a solvent-free process and a distillation process to produce PLA with controlled molecular weights in a multi-step process. The LA is first condensed to form low  $M_w$  prepolymer PLA. With controlled depolymerization, the cyclic dimer, also referred as lactide, is produced from the low  $M_w$  prepolymer PLA [24]. The lactide in the liquid form is purified by distillation. The PLA with controlled molecular weight is produced by the ring opening of lactide and then polymerization with catalyst [16,17,25,26]. Fig. 4 shows the basic process design to produce high  $M_w$  PLA.

PLA produced from this process can be derived from different amounts of L- and D-lactide. The lactide reactor produces a combination of LA, LA oligomers, water, *meso*-lactide and impurities [18]. The mixture must be purified, in this case by vacuum distillation through a series of columns. Due to the difference in boiling points of lactide and *meso*-lactide (Fig. 5), the highest  $M_w$  PLA is derived from L-lactide and a small amount of *meso*-lactide. The higher the stereochemical purity of the lactide mixture, the higher the stereochemical purity of the PLA. The NatureWorks LLC process results in a large amount of *meso*-lactide, so the properties of the PLA resin obtained through this process can vary according to the amount of *meso*-lactide in the mix. PLA with a large amount of 93% L-LA can crystallize.

Although a higher amount of *meso*-lactide in the monomer of PLA contributes to some advantages, such as easier processing and production of amorphous PLA, its presence compromises the thermal stability

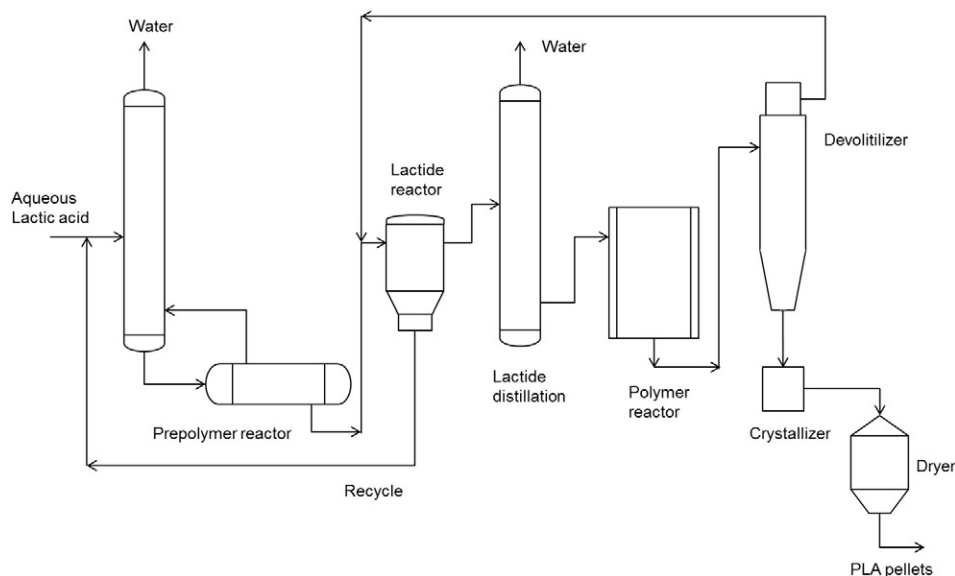
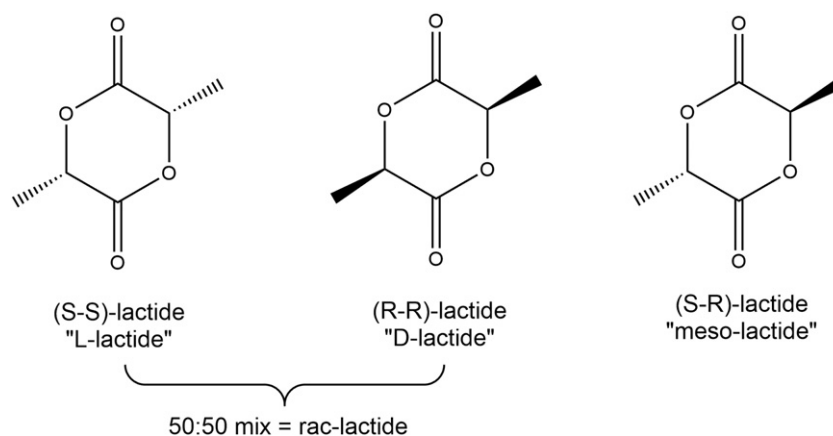


Fig. 4. NatureWorks LLC commercial process for producing high molecular weight PLA, adapted from Auras et al. [2] and Vink et al. [5].



**Fig. 5.** Diastereomeric structures of lactide (3,6-dimethyl-1,4-dioxane-2,5-dione).  $T_m$  of L-lactide, D-lactide, *meso*-lactide, and *rac*-lactide are 96, 97, 53, and 125 °C, respectively, adapted from Vert et al. [18].

of PLA (*i.e.*, low heat deflection temperature (HDT)) for a wide range of applications [18]. The presence of *meso*-lactide in poly(L-lactic acid) (PLLA) also may cause deteriorative changes of the crystallinity and biodegradation properties of the materials [27]. Therefore, it is generally desirable for PLA monomer to contain a low amount of *meso*-lactide. Although the production of *meso*-lactide is considered undesirable and often is associated with impurities, NatureWorks LLC has made it possible to refine this monomer into various functionalities. Applications of the *meso*-lactide by-product include its use as chemical intermediates in various surfactants, coatings, and copolymers [28]. *Meso*-lactide can be separated easily from either (S,S)-lactide or (R,R)-lactide due to its volatile nature. Commonly used methods to perform separation of *meso*-lactide from either (S,S)-lactide or (R,R)-lactide are fractional distillation, melt crystallization and solvent recrystallization [29]; however, these methods pose some difficulties in separating *meso*-lactide from other impurities. NatureWorks LLC has patented a process in which *meso*-lactide can be separated from crude lactide efficiently by means of an enriched stream of a minimum 0.8-mole-fraction of *meso*-lactide and forming a purified (S,S)- and (R,R)-lactide stream. Futerra S.A., a joint venture company between Galactic and Total Petrochemicals, has also patented a method to produce *meso*-lactide, D-lactide, and L-lactide by back biting depolymerization of PLA. The process starts by employing a controlled temperature (200–290 °C) and a reduced pressure in a presence of catalyst and co-catalyst to depolymerize PLA into its dimeric cyclic esters form. The resultant PLA components are depolymerized into a vaporized form in a reaction zone. This vaporized form is then condensed and the *meso*-lactide, D-lactide, and L-lactide produced are recovered separately or together. This invention, which is regarded as the second generation of PLA, can produce D-lactide and *meso*-lactide with high throughput for the production of poly(D-lactic acid) (PDLA) or co-polymers consisting of L- and D-LA enantiomers without the need to start off with LA [30].

Extensive research has also been conducted to produce lactide and PLA via low manufacturing and production costs and with enhanced properties [31,32]. Various catalysts, ranging from metal, cationic, and organic, have been used during polymerization of PLA to achieve high  $M_w$  and high optical purity [33]. Metal complexes are reported to be one of the most efficient catalysts for the production of stereoblock isotactic PLA via ROP of *rac*-lactide due to its ability to control parameters such as molecular and chain microstructure [34]. Dusselier et al. [35] reported the production of lactide through a direct Brønsted acidic zeolite-based catalytic process, which obtains considerably larger lactide yields than with the controlled ROP of low  $M_w$  PLA. Yang et al. [34] investigated the production of PLA by *rac*-lactide using monoanionic aminophenolate ligands with metal complexes in the presence of solvents such as tetrahydrofuran and 2-propanol. Monomeric zinc silylamido complexes with arylamine coordination ligands

produced a low degree of heterotactic PLA, and similar complexes with alkylamine coordination ligands produced isotactic PLA. The stereoselectivity of the *rac*-lactide polymerization was affected by the pattern of the monoanionic aminophenolate ligands coordination. Moreover, complexes of tetrametallic lithium and sodium diamino-bis(phenolate) were investigated for their efficacy in the polymerization of *rac*-lactide, and these complexes were able to produce PLA with narrow  $M_w$  dispersities [36].

A recent study reported the use of a biodiesel fuel by-product, glycerol, to produce *rac*-lactide, a monomer for producing stereoblock PLA [37]. The method employed a hydrothermal reaction in the presence of alkaline catalyst to produce racemic lactide. The lactide was further purified by acidizing sodium lactate with sulfuric acid, and the resultant lactide was extracted with ethyl acetate to obtain refined lactide. A mixture of lactide isomers (crude lactide) containing both *rac*-lactide and *meso*-lactide was produced via dimerization of lactic acid (*i.e.*, reactive distillation at temperature of 210–230 °C and a pressure of 5–10 mm Hg). The levels of *rac*-lactide and *meso*-lactide in the crude lactide were reported to be 32.8% and 32.6%, respectively, with 34.6% impurities (*i.e.*, LA and oligomer). This crude lactide was then purified with ethyl acetate in a  $N_2$  atmospheric condition via three-time recrystallization to obtain a refined *rac*-lactide of 99.1% purity, with *meso*-lactide (0.2%) and other impurities (0.7%) [37].

Zhu and Chen [38] also reported a new approach to convert *meso*-lactide to *rac*-lactide. On the basis of the “frustrated Lewis pair” concept, this approach utilized the epimerization of *meso*-lactide to *rac*-lactide using 1,4-diazabicyclo[2.2.2]octane (DABCO)/tris(pentafluorophenyl) borane 95% ( $B(C_6F_5)_3$ ) at 2M in toluene, which resulted in 95.4% conversion. This study investigated different types of Lewis acids with different molar concentrations and different polar and non-polar solvents to find optimized conversion of *meso*-lactide to *rac*-lactide. The epimerization method used in this study is versatile since it was able to effectively convert lactide stereoisomers regardless of ratio into *rac*-lactide [38].

### 3. PLA processing

The methods for processing PLA are well-established polymer-manufacturing techniques used for other commercial polymers such as PS and PET [39]. Melt processing is the main technique for mass production of high  $M_w$  PLA in which the PLA resin obtained (as shown in Fig. 4) is converted into end products such as consumer goods, packaging, and other applications. Melt processing is characterized by heating the material above its melting temperature, shaping the molten polymer into desired shapes, and finally cooling to stabilize its final dimensions. Processing of PLA has been extensively reviewed [1,40]. The main objectives of this section are to summarize the key methods used to process PLA and then to provide a short update of new research since our



last review of PLA processing [1]. Additionally, we direct the reader to a number of contributions that explain each processing technique in further detail.

The limiting factors for processing PLA are similar to those for fossil-based polymers: degradation at the upper limits of temperature and shear, and poor homogeneity at the lower limits [39]. However, understanding PLA's thermal, crystallinity, and melt rheological behaviors is critical to optimize its processing and component qualities. Detailed information about these properties is provided elsewhere [13]. PLA is a hygroscopic material and very sensitive to high relative humidity (RH) and temperature [39]. Before PLA can be processed, it should be dried to a water content less than 100 ppm (0.01%, w/w) to avoid hydrolysis ( $M_w$  reduction), as discussed in Section 6.1. During industrial production, PLA is mostly dried to values below 250 ppm water (0.025%, w/w). If PLA is processed at temperatures higher than 240 °C or with longer residence times, the PLA resin should be dried below 50 ppm water (0.005% w/w) to avoid number average molecular weight ( $M_n$ ) reduction [1,41]. To achieve effective drying, the dew point of the drying air should be equal or lower than  $-40$  °C, with an airflow rate greater than  $0.03 \text{ m}^3 \text{ h}^{-1} \text{ kg}^{-1}$  of resin throughput. After the PLA resin is properly dried, melt extrusion is the most important technique for continuous melt processing of high  $M_w$  PLA consumer goods.

### 3.1. Extrusion

Extrusion of PLA in a heated screw is the first step before any further processing of PLA, such as injection, thermoforming or spinning, takes place. Commercial PLA resins can be processed by using conventional screws equipped with a general-purpose screw of L/D ratio (ratio of flight length of the screw to its outer diameter) of 24–30. If PLA is processed in extruders designed for polyolefins, and the extruder is working near to its maximum power, the extruder may not have enough torque to process PLA. So, it is recommended to process PLA in extruders regularly used for polyesters or PS, with similar performance profile. The recommended compression ratio (ratio of the flight depth in the feed section to the flight depth in the metering section) for PLA processing is in the range of 2–3. The extruder provides the heat to melt the resins by heater bands wrapped around the barrel; however, the majority of heat input is provided by the friction of the resin between the screw and the barrel. Thus, to ensure that all the crystalline domains of the semicrystalline PLA are melted, and to achieve an optimal melt viscosity for processing, the heaters are usually set at 40 to 50 °C higher than the melting temperature ( $T_m$ ). The melt rheological properties of PLA play an important role in how the polymer flows during extrusion. Melt viscosities of high  $M_w$  PLA melt viscosities are in the order of

5000–10,000 P (500–1000 Pa s) at shear rates of  $10\text{--}50 \text{ s}^{-1}$ ; these polymer grades are equivalent to  $M_w$  of  $\sim 100,000$  Da for injection molding to  $\sim 300,000$  Da for cast film extrusion applications [1]. Extruding PLA at high temperatures can cause thermal degradation (as explained in Section 6.2), so the temperature profile during extrusion of PLA should be tightly controlled. The thermal degradation of PLA can be attributed to several factors: (a) hydrolysis by trace amounts of water; (b) zipper-like depolymerization; (c) oxidative, random main-chain scission; (d) intermolecular transesterification to monomer and oligomeric esters; and (e) intramolecular transesterification resulting in formation of monomer and oligomer lactides of low  $M_w$  [40]. Processing PLA above 200 °C can degrade PLA through intra and intermolecular ester exchange, *cis*-elimination, and radical and concerted non-radical reactions resulting in the production of CO, CO<sub>2</sub>, acetaldehyde, and methyl ketone [42]. Depending on the rate of the degradation reaction, the end product can be lactide or acetaldehyde. Formation of lactide during extrusion can affect the optical purity of the final extruded PLA; reduce the melt viscosity; produce fuming of lactide (i.e., lactide vapor produced during extrusion); and can condense lactide on equipment surfaces, such as chilled rollers and molds, which is known as “plate out.” To avoid lactide fuming and condensation, the temperature of the surfaces should be increased. Table 1 shows the recommended processing temperatures for a number of commercially available NatureWorks LLC PLA resins known as Ingeo™ PLA.

### 3.2. Injection molding

PLA is primarily injected on machines that have a reciprocating screw extruder, as shown in Fig. 6. In this case, the screw is designed to reciprocate within the barrel to inject the molten polymer into the mold cavities. At the start, the molds close and the nozzle opens, and the screw moves forward, injecting the molten polymer into the mold cavity. Since the polymer shrinks during cooling, the screw is maintained in the injection position by holding pressure steady. Then, the nozzle is closed and the screw starts retracting. During the cooling cycle of the molds, the screw rotates and conveys the melt polymer forward; sufficient cooling time should be provided to produce stable parts. Cycle time of the injection part is extremely important to control shrinkage of the PLA injection-molded parts, which are generally brittle due to the accelerated physical aging of PLA, which is attributed to its low glass transition temperature ( $T_g$ ). PLA parts produced with low  $M_n$  are subjected to faster aging. Likewise, PLA injection-molded parts could exhibit low crystallinity due to the slow crystallization rate of PLA. Furthermore, to avoid excessive shrinkage, processing parameters such as mold temperature, packing pressure, cooling rate, and post-

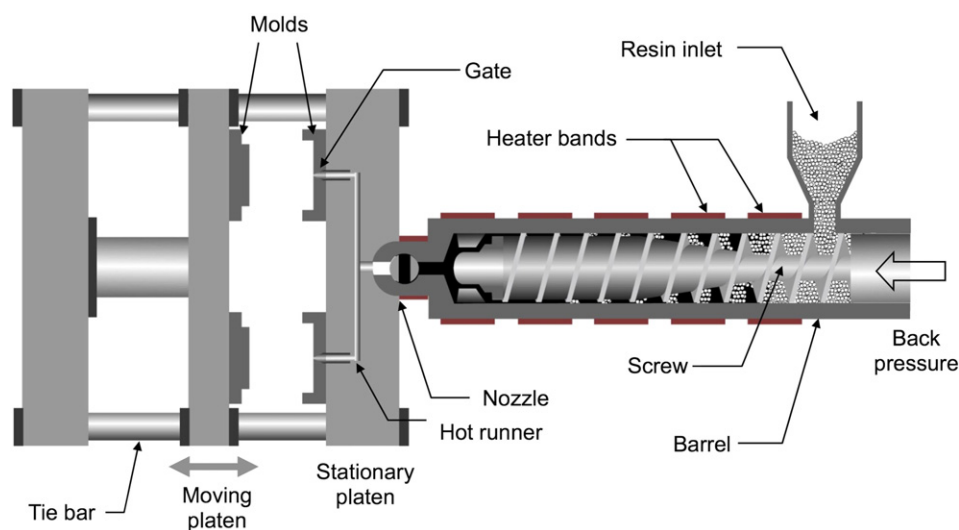
**Table 1**  
Properties and processing temperatures of selected commercially available Ingeo™ PLA resins.

Application	2500HP [43]	3001D [44]	4032D [45]	6060D [46]	7001D [47]	8052D [48]
	Extrusion-crystalline sheets	Injection molding	Biaxially oriented films	Fiber melt spinning	Injection stretch blow molding	Foam
Specific gravity, ASTM D792	1.24	1.24	1.24 <sup>a</sup>	1.24	1.24	1.24
MFR, g/10 min (210 °C, 2.16 kg) ASTM D1238	8	22	N/A	8–10	6	14
Melt temperature, °C	210	200	210	N/A	200–220	200
Feed throat, °C	45	20	45	N/A	20	20
Feed temperature, °C	190	150/165 <sup>b</sup>	180	N/A	180	165
Compression section, °C	200	195	190	N/A	210	195
Metering section, °C	210	205	200	N/A	210–220	205
Nozzle, °C	N/A	205	200	N/A	210–220	205
Adapter, °C	210	N/A	N/A	N/A	N/A	N/A
Die, °C	210	N/A	N/A	N/A	N/A	N/A
Mold, °C	N/A	25	200	N/A	21–38	25
Screw speed, rpm	20–150	100–175	20–100	N/A	N/A	100–175
Back pressure, MPa	N/A	0.345–0.689	0.414–0.483	N/A	0.689–1.379	0.345–0.689

N/A: not available.

<sup>a</sup> ASTM 1505.

<sup>b</sup> 150 °C amorphous/165 °C crystalline.

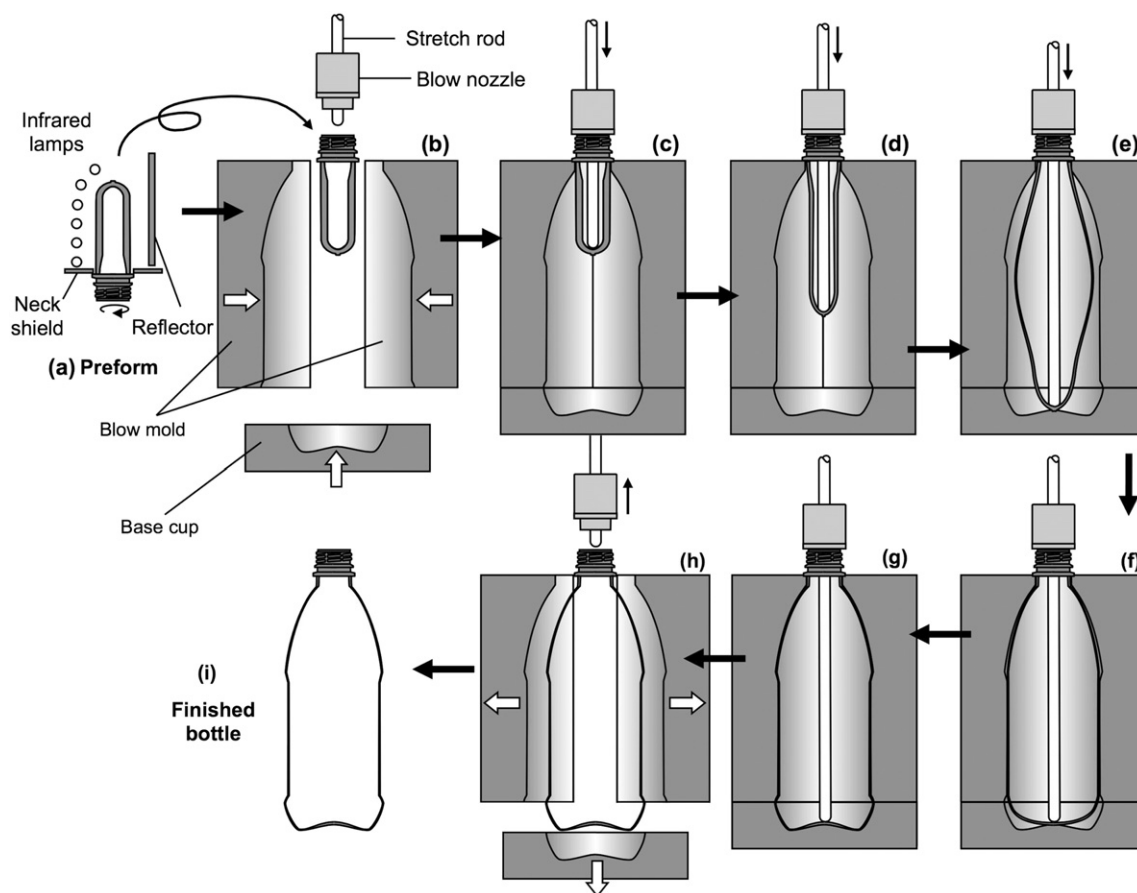


**Fig. 6.** Major components of an injection molding machine showing the extruder (reciprocal screw) and clamp units. "Reprinted from Progress in Polymer Science, 33, Lim et al., Processing technologies for poly(lactic acid), 820–852, copyright (2008), with permission from Elsevier" [1].

mold cooling treatment should be properly controlled. A complete explanation of how to optimize the cycling time for PLA injection-molded parts and reduce shrinkage is provided elsewhere [1].

Shear-controlled orientation in injection molding (SCORIM) is a technique that allows the enhancement of mechanical properties of semicrystalline polymers, like PLA, by tailoring the morphology of the

solidifying polymer melt using an in-mold shearing action that is externally controlled [39]. As in conventional injection molding, the processing cycle begins with the filling of the cavity. The SCORIM unit, which has two cylinders with their own melt flow path and three operation modes (A, B and C), then can manipulate the melt. Mode-A consists of an out of phase reciprocation of the two pistons; mode-B consists of



**Fig. 7.** Injection stretch blow molding (ISBM) of PLA bottle. "Reprinted from Progress in Polymer Science, 33, Lim et al., Processing technologies for poly(lactic acid), 820–852, copyright (2008), with permission from Elsevier" [1].

an in-phase operation to pump more melt into the cavity; and mode-C consists of applying hydrostatic pressure by two cylinders for offsetting volumetric shrinkage [3].

### 3.3. Injection stretch blow molding

Injection stretch blow molding (ISBM) is primarily used to produce bottles. Fig. 7 shows a general ISBM process for making PLA bottles. ISBM requires the initial production of a parison or preform by injection molding. Then, the preform is transferred to a blow molding machine where it is heated at around 90 °C, and the preform is stretched in both the axial and hoop directions to achieve biaxial orientation, which improves the physical and barrier properties of PLA bottles. Additives are added to the PLA resins to optimize the absorption of energy by the preform from the infrared lamps, so that optimal stretching is achieved. PLA preforms tend to shrink after reheat in regions near the neck and the end cap (i.e., regions where the residual injection stresses are largest). Residual stresses can be minimized by properly designing the preform. ISBM can be conducted in one or two stages where the preform is produced during the same step as blowing or it is just produced in two consecutive steps [1]. PLA resins show strain-hardening when stretched to a high strain ratio. Therefore, stretching of PLA should be programmed to obtain PLA bottles with optimal sidewall orientation and thickness. Under-stretched preforms result in bottles with large wall thickness variation and lower mechanical properties. Over-stretched preforms result in stress whitening due to the formation of micro-cracks on the bottle surface that diffract light. Preform axial stretch ratios of 2.8–3.2 and hoop stretch ratios of 2–3, with the desirable planar stretch ratio of 8–11, are recommended [1]. Introducing standard features in the bottle design, such as transition shape, step changes, and pinch points on the core and cavity, may help to improve PLA bottle performance. Preform designs are also important for obtaining bottles with good clarity and physical properties, which usually depends on the bottle design and the blow mold equipment; however, there is little information about that in the literature due to the proprietary nature of this information.

### 3.4. Cast film and sheet

Cast is the main method to produce films with thickness  $\leq 0.076$  mm and sheets with thickness typically  $\geq 0.25$  mm. During the production of cast films, molten PLA is extruded through a lip die and quenched on polished chrome rollers refrigerated with cooled water. Cast films usually have a low crystallinity and transparent appearance due to the rapid cooling provided by the chilled rolls. Cast film extrusion has the advantages of providing good optical properties, high production rate, and good control of film thickness [39]. Deckle systems to control film and sheet edge trimming are generally avoided to reduce the effect that the degraded molten PLA introduces in the edge instability. The gap of the die is set to around 10% higher than the thickness of the film and/or sheet to obtain the right film and sheet dimensions. Table 1 shows the recommended temperatures to extrude PLA films and sheets (PLA 4032D and 2500HP). Horizontal roll stacks are used to produce PLA films and sheets due to the polymer's low melt strength. Roller temperature between 25 and 50 °C is recommended to avoid lactide condensation, and by using an exhaust system around the die, lactide buildup can be controlled. Additionally, good contact between the web and the rolls is recommended to minimize lactide buildup. Slitting and web handling of PLA is similar to that for PS. Rotary shear knives are recommended for trimming the edge of PLA web since razor knives could yield rough edges and break the web. Orientation between 2 and 10 times its original length will improve PLA thermal and impact sheet properties. PLA films produced from 98% L-lactide can be subjected to 2–3 times machine direction (MD) stretch ratios, and 2–4 times transverse stretch ratios. When a larger amount of D-lactide is present in PLA, more amorphous sheet or film is produced, and larger

stretch ratios can be obtained. Extruded PLA films and sheets have excellent optical properties and high Young's modulus, but low elongation at break and toughness [40]. Table 2 shows the main optical, physical,

**Table 2**

Selected average optical, physical, mechanical, and barrier properties of PLA films reported from a number of studies using different grades of PLA, adapted and modified from Auras [49].

<b>Optical</b>	
Refractive index <sup>a</sup> [50]	1.35–1.45
Clarity	Clear-yellow
<b>Thermo-physical</b>	
Density amorphous, kg m <sup>-3</sup> [51]	1250
Density 100% crystalline, kg m <sup>-3</sup> , b [50]	1490
Van der Waals volume (V <sub>w</sub> ), cm <sup>3</sup> mol <sup>-1</sup> , c [50]	34.45
Molar volume of glassy amorphous (V <sub>g</sub> ), cm <sup>3</sup> mol <sup>-1</sup> , c [50]	55.12
Molar volume of semicrystalline polymer (V <sub>c</sub> ), cm <sup>3</sup> mol <sup>-1</sup> , c [50]	49.44
Solubility parameter ( $\delta_p$ ), 25 °C, MPa <sup>0.5</sup> [2]	19–20.5
T <sub>g</sub> , °C [52]	50–80
T <sub>m</sub> , °C [52]	130–180
Initial decomposition temperature (T <sub>d,0</sub> ), °C [53]	335
Half decomposition temperature (T <sub>d,1/2</sub> ), °C [53]	395
Average energy of activation (E <sub>act</sub> ), kJ mol <sup>-1</sup> [53]	205–297
Enthalpy ( $\Delta H_m$ ), 100%, J g <sup>-1</sup> [54]	93
Crystallinity, % [53]	0–40
Heat deflection temperature, °C [55]	55–65
Vicat penetration temperature, °C [55]	59
Thermal conductivity $\times 10^{-4}$ , cal cm <sup>-1</sup> s <sup>-1</sup> °C <sup>-1</sup> [1]	2.9
Heat capacity, cal g <sup>-1</sup> °C <sup>-1</sup> [1]	0.39
Thermal expansion coefficient $\times 10^{-6}$ , °C <sup>-1</sup> [1]	70
Surface tension, dyn cm <sup>-1</sup> [2]	42.0
Friction coefficient, [2]	0.37
Melt flow index, g min <sup>-1</sup> , d [2]	0.85
<b>Rheological</b>	
Mark-Houwink constants	
K, mL g <sup>-1</sup> , e [56]	0.0174
a <sup>e</sup> [56]	0.736
<b>Mechanical</b>	
Tensile strength at yield, MPa [2]	0.88
Elastic modulus, GPa [2]	8.6
Elongation at break, % [2]	3–30
Flexural strength, MPa [55]	70
Flexural modulus, GPa [55]	3.8
Unnotched izod impact, J m <sup>-1</sup> [55]	106
Notched izod impact, J m <sup>-1</sup> [55]	26
Rockwell hardness [55]	88
Impact strength	Poor
<b>Barrier</b>	
Oxygen permeability $\times 10^{-18}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> at 25 °C f [52,54]	1.21 $\pm$ 0.07
Oxygen activation energy, kJ mol <sup>-1</sup> [25–45 °C] f [52,54]	41.43 $\pm$ 3.5
Carbon dioxide permeability $\times 10^{-17}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> at 25 °C g [52]	2.77 $\pm$ 0.05
Carbon dioxide activation energy, kJ mol <sup>-1</sup> , g [52]	15.65 $\pm$ 0.63
Nitrogen permeability $\times 10^{-19}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> [57]	468
Nitrogen activation energy, kJ mol <sup>-1</sup> [57]	11.2
Water permeability $\times 10^{-14}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> at 25 °C h [52,54]	1.75 $\pm$ 0.05
Water activation energy, kJ mol <sup>-1</sup> h [52,54]	–9.73 $\pm$ 0.27
D-limonene permeability $\times 10^{-19}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> , i [58,59]	<1.0
Ethyl acetate permeability $\times 10^{-19}$ , kg m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> , i [58,59]	5.34
Methane permeability $\times 10^{-18}$ , m <sup>3</sup> (STP) m m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> [57]	7.50
Methane activation energy, kJ mol <sup>-1</sup> [57]	13
Helium transmission rate $\times 10^{-6}$ , cm <sup>3</sup> cm m <sup>-2</sup> s <sup>-1</sup> kPa <sup>-1</sup> , j [60]	10.30

N/A: not available.

<sup>a</sup> Refractive index values for PLA were calculated by Gladstone and Dale, Vogel, and Lloyenga methods.

<sup>b</sup> Density of 100% PLA was calculated according to the group contribution method.

<sup>c</sup> PLA value was calculated using the group contribution method.

<sup>d</sup> PLA value measured at 200 °C and 5 kg according ASTM D1238.

<sup>e</sup> PLA value was measured according to ASTM D445 and D446 (PLA values were determined in tetrahydrofuran at 30 °C).

<sup>f</sup> Oxygen activation energy is reported for temperatures between 25 and 45 °C.

<sup>g</sup> Carbon dioxide activation energy is reported for temperatures between 25 and 45 °C.

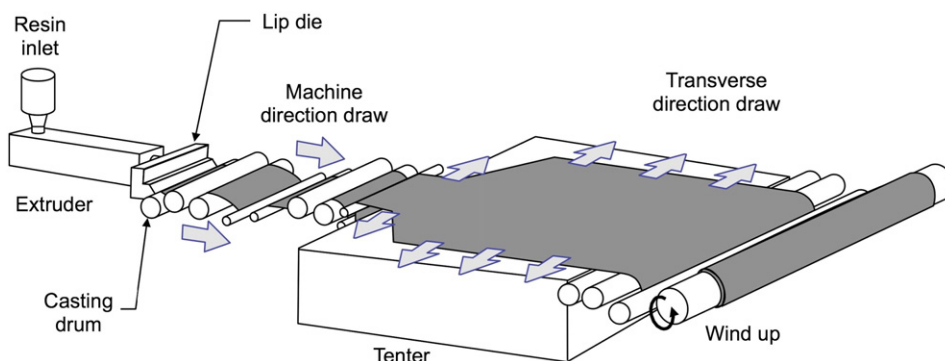
<sup>h</sup> Water activation energy is reported for temperatures between 10 and 37.8 °C.

<sup>i</sup> Ethyl acetate values of PLA at 3030 Pa and 30 °C and 9435 Pa and 30 °C, respectively;

D-limonene values of PLA at 245 Pa and 45 °C and 45 Pa and 23 °C, respectively.

<sup>j</sup> Value of amorphous PLA at 23 °C and 0% RH.





**Fig. 8.** Biaxial oriented extrusion cast film machine. "Reprinted from Progress in Polymer Science, 33, Lim et al., Processing technologies for poly(lactic acid), 820–852, copyright (2008), with permission from Elsevier" [1].

thermal, mechanical, and barrier properties of PLA films. Fig. 8 shows the production of biaxially oriented PLA extrusion cast film.

Production of PLA film by blown film technologies is rarely done since PLA has weaker melt strength, and so formation of a stable bubble during extrusion is challenging. Attempts to create PLA blown film have been conducted by using viscosity enhancers. Most of the additives used to increase the melt strength of the PLA are proprietary [40]. Besides low melt strength, PLA is stiff, so when collapsing the bubble during blown film production, permanent wrinkles may be produced. The problem of dead-fold properties can be overcome by also introducing additives.

### 3.5. Thermoforming

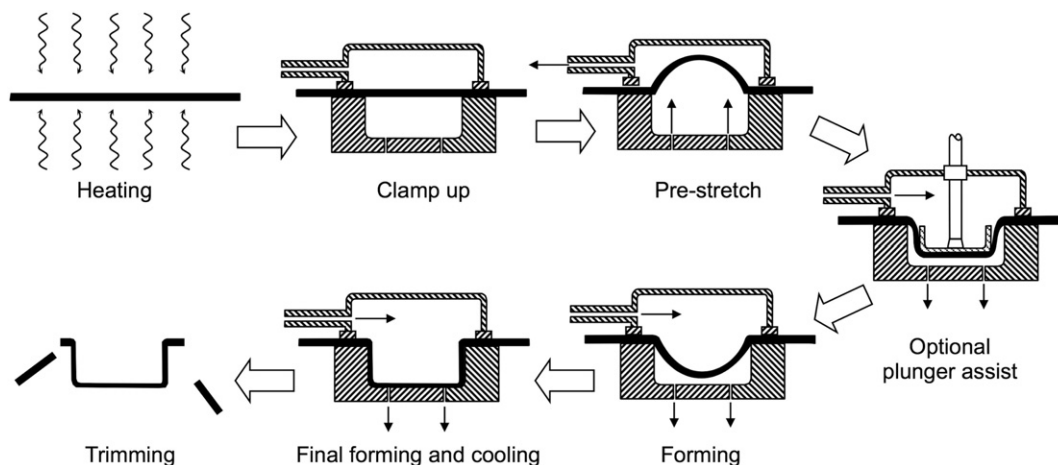
Thermoforming is a standard method to produce PLA containers, such as clamshell, cups, and food trays, extensively used for short-shelf-life product packaging applications. Thermoforming is a process in which a pliable plastic is pressed into a final shape by vacuum or air pressure. Fig. 9 shows the steps to produce a thermoformed PLA part. Generally, a PLA sheet (thickness > 10 mil or 254  $\mu\text{m}$ ) is extruded as previously described, heated, introduced to a mold where it is pre-stretched and then formed (assisted or not by a plunger) to obtain the final PLA container. Initial heating of the PLA film is by infrared (IR) lamps; the IR wavelength should match the maximum absorbance of the polymer being thermoformed. PLA sheets are thermoformed at temperatures around 80–110  $^{\circ}\text{C}$ . Aluminum molds are recommended for thermoforming PLA. As in the case of ISBM, orientation improves toughness of PLA containers; therefore, thermoformed parts are less brittle

than PLA sheet, especially in regions highly stretched during the forming operations rather than flanges and lips. Clamshells produced from PLA sheets show better drop-impact properties at freezing temperature ( $-20\text{ }^{\circ}\text{C}$ ) than PET and PS clamshells [61]. PLA sheets produced with 100% recycled PLA flakes showed a reduction of  $M_n$  of around 5% compared with the original PLA samples; however, this reduction did not affect the production of PLA containers with 100% post-consumer recycled (PCR) PLA content [62].

### 3.6. Other processes—Foaming and fibers

PLA resins are used in foam and textile applications. Although methodologies for these applications are well established for other commercial polymers, until now the amount of commercial PLA (by weight) marketed in these forms has been minor. Obtaining lightweight materials with improved cushioning, insulation, and structural performance is a major reason to produce PLA foam parts. Initially, PLA foams were extensively used for medical applications (sutures, implants, and screws), but it is also a promising bioplastic for use in relatively short-lived applications like transport packaging (loose-fill packaging, insulation, and cushioning) or disposable cutlery. In this context, PLA would allow an alternative disposal route and replace fossil-based foams since the polymer is biodegradable and based on renewable resources [63].

Most commercial foaming of PLA is obtained by batch or continuous processes. In these processes, a physical or chemical foaming agent (PFA or CFA) is introduced in the PLA matrix. PFAs are dissolved in the molten PLA matrix and undergo a physical change, such as volatilization of a liquid or release of compressed gas, during foaming. Examples of PFAs



**Fig. 9.** Production of a thermoforming part. "Reprinted from Progress in Polymer Science, 33, Lim et al., Processing technologies for poly(lactic acid), 820–852, copyright (2008), with permission from Elsevier" [1].

are hydrocarbons and halogenated hydrocarbons and gases such as  $N_2$ ,  $CO_2$ , and Ar. CFAs are chemical compounds which are stable at room temperature, such as sodium bicarbonate, azodicarbonamide, *p,p'*-oxybis(benzene)sulfonyl hydrazide, *p*-toluenesulfonyl semicarbazide, and 5-phenyltetrazole, but after a set change of temperature and pressure conditions, these compounds convert to gas by undergoing a chemical reaction that provides gas to nucleate bubbles inside the PLA matrix and create the foam structure. CFAs can react endothermically (i.e., absorption of heat during decomposition), or exothermically (i.e., release of heat during decomposition) [64]. Generally, CFAs are selected to be used at temperatures close to the processing temperature of the polymer. In the case of PLA, a number of PFAs and CFAs have been used such as  $CO_2$ ,  $N_2$ , and BIH40 (a CFA produced by Boehringer Ingelheim Chemicals) [64].

During the batch process, a gas ( $N_2$ ,  $CO_2$  or a mixture) is saturated into the PLA matrix at a pressure below 800 MPa at room temperature in a chamber. Then, the saturated PLA sample is removed from the chamber, and the solubility of the blowing agents is suddenly reduced by increasing the temperature and/or reducing the pressure, so that bubbles can nucleate. Finally, the produced cells are vitrified by reducing the temperature below the  $T_g$  of the PLA matrix. Fig. 10a shows a representation of a batch process.

The continuous microcellular foaming process was developed to overcome some of the drawbacks of the batch process, for example, the time required to saturate the samples. In a continuous process, a blowing agent, generally a gas, is introduced into the molten PLA matrix in a modified extruder (Fig. 10b). After that, the saturated gas PLA matrix is solution mixed and transferred to a static mixer, which guarantees the single-phase solution. Finally, the microcellular nucleation occurs in the nozzle of the extruder unit due to the rapid pressure drop. PLA foaming is affected by a number of parameters such as initial crystallinity, melt rheology, fillers, amount of CFAs, and processing conditions. A detailed review of PLA microcellular foams can be found elsewhere; PLA foam samples have been reported to increase notched izod impact strength by more than triple while reducing the specific density by almost half [64].

PLA's low melt strength is the main drawback of using it for foaming applications; however, new modifiers are being investigated to induce crosslinking, chain extension, or grafting to increase the molecular weight and the melt properties such as shear and elongational viscosity. Gottermann et al. [63] reported that the use of modifiers, such as organic peroxide, multifunctional epoxide, styrene maleic anhydride,

isocyanurate + diisocyanate, and bisoxazoline + diisocyanate, helps to increase the  $M_w$  of commercially available PLA. In most cases the foam density decreased and cell size increased (except with multifunctional epoxide), and when modified with organic peroxide and multifunctional epoxide the elongational viscosity of PLA increased [63].

Spinning of PLA fibers has been used to produce PLA fibers for suture applications. PLA fibers are gaining importance since they have lower water barrier properties. Conventional processes and finishing technologies can be used for processing PLA fabrics; PLA shows similar properties to other synthetic fibers, but requires modified dyeing and finishing techniques due to its low affinity to conventional water-soluble dyes [65]. PLA fibers can be used to produce breathable garments. Among the important criteria to produce fibers are: i) to control moisture content to be less than 50 ppm to avoid any possible hydrolytic degradation, and ii) to achieve an optimum drawing temperature ( $>PLA$ 's  $T_g$ ) and drawing speed ( $200\text{--}9000\text{ min}^{-1}$ ) to obtain appropriate crystallinity and strong PLA fibers [66]. During spinning of PLA fibers, the microstructure of the polymer chains is oriented in the axis direction of the fiber, so a fiber with very high aspect ratio (length to diameter) and orientation can be produced. Spinning of fibers produces a controlled molecular orientation and spatial arrangement of the PLA structure. In modern spinning processes, a molten polymer or solution is extruded through a small orifice and is elongated by applying an external force. Then, the polymer filament is cooled and precipitated. Further processing of the polymer filament may take place, such as drawing, unidirectional stretching, and texture control. PLLA with a  $M_w$  around  $0.5\text{ to }3.5 \times 10^5\text{ Da}$  is used for melt spinning through a two-stage process that includes melt spinning and hot drawing [67]. A standard melt spinning process is represented in Fig. 11. A typical melt temperature profile for PLA resin melt spinning is shown in Table 2. A general extrusion process, as described in Section 3.1, is used to produce the fibers; however, the spin pack plays an extremely important role since it delivers the molten PLA previously filtered to remove impurities to the spinneret plate through the spinneret holes. The spinneret holes have a specific ratio of length to diameter to achieve the desirable shear flow mode. Spinneret plates can be monofilament or multifilament. Denier, the unit used to quantify filaments, is defined as weight in grams of a 9000-m long filament. For PLA, the recommended diameter of the spinneret holes ranges from 0.2 to 0.35 mm with a typical ratio of 2–3. Larger hole diameters are necessary for filaments greater than 6 deniers. After the filament is produced, it is air cooled at temperatures about  $15\text{--}30\text{ }^\circ\text{C}$  in an air quench zone or chamber, which cools the filament

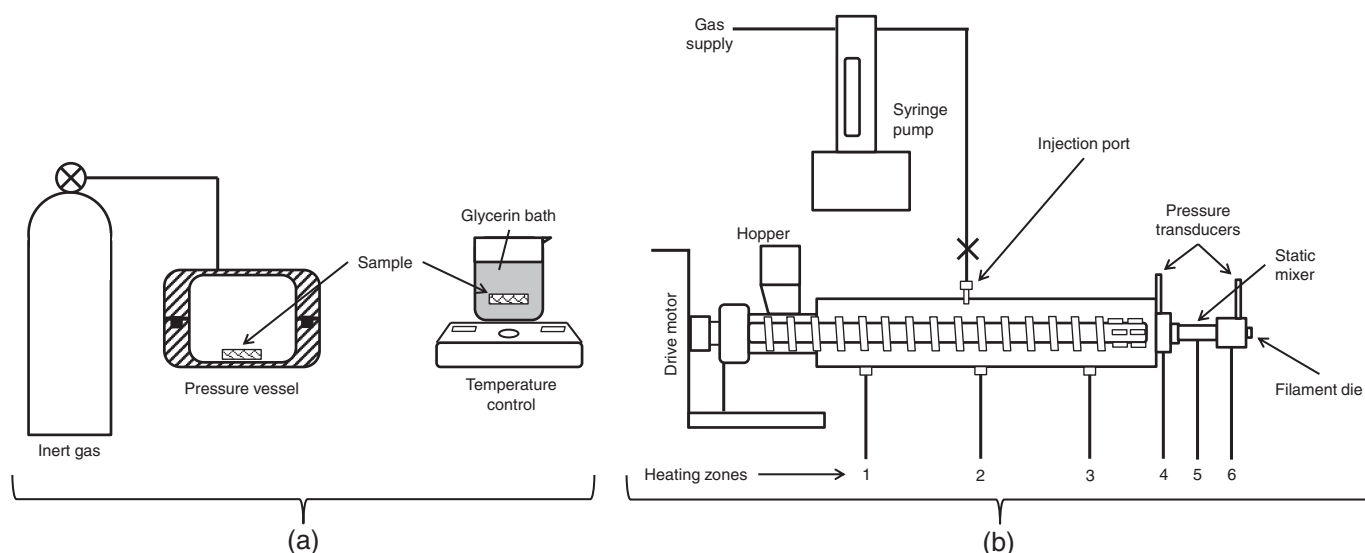
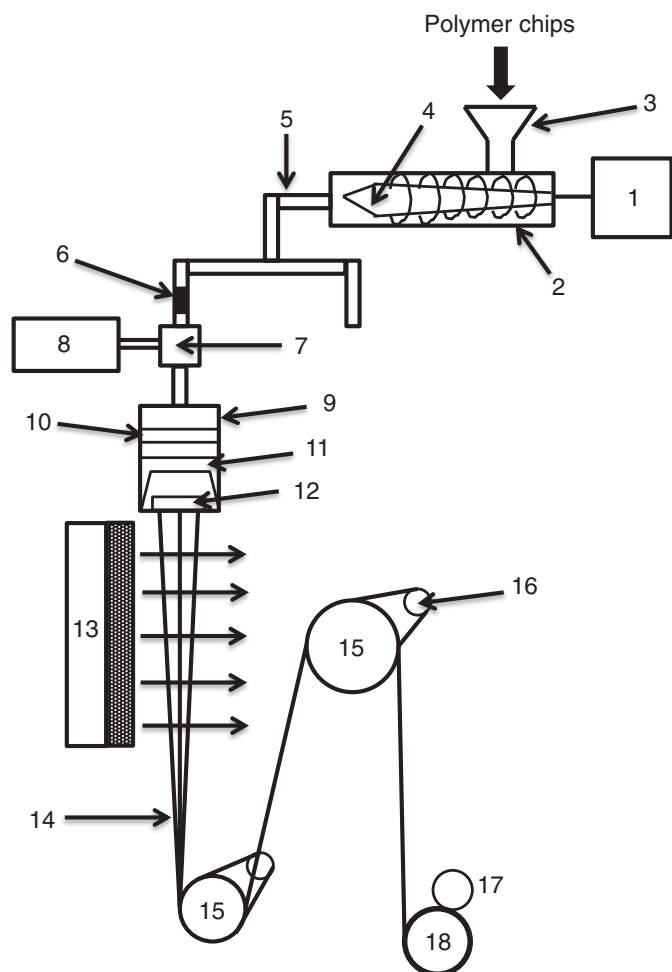


Fig. 10. Schematic of microcellular foaming process: (a) batch process, (b) continuous process; 1 to 6 are the main regions of the extruder; adapted from Matuana [64].



**Fig. 11.** Schematic representation of melt spinning setup: (1) extruder drive, (2) single-extruder—24–36:1 L/D ratio, (3) hopper, (4) screw, (5) manifold, (6) static mixer, (7) metering pump, (8) metering pump drive, (9) spin pack, (10) mesh filters, (11) distributor, (12) spinneret, (13) cross-flow quench chamber, (14) freshly spun yarn, (15) godet, (16) idler roller, (17) friction-driven winder, and (18) yarn bobbin, adapted from Agrawal [67].

through its melt crystallization temperature ( $T_{mc}$ ) and to its  $T_g$ . When the spun filament temperature is below the  $T_g$ , the spinning process is considered complete. Then, the spun filament needs to be finished and wound up. A detailed description of the production of melt spinning PLA fibers can be found elsewhere [67].

Solution spinning of PLA can also be carried out to avoid the substantial hydrolytic degradation that happens during melt spinning. During solution spinning, PLA is extruded as in melt spinning, but then the spinneret is submerged in a spinning bath, so that the PLA melting point is immediately depressed to below room temperature. After that, the solvent is removed by solvent-assisted coagulation or evaporation. Two main methods are used for solution spinning: wet and dry spinning. During wet spinning, PLA is dissolved in a solvent such as tetrahydrofuran, chloroform and/or dichloromethane, and then it is extruded in a submerged bath with a mixture of a solvent and a non-solvent (e.g., toluene at 110 °C) to induce coagulation. Generally, PLLA with  $M_w < 3 \times 10^5$  Da is not suitable for wet spinning. During dry spinning, after the PLLA dope solution (e.g., PLLA in chloroform) is extruded, and pumped through a multi-hole spinneret, it is introduced in a chamber with circulating heated air/gas, so that the solvent can evaporate. PLA fibers are used for textiles and medical applications; examples of these applications are presented in Section 5.2.

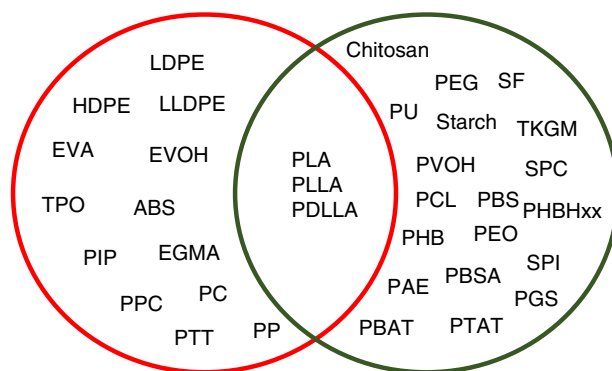
#### 4. Tailoring PLA properties

Although PLA has many desirable properties for consumer good applications, there are limitations for all-purpose use, as with any polymer. Researchers have been trying to expand PLA use and applications by blending PLA with a number of biodegradable and non-biodegradable resins, and/or by compounding PLA with a number of fillers such as fibers and micro- and nanoparticles. Covering all of the blends and composites in a short overview is a daunting task, and a number of review papers have been written to discuss the improvements of PLA properties [68–73]. Therefore, this section provides a summary of the main resins used to blend and/or compound with PLA, and it will direct the reader to the original work to obtain additional information.

Blending of PLA with biodegradable and non-biodegradable polymers has been extensively reported [71–73]. Fig. 12 shows the main biodegradable and non-biodegradable resins blended with PLA. PLA is considered a brittle polymer, so extensive research has been conducted to improve its toughness for different applications [74,75]. In general, a rubbery polymer with low  $T_g$  (generally below 20 °C of the use temperature) is blended with PLA at a low ratio to create small rubber domains between 0.1 and 1.0  $\mu\text{m}$  with good interfacial adhesion to PLA, so that the rubber domains can dissipate the impact energy when PLA is failing through fracture [76]. Beside an improvement in toughness, different polymers have been blended to PLA to improve properties such as optical [75,77], barrier [78–83], thermal [74], and biodegradation [84–88].

A polymer composite is defined as a material that has two or more distinct phases. One of the phases is a discontinuous phase considered as the reinforcement phase dispersed in a continuous or matrix phase. The reinforcement phase can be fibers and/or micro- and nanoparticles. The main goal of adding a reinforcement phase to PLA is to tailor its properties, such as elongation at break [81,132–141], heat resistance [138,142,143], dimensional stability [137,144–147], barrier [132,137,140,148,149], and cost [150], to overcome some of PLA's shortcomings properties compared with fossil commodity polymers, as well as brittleness and low thermal stability [2]. Since the main engineering properties of a composite result from the discontinuous phase, PLA has been reinforced with natural and synthetic fibers, micro- and nanofillers [73,151].

Fibers with a larger length to diameter ratio can be used to carry load in fiber-PLA composites, and increase their applications [73]. Natural and synthetic fibers have been used to reinforce PLA. Dispersion and orientation of the fibers play a crucial role in obtaining PLA composites with the desired properties. Adhesion between the PLA matrix and the



**Fig. 12.** Selected biodegradable and non-biodegradable blends of PLA polymers: PLA-LDPE [89], PLA-LLDPE [90], PLLA-LDPE [90–92], PLLA-HDPE [91], PLA-PS [93], PLLA-PEVA [94], PLLA-EVOH [95], PLA-TPO [96], PLLA-ABS [97], PLLA-PIP [98], PLA-PVOH [99], PLA-PHB [100], PLLA-PBS [101,102], PLA-PBSA [103], PLA-PBAT [104,105], PLLA-PTAT [106], PLA-PAE [107], PLA-PU [108], PLA-PEG [109], PLA-SPI [110], PLA-SPC [110], PLA-SF [111], PLA-TKGM [112], PLA-chitosan [83,113], PDLLA-chitosan [114], PLLA-chitosan [114], PLLA-PBSL [115], PLLA-PEO [116], PLA-PCL [117–119], PDLLA-PCL [117], PLA-PCL [120], PLA-starch [121–124], PLA-PHBHxx [125], PLA-PPC [126], PLA-PP [127], PLA-PC [128], PLA-PGS [129], PLA-PTT [130], and PLA-EGMA [131].

fibers is a strong controlling parameter of the final composite properties since enhancement of the composite performance is strongly attributed to the adhesion between the continuous and discontinuous phases. Wood and non-wood natural fibers, such as cotton, jute, flax, kenaf, sisal, and hemp, are extremely attractive to be compounded with PLA since they are 100% renewable and so a fully bio-based composite is obtained. Synthetic fibers, such as glass and carbon-based, are also commonly used to reinforce PLA parts since they have extremely high tensile strength, which improves the final mechanical properties of the composite [73].

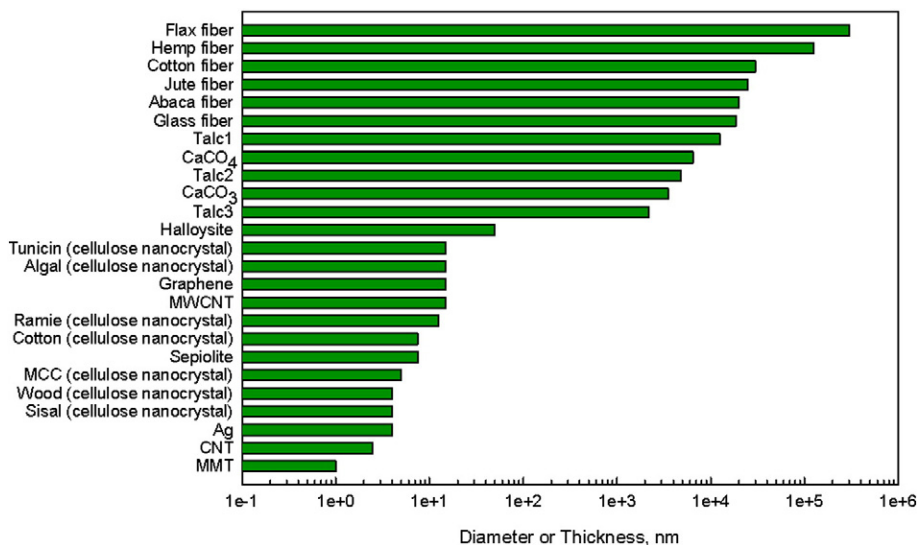
Fillers in micro- and nanosizes have played an increasing role in creating composites with lower cost and environmental footprint. Inorganic fillers, such as talc, mica, hydroxyapatite, carbon black, and gypsum, have been used for many decades to reinforce polymers since they can enhance PLA mechanical properties with a small amount of composite. Lately, the addition of nanoparticles has gained attention since adding nanoscale clay particles results in a significant improvement of material performance. Some of the specific nanocomposite properties that are enhanced through the exfoliation of these nanoparticles include mechanical [152–160], barrier [132,137,140,148,149,160,161], and thermal properties [156,157,160]. The mechanical property of polymers with a nanoclay loading of 3–6% can achieve equivalent mechanical properties (*i.e.*, tensile strength, impact strength, flexural modulus) to a polymer with up to 30 wt.% fillers at the microscale (*i.e.*, glass and mineral fibers, etc.) [162,163]. Since clay platelets are considered impermeable to small molecules (*e.g.*, gasses, liquids), and their presence in the polymer matrix extends the diffusion path of small molecules through a tortuous path, nanoclays can improve the barrier of the nanocomposite [164]. Although a recent study showed that in the case of organic compounds, it is the sorption of the compound to the surfactant added to the nanoclay that modifies the barrier property of PLA (*i.e.*, by modifying the solubility parameters) [165]. The high thermal stability of clays allows their use in polymers for heat-resistant and flame-retardant applications. Enhancement in polymer thermal stability is affected by the size of clay particles; nanoclays with an aspect ratio (lateral dimension vs thickness) greater than 100 are usually preferred [163]. Well-dispersed nanoclay particles in a polymer matrix can act as both a superior heat insulator [166] and mass transport barrier [167]. Fig. 13 shows the diameter or thickness of selective micro- and nanofillers that have been added to PLA.

## 5. PLA industrial applications

Production of PLA for industrial applications has risen steeply due to its competitive cost and the positive public perception of the polymer's environmental footprint. Industrial applications for PLA can be categorized into two main groups: consumer durable goods and consumer non-durable goods. From an economic perspective, consumer durable goods are commodity products with a lifetime of more than 3 years such as appliances, cars, and medical products. Consumer non-durable goods are products having a lifetime up to 3 years such as packaging, short-term medical items, and serveware [189]. In some cases these product categories may overlap, depending on the PLA design. The next section lays out the industrial applications for PLA according to commercial usage categories: medical, fibers and textiles, packaging and serveware, environmental remediation, and others.

### 5.1. Medical

Since the early 1960s, PLA has been used for medical applications such as implants and medical devices. PLA found a favorable niche for medical implants since it degrades over time; therefore, the removal step of an implant is not required. Also, LA is naturally produced by the body and has no known toxicity effect on humans. Various applications for PLA as medical implants include tissue growth, bone grafting, and fracture fixation devices. PLA is commonly used in combination with other polymers and/or proteins, such as polyglycolic acid (PGA), glass fiber, collagen, carbon fiber, and hydroxyapatite (HA) ceramic, to improve its functionality for stabilization of fractures, fixation of tendons and ligaments, and improvement of mechanical properties. On the other hand, degradation of PLA has been reported to lower the pH of cells/tissues due to the accumulation of LA, leading to inflammation of the in-contact tissue [190]. Zhou and Li [191] reported that a composite of PLA–chitosan could alleviate this inflammation issue, as the presence of chitosan neutralizes the PLA-induced pH sites [10,191]. In addition, PLA composite implants may help treat any organ loss or malfunction by stimulating the growth of the natural cells around the polymer part. The American Society of Plastic Surgeons has recently promoted dermal fillers made of PLA. Such a filler works by stimulating the production of collagen in the human body and is intended for facial improvement [192]. Although extensive documentation is available on



**Fig. 13.** Average scale dimensions of selected fillers in PLA composites: MMT (montmorillonite) [168], CNT (carbon nanotube) [169], Ag [170], sisal [171], wood [168,172,173], MCC (microcrystalline cellulose) [174], sepiolite [168], cotton [175,176], ramie [177,178], MWCNT (multiwall carbon nanotube), graphene, algal [179,180], tunicin [181], halloysite [148], talc3 [182], CaCO<sub>3</sub> [183], talc2 [182], CaSO<sub>4</sub> [184], talc1 [182], glass fiber [185,186], abaca fiber [187], jute fiber [187], cotton fiber [187], hemp fiber [187], and flax fiber [186,188].



the use of PLA composites as medical implants, reports on clinical practice using these implants are scarce, which could be due to possible compatibility issues between the human body and PLA implants. Fast or slow degradation of PLA implants may cause some defense reaction from the human host. Moreover, the toxicity effect may occur for long-term use [190].

The use of PLA medical devices to replace metallic medical devices has been researched for more than a decade. PLA has been sought as an alternative to solve issues associated with metal device implants such as possible corrosion and distortion of magnetic resonance images [192]. For example, Zimmer Biomet®, a musculoskeletal health solutions company, produced Bio-Statak®, a tissue attachment device made of PLLA that is resorbable and was reported to have comparable pullout strength to metal devices [193]. Researchers from the Fraunhofer Institute in Germany in 2010 developed PLA composite screws that are claimed to closely mimic real bone strength as an alternative to titanium surgical implants [194]. Other companies, such as Arthrex™, Phusis, Gunze, Takiron, and Linvatec, have commercialized PLA medical devices for use as interference screws, miniplates, rods, and suture anchors. Most of the aforementioned medical devices are made through a drawing process of PLLA with  $M_w > 7.0 \times 10^4$  Da [190]. This process helps to strengthen the property of the devices to be as close as possible to real bones, and is achieved as a result of the orientation and crystallinity of PLA. The drawing process of PLLA also seems to affect the piezoelectricity property of the devices; this property is associated with stimulation of bone growth [190]. PLA seems to be a better option than metal, but in the case of bone grafting, PLA has slower effect on bone resorption. Moreover, some mechanisms of PLA degradation in the human body are not fully understood. In 2005, Mitek Sports Medicine launched a biocomposite implant known as Biocryl® Rapide®, with the claim of superior function over PLA. By 2013, this biocomposite had reportedly been used for knee and shoulder implants in more than 250,000 patients [195]. Additional examples of PLA use in medical applications are provided in the other reviews of this series. Advanced tailoring and molecular modification of PLA are still needed to expand PLA's function as medical implants.

### 5.2. Fibers and textiles

PLA can be processed into fibers by spinning, as explained in Section 3.6. PLA is suitable for fiber applications due to its ability to absorb organic compounds and its wicking properties. Since the polymer is fairly polar, it can absorb moisture, which makes PLA a suitable candidate for wipes. For example, Biovation® developed a PLA single-use antimicrobial wipe. Fraunhofer UMSICHT and FKUR developed water filters based on PLA blend fibers (Bio-Flex® S 9533)—this blend is reported to contain adsorbent carbon made of coconut shells [196]. Since PLA has excellent wicking properties, the polymer also can be used for disposable products. For example, Biovation launched disposable antimicrobial blood pressure cuff shields called Bioarmour™—this product is composed of 74 wt.% PLA and is intended to protect a patient's skin from being directly in contact with the cuff and provides comfort for patients due to its breathability [197]. Ahlstrom Corporation recently introduced a fine-filament web filter for tea made from PLA fibers—the polymer's wicking ability allows the infusion of the tea flavor into hot water [198].

PLA fibers also are of interest to the automotive industry. Approximately 10% of a vehicle compartment is made of plastic. Various companies, including Ford Motor Company, are looking into environmentally friendly polymer options for car interior parts such as carpets, floor mats, and trim parts. Some companies have started producing parts with different bio-products such as PLA, flax, jute, and cotton. A conference on bio-based materials for automotive applications (bio!CAR) was held in Stuttgart, Germany, in September 2015. However, some obstacles must be solved, such as emission of undesirable odors when the polymer is at high temperature, time span of degradation processes,

and moisture effects toward materials, before PLA can be fully implemented for such applications [199]. A study comparing PET and PLA-based seat fabrics to investigate automotive requirement properties such as seam fatigue, flammability, resistance to abrasion and snagging was performed. The study found that PLA met most of the requirements for automotive fabrics and had comparable performance to PET, but failed in the flammability and abrasion tests [200]. Other biopolymers, such as polyurethane and soy-based polymers, have been investigated for their use in the automotive industry by Daimler AG, Fiat, and the Toyota Motor Group. These major car producers are primarily concerned with the durability of the biopolymers [201]. Some improvements are needed before PLA can replace fossil-based polymers in the car industry.

The use of PLA to replace major synthetic polymers, such as nylon and PET, in the textile industry is increasing. PLA textiles are being used by garment industries (*i.e.*, apparel, homeware). Although PET-cotton blends are a common combination in apparel for established brands like Nike®, Gap®, and Under Armour®, PLA itself is seen as a promising alternative due to its wicking properties and breathability, making PLA a comfortable material for apparel manufacturing. The Hohenstein Research Institute tested the use of PLA and PLA-cotton blends in garments, and found that PLA is suitable for sports apparel due to its thermal insulation and buffering capacity to sweat, among other specifications [202]. PLA had high resiliency when used for making jackets. Also, the ability of PLA to withstand laundry service with multiple washing was tested and was in accordance with the American Association of Textile Chemists and Colorists (AATCC) standards. However, some issues are associated with PLA textiles, such as the pressing and ironing temperatures, which are limited to temperatures lower than those acceptable for PET and cotton [202]. The dyeing and finishing processes for textiles often undergo conditions involving temperature, pH, and time, thus imposing a challenge for PLA since the polymer is susceptible to degradation under the aforementioned conditions [202]. PLA has good retention and crimp properties, so it is suitable for knitted and embroidered textiles. Another application for PLA textile is in homeware use such as curtains, pillowcases, and rugs [203]. Early in 2015, Kansai University and Teijin™ developed a new wearable piezoelectric device to detect “directional changes and arbitrary displacement”—this device is made of laminated PLLA and PDLA [204]. In summary, there is significant potential for PLA to be used by the fiber and textile industries, but its limitations remain an issue and more development and changes are needed for PLA to compete with existing fossil-based polymers.

### 5.3. Packaging and serveware

The use of PLA in packaging and serveware has largely increased over the last 5 years. Research is being performed by both academia and industry with collaborative works between the two to strengthen the green-packaging market to meet consumer demands for packaging derived from renewable resources. PLA has numerous challenges for commercial packaging applications due to its limited mechanical and barrier performance. However, PLA package performance has been improved significantly by tailoring polymer processing, blending with other polymers, and adding compounds, such as nucleating agents, antioxidants, and plasticizers, to meet the end needs [205].

For example, oriented and non-oriented PLA can be produced by tailoring PLA processing. Oriented PLA has considerable thermal resistance with good clarity over non-oriented PLA. Although oriented PLA films pose desirable characteristics, their brittleness is still of concern due to the fragility and loud noise produced by the packages. Frito Lay introduced a compostable PLA bag for their SunChips® brand in 2010, but this bag underwent major public scrutiny over the loud crinkling sounds during bag handling. The bags were later removed completely from the market [206,207]. Oriented PLA films are also used for bakery packaging and gift cards [205]. Meanwhile, non-oriented PLA sheets are preferred for use as thermoformed clamshells to package fresh products



[208] and other products with short shelf life. These clamshells are still being used to pack some Wal-Mart products. Other companies have claimed that the shelf life of the packaged fruits is 10%–15% longer in PLA containers [209]. However, the low barrier properties of PLA toward moisture and gases may cause limitations in other applications. Table 3 shows examples of products that have been and/or continue to be packaged in PLA containers.

Major European markets showed early interest in the use of commercialized PLA. Danone®, for example, launched yogurt cups made of PLA for its Germany market, which accounted for 80% of the total volume of their Activia product line [210]. Other thermoformed PLA products also are available by various companies (Table 3). Packages

produced from non-oriented PLA, however, are limited to non-heat applications. Some other commercial packaging applications for PLA include shrink films and shrink labels. For PLA to meet the requirements for these types of applications, it needs to exhibit shrinkage, which is commonly observed for oriented PLA at temperature above 60 °C with a reported shrinkage ratio of 70% [205]. ConAgra Foods uses recycled PLA shrink film (produced and supplied by EarthFirst®) as tamper-evident seals for its three leading table spread brands: Fleischmann's®, Blue Bonnet®, and Parkay® [211] (Table 3). The use of oriented PLA as shrink labels does have a slight limitation since PLA's shrinkage ratio is low at around 70 °C, which results in whitening of the label due to the crystallization process. Thus, lamination with other polyester films or

**Table 3**  
Selected examples of packaging containers produced from PLA.

Trademark/Commercialized brand	Year active	Improved functions	Applications	Remarks	Ref.
Tenova, Sweden	2003–current	None	Shopping bags	Bags composed of 45 wt.% PLA and 55 wt.% Ecoflex	[220]
Biota®, USA	2004–2006	None	Bottled waters	Advertised as biodegradable bottles No longer on market due to company bankruptcy	[221,222]
Wal-Mart, USA	2005–current	None	Strawberries, brussel sprouts	Advertised as biodegradable clamshells Among the first company to use commercialized PLA	[208]
Del-Monte, USA	2005–current	None	Fresh-cut produce	Advertised as biodegradable clamshells	[223]
SPAR, Austria	2005–current	None	Organic pears, apples, tomatoes	Advertised as biodegradable thermoformed with flexible PLA lid	[209]
Hypermarket chain Auchan, France	2005–current <sup>a</sup>	None	Fresh salads	Advertised as biodegradable containers	[224]
Newman's Own, USA	2005–current <sup>a</sup>	None	Organic salads	Advertised as biodegradable containers	[225]
Pacific Pre-Cut, USA	2005–current <sup>a</sup>	None	Freshly prepared salads	Advertised as biodegradable containers	[226]
Vitamore®, Ihr Platz (drugstore chain), Germany	2006–current	None	Bottled beauty, energy and memory drinks	Advertised as 100% bio-based bottles	[212]
Huhtamaki, Finland	2006–current	None	Dessert cups	Advertised as biodegradable containers	[227]
Greenware®, Fabri-Kal, USA	2008–current	None	Cold drink cups, lids and portion containers	100% biodegradable	[228]
Noble Juice, USA	2008–current	None	Organic and non-organic citrus juice bottles	100% biodegradable	[229]
Apple Inc., USA	2008–current <sup>a</sup>	None	iTunes prepaid gift cards	Current status in market unknown	[230]
Sant' Anna, Italy	2008–current	None	Bottled water	100% biodegradable bottles with PE lids	[231]
Fleischmann's®, Blue Bonnet®, Parkay®, ConAgra Foods, USA	2009–current	Improved shrinkage performance	Tamper evident seals for table spreads	Made of recycled PLA Claimed to reduce 20% of facility's energy consumption	[211]
Reddi-Wip®, PAM®, ConAgra Foods, USA	2009–current	Improved shrinkage performance	Shrink labels for cream whipped topping and cooking spray	Made of recycled PLA Claimed to reduce 20% of facility's energy consumption	[211]
Shiseido-Urara, China	2009–current	None	Bottled shampoo	Favorable reception in Chinese market as an environmentally friendly option	[232]
Wal-Mart; Sams-Club, Mexico	2010–current <sup>a</sup>	None	Small white onion	Bottles are 50 wt.% PLA and 50 wt.% HDPE No longer on the market	[233]
Sunschips®, Frito Lay, USA	2010–2014	Thermal resistance	Potato chips bags	Advertised as biodegradable clamshells Bags withdrawn from the market within a year due to loud crinkling noise Original flavor was retained for a while after incident, but is no longer available	[206,207]
Activia®, Danone, Germany	2010/2011–current	None	Yogurt	Bags composed of 94 wt.% PLA, 6 wt.% adhesive and ink, 0.2 wt.% aluminum liner Improved carbon footprint by 25%	[210]
Stonyfield Farm®, USA	2010/2011–current	None	Organic yogurt multipack cups	43% less fossil resource usage than original package Cups composed of 93 wt.% PLA, 4 wt.% titanium dioxide and 3 wt.% compounded additives	[234]
Polenghi LAS, Italy	2010–current	None	Bottled lemon juice	48% reduction of greenhouse gas emissions Claimed to be the first blown extrusion PLA bottle in EU market	[235,236]
Ceramis®, Amcor's Swiss	2011–current	High barrier toward O <sub>2</sub> , moisture, aroma compounds	Snacks (pouches) Fruits and vegetables (thermoformed) Breads	Silicon oxide coating provides excellent barrier for PLA	[237]
Track & Field, Brazil	2011–current <sup>a</sup>	None	Capsules for athletic apparel		[238]
PURALACT®, the Netherlands	2013–current	Thermoformed containers able to tolerate boiling temperature	Single-use hot beverage cups	Conversion to PLA packaging line is feasible by using an existing PS line	[239]
PURALACT®, the Netherlands	2013–current	Comparable impact resistance to ABS	Serviceware	Safe food contact application, and the containers are microwavable	[217]

<sup>a</sup> Current (2016) market availability could not be confirmed.

blending other polymers with amorphous PLA is used to ameliorate PLA shrinkage properties [205]. Commercial use of PLA shrink labels was reported for soft drink products manufactured by S&B Foods, Nisshin Oilco, and Asahi [205].

PLA is used to produce bottles for water and juices; however, this market is not extensive. Common production for PLA bottles is ISBM, as previously explained. Application for PLA bottles is limited only to non-carbonated beverages due to the insufficient creep behavior of PLA and low barrier toward CO<sub>2</sub> (which results in products with a lack of carbonation). Vitamore<sup>®</sup> carbonated drink in PLA was reported to have shelf life of about 6 months with a moderate loss of CO<sub>2</sub> [212]. Further improvements are needed to tailor the barrier properties of PLA for products with a longer shelf life to expand commercial applications. Some examples of PLA bottled products for the beverage market are listed in Table 3. Despite numerous efforts by manufacturers in introducing PLA-based bottles into the market, further development is needed to obtain PLA bottles with the required commercial properties to compete with the established fossil-based polymers. Nevertheless, Coca Cola<sup>®</sup> has shown interest in bio-based materials, such as high density poly(ethylene) (HDPE) made from sugarcane molasses, for their Odwalla juice beverage line [213]. Tetra Pak, one of the world's leading packaging companies, recently launched a new bio-based carton made of certified paperboard, and bio-based low density poly(ethylene) (LDPE) films with bio-based HDPE caps named Tetra Rex<sup>®</sup>. Valio, a dairy producer in Finland, is currently using these Tetra Pak<sup>®</sup> cartons for Eila lactose-free semi skimmed milk drink for the Finnish market [214].

Production of PLA containers for serviceware applications, such as microwaveable containers and single-use disposable drinking cups, is challenging since PLA is susceptible to heat deformation. For such applications, a higher heat deflection temperature (HDT) is desirable as it allows the molten polymer to mold faster and to retain its dimensional shape once the formed polymer is removed from the mold. The HDT of PLA is reported to be between 55 and 65 °C [1,215], which is too low for producing thermally stable PLA containers for a non-refrigerated supply chain. Therefore, nucleating agents, such as alkylene bisamide [205], Ecopromote<sup>®</sup>—a biodegradable nucleating agent by Nissan Chemical [216], talc, and PDLA, are often incorporated into the PLA [205]. The presence of a nucleating agent helps to induce faster crystallization of PLA, so an increase in HDT can be achieved. For example, Corbion Purac<sup>®</sup> produces PURALACT<sup>®</sup> lactide serviceware, which is microwaveable and has a comparable impact resistance to acrylonitrile butadiene styrene (ABS); production is achieved by manipulating the stereochemistry of PLA with D-lactide monomers, but no further process details have been disclosed by the company [217]. SelfEco, a company under VistaTek LLC, has produced party serviceware items from PLA and its blends [218]. Teknor Apex has developed a PLA series (Terraloy BP-34001) with improved impact strength and HDT of 135 J m<sup>-1</sup> and

112 °C, respectively, which are higher than those of standard PLA (impact strength = 33 J m<sup>-1</sup>; HDT = 55–65 °C). Teknor Apex claimed that this new compound contains 78 wt.% PLA and has the ability for rapid processing with shorter cycle times [219]. It is likely that thermal resistant food serviceware made of PLA will become more available in the coming years.

#### 5.4. Plasticulture

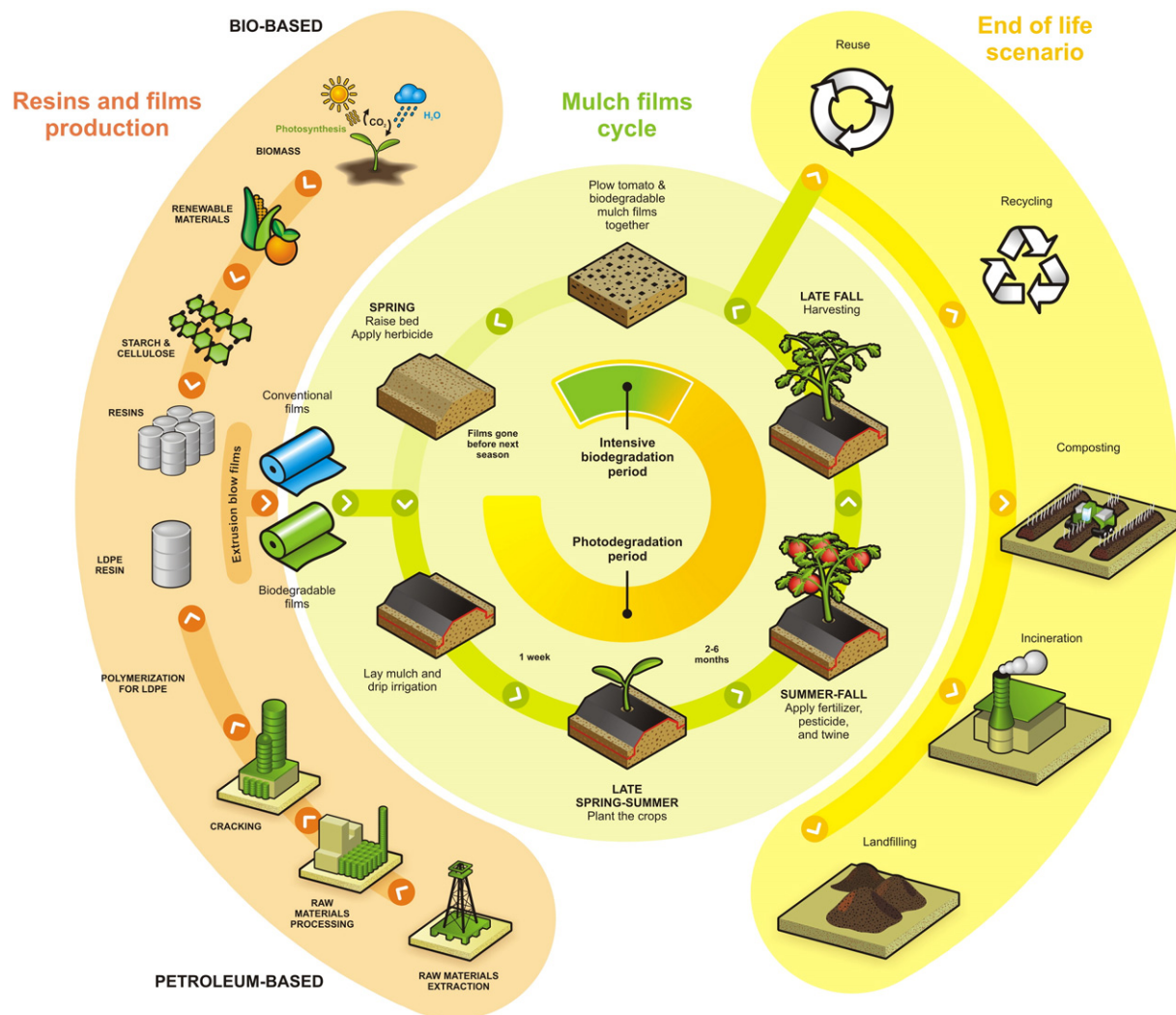
Plasticulture is the use of plastics for agricultural applications. Plastics are used for applications such as i) to protect soils from erosion and plants from weed, insects, and birds via mulch films, ii) to function as drip irrigation tubing, and iii) to cover tunnels of greenhouses (Figs. 14 and 15). The use of plastics for agricultural applications started in the 1950s to improve and increase the growth and production of agricultural products [240]. Conventional non-renewable plastics are the default choice in the plasticulture industry, and poly(ethylene) (PE) is the main polymer in use. However, various issues regarding the use of non-renewable plastics are of increasing concern among agricultural personnel and consumers. Among these issues are cost of waste management, end-of-life options, and consumer demands for more environmentally friendly options. Waste management handling is expensive, due to the additional labor cost for the removal of conventional plastics after use and associated transportation costs. Also, the end-of-life option is not feasible since landfill soil may become contaminated with pesticide residues from the used plastics. Similarly, recycling is not an option and open burning is illegal in several states in the USA [241]. Therefore, biodegradable plastics, such as PLA, poly(hydroxyalkanoates) (PHAs), starch, and poly(butylene adipate-co-terephthalate) (PBAT), are seen as attractive options to help solve these issues [242].

The implementation of biodegradable plastics in the plasticulture industry is still at the early stage and is mostly done at the research level due to the high per-pound cost of the polymers. The most promising outcome to be expected from the use of biodegradable plastics for plasticulture is that they are able to biodegrade after use.

Although, as discussed above, PLA has considerable potential for various industrial applications, the use of homopolymer PLA in the plasticulture industry has been limited due to its poor mechanical and thermal properties. Mulch films (Fig. 15) made with PLA alone are deemed insufficient to protect soils and plants due to brittleness. The relatively high *T<sub>g</sub>* of PLA and less available amorphous region limit the food sources for microorganisms to initiate the biodegradation process at low temperatures [240]. Consequently, PLA is blended with other biodegradable polyesters to produce commercialized PLA-based mulch films [240]. Commercialized PLA-based mulch films are commonly made with plasticizers, and those that incorporate LA derivatives or oligomers demonstrate an accelerated biodegradation process [243, 244]. The accelerated biodegradation of plasticized PLA-based mulch



Fig. 14. (Left) Tomato plots covered with mulch films; (right) high tunnel or overwintering house.



**Fig. 15.** Cradle to gate, grave, and cradle life cycle flowchart of plastic mulch films. After removal of conventional mulch films, they can be reused, recycled, incinerated, and/or landfilled. Biodegradable mulch provides the same end-of-life scenario routes and also can be composted.

films could be attributed to the introduction of free volume in the PLA polymer matrix, allowing the diffusion of surrounding water into the polymer, thus promoting hydrolysis and, in turn, increasing the accessibility of microorganisms to their food sources. This described phenomenon is called bulk erosion. Another phenomenon involved in the biodegradation process is known as surface erosion [2]. Details on hydrolysis of PLA-based films in non-medical environments are provided in Section 6.

### 5.5. Environmental remediation

Removal of contaminants from the environment is known as environmental remediation or bioremediation. Remediation is a waste management method available today to treat water and wastewater by employing mostly sorption and denitrification mechanisms. Theoretically, it is believed that the efficiency of these mechanisms relies on Van der Waals interaction and electronic affinity between contaminants and sorption/source media [245]. The sorption/source media may be adsorbents such as activated carbon, zeolite, and polymers. Biodegradable polymers, such as PCL, PBS, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and PLA, have the potential to be used for environmental remediation [246]. These polymers act either by absorbing the contaminants from any contaminated system (sorption

mechanism) or by supplying carbon and energy to microorganisms to facilitate the denitrification mechanism.

PLA, among other biodegradable polymers, is being investigated for possible use in environmental remediation due to its availability as a raw material and its relatively lower price. One example of commercialized PLA used for environmental remediation is hydrogen release compound (HRC<sup>®</sup>), produced by Regenesys Bioremediation Products (San Clemente, CA). This product is manufactured in a liquid and a gel-like form intended for controlled-release of LA for certain durations [247]. However, to a certain extent, PLA characterization and research for environmental remediation applications are limited. The efficiency of biodegradable polymers for environmental applications relies on their  $T_g$ . In the case of PLA, its ability to adsorb contaminants would be limited to conditions  $>60^\circ\text{C}$  [246]. In addition, PLA has more resistance to microbial activity than that of other biodegradable polymers like PCL [248]. The resistance of PLA toward microbial activity is mainly due to the high molecular weight of commercial PLA ( $\geq 2.0 \times 10^5$  Da). Thus, microorganisms need more time to use PLA as their food source; hydrolysis should reduce the  $M_w$  to be manageable for the microorganisms to use it. Consequently, lower molecular weight PLA is likely a better candidate for the denitrification mechanism. Studies on PLA with  $M_w < 1.0 \times 10^4$  Da showed a significantly greater removal rate of nitrogen than for PLAs of higher molecular weight [246]. Meanwhile, the focus



for environmental remediation applications seems to lie with other aforementioned biodegradable polymers (*i.e.*, PCL, PBS, PHBV) due to their effectiveness in adsorbing contaminants, such as chlorophenols, at room temperature [246].

### 5.6. Other applications

Some other commercialized or potential applications of PLA include paints, cigarette filters, 3D printing, and parts for space exploration [249]. A 3D portable on-board printer was developed by collaborative work of Altran Italia, Thales Alenia Space, and the Italian Institute of Technology for use in space; the printer was produced with approximately 5.5 kg of PLA. PLA characteristics, such as glossiness and multi-color appearance, make PLA one of the main choices for 3D printing. A high accuracy for dimensional parts can be achieved with PLA because it poses less warp behavior than commonly used printing filament materials like ABS [249]. PLA has been used to develop tow fibers for cigarette filters by D.M. Enterprises Pvt. Limited (Hong Kong) to replace cellulose acetate tow. Although cellulose acetate is a natural product, its degradation is relatively slow; the addition of concentrated acid may improve the degradation rate. However, it is not a safe choice for such applications [250]. Therefore, the use of biodegradable polymers like PLA may alleviate the current degradation issue associated with cigarette filters.

Another newly developed application of PLA is as a water-based paint: Fujitsu Laboratories Ltd. developed this product to reduce the level of volatile organic compounds commonly found in solvent-based paints. Isocyanate reactant was used to improve the stability of PLA emulsion and, in turn, the quality for its final application as water-based paint [251]. Additionally, Fujitsu in collaboration with Toray Industries, Inc. in 2005, developed a PLA alloy that had high heat resistance and flame retardant used to mass produce the Fujitsu's FMV-BIBLO notebook models [252]. Similarly, PEGA D&E of PEGATRON Corp. collaborated with the Plastic Industry Development Center (Taichung, Taiwan) to produce an alloy consisting of both PLA and medical recycled PC for use in consumer electronics [253].

Many newer applications of PLA surfaced with the help of existing and newly developed technologies. Most of these applications were achieved through a fundamental understanding of the physicochemical, mechanical, stereo-chemical, and morphological properties of PLA.

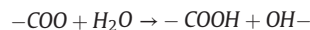
## 6. PLA degradation

PLA polymeric parts can be exposed to different environments during their lifetime, which may promote their degradation. Degradation leads to irreversible changes of the polymer until it gradually fails due to the loss of various properties. Such loss of properties can occur under different mechanisms, including chemical hydrolysis, microbial, photochemical, thermal, and enzymatic degradation, which mainly occur by main chain scission or side chain scission [2,254,255]. Depending on the application, degradation of PLA can be an advantage or a disadvantage. In the case of mulch films or contaminated packages, degradation through different mechanisms is one of the advantages of PLA. In this section, the main mechanisms of PLA degradation in commercial applications are discussed. Biodegradation in medical settings can be found in the other sections of this PLA series.

### 6.1. Hydrolysis

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 products of the hydrolysis self-catalyze the reaction [256–258]. Thus, hydrolysis of PLA starts by the diffusion of water molecules into the amorphous regions, which in turn initiates the cleavage of the ester bonds. Then, degradation continues in the

boundary layer of the crystalline domains [259,260]. The following reaction shows the hydrolysis of the ester groups of aliphatic polyesters, as in PLA, in the presence of water:



Information regarding PLA hydrolysis in non-medical applications, such as in food packaging, plasticulture, and environmental remediation, is scarce. There were only a few studies done in different environments and media (other than in medical settings) in which PLA was in contact with water during its use, leading to hydrolysis reactions.

For example, PLA has been used in plasticulture as mulch films (as shown in Section 5.4) where PLA can be affected by a number of abiotic factors, such as temperature, pH, soil moisture, and UV radiation, which all play relevant roles in the degradation. During abiotic degradation, the mulch films are fragmented, the tensile strength of the material weakens, and a slight reduction of  $M_w$  occurs [240], then PLA is converted into  $\text{CO}_2$ , water, and inorganics. Hydrolysis is one of the mechanisms that helps degrade PLA in this environment. Furthermore, in other agriculture applications, for example during controlled release of herbicides for stimulating the plant growth and improving yield, hydrolysis of PLA takes place since the material is exposed to high RH or put in direct contact with water [8,261,262].

In packaging applications, when PLA is used for fresh produce or beverage containers, it is exposed to humid environments that can trigger hydrolysis reactions. Copinet et al. reported that at high RH, the rate of hydrolysis increases due to absorption of water molecules into PLA. As a result, a decrease of the  $M_w$  was observed, leading to a reduction in  $T_g$  from 60 to 19.4 °C when exposed to 100% RH, and a 50% reduction of the initial percent elongation at break at 30 °C in 15 and 10 weeks when PLA films were exposed to 50% and 100% RH, respectively [263].

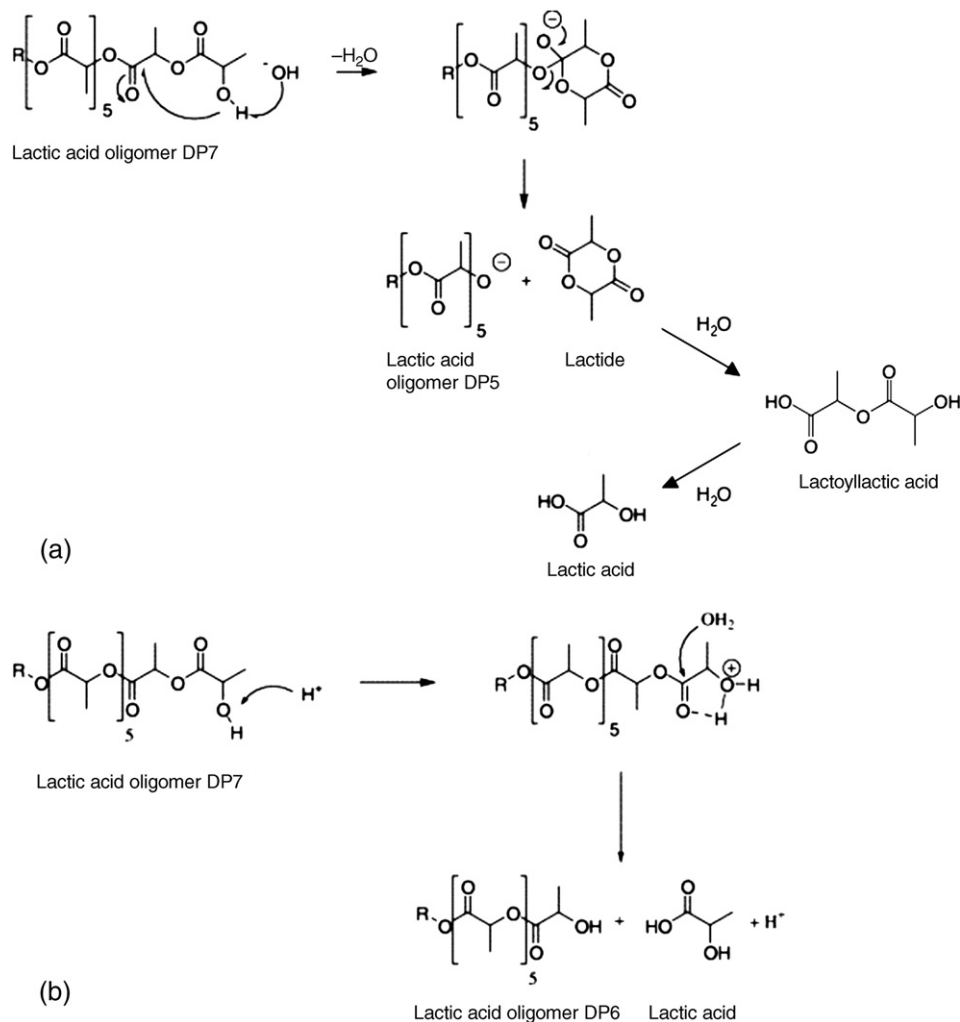
PLA containers have been developed to be in contact with water, cold-chain dairy, and juices, so the PLA is in contact with different environments at different pH and polarity. The medium pH influences the rate of hydrolysis of PLA-based materials. In strong acidic and basic media, polymer chains are more easily degraded since the hydrolysis reactions are catalyzed by the presence of hydronium and hydroxide ions (Fig. 16) [264–267]. For example, if PLA is used for a citrus juice bottle, the PLA will be exposed to an acidic medium (pH < 4) making the hydrolysis mechanism proceed via chain-end scission [257,268].

In PLA containers used for alcoholic products, ethanol will swell the PLA matrix, act as plasticizer, and increase the chain mobility; as a result, the PLA will be subjected to solvent induced crystallization (SIC) [269–271]. To certify polymers for food contact applications, common food simulants are used for migration studies, including 95% ethanol, 50% ethanol, and water for fatty, alcoholic, and aqueous liquid products, respectively [272,273]. PLA films exposed to alcohol solutions at 40 °C undergo hydrolysis, in turn causing a large reduction of  $M_n$ , especially when PLA films are exposed to 50% ethanol [274] (Fig. 17).

Temperature also plays a crucial role in the hydrolysis of PLA in non-medical applications. The rate of degradation of PLA increases with temperature, resulting in faster cleavage of the ester bonds [258,263,275,276]. When PLA is immersed in water at 30, 40, and 50 °C, chain scission is accelerated as temperature increases, and an increment of carbonyl index attributed to the formation of carboxyl groups during hydrolysis is also expected [277].

### 6.2. Thermal degradation

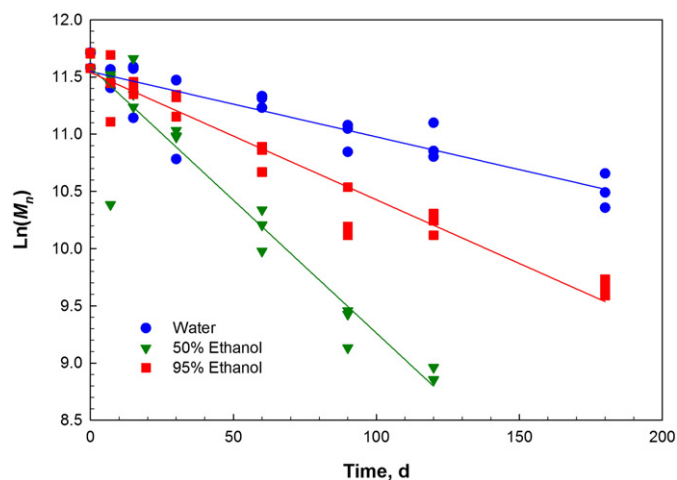
PLA is susceptible to thermal degradation during processing, leading to a decrease in  $M_w$  and the rheological and mechanical properties of processed PLA parts. Thermal degradation of PLA can be attributed to the hydrolysis initiated by residuals of water during processing, unzipping depolymerization reaction, random main-chain scission, and intramolecular and intermolecular transesterification (Fig. 18)



**Fig. 16.** Hydrolytic chain cleavage mechanisms of PLA in alkaline (a) and acidic (b) media. "Reprinted from Polymer, 42, Jong et al., New insights into the hydrolytic degradation of poly(lactic acid): participation of the alcohol terminus, 2795–2802, copyright (2001), with permission from Elsevier" [257].

[278]. Therefore, drying PLA resins before processing is highly recommended.

A number of studies have addressed the complex mechanism of the thermal degradation of PLA. Kopinke et al. [279,280] proposed that the

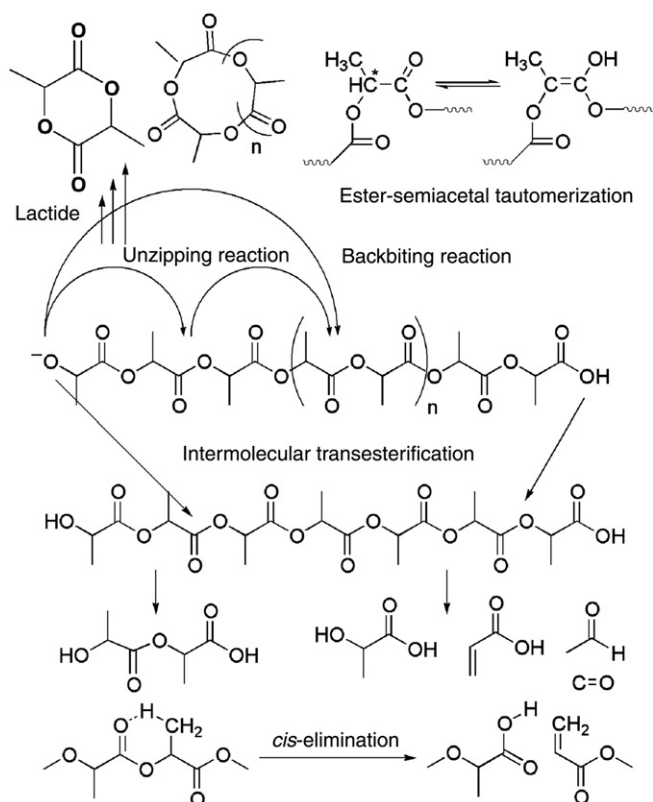


**Fig. 17.**  $\ln(M_n)$  as a function of time during hydrolysis of PLA films into water, 95% ethanol, or 50% ethanol at 40 °C.

dominant pathway of the PLA thermal degradation above 200 °C is intra- and intermolecular ester exchange, *cis*-elimination, radical and concerted non-radical reactions. McNeill and Leiper [281] stated that the mechanism is based upon a hydroxyl end-initiated ester interchange, non-radical process. Aoyagi et al. [282] and Abe et al. [283] proposed that PLA not only follows one mechanism during pyrolysis but this thermodegradation also involves more than two pathways, such as random scission, unzipping depolymerization, and intermolecular transesterification. Furthermore, changes of activation energies of the thermal degradation process have been reported, with increasing weight loss using isothermal methods going from 103 to 72 kJ mol<sup>-1</sup>, 80 to 160 kJ mol<sup>-1</sup> and 170 to 190 kJ mol<sup>-1</sup> involving complex kinetic mechanisms [282,284,285].

Thermal degradation of PLA is a complex phenomenon leading to the appearance of different compounds such as low molecular weight molecules and linear and cyclic oligomers with different  $M_w$  and lactide. Other degradation products have been detected such as CO, CO<sub>2</sub>, acetaldehyde, and methyl ketone [280,281,285]. Kopinke et al. [280] found that temperatures above 270 °C lead to degradation of PLA and that the formation of acetaldehyde increases with temperature. However, McNeill and Leiper [281] showed that during degradation temperatures in the range of 230–440 °C, acetaldehyde was formed in the highest concentration at 230 °C and then a decreasing effect was observed at 440 °C. The decrease in proportion can be explained by the thermal degradation of acetaldehyde, involving chain reactions to obtain the by-products CH<sub>4</sub> and CO.





**Fig. 18.** Thermodegradation mechanisms of PLA. "Reprinted from: Poly(Lactic Acid). Synthesis, Structure, Properties, Processing, and Applications, Nishida, Thermal degradation, 401–412, copyright (2010), with permission from John Wiley & Sons, Inc." [286].

PLA thermal degradation is influenced by several factors such as initial  $M_w$ , moisture, and residual polymerizing catalysts [287,288]. Moisture in the resin, temperature, and residence time in the extruder during processing contribute to the decrease in  $M_n$  and stress and strain at break due to the dependency of these parameters on  $M_w$  [289,290]. The presence of residual metals is a parameter that also causes drastic thermal degradation of PLA. Kopinke et al. [280] showed that PLA in the presence of residual Sn from the polymerization process leads to a selective depolymerization step producing lactide. Cam and Marucci [291] observed that the presence of residual metals assists thermal degradation in PLA, affecting the onset temperature in the order of  $\text{Fe} > \text{Al} > \text{Zn} > \text{Sn}$ . Furthermore, the presence of stannous octoate catalyst ( $\text{Sn}(\text{Oct})_2$ ) in a proportion of 0.5, 1, and 5 wt.%, accelerated the

degradation of PLA. The presence of 5 wt.% of  $\text{Sn}(\text{Oct})_2$ , even at the low temperature of 160 °C, accelerates PLA degradation [278,292]. Abe et al. [283] found that Zn catalyzes intermolecular transesterification to produce linear PLA oligomers, and selective unzipping depolymerization of cyclic PLA oligomers to produce lactides.

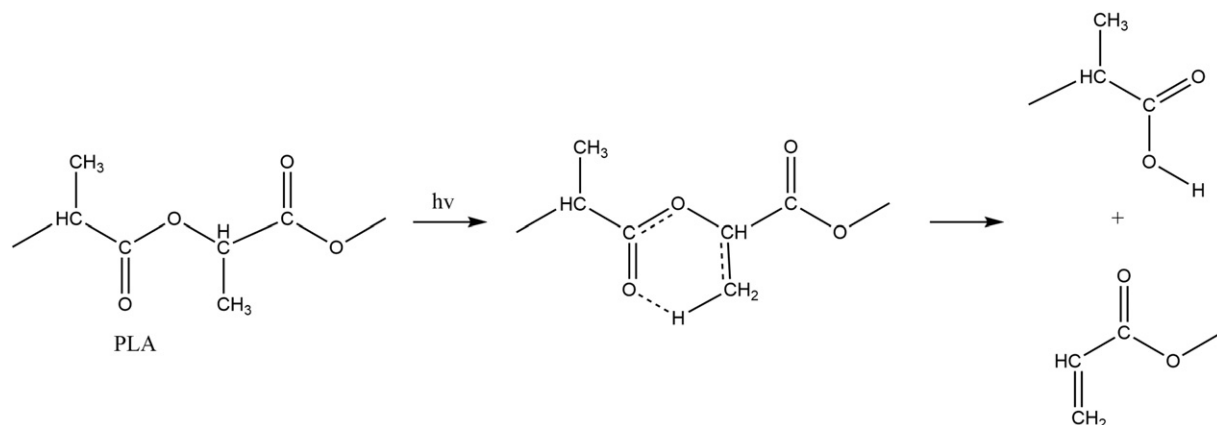
Improving the thermal stability of PLA to avoid the degradation of the polymer during processing, via end-protection or using chain extenders, has been studied. End-protection of the hydroxyl group has been assessed due to the mechanism of pyrolysis in PLA by a backbiting reaction, which causes an unzipping depolymerization starting from the hydroxyl ends of the chains [280,281,284]. One method is by the acetylation process, which not only achieves end-protection, but also is capable of removing residual metals that accelerate degradation of PLA [283,288,291,293]. Fan et al. [293] studied the relationship between the effects of the acetylation and metal content by acetic anhydride where the stabilization was due to the elimination of residual Sn. On the other hand, chain extenders, such as tris(nonylphenyl) phosphite (TNPP), polycarbodiimide (PCDI) and Joncryl<sup>®</sup>, have been used where the onset temperature of degradation is increased due to the reduction of active sites on the chain end per mass by the production of longer polymer chains [273,294,295].

### 6.3. Photodegradation

PLA is exposed to sunlight during its lifetime for applications in plasticulture, packaging containers, or films, thereby inducing plastic degradation due to the low wavelength and high-energy UV radiation. Other applications involve the use of UV irradiation for sterilization of biomedical and pharmaceutical products. The carbonyl group presence in the PLA chemical structure absorbs UV radiation at about 280 nm via  $n-\pi^*$  electron transition, thus increasing the susceptibility of PLA to photodegradation [296].

Aliphatic polyesters, including PLA, photodegrade under UV and sunlight exposure via the Norrish II mechanism (Fig. 19) whereby chain scission of the main chain occurs and the formation of  $\text{C}=\text{C}$  double bonds takes place along with carboxyl end groups and where the reaction is triggered by the electron transition at  $\text{C}=\text{O}$  [297–300]. The main-chain scission of PLA during photodegradation occurs randomly; the photodegradability is higher in the amorphous regions than in crystalline regions, resulting in the reduction of  $M_w$  where anhydride groups are formed and decreasing the rate of crystallization [299,301,302]. When UV radiation penetrates the polymer, the degradation proceeds via bulk erosion where the light penetrates the polymer without a significant reduction in its intensity regardless of the chemical structure and the crystallinity of the polymer [302].

Other basic mechanisms have been proposed to predict the degradation of PLA products by UV irradiation. Janokar et al. [303], studying



**Fig. 19.** Photodegradation of PLA via Norrish II mechanism, adapted from Tsuji et al. [302].

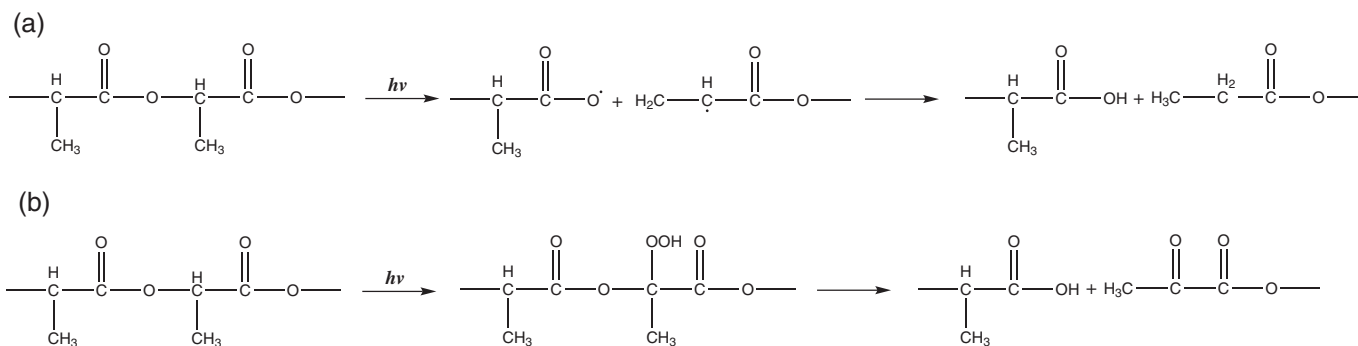


Fig. 20. Mechanisms of photodegradation of PLA, adapted from Janokar et al. [303].

the effect of wavelength on PLA photodegradation at a range of 232–500 nm, concluded that photodegradation mainly occurs between 200 and 300 nm and proposed two mechanisms. One mechanism leads to breakage of the main chain C–O by a photolysis reaction (Fig. 20a), and the other leads to the formation of hydroperoxide derivatives and subsequent degradation compounds containing carboxylic acid and diketone end groups by photooxidation (Fig. 20b).

UV irradiation can have different effects in PLA. UV irradiation can cause a decrease in  $M_w$  of PLA; UV also causes an increase in  $M_w$  distribution, which has an effect on mechanical properties, such as the decrease in stress and strain at break, where PLA becomes brittle over time [302–305]. Furthermore, a faster degradation takes places when exposure time to UV light increases [301].

The combination of different factors can affect the degradation of PLA. Copinet et al. [263] studied the effect of temperature and humidity of PLA exposed to UV irradiation at 315 nm, where the UV light accelerated the reduction of molecular weight,  $T_g$ , percentage of elongation at break, and crystallinity at different temperatures and RH. During this study, from the cleavage of C–C bonds of the main chain, two radicals were supposed to be produced (Fig. 21), and two others from cleavage at C–O of the main chain (Fig. 22a), and from cleavage of ester bonds (Fig. 22b).

Besides UV light, PLA can be exposed to different kinds of radiation such as  $\gamma$ -irradiation when the material undergoes a  $\gamma$ -sterilization process. The effect of  $\gamma$ -radiation has been studied by Balbanalbi et al. [306] using electron spin resonance (ESR) spectroscopy, where the radicals formed during degradation were the result from the scission of the ester bonds and hydrogen abstraction from the methane groups of PLA main chain. Birkinshaw et al. [307] examined the effect of  $\gamma$ -radiation on the molded poly-D,L-lactide, where changes in mechanical properties and reduction in  $M_w$  were observed, making the sample brittle due to random chain scission of the polymer.  $\gamma$ -radiation occurs mainly in the amorphous region of the polymer [308].

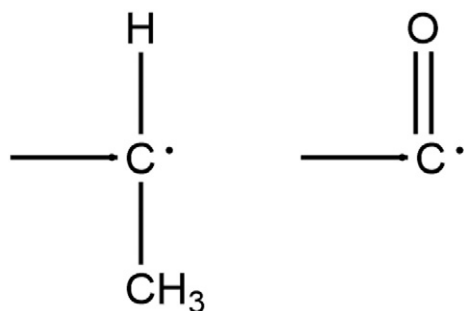


Fig. 21. Radicals generated during photodegradation of PLA from cleavage of C–C bonds, adapted from Copinet et al. [263].

## 7. End-of-life scenarios for PLA

According to the 2015 Global Sustainable Development Report, the increasing global awareness of sustainability is noticeably changing consumer preferences, and producers have to adapt to meet those preferences [309], along with the need of tools that allow the assessment of environmental impacts of materials [310]. Consequently, there is increasing demand for bio-based polymers to replace traditional fossil-based polymers, as the latter are perceived to have higher environmental footprints [3,5,311].

PLA is likely the most popular bio-based polymer. It is recyclable and biodegradable under industrial composting (IC) conditions through an initial hydrolysis process [2], and it has been proposed to be used especially in cases where plastics become highly contaminated and are difficult to recover through recycling such as food packaging and agricultural mulch films. While PLA is derived from renewable resources and offers an alternative disposal route (i.e., composting), there are limitations to its implementation due to the lack of suitable infrastructure for sorting, recycling, and/or composting PLA products at their end of life [3].

The European Commission introduced a five-level waste hierarchy in the European Waste Directive 2008/98/EC, which includes: 1) prevention, 2) reuse, 3) recycling, 4) other recovery, and 5) disposal [312]. Likewise, the US Environmental Protection Agency (EPA) has a four-level integrated waste management hierarchy, including: 1) source reduction (including reuse), 2) recycling (including composting), 3) combustion with energy recovery, and 4) disposal through landfill [313,314]. The four components are important within the integrated waste management system as shown in Fig. 23.

PLA is a special polymer since it can be treated in all levels of the hierarchy, including composting as an end-of-life scenario [315]. However, according to US EPA Advancing Sustainable Materials Management: Facts and Figures 2013 [314], about 254,110 thousands of tons of MSW were generated in the USA in 2013, from which about 25.5% was recycled, 8.8% was composted, 12.9% was combusted with energy

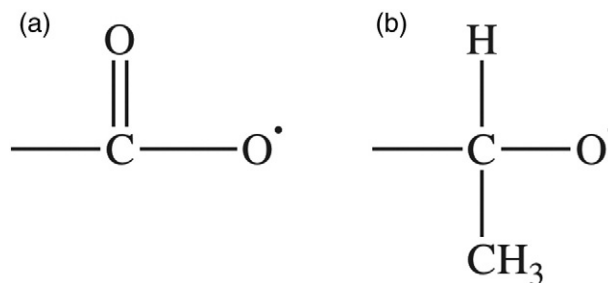


Fig. 22. Radicals generated during photodegradation of PLA (a) from C–O and (b) ester bond cleavage, adapted from Copinet et al. [263].

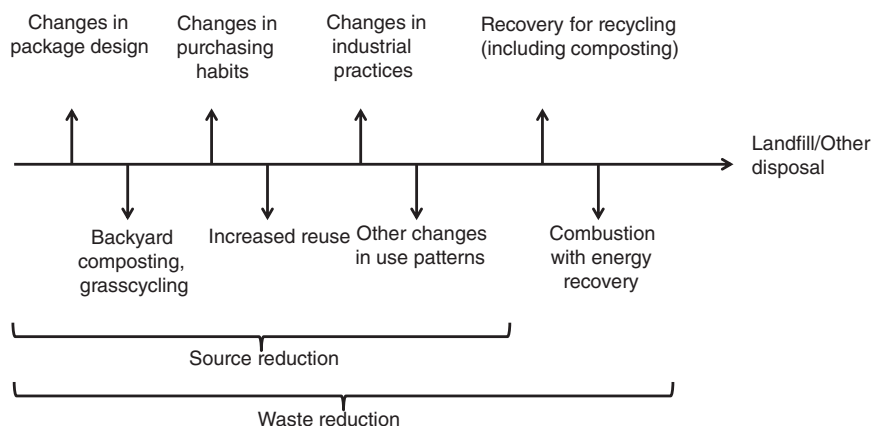


Fig. 23. Diagram of solid waste management, adapted from the US Environmental Protection Agency in Advancing Sustainable Materials Management [314].

recovery, and 52.8% was discarded in landfills. Packaging and containers comprised the biggest portion (29.8%) of the MSW, from which only about 5.2% of plastic packaging was recovered, mostly PET (24.8%) and HDPE (16%). On the other hand, from the 50,000 tons of PLA waste that was generated (mostly for plates and cups, packaging, and other non-durable goods), only a negligible amount (less than 5000 tons, 10%) was recovered through recycling and/or composting [313,314].

#### 7.1. Source reduction (reuse)

For new applications of PLA to enter the market, it is important to analyze in more detail the preferred end-of-life scenarios [315]. Waste management hierarchy emphasizes source reduction by designing products, especially packaging, to achieve material reduction (lightweighting), longer product life, and reuse [313,314,316].

Lightweighting of PLA has been of great interest not only for its economic value but also for waste reduction. Nevertheless, with this approach one must consider the possibility of reduced mechanical functionality of the PLA. Efforts made over the years to produce lightweight PLA materials with good physical and mechanical properties include producing reinforced PLA with fibers/fillers, PLA composites, and foamed PLA, to name a few. PLA-sugar-beet composite materials produced by compression-heating techniques have reduced density compared with PLA; however, the mechanical properties of the composite materials were affected negatively with increasing amounts of sugar beet pulp [317]. Peinado et al. [318] fabricated PLA reinforced with functionalized sepiolite-aminosilane grafted filler and CFA to produce lightweight PLA with improved mechanical properties. Although the addition of CFA significantly reduced the material density, its mechanical properties were compromised in the absence of the functionalized sepiolite filler. A synergistic effect of the CFA and the functionalized sepiolite was reported, where the density of the material was significantly reduced with an improved modulus. Additionally, the application of lightweight PLA-cellulose fiber composite was extended to the automotive industry for use as floor-load materials [319]. The composite with 50 wt.% fiber fraction demonstrated the highest tensile strength due to the ability of this fiber to form hydrogen bonding networks within PLA matrices. The composites with 50 wt.% fiber fraction with fixed nominal density of 0.2, 0.3, and 0.4 g/cm<sup>3</sup> met the flexural stress and stiffness for the supportable load floor weight of vehicle specifications [319]. As the market for PLA parts increase, we expect additional research of technologies to lightweight PLA.

In the case of retail packaging, a wide-scale reuse system for materials has restricted potential due to the logistics and cost involved in returning empty containers to suppliers [320]. PLA packaging is not the exception. On a much smaller scale, PLA products and packaging could be reused (whether for its primary purpose or not) by

households, assuming the PLA products and packaging maintain the desired properties, functionality, and safety.

#### 7.2. Recycling

Following the hierarchy, the next preferable disposal route of PLA would be recycling, which can be either chemical or mechanical [62,321,322]. PLA packaging, such as water bottles or blisters, usually has low contamination, making recycling a viable route to recover the material [62]. However, as previously mentioned, the lack of infrastructure to collect PLA and the logistics required to recover make it challenging to collect and recycle PLA. The economic cost involved in recycling at the post-consumer level does not usually favor the recovery and recycling of plastics other than HDPE and PET (mostly bottles); these two post-consumer resins have a big market demand since they can be used to form new bottles or other products like fibers, clothes, carpets, and textiles [62,323].

During chemical recycling, PLA is hydrolyzed at a high temperature to yield LA, which can be readily polymerized to high  $M_w$  PLA [62,321, 322]. The disadvantage of chemical recycling is that it is still complex and expensive [62]. NatureWorks LLC have successfully recycled off-grade Ingeo™ by using chemical recycling [324].

Mechanical recycling (MR) would be the easiest and cheapest way to recycle post-consumer PLA, and it involves recovering, sorting, regrinding, and reprocessing (i.e., melt processing) the PLA waste [62]. However, there is a debate on whether PLA can be successfully recycled in the current plastics recycling infrastructure due to the contamination of the recycling stream. According to Cornell [323], for PLA to be mechanically recycled, it must be either completely fungible with existing recycled resins or be available in sufficient quantity to achieve the needed critical mass. On the one hand, there are some initiatives to facilitate the recycling of PLA through the existing infrastructure for recovery and sorting. One initiative is to improve the material identification by establishing a new resin identification code (RIC) exclusive to PLA since it currently falls in the category of “7-OTHER” according to the ASTM D7611—Standard Practice for Coding Plastic Manufactured Articles for Resin Identification; this category is shared with other uncoded materials such as polycarbonate, ethylene vinyl alcohol, to name a few. Other initiatives are focused on the use of technologies like near-infrared or black light illumination to facilitate the sorting of PLA from the waste stream [325]. Thus, if there are sufficient PLA containers entering the waste stream, recycling entrepreneurs may explore means of recovering and recycling PLA in a cost-effective fashion. Various organizations, such as the Bioplastics Recycling Consortium and Greenplastics Inc., were formed to develop solutions for post-consumer bioplastic materials [326,327]. On the other hand, the National Association for PET Container Resources (NAPCOR) and the

Association of Postconsumer Plastic Recyclers (APR) have refuted the idea of mixing biopolymers like PLA into the existing stream of recycled containers, expressing concerns regarding the cost of separation and processing, increased contamination, and reduced quality of the recycled material [323,328].

### 7.3. Composting

Biodegradation is considered to be nature's way of recycling [4,329]. PLA is biodegradable under IC conditions starting with an hydrolysis process, in which ultimate PLA degradation results from the action of naturally occurring microorganisms at a high temperature (58 °C) and 50% RH [329]. Fig. 24 shows a typical large-scale composting process in which biodegradable materials decompose, resulting in compost, CO<sub>2</sub>, H<sub>2</sub>O, and minerals. There are three indispensable factors for polymer biodegradation to take place: substrate (chemical structure and conformation), environment (temperature, oxygen, and moisture) and microorganisms (metabolic pathways and enzymes) [330,331].

Biodegradation of polymers (including PLA) usually takes place in two main steps: primary degradation, in which fragmentation of the polymer chain occurs due to hydrolysis or another oxidative reaction, and ultimate biodegradation, in which the microorganisms assimilate the low  $M_w$  chains formed (Fig. 25) [330–332].

Biodegradation can be evaluated by different analytical techniques, either in a direct or an indirect approach [333], but respirometric methods are usually preferred to evaluate biodegradation of polymers in laboratory settings [330]. Respirometric methods directly measure

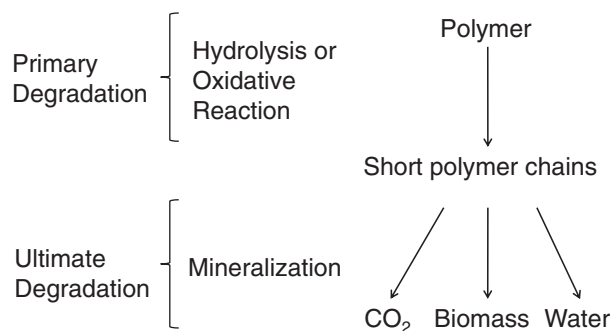


Fig. 25. Schematic of polymer biodegradation mechanism, adapted from Leejarkpai et al. [332].

the consumption of oxygen or the evolution of CO<sub>2</sub> [333]. A number of standards have been developed to define the requirements and the methodologies to assess the biodegradability of plastic materials [4]. ASTM D5338 and ISO 14855 are the main standards describing the measurement of an aerobic biodegradation of plastic materials under composting conditions by analysis of evolved CO<sub>2</sub> [334,335]. Table 4 shows a basic comparison between these two standards.

The aerobic biodegradation of PLA film (Ingeo™ 2003D) in compost was evaluated by using an in-house-built direct measurement respirometer (DMR) following the methodology described by Selke et al. [337], in which bioreactors containing PLA, blank (compost only), and

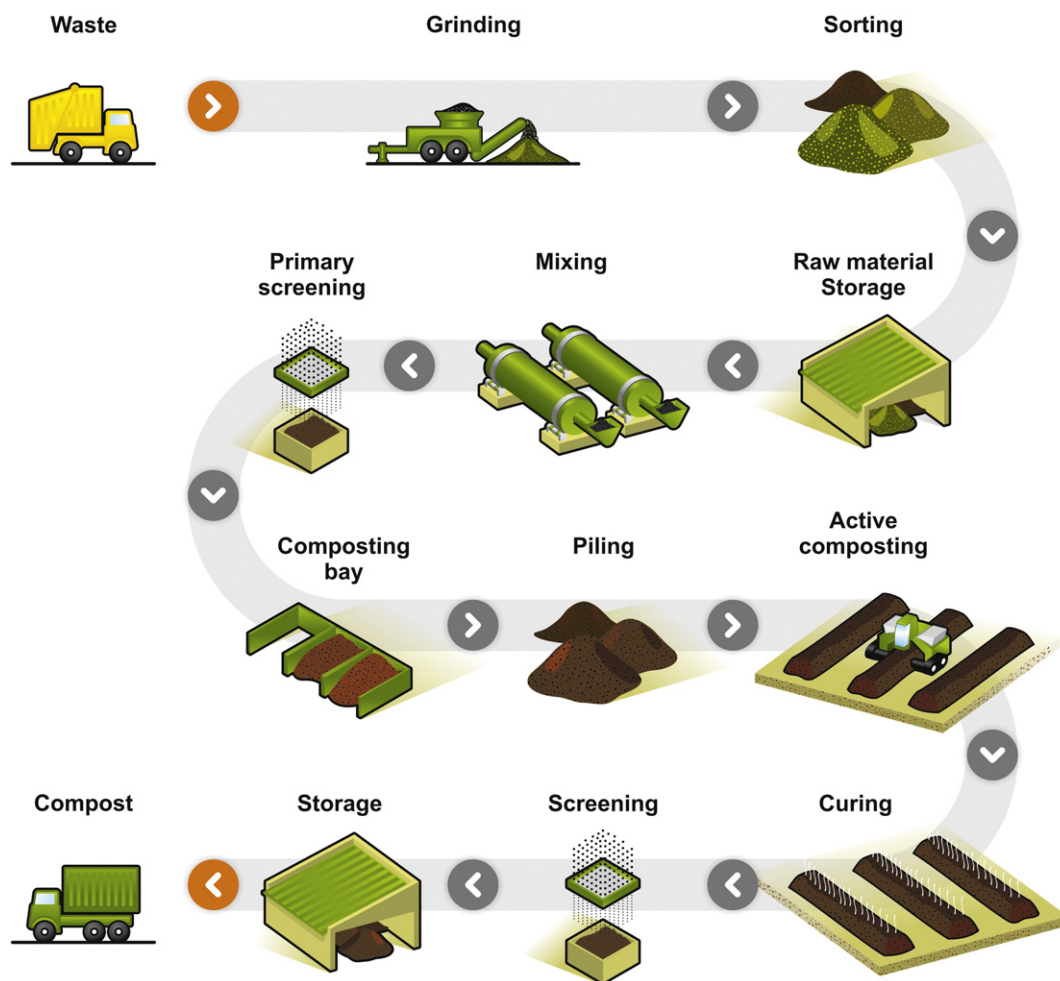


Fig. 24. Large-scale commercial composting process. "Reprinted from Polymer International, 57, Kijchavengkul et al., Compostability of polymers, 793–804, copyright (2008), with permission from Wiley" [329].



**Table 4**

General requirements to test biodegradation under laboratory conditions and comparison between ASTM D5338 and ISO 14855 standards [334,335], reproduced from Castro-Aguirre, E. [336].

Requirement		ASTM D5338	ISO 14855
Apparatus	Number of bioreactors	At least 12	At least 9
	Volume of bioreactors	2 to 5 L (sufficient headspace)	2 L or higher (sufficient headspace)
	Aeration	Water saturated CO <sub>2</sub> -free Accurate flow rate	Dry or water saturated CO <sub>2</sub> -free At pre-set flow rate
Compost inoculum	Sensor	Specific sensors or appropriate gas chromatographs	Infrared analyzer Gas chromatograph
	Age	2–4 months old	2–4 months old
	Homogeneity	Sieved on a screen < 10 mm Allows addition of structural material	Sieved on a screen of about 0.5 to 1 cm Allows addition of structural material
Substrate	Dry solids	Between 50% and 55%	Between 50% and 55%
	Volatile solids	Ash content < 70%	No more than 15% of wet or 30% of dry solids
	pH	Between 7 and 8.2	Between 7 and 9
Other	Production of carbon dioxide	Between 50 and 150 mg of CO <sub>2</sub> per gram of volatile solids over the first 10 days	Between 50 and 150 mg of CO <sub>2</sub> per gram of volatile solids over the first 10 days
	C/N ratio	Between 10 and 40	Between 10 and 40
	Shape	Granules, powder, film, simple shapes	Granules, powder, film, simple shapes
Substrate	Surface area	2 × 2 cm max.	2 × 2 cm max.
	Positive control	Cellulose (particle size < 20 μm)	Cellulose (particle size < 20 μm)
	Negative control	Polyethylene	Not required
Other	Temperature	58 ± 2 °C	58 ± 2 °C
	Water content	About 50%	About 50%
	Ratio of mixture	6:1 sample (dry solids)	6:1 sample (dry solids)
Frequency of measurement	Frequency of measurement	At least daily	At least twice per day
	Test period	At least 45 days	Not exceeding 6 months
	Incubation	Dark or diffused light	Dark or diffused light
Oxygen concentration	Oxygen concentration	6% or higher	6% or higher

cellulose (positive reference) were tested. Fig. 26a shows that the PLA film produced a significantly higher amount of CO<sub>2</sub> than the blank, meaning that microorganisms were able to use the carbon from the polymer for their metabolic processes. The amount of CO<sub>2</sub> produced by the PLA film is comparable with that for the positive reference in the same time period. Fig. 26b shows that the PLA film mineralized above 70% after 2 months of composting. PLA also presented a lag time during the first 3 weeks of the test, which is related to the primary degradation where the  $M_w$  of the polymer is reduced to around  $9.0 \times 10^3$  Da for the microorganisms to start the ultimate degradation or mineralization.

Composting would be the optimal end-of-life option for contaminated PLA. However, there are only few existing composting facilities that accept biodegradable plastic materials since most are concerned that biodegradable plastics are not easily distinguishable from conventional plastics and that quality control is difficult [315].

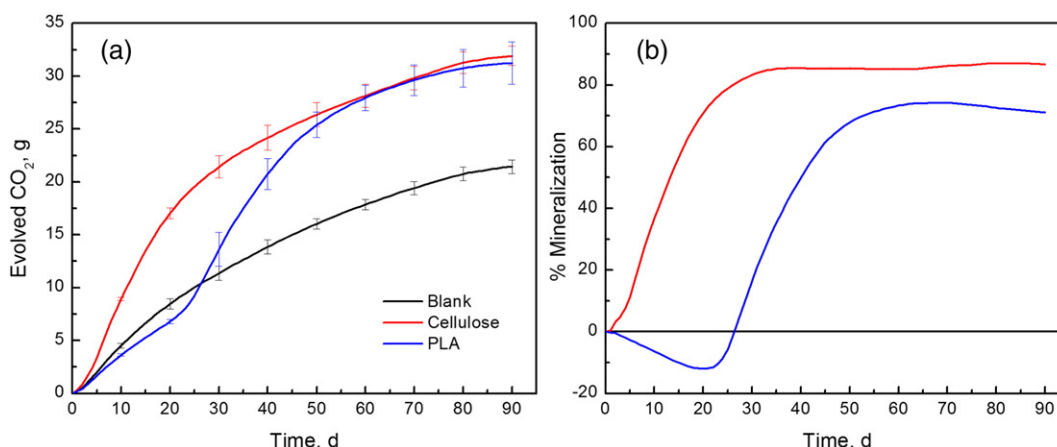
Similar to recycling, there is a big challenge for collecting and sorting PLA waste from other MSW so that the PLA can be sent to the

composting facilities. Hence, the benefit provided by PLA of offering an additional disposal route (biodegradation or composting) is only realized if PLA is disposed in an appropriate waste management system that uses their biodegradable features [320]; otherwise, the PLA would accumulate like other plastic materials in the landfill.

#### 7.4. Incineration with energy recovery

The incineration of waste is not only a volume-reduction practice but has also evolved to waste-to-energy plants in which energy is recovered from waste materials to produce heat or electricity, followed by the disposal of the fly and bottom ashes. Incineration of waste with energy recovery also reduces the dependency of using fossil resources and other fuel sources. Even though air pollution is often the main concern about incineration, the improvements in gas cleaning technology allow the reduction of pollutants released to the atmosphere [338,339].

Thus, some of the energy content of plastics can be recovered by incineration, and reasonable energy efficiency can be achieved through



**Fig. 26.** a) Amount of CO<sub>2</sub> evolved from blank, cellulose, and PLA film; b) percentage mineralization of cellulose and PLA film.



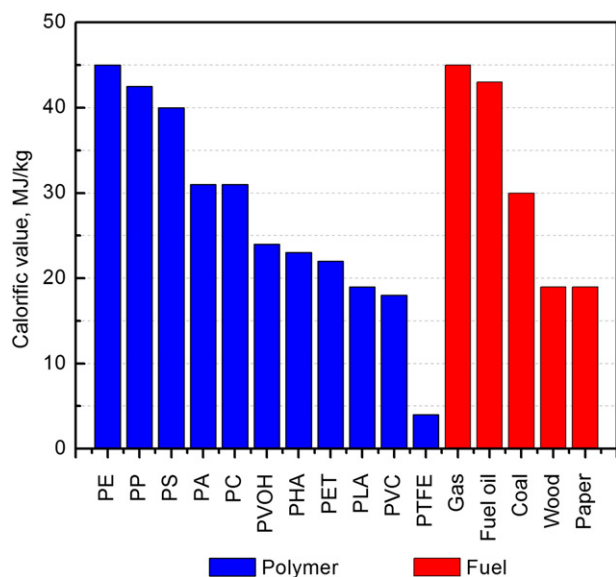


Fig. 27. Calorific values of selected materials, adapted from Laußmann et al. [340].

various approaches such as co-fuelling of kilns [320]. Disposing PLA waste via incineration recovers the energy embedded in PLA, representing a CO<sub>2</sub>-neutral method of energy production, and it contributes to the conservation of fossil resources [340]. However, energy recovery does not reduce the demand for raw material used in plastic

production [320], and it is also important to consider the composition of the emitted combustion gases [340].

NatureWorks LLC reported that Ingeo™ resin heat content is about 19.5 MJ kg<sup>-1</sup> [341]. This value is in agreement with the calorific values reported by Laußmann et al. [340] (Fig. 27), who carried out comparative experiments between biopolymers, fossil-based polymers, and fuels. They concluded that biopolymers, including PLA, are suitable for thermal energy recovery since they have calorific values comparable to cellulosic-based materials, and they do not produce additional toxicologically critical substances during combustion [340].

### 7.5. Landfill

The less preferable option to dispose PLA is landfilling (LF). According to the US EPA, although disposal of MSW to landfill decreased from 145.3 million tons in 1990 to 134.3 million tons in 2013, landfill remains the most economic and attractive method for handling MSW [313,314]. LF has some environmental impacts primarily due to gas and leachate formation, including health hazards, fires and explosions, vegetation damage, unpleasant odors, landfill settlement, ground water pollution, air pollution, and global warming [342]. The drawback of disposing plastics in landfills lies in the fact that most plastic materials do not degrade in a practical period of time and end up accumulating [343]. Landfills usually do not provide the appropriate environment to promote degradation, and their conditions vary considerably by geography [344]. On the other hand, PLA biodegradation is highly dependent on temperature and moisture since these two factors promote hydrolysis of the polymer chains, and in turn accelerate biodegradation. At mesophilic temperatures little or no degradation of PLA is observed [344].

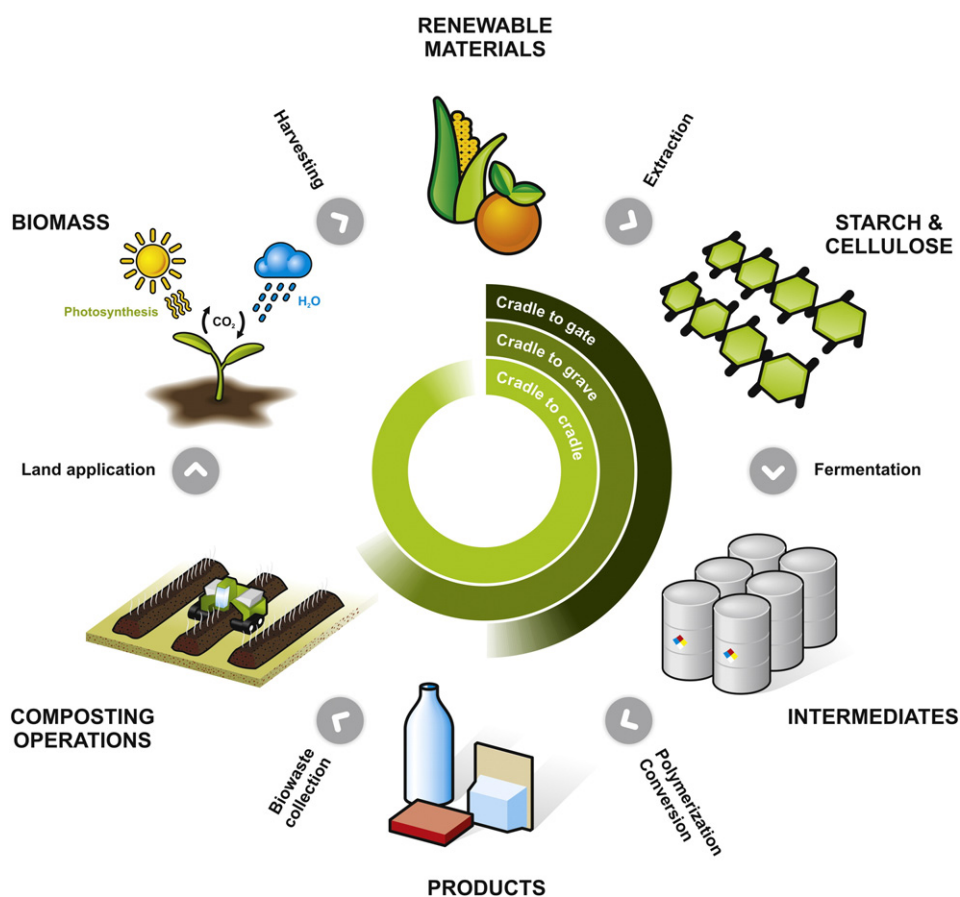
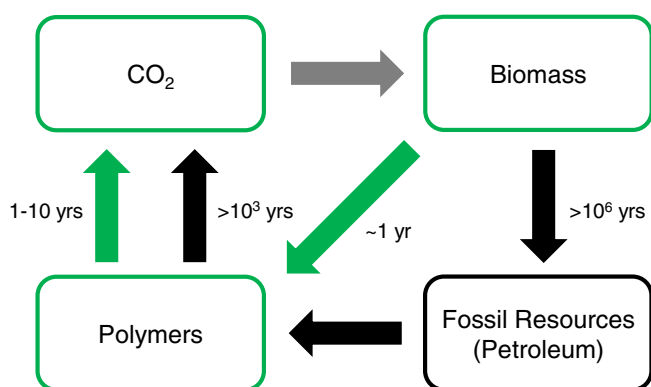


Fig. 28. Cradle-to-gate, cradle-to-grave, and cradle-to-cradle representations of production, consumption, and disposal of bio-based polymers from renewable resource via composting. "Reprinted from Polymer International, 57, Kijchavengkul et al., Compostability of polymers, 793–804, copyright (2008), with permission from Wiley" [329].



**Fig. 29.** Carbon cycle of fossil-based polymers and bio-based polymers. Renewable resource pathway (green arrows); fossil resource pathway (black arrows); and pathway for both renewable and fossil resources (gray arrow), adapted from Kijchavengkul et al. [329].

According to NatureWorks LLC, their resin Ingeo™ is stable in landfill conditions with no statistically significant quantity of methane released. Studies performed under accelerated landfill conditions at different temperatures and moisture levels found that the amorphous PLA did generate a small amount of methane in the test at 35 °C, but no methane was generated in the test at ambient temperature. Semicrystalline PLA did not generate a significant amount of methane in any of the tests. The company also pointed out that it is likely that any degradation of PLA in a landfill would require a chemical hydrolysis step prior to any biodegradation [344].

## 8. Environmental footprint of PLA

The increasing global awareness of sustainability is changing the perceptions and preferences of consumers; therefore, environmental assessment tools are being used to evaluate the EFP of systems and products [310]. An EFP is a quantitative measurement describing how human activities can inflict different impacts on global sustainability considering the environmental, social, and economic indicators [345].

Life cycle assessment (LCA) can be used to evaluate the EFP of PLA. LCA is a method to assess the environmental performance of products and/or potential impacts of a system considering raw materials acquisition, production, use, and disposal [346,347]. LCA is conventionally thought of as a “cradle-to-grave” approach; however, in the last few years a “cradle-to-cradle” approach has been introduced [345] (Fig. 28).

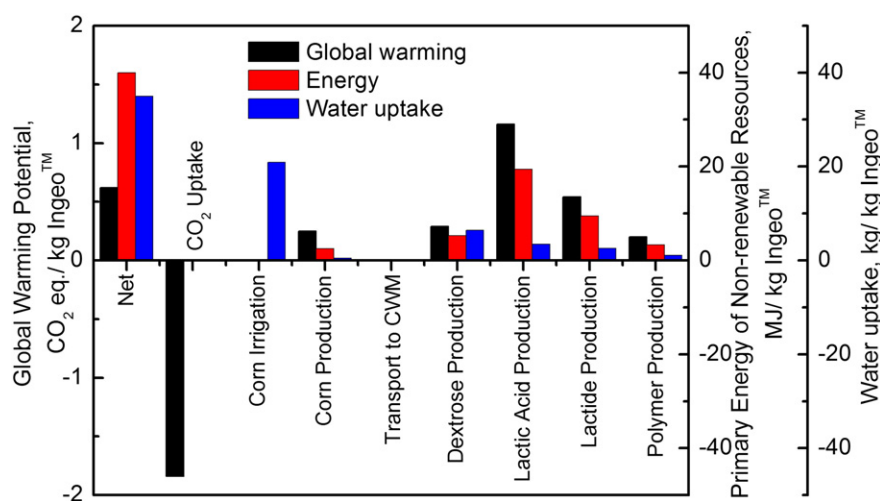
In other words, LCA systematically evaluates each of the life stages of a product or product system, in which environmental inputs (resources) and environmental outputs (emission and waste) are produced and the impacts to human health and environment are calculated. LCA results are interpreted in relation to the objectives of the study [346,347]. LCA studies are mostly conducted under the framework of the international standards ISO 14040 and 14044 [348,349], which provide requirements, recommendations, and guidelines about methods and techniques for quantifying inputs and outputs, and impact characterization [346,347].

The EFP of PLA resins and/or PLA products can be evaluated using midpoint impact categories [350]. Additionally, measuring key indicators such as greenhouse gases (GHG) emissions and non-renewable energy use, and comparing the data between PLA and traditional polymers (e.g., PET and PS) can give insights about PLA environmental performance.

In 2003, NatureWorks LLC published the first cradle-to-gate life cycle inventory data (ecoprofile) for its PLA (Ingeo™) based on the 140,000 tons/year plant design, in which they provided some information regarding the production technology [351]. In 2007, the company provided an updated ecoprofile based on the actual data collected from its production facilities, and also provided a more accurate description of the manufacturing system and LCA calculation procedure [352]. In 2010, NatureWorks LLC published an updated ecoprofile based on the production technology improvements and also benchmarked the results for energy requirements and GHG emissions with data for a selection of fossil-based polymers [353]. Recently (2015), the company published an updated PLA ecoprofile providing a detailed description of the production of its resin (now 150,000 tons/year plant) and focused on the corn feedstock used to produce Ingeo™ and on the PLA intrinsic zero material carbon footprint, as explained below [5,345].

One of the advantages of using bio-based biodegradable polymers like PLA is to help replenish the carbon cycle (Fig. 29) [329]. When using renewable carbon feedstock to manufacture plastic materials instead of fossil carbon feedstock, there is an intrinsic zero material carbon footprint value proposition; in other words, the carbon footprint reduction arises from the material itself and not necessarily from the process of converting the feedstock to products (process carbon footprint) [354].

Fossil resources could be considered renewable, but it takes more than a million years for biomass to be converted into fossil fuels. Since the rate of consumption is much greater than the rate of replenishment, mass imbalance occurs in the carbon cycle. In contrast, biodegradable polymers made from bio-based materials, such as corn and corn starch, can be produced and converted into biomass in similar time frames [329]. Fig. 30 shows the global warming potential (GWP), primary



**Fig. 30.** GWP, primary energy of non-renewable resources expressed as higher heating values (HHV), and net water uptake for the production system of Ingeo™ resin, adapted from Vink and Davies [5].

energy from non-renewable resources (PENNR), such as oil, gas, coal, and uranium, and water uptake for 1 kg of Ingeo™ PLA resin [5]. One of the main value propositions for using PLA to replace other fossil-based polymers, is the lower GWP due to carbon sequestration during the corn-growing stage.

Several authors have done LCAs regarding the performance of PLA in comparison with other materials like PET and PS for different applications, in which PLA could be a good substitute for clamshell containers, trays, and water bottles [311,355–358]. Table 5 and Fig. 31 show general information about the EFP of PLA in comparison with other polymers.

Such a comparison is effective only if: a) polymer weights in the studied applications are quite similar; b) contributions to impact categories are dominated by the polymer-pellet production; c) energy requirements for converting the polymer into product are relatively small or relatively similar; d) use phase is similar; e) the same recycling or end-of-life routes are employed; f) the same level of detail in the life cycle inventory data-collection process was used; g) the same LCA methodology was used; h) the same database for upstream inventory data was used; and i) the same life cycle impact assessment methodology, indicators, and characterization factors (+ version) were used [5]. Given the above, the climate change of Ingeo™ and PLA have large differences since carbon sequestration has not been accounted for in PLA. If this factor is taken into consideration, a global warming potential of PLA would be 0.9 kg CO<sub>2</sub> eq per kg of resin vs 0.62 kg CO<sub>2</sub> eq per kg of resin for Ingeo™. Thus, a large benefit is obtained using the new reported data for Ingeo™ [5]. In the case of non-renewable energy, similar values are reported by Vink and Davies and the current data are available in Ecoinvent 3.2. In the case of water depletion, the new values reported by Vink and Davies make sure to properly account for water uptake from river and ground for the Blair manufacturing plant, excluding the water for hydropower installations and rainwater. So, a much lower water EFP is reported for Ingeo™, provided that water consumption is similar to that for polyolefins.

A large controversy exists regarding the use of the arable food land for plastic materials [359–361]. Vink and Davies reported, based on Carus [362], that 0.00046% of the 5 billion ha of agricultural land available will be required to supply the corn needed for the 150,000 tons/year Ingeo™ production in Blair, and if we imagine a scenario where the 300 million tons of plastics annually produced in the world were to be replaced by bio-based polymers with the same land use per kilogram of PLA, 0.9% of the 5 billion ha of agricultural land available will be required [5,362,363].

An LCA study has been done recently regarding the end-of-life options for PLA [315]. In their study, Rossi et al. performed an LCA of the

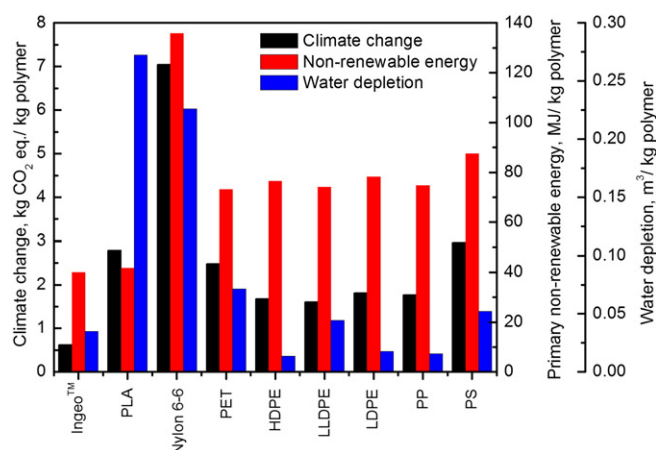


Fig. 31. Climate change, non-renewable energy, water depletion for 1 kg of PLA and other commercial polymers as available in Ecoinvent 3.2 and reported using Simapro 8.0.5 with ReCiPe (E) midpoint indicator considering the world as the geographical region, and Ingeo™ adapted from Vink and Davies [5].

end-of-life options for biodegradable packaging based on the waste hierarchy mentioned in Section 7. Fig. 32 shows the system boundary, which covers the primary material production and end-of-life treatment processes such as MR, IC, anaerobic digestion (AD), direct fuel substitution in industrial facility (DFS), incineration with heat recovery in MSW incinerator (MSWI), and LF. Details of the life cycle inventory for each scenario can be found elsewhere [315].

Rossi et al. [315] used IMPACT 2002 + LCIA method to evaluate the environmental impacts for the different end-of-life scenarios complemented by water withdrawal and turbinated water indicators. Global warming impacts for PLA dynamically assessed over a 100-year time horizon are presented in Fig. 33, in which IC has the highest net impact (measured in kg of CO<sub>2</sub> eq per kg of dry PLA packaging without food contamination after deduction of the treatment credits) and MR has the lowest net impact.

Likewise, Fig. 34 shows the non-weighted scores of the PLA production and end-of-life scenarios for each midpoint category, in which for most impact categories MR was the least-burdening option. On the other hand, IC and LF were the least favorable options for most impact categories.

However, the authors emphasize that those conclusions are only valid under the stated hypotheses since other factors may lead to different conclusions. Additional studies are needed to ensure that this

**Table 5**  
Environmental footprint of 1 kg of selected commercial polymer resins as available in Ecoinvent 3.2 and reported using Simapro 8.0.5 with ReCiPe (E) midpoint indicator considering the world as the geographical region.

Impact category	PLA	Nylon 6-6	PET	HDPE	LLDPE	LDPE	PP	PS
Climate change, kg CO <sub>2</sub> eq	2.7907	7.0460	2.4813	1.6815	1.6055	1.8154	1.7666	2.9690
Ozone depletion, kg CFC <sup>-11</sup> eq	2.18E-07	2.61E-09	1.48E-07	1.18E-09	4.75E-08	1.13E-09	8.85E-10	5.46E-09
Terrestrial acidification, kg SO <sub>2</sub> eq	0.0218	0.0295	0.0121	0.0064	0.0057	0.0078	0.0062	0.0112
Freshwater eutrophication, kg P eq	0.0004	0.0003	0.0001	1.23E-06	9.03E-07	1.42E-06	4.33E-05	3.56E-06
Marine eutrophication, kg N eq	0.0065	0.0091	0.0002	0.0001	0.0001	0.0002	0.0002	0.0003
Human toxicity, kg 1,4-DB eq	9.4123	1.7760	4.6504	0.4946	0.2917	0.6967	0.4113	0.6617
Photochemical oxidant formation, kg NMVOC	0.0115	0.0205	0.0087	0.0086	0.0065	0.0093	0.0076	0.0096
Particulate matter formation, kg PM10 eq	0.0063	0.0082	0.0040	0.0020	0.0021	0.0023	0.0019	0.0033
Terrestrial ecotoxicity, kg 1,4-DB eq	0.0089	0.0002	0.0018	1.51E-05	1.13E-05	2.04E-05	1.21E-05	0.0003
Freshwater ecotoxicity, kg 1,4-DB eq	0.0090	0.0037	0.0021	0.0004	0.0002	0.0005	0.0003	0.0009
Marine ecotoxicity, kg 1,4-DB eq	3.5355	2.5132	2.9761	0.2391	0.1561	0.3246	0.1915	0.9059
Ionizing radiation, kBq U235 eq	0.1398	0.0006	0.0785	0.0002	0.0002	0.0003	0.0002	0.0004
Agricultural land occupation, m <sup>2</sup> a	1.1321	0.0009	0.1035	0.0004	0.0003	0.0003	0.0003	0.0006
Urban land occupation, m <sup>2</sup> a	0.0674	0.0006	0.0147	0.0002	0.0001	0.0002	0.0002	0.0004
Natural land transformation, m <sup>2</sup>	0.0004	-2.04E-06	0.0004	-3.77E-07	-4.39E-08	-7.27E-07	-3.98E-07	-1.25E-06
Water depletion, m <sup>3</sup>	0.2726	0.2262	0.0714	0.0136	0.0443	0.0176	0.0156	0.0524
Metal depletion, kg Fe eq	0.1538	0.0046	0.1646	0.0015	0.0019	0.0029	0.0015	0.0108
Fossil depletion, kg oil eq	0.8246	2.6814	1.5455	1.5908	1.5628	1.5684	1.5716	1.8711
Non-renewable energy, MJ primary	41.739	135.86	73.182	76.398	74.090	78.223	74.636	87.542

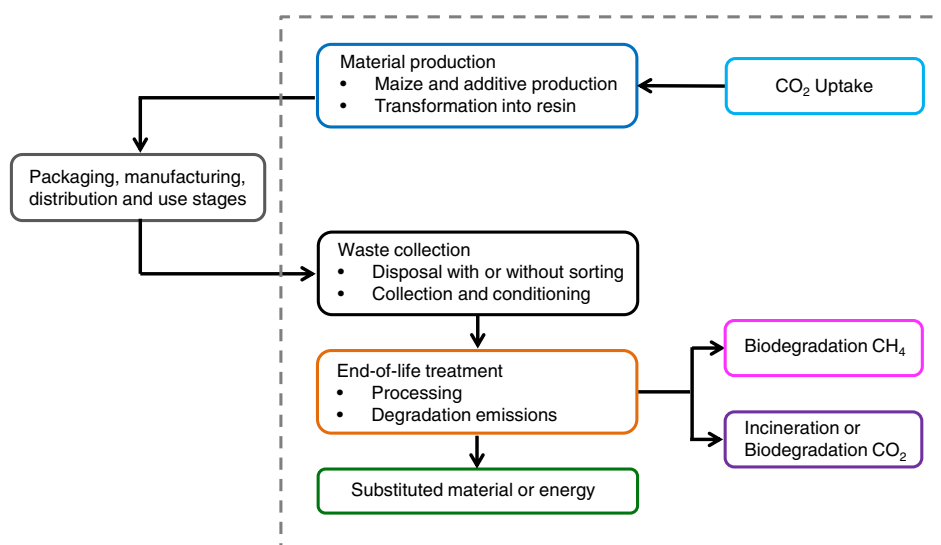


Fig. 32. PLA life cycle and boundary of the studied system, adapted from Rossi et al. [315].

preliminary finding can be translated to other boundary conditions and can be applied to other regions.

## 9. Final remarks

The range of PLA applications for consumer durable and non-durable goods has increased significantly since industrial methodologies, such as polycondensation and ROP, allowed the production of high  $M_w$  PLA to reach the market. At present, the main producer of the commercially available high  $M_w$  PLA derived from corn is NatureWorks LLC. Additional producers (e.g., Corbion®) are expected to reach the market with PLA derived from plant-based materials and/or biomass waste, which should increase its availability and further commercial applications.

Additional research has been focused on understanding and enhancing the physical and mechanical properties of PLA by, for example, deriving commercial PLA from *rac*-lactide. Extensive work has been conducted on blending PLA with biodegradable and non-biodegradable

polymers and on using fillers at the micro- and nanoscales to create blends and composites with optimal properties, lower cost, and less environmental footprint. All these new variations of PLA-based materials target enhanced performance of PLA while sometimes at the expense of losing the biodegradability of the polymer matrix and reducing its industrial commercial recovery. Thus, new materials should be produced while keeping in mind that they need to be recovered by the more preferred routes of the waste management hierarchy (i.e., source reduction, recycling, composting, incineration with energy recovery, and landfill).

The methods used for PLA mass production are well-established polymer-manufacturing techniques (i.e., extrusion, injection molding, blow molding, thermoforming, foaming, and spinning). Therefore, PLA has found extended applications such as fibers, textiles, plasticulture, serveware, and packaging containers via established processing technologies. However, use of different PLA structures may complicate the performance and/or use of these methods. Additional research may be needed in the production of the new *rac*-lactide derived PLA.

One of the main value propositions for PLA is its intrinsic degradation, which can be triggered when PLA is exposed to different environments. Thus, degradation of PLA can be seen as an advantage or disadvantage depending on the application. Extensive research has been conducted on the degradation of PLA in human, processing, and composting environments. However, additional research is needed to assess the degradation of PLA and its modification when in contact with different solvents and simulants.

Furthermore, the increasing awareness of sustainability is highly influencing consumer preferences toward bio-based polymers, and PLA has the potential to become one of the major commercialized polymers. PLA can be derived from renewable resources, such as regular crops, plant-based materials, and biomass waste, and it could be treated in all levels of the waste management hierarchy. In this regard, however, there are still limitations due to the lack of suitable infrastructure for sorting, recycling, and/or composting PLA products at their end of life. So, efforts should be centered on working with industries, commodity groups, industry associations, and government groups to improve the recovery rate of PLA.

Finally, life cycle assessment has been used to evaluate the environmental footprint of PLA, providing useful information about the environmental impacts that PLA may have during raw material acquisition, production, use, and disposal. Robust data exists about the PLA resin production from one producer, NatureWorks LLC. However, information is missing regarding the use and end-of-life scenarios of PLA parts.

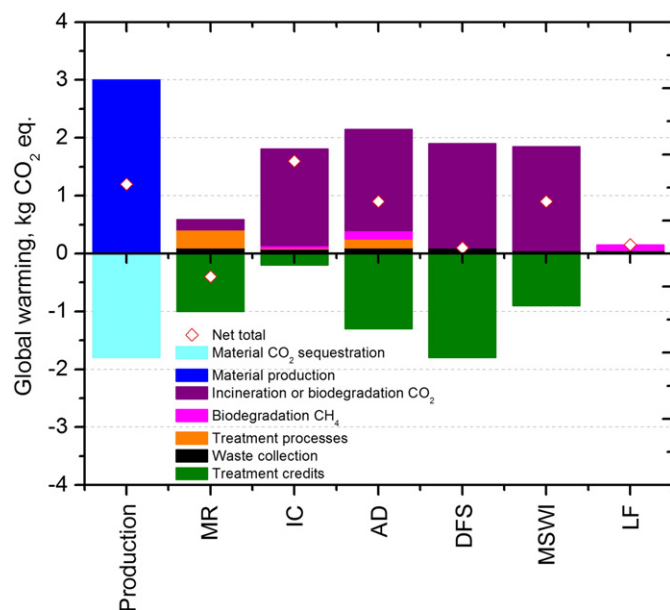


Fig. 33. Comparison of dynamically-assessed global warming impacts over 100 years associated with the six end-of-life treatments for PLA. The bars on the left side present production impacts of the resin (cradle-to-gate) for comparison purposes, adapted from Rossi et al. [315].



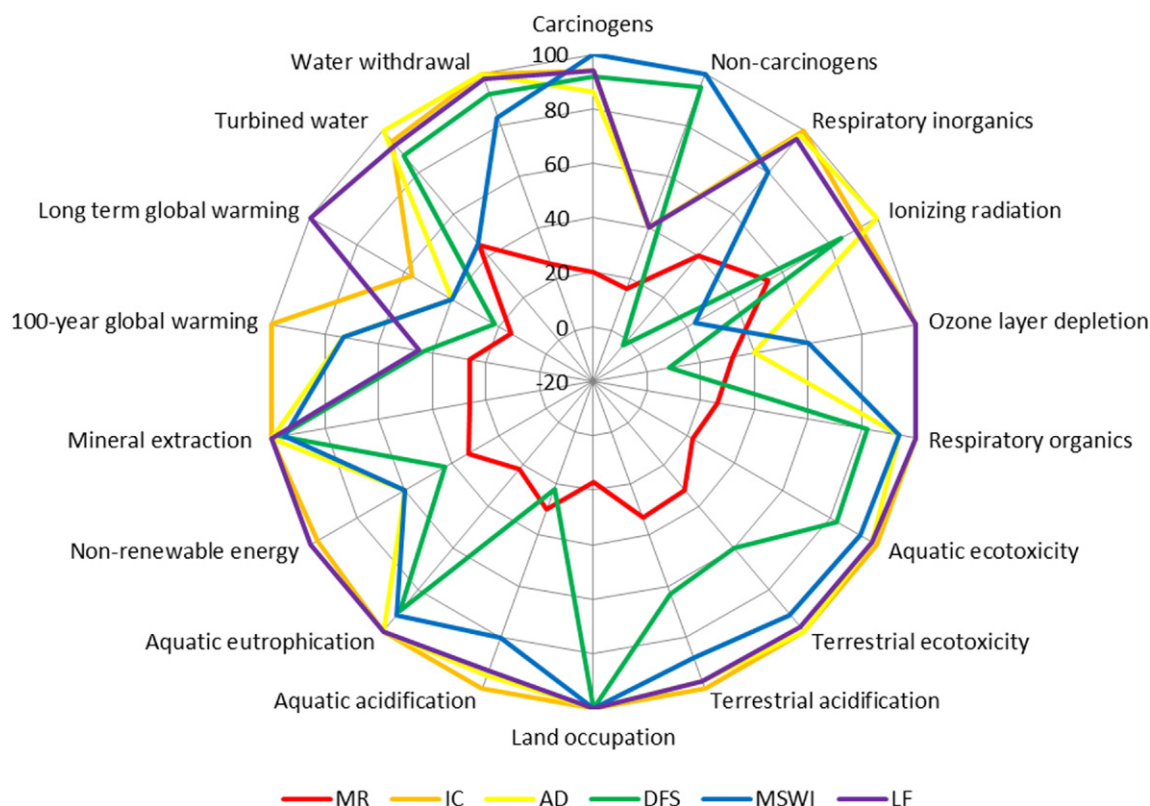


Fig. 34. Comparison of end-of-life options for PLA for each midpoint category, adapted from Rossi et al. [315].

In conclusion, PLA has transcended from a minor bio-based polymer player in the market of commercial fossil-based polymers to be considered as part of a new solution for an increasingly recognized new bio-based economy. Present and future efforts in developing PLA for an array of applications should secure PLA's status as one of the major new bio-based polymers.

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