


# Synthesis, properties, and applications of polylactic acid-based polymers

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## Abstract

Poly(lactic acid) (PLA) is known as one of the greatest promising bioabsorbable and compostable polyesters with the capability of high molecular weight synthesis. Lactic acid condensation, azeotropic dehydration, and condensation ring-open polymerization of lactide are three methods for PLA polymerization. Comprehension of material properties is critical for choosing the right processing method and adjusting PLA characteristics. A variety of mechanical properties of this material, from soft and elastic to stiff and high strength makes PLA suitable for a wide range of applications. Besides, PLA can be blended or copolymerized with other polymeric or non-polymeric substances. Thus, this polymer can achieve suitable chemical, mechanical, and rheological properties. Understanding the role of these properties and selecting a suitable processing technique is necessary for its intended consumer and various applications. This study elaborated a general summary of the polymerization, processing, and characteristics of PLA (i.e., structural diversities, rheological performances, mechanical properties, and permeability). Besides, this work presented some information regarding essential factors that can be used for modifying PLA properties to address the requirements for various applications such as biomedical, food packing, biocomposite, and additive manufacturing.

## KEYWORDS

biodegradable polymer, PLA, poly(lactic acid), properties, synthesis

## 1 | INTRODUCTION

More than 368 million tons of plastic are manufactured per year. With an annual increase rate of 2.5% of the bioplastic market, the global bioplastics production capacity is increased from around 2.11 million tons in 2020 to approximately 2.87 million tons in 2025.<sup>[1]</sup> Although 43% of these manufactured products are biodegradable, and 30% of these products are known as both bio-sourced and biodegradable.<sup>[2]</sup> Bioplastics such as bio-based

polyethylene terephthalate (PET) (nonbiodegradable) and biodegradable starch-based blends represent 27 and 18% of the bioplastics market, respectively. Subsequently, bio-based polymers such as polyamide (PA) as a nonbiodegradable polymer, polylactic acid (PLA) as a biodegradable polymer and Polyethylene (PE) as a nonbiodegradable polymer, represent 10% of the world market. European Bioplastics association predicted that PLA (biodegradable) and poly(hydroxyl alkanooates) (PHA) (biodegradable) will be the major market drivers in the years ahead.<sup>[2]</sup>

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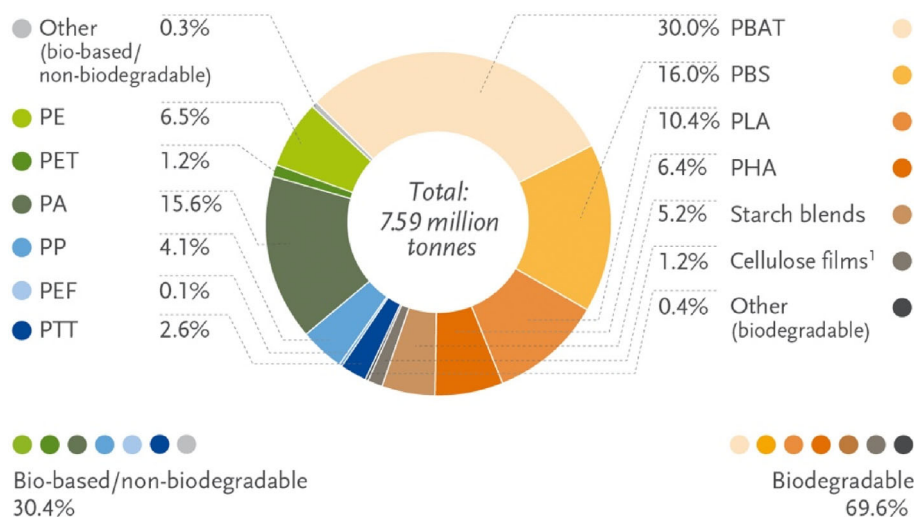


FIGURE 1 Worldwide production capacities of bioplastics 2026.<sup>[1]</sup>

Bio-based and biodegradable plastics are environment-friendly by contributing to reducing CO<sub>2</sub> emissions during production, digestion, or composting. Thus, production of bio-based and biodegradable polymers such as PLA are necessary for growing bio-economy area.<sup>[1]</sup>

PLA is a bio-sourced, bioabsorbable, bio-compostable, and biodegradable polymer.<sup>[3-9]</sup> In addition, PLA has a high production capacity among bioplastic materials being commercially available (Figure 1). PLA with high productivity and easy access is known as an economical substance.<sup>[10]</sup> PLA is a green alternative substance for the manufacturing of biodegradable bioplastic derived from petrochemical sources.<sup>[11,12]</sup> This study goes throughout an in-depth review of PLA, starting from the economic aspect of PLA production, PLA synthesis, as well as polymerization mechanisms. This review also gives a general and critical review about PLA properties, limitations, the tools for improving these features, applications, and future opportunities. Moreover, the biodegradability and compostability aspects of this polymer have been discussed in detail.

PLA with helix structure,<sup>[8,9]</sup> has an orthorhombic unit cell<sup>[13,14]</sup> and has made of biodegradable polyesters L and/or D-lactic acid monomers. PLA polymerization can be either by microbial fermentation or chemically polymerization. The content of lactic acid enantiomers with the PLA chain affects the final characteristics of PLA such as the degree of crystallization rate, melting temperature, and glass transition temperature.<sup>[15]</sup> PLA chains can be made of homopolymers and heteropolymers. By comprising either optically pure L-lactic acid or D-lactic acid, PLA homopolymers produce. PLA homopolymers are semicrystalline polyesters with a melting temperature ( $T_m$ ) of about 175°C. While due to disorders of polymer chains PLA heteropolymers (poly DL-lactic acid) are amorphous.<sup>[16]</sup> Industrial PLA production can be

obtained either by the polymerization of lactic acid (LA) or by the ring-opening polymerization (ROP) of lactide.<sup>[16-20]</sup> Based on the processing grade, PLA  $T_g$  varies from 50 to 59°C with a melting point of 159–178°C.<sup>[21]</sup>

PLA is recyclable, eco-friendly,<sup>[22]</sup> energy-saving,<sup>[23]</sup> with improved thermal processibility, compared to other biopolymers such as PHAs, poly(ethylene glycol) (PEG), poly(-caprolactone) (PCL), and so forth.<sup>[24]</sup> Although this polymer has some drawbacks such as a slow degradation rate, a high degree of hydrophobicity, and the absence of reactive side-chain groups.<sup>[25]</sup> PLA with less than 10% elongation at break is a highly brittle material which is due to its poor toughness.<sup>[26]</sup> Due to the low rate of crystallization, PLA has a long injection molding cycle time, with great sensitivity to humidity and low resistance to hydrolysis.<sup>[27,28]</sup>

The relatively low  $T_g$  of PLA with high isomer purity comparing to other polymers frequently utilized in the packaging (e.g., PS, PMMA, etc.) is another important disadvantage that should be considered.<sup>[29]</sup> The following strategies can be used to address the low  $T_g$  of PLA and making it applicable for high temperatures processing:

- addition of reinforcements;
- promoting PLA crystallization;
- nano-alloying PLA;
- blending PLA with polymers having high  $T_g$  (e.g., PC, PMMA) or crystallization ability such as PA;
- chain extension (e.g., with diisocyanates).

The global PLA market size was esteemed to \$566.74 million in 2021 and is estimated annual growth rate (CAGR) of over 26.6% from 2022 to 2030.<sup>[30]</sup> PLA has a high interest in diversity of applications such as biomedical,<sup>[31]</sup> food packaging,<sup>[32]</sup> composite,<sup>[29,33]</sup> automotive,<sup>[34-38]</sup> electronics, and so forth.<sup>[39-47]</sup> Indeed, due to low melting point and

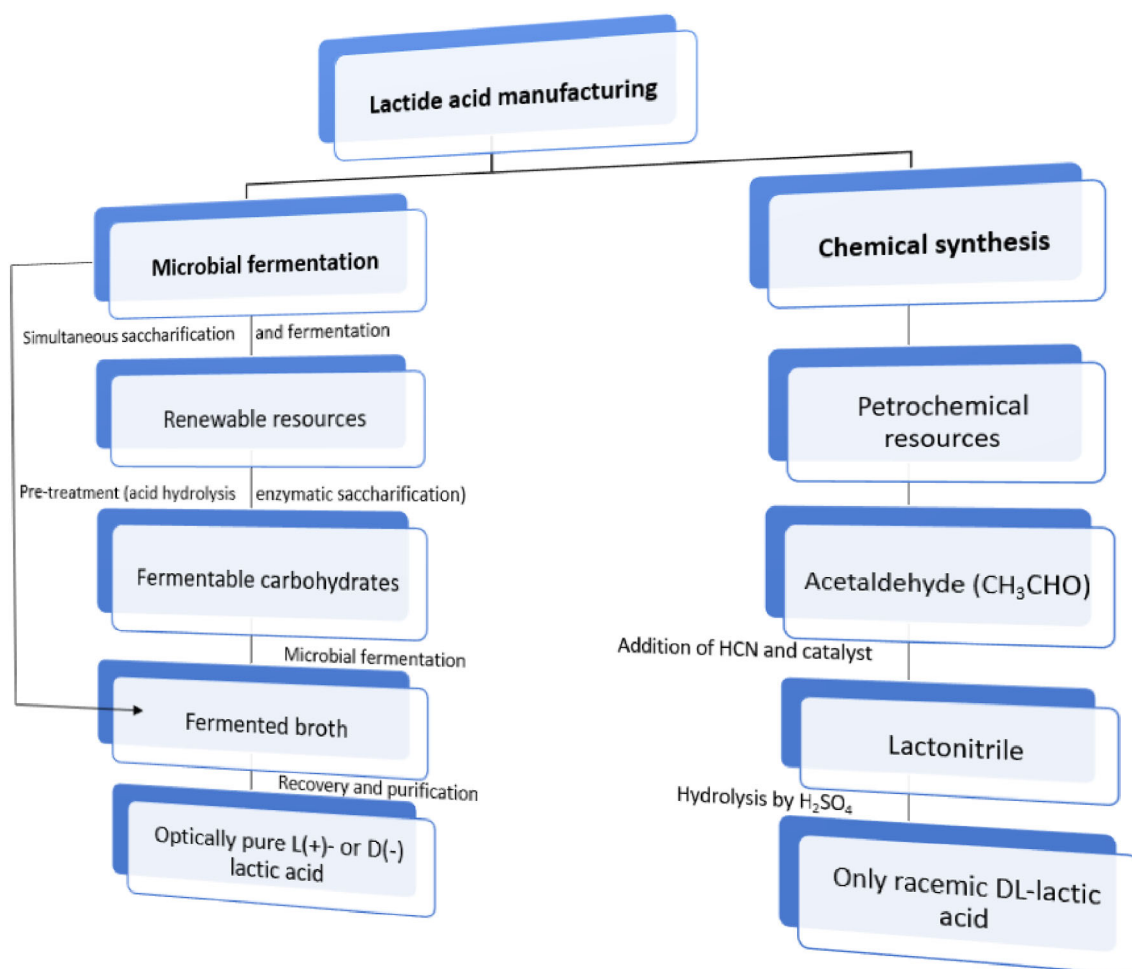


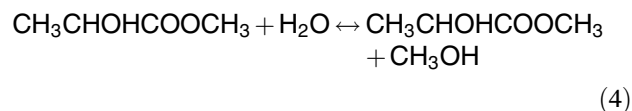
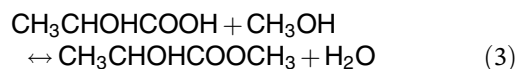
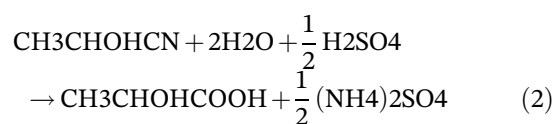
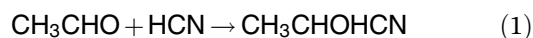
FIGURE 2 Summary of chemical synthesis and microbial fermentation processes, two routes of lactic acid manufacturing.

requiring less energy during the process, PLA has been widely adopted in additive manufacturing (AM) technique.<sup>[48–53]</sup> The increasing demand for PLA is essentially driven by the end-use industries such as packaging, agriculture, transport, automobiles and textile. PLA application in packaging accounts for 65% of the total uses, which is ahead of textiles, automobiles and transportation. This review article attempts to highlight a brief overview of the PLA manufacturing process, and PLA properties followed by its applications in different fields from biomedical to technical domains.

## 2 | PLA SYNTHESIS AND POLYMERIZATION

Lactic acid is the basic building block of PLA. Figure 2 shows lactide acid industrially manufactured by fermentation of carbohydrates or chemical synthesis of resources such as coal, petroleum product, and natural gas.

Lactic acid reactions are described in Equations (1)–(4)<sup>[54]</sup>:



Naturally, lactic acid molecules can be obtained in plants, microorganisms, and animals. Based on the application requirements, lactic acid with different degrees of purities can be determined. Different stereoisomers of lactide are shown in Figure 3. In cyclic dimer processing of lactic acid two of PLA molecules combine, it rises to l-lactide or ll-lactide, d-lactide, or dd-lactide. Meso-lactide

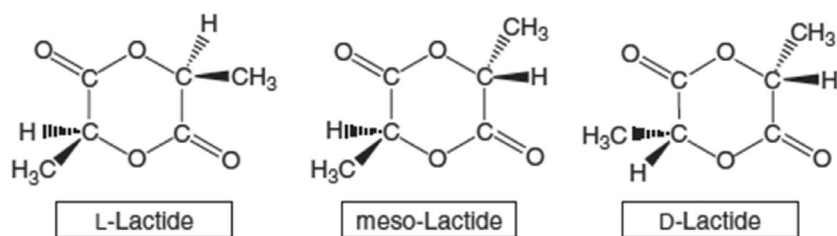


FIGURE 3 Illustrates the chemical structures of L-, meso-, and D-lactides, adapted from Avérus.<sup>[55]</sup>

or D-lactide also can be made by both molecules of L-lactic acid and D-lactic acid. Rac lactide, a racemic lactide, is formed by the mixture of L- and D-lactides. By depolymerization of low molecular weight PLA under decreased pressure lactide can be obtained. Previous studies have emphasized that lactic acid isomer feedstock, temperature, the catalyst's nature as well as content are the effective parameters for the amount of lactide isomer formed during the process.<sup>[24,55,56]</sup> Indeed, the separation between each stereoisomer is essential to examine the final PLA structure during the process. This process can be determined due to the difference in boiling points between meso- and L- or D-lactide.<sup>[55]</sup>

Lactic acid (2-hydroxy propionic acid), the simplest hydroxy acid exists in two optically active configurations of L(+)-isomer and D(-)-isomer. The L(+)-isomer is specified to be made in humans and other mammals. Furthermore, the bacterial system is the source of both D(-)- and L(+)-enantiomers processes.<sup>[56]</sup> *Lactobacilli amylophilus*, *L. bavaricus*, *L. casei*, *L. maltaromicus*, and *L. salivarius* are known as the organisms that mainly yield L(+)-isomer. Besides, *L. delbrueckii*, *L. jensenii*, or *L. acidophilus* yield the D-isomer or mixtures of both.<sup>[56]</sup> Based on the particular strain of *Lactobacillus*, a wide range of carbohydrates can be utilized in fermentation. This process is mostly prepared in great quantities (around 200 kT per year) by the bacterial fermentation of carbohydrates. According to the type of bacterial used, the fermentation process can be categorized into different types (I) the heterofermentative method, and (II) the homofermentative process. Therefore, it modifies the process of lactic acid with an inferior level of by-products, and principally with the industrial application.<sup>[55,56]</sup> The previous study has suggested that during this process most of the simple sugars with agronomic sources can be employed. These sources can be (1) glucose, maltose, and dextrose from corn or potato starch; (2) sucrose from cane or beet sugar; and (3) lactose from cheese whey. Furthermore, protein, complex nutrients such as B-vitamins, amino acids, and nucleotides are other materials that organisms require during the process. These materials can be purveyed from corn steep liquor, yeast extract, cottonseed flour, or soy flour.<sup>[57]</sup> Finally, lactide units can be considered as a

more complex macromolecule architecture known as copolymers.

## 2.1 | Different syntheses of PLA

Generally, polymer materials can be classified in different ways. Polymerization mechanisms, production procedures, specialized features, applications, and structure are only a few examples. Furthermore, the diversity of structures can be obtained based on the type, order of repeating units, and the form of branching. PLA synthesis is multiple processes beginning from the formation of lactic acid and finishing with polymerization.<sup>[24,55–57]</sup> The primary step of this procedure is the production of lactide. Figure 4 demonstrates high molecular weight PLA which can be synthesized by three diverse ways of polymerization. Condensational polymerization of lactic acid is a technique to rectify the problems of low molecular weight, brittle, and the glassiness. External coupling agents also are a method for overcoming these shortages. Although due to the melt viscosity, the presence of water, impurities, the lack or low concentration of reactive end group, and the back-biting equilibrium reaction the molecular weight of the condensation polymer is low. As a result, this approach is not suitable for a broad range of applications. In the second route of yielding a high weight average ( $M_w$  100,000) PLA process, different steps of collecting, purifying, and ring-open polymerize (ROP) should be followed.<sup>[57]</sup> In the third process, to achieve PLA with an average molecular weight of more than 300,000 both lactic and catalyst are azeotropically dehydrated in refluxing great boiling aprotic solvent under decreased pressure.<sup>[56–58]</sup>

## 2.2 | Polymerization mechanisms

As mentioned before, lactic acid condensation, azeotropic dehydration and condensation, and ROP of lactide are three methods for PLA polymerization. It is worth mentioning that condensation polymerization is known as the least expensive approach. However, this method is an

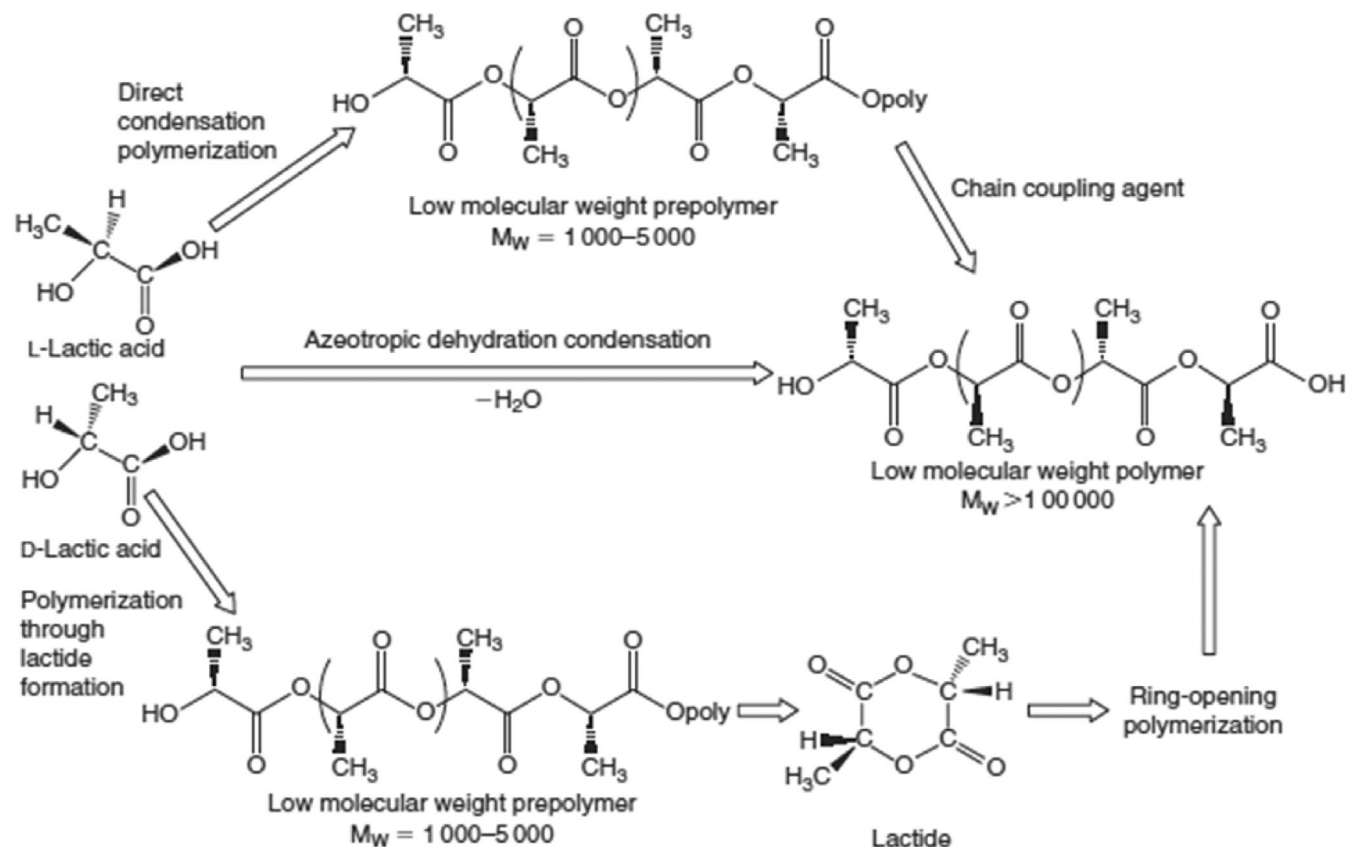


FIGURE 4 A schematic representation of different synthesis approaches for obtaining high molecular weight PLA, reprinted from Avérous.<sup>[55]</sup>

inconvenience as the processing of high molecular weight is complex.<sup>[55]</sup> In this process, the latter can be tackled by coupling or esterifying cation-promoting agents.<sup>[24,56]</sup> Thus, coupling agents react with both hydroxyl (OH) or the carboxyl PLA end-groups.<sup>[55,56]</sup> It is important to consider that the nature of the chain end-groups should be fully verified.<sup>[55]</sup> That chain-extending agent's method is economically visible. Moreover, this technique has the possibility of designing copolymers with various functional groups. Although there are certain disadvantages to this method such as: containing the unreacted chain-extending agents, oligomers, and remaining metallic impurities from the catalyst in the final polymer, residual metal, or polymer impurity. In this technique, the chain-extending agents can be non-biodegradable or non-bioabsorbable.<sup>[55,56]</sup>

### 2.2.1 | Azeotropic dehydration and condensation

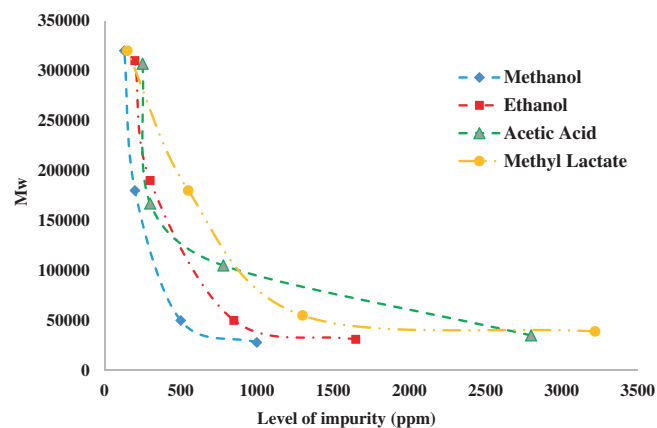
PLA with high molecular weight can be manufactured by azeotropic dehydrative condensation of lactic acid, without requiring the addition of chain extenders or

adjuvants. Mitsui Chemicals (Japan) has industrialized a method to produce high molecular weight PLA ( $M_w$   $^3$ 300,000). In this procedure, lactic acid and catalyst are azeotropically dehydrated in a refluxing, high boiling, aprotic solvent under lesser pressure.<sup>[22,55-57]</sup> The process involves decreasing the distillation pressure of lactic acid for 2–3 h at 130°C to remove the majority of condensation water. In the next step, the catalyst was added along with diphenyl ester. A tube was packed with a 3 Å molecular sieve, and it was attached to the reaction vessel. The solvent was joined to the response vessel via the molecular sieves during an expansion of 30–40 h at 130°C. Finally, the polymer was separated or dissolved and participated in more purification.<sup>[24]</sup> It has been determined that solvent, catalyst, reaction temperature, and level of impurities are the effective parameters on the rate of polymerization and final molecular weight.<sup>[56]</sup>

Table 1 provides the list of various catalysts that were tested to determine how they affect molecular weight during the process. In this table, the reactions were performed at 130°C for 24 h in diphenyl ether. In addition, if the molecular weights were less than 5000 at this step, the reactions were continued over 16 h at 160°C.

**TABLE 1** The effect of various catalysts on molecular weight<sup>[56,59]</sup>

Catalyst	Cat./PLA (wt%)	Temp. (°C)	$M_w$
H <sub>3</sub> PO <sub>4</sub>	2.5	160	1300
H <sub>2</sub> SO <sub>4</sub>	2.5	130	65,000
PTSA	2.5	130	100,000
Nafion-H	2.00	160	4000
Mg	0.50	160	2100
Al	0.50	160	5400
Zn	0.50	160	35,000
Sn	0.50	130	240,000
TiO <sub>2</sub>	0.83	160	1600
ZnO	0.62	160	20,000
SnO	0.57	130	230,000
ZnCl <sub>2</sub>	1.04	160	18,000
SnCl <sub>2</sub>	0.80	130	230,000
Mn(AcO) <sub>2</sub>	1.57	1.60	19,000
Fe <sub>2</sub> (LA) <sub>3</sub>	1.70	160	27,000
Ni(AcO) <sub>2</sub>	1.51	160	140,000
Cu(OA) <sub>2</sub>	2.75	160	1900
Y(OA) <sub>3</sub>	2.92	160	20,000
Ti(BuO) <sub>4</sub>	3.55	130	8000
(Bu) <sub>2</sub> SnO	1.05	130	130,000

**FIGURE 5** The impact of impurities on final molecular weight, adapted from Hartmann.<sup>[56]</sup>

As mentioned before impurities have significant effects on the final molecular weight, which is due to the end-capping of the polymer.<sup>[56]</sup> In general, lactic acid processed by the fermentation technique comprises impurities that can be the result of fermentation itself or the isolation and purification phases. These purities can be methanol, ethanol, acetic acid, pyruvic acid, fumaric acid, methyl lactate, or ethyl lactate. Figure 5 provides

the influence of impurities on the final molecular weight. The figure clarifies that to obtain the PLA with the highest molecular weight the maximum level of impurities should be less than 0.01% (100 ppm).<sup>[56]</sup>

## 2.2.2 | ROP of lactide

Ring opening is a polymerization technique for producing high molecular weight PLA. Although catalysts are required during the ROP process, PLA molecular weight can be controlled.<sup>[60,61]</sup> In this process, residence time, processing temperature, catalyst category, concentration,<sup>[61]</sup> the type of monomer, the rapport, and sequence of D- and L-lactic acid units can be controlled.<sup>[60]</sup> Furthermore, adopting high-purity lactide during the process is crucial to consider.<sup>[58]</sup> The procedure entails decompression, which involves removing water from the system, followed by the addition of catalysts to the reactor. After a few hours, the final product, lactide with an open ring for polymerization obtain.<sup>[59]</sup> Figure 6 demonstrates the global polymerization mechanism occurring in two steps. Diverse factors such as the polymerization temperature, processing time, the monomer/catalyst ratio, and the category of catalyst can affect polymerization yield and transesterification effect.<sup>[55]</sup> In addition, the interaction between time and temperature plays a substantial role in the matter of restraining the degradation reactions, the molecular weight, and the reaction kinetics.<sup>[55]</sup> Additionally, the chain length can be regulated by the amount of OH impurities.<sup>[55]</sup>

## 3 | PLA PROPERTIES

PLA is a biodegradable, bioabsorbable, pseudoplastic, and renewable thermoplastic polymer.<sup>[25,26,62–67]</sup> Thermoset PLA can be extracted from vegetable oils, like soybean oil, and rapeseed oil.<sup>[68]</sup> Although it has been proved that most thermoset PLA materials, like AESO (acrylic epoxy soya oil resin) are nondegradable as the synthetic processes can be varied.<sup>[69]</sup> Previously, bio-based thermoset PLA was successfully tuned to be completely degradable and more environmentally friendly.<sup>[69]</sup>

Bio-based resin can be composed either by direct condensation of pentaerythritol, itaconic acid, and lactic acid<sup>[70,71]</sup> or based on lactic acid, glycerol (GLA), and methacrylic anhydride.<sup>[70,72]</sup> The star-shaped PLA resin contains GLA, and methacrylic anhydride can yield mechanical characteristics with lower viscosity comparing to the resin synthesized from pentaerythritol.<sup>[70]</sup> Bakare et al.<sup>[70]</sup> synthesized different bio-based thermoset

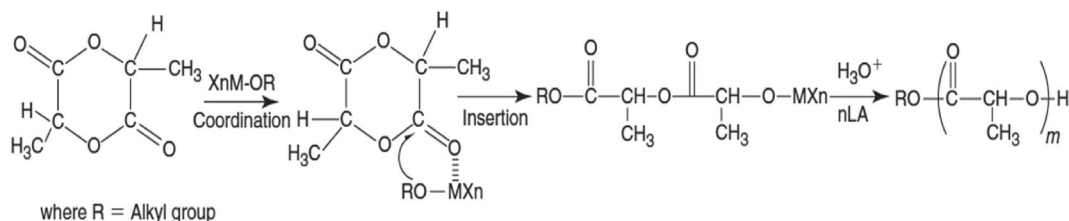


FIGURE 6 The coordination–insertion polymerization approach, reprinted from Avérous.<sup>[55]</sup>

resins of (I) allyl alcohol lactic acid resin (ALA), (II) methacrylate pentaerythritol lactic acid resin (PMLA), and (III) MLA resin that was comprised of allyl alcohol terminated lactic acid oligomer. The PMLA resin had a rather bio-based content compared to MLA with a glass transition of 100 and 79°C, respectively. This result was higher than GLA resin properties with a glass transition of 76°C and the marketable unsaturated polyester (UPE) at 71°C. Besides, both MLA and PMLA resins had considerably lower flow viscosities than the GLA and UPE resins.<sup>[70]</sup>

### 3.1 | Rheological properties

PLA melt is known as a viscoelastic and non-Newtonian fluid. This polymer is a good candidate for sheet extrusion, film blowing, as well as fiber spinning.<sup>[22]</sup> Physical properties such as density, heat capacity, and rheological characteristics of PLA can be tuned by  $T_g$ .<sup>[41]</sup> As a drawback, the melting stability of PLA can be detected during processing and rheological testing.<sup>[63]</sup> Semicrystalline PLA has higher shear viscosity than amorphous PLA which is owing to differences in macromolecular structure. Increasing the temperature decrease the shear viscosity for both categories of PLA. Furthermore, raising the shear rate reduces the viscosity of PLA melts by deteriorating the chain length of PLA molecules. Polymer processes such as extrusion, injection, and spinning can alter the PLA thermal degradation.<sup>[73]</sup> The multi-extrusion process, for instance, impacts the tensile properties, strength, melt flow, and penetrability of water vapor and oxygen.<sup>[73,74]</sup> The tensile and impact properties of PLA decrease slightly after the multi-extrusion process. By contrast, the melt flow index and permeability of H<sub>2</sub>O vapor and oxygen increase by multi-extrusion cycles.<sup>[73,74]</sup> The viscosity reduces as the extrusion temperature rises, owing to a reduction in molecular weight induced by the extrusion screw's shear deformation. Figure 7 shows the influence of extrusion temperature on the complex viscosity of PLA.<sup>[75]</sup> Molecular weight diminution and weight loss happen from 180 to 220°C<sup>[75]</sup> To resolve this issue, and improve thermal stability, shear sensitivity, and/or melt strength of PLA during

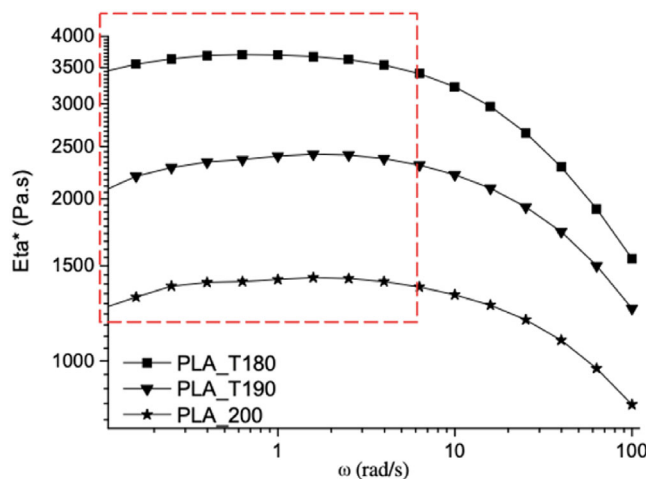


FIGURE 7 Schematic representation of polylactic acid (PLA) rheological behavior at different temperatures, under an inert atmosphere, adapted from Al-Itiry.<sup>[75]</sup>

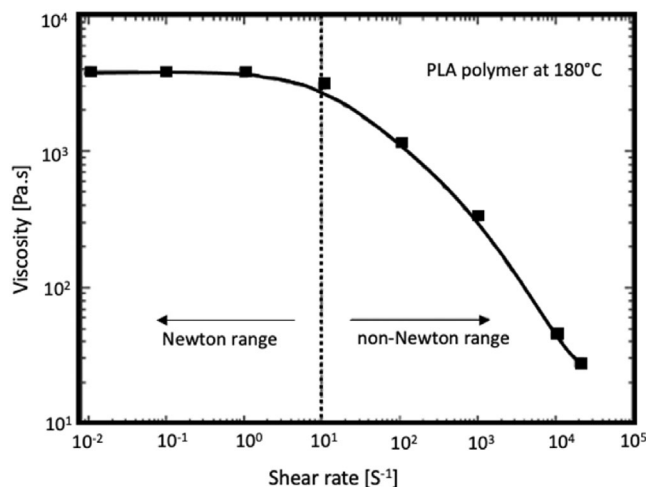


FIGURE 8 The viscosity behavior of polylactic acid (PLA) at 180°C as a function of the shear rate, adapted from Hamad.<sup>[73]</sup>

the extrusion process, chain extenders with polymers can be applied. This process has the final result of increasing the complex viscosity of the extended polymer.<sup>[73,75]</sup> Octoate catalysts such as tris (nonylphenyl) phosphite are good candidates for balancing chain extension during degradation reaction, thus enhancing PLA melt stability.<sup>[63,73]</sup>

**TABLE 2** Indicates the mechanical characteristics of poly(L-lactide) with the different molecular weights<sup>[24,57]</sup>

	L-PLA ( $M_w = 66,000$ )	Annealed L-PLA ( $M_w = 66,000$ )	D,L-PLA ( $M_w = 114,000$ )
Tensile strength (MPa)	59	66	44
Elongation at break (%)	7.0	4.0	5.4
Elastic modulus (MPa)	3750	4150	3900
Yield strength (MPa)	70	70	53
Flexural strength (MPa)	106	119	88
Unnotched izod impact ( $J m^{-1}$ )	195	350	150
Notched izod impact ( $J m^{-1}$ )	26	66	18
Rockwell hardness	88	88	76
Heat deflection temperature ( $^{\circ}C$ )	55	61	50
Vicat penetration ( $^{\circ}C$ )	59	165	52

Abbreviation: PLA, poly(lactic acid).

Figure 8 illustrates PLA Newtonian behavior at the low shear rates ( $<10 s^{-1}$ ) while at the high shear rates ( $>10 s^{-1}$ ) it exhibited non-Newtonian behavior (shear thinning).<sup>[73]</sup> For the L/D-isomer mixture, there is a direct connection between the shear viscosity of the polymer, L-isomer, and the crystallinity of PLA.<sup>[73,76]</sup> The viscosity of branched PLA is higher than that of linear PLA in Newton ranging. By contrast, in the non-Newtonian range, the viscosity of the branched PLA is lower than linear PLA.<sup>[73]</sup>

A variety of rheological characterization methods such as capillary and rotational rheometers are applicable to determine the rheological properties of PLA. Following volumetric measurement, it was determined that PLA and lactide isomers in the liquid state have a nearly equal density as a function of temperature. The density of amorphous and crystalline PLLA has been determined as 1.248 and 1.290  $g cm^{-3}$ , respectively.<sup>[24,63]</sup> PLA in solid form has a density of 1.36  $g cm^{-3}$  for L-lactide, 1.33  $g cm^{-3}$  for meso-lactide, and crystalline. In an amorphous state, the PLA densities for meso and crystalline forms are 1.36 and 1  $g cm^{-3}$ , respectively.<sup>[24]</sup> Two polylactides of poly(98% L-lactide) and poly(94% L-lactide) have a density of  $\sim 1.2400$  and  $\sim 1.243$   $g cm^{-3}$ , respectively.<sup>[24]</sup>

### 3.2 | Mechanical properties

PLA is a talented thermoplastic aliphatic polyester with good mechanical strength, great optical properties, good compostability, high biocompatibility capacity, and good processing ability.<sup>[74,77,78]</sup> A variety of mechanical properties of this material, from soft and elastic to stiff and high strength makes PLA suitable for a wide range of applications.<sup>[41]</sup> Table 2 shows the summary of information related to PLA mechanical characteristics. PLA

applications in packaging such as films have provided better mechanical characteristics than polystyrene (PS), and are comparable to PET.<sup>[24,25]</sup> Although PLA has some drawbacks such as reduced ductility and poor degradation rate. Durable toughening without compromising tensile strength, modulus, and degradability is the main challenge in improving PLA toughness. Besides, toughened PLA exhibited a propensity to lose toughness with physical aging. To be able to progress mechanical properties, degradation behavior, processability, and crystallinity several bulk-modification approaches have been engaged. It was determined that a mixture of pure poly(L-lactide) and poly(lactide) with a ratio of 1:1 increases the melting temperature ( $230^{\circ}C$ ) and tunes the mechanical properties of the pure polymer. Although blending is the most broadly utilized technique to increase PLA mechanical characteristics.<sup>[25]</sup> Both biodegradable and nonbiodegradable plasticizers can be applied to decrease the  $T_g$ , increase ductility, and improve the processability.<sup>[25]</sup>

Toughen's property can be modified by blending PLA with low-density poly(ethylene) (LDPE). The incorporation of PLA with organic/inorganic fillers is an approach to improve Young's modulus. PLA blends with starch are of specific interest as the starch is freely accessible at low cost, is naturally biodegradable, and can be obtained from renewable sources.<sup>[79]</sup> Although the diminution of toughness with physical aging rests a challenge for PLA-based blends. Table 3 shows the mechanical properties of pure PLA and LDPE, as well as binary and ternary blends with starch.

### 3.3 | Permeability characteristics

The diffusion and sorption of gases in semicrystalline polymers depend on physical aging, polymer thermal



TABLE 3 Mechanical properties of pure PLA, and LDPE, blend, as well as PLA–LDPE blend with starch<sup>[79]</sup>

Material	Ratio	Elastic modulus (MPa)	Tensile (MPa)	Elongation at break (%)
LDPE	-	200 ± 5	13.3 ± 0.2	460 ± 10
PLA	-	2625 ± 65	52 ± 1.0	4.7 ± 0.1
LDPE–PLA	80:20	383 ± 15	8.6 ± 0.2	20 ± 1.5
	70:30	419 ± 20	8.7 ± 0.2	15 ± 1.0
	60:40	488 ± 35	8.8 ± 0.2	3 ± 0.8
	50:50	1190 ± 42	17.8 ± 0.4	3 ± 0.8
LDPE–starch	80:20	220 ± 10	8.1 ± 0.1	105 ± 15
	70:30	290 ± 10	7.1 ± 0.2	105 ± 5
	50:50	255 ± 5	7.4 ± 0.2	85 ± 10
PLA–starch	80:20	3070 ± 86	48.6 ± 1.5	2.12 ± 0.1
	70:30	3120 ± 72	37.1 ± 2.9	1.92 ± 0.1
	60:40	3230 ± 84	42 ± 2.0	2.0 ± 0.1
LDPE–PLA–starch	40:20:40	650 ± 5	7.4 ± 0.2	2.3 ± 0.1
	50:20:30	571 ± 16	7.1 ± 0.2	2.9 ± 0.2
	60:20:20	490 ± 12	6.3 ± 0.5	8.0 ± 0.5
	50:30:20	563 ± 21	5.1 ± 0.2	3.5 ± 0.3
	50:20:30	571 ± 16	7.1 ± 0.2	2.9 ± 0.2
	50:10:40	497 ± 4	5.6 ± 0.1	4.0 ± 0.2

Abbreviations: LDPE, low-density poly(ethylene); PLA, poly(lactic acid).

history, polymer-gas molecule chemistry, free volume in the amorphous state, and crystallinity.<sup>[80]</sup> In addition, permeation properties in the amorphous state can be adjusted by polymer chain branching and small changes in L:D stereochemical content.<sup>[41,80]</sup> PLA has low gas barrier properties with a slow crystallinity rate. The crystalline phase of polymer is known to be impermeable; hence, to improve PLA barrier properties, it is important to optimize its crystallization condition.<sup>[41,80]</sup> Besides, gas permeation and sorption characteristics of PLA in both glassy and amorphous states are principally subtle to the film realization protocol and physical aging.<sup>[80]</sup> By film physical aging, the permeability decreases, which is due to increasing densification and decreasing free volume.<sup>[80]</sup> Diffusion of small molecules like He, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> through glassy, partially crystalline polymers and polymer membranes make the polymer a good candidate for current and possible future applications. PLA is a fairly weak barrier to water vapor and CO<sub>2</sub>.<sup>[80]</sup> Moreover, N<sub>2</sub> has inferior diffusivity and permeability compared to O<sub>2</sub> in the greatest polymer films. There is a linear relationship between PLA permeability of CO<sub>2</sub> and temperature, while by increasing the temperature the permeability of CO<sub>2</sub> increases.<sup>[80]</sup> The permeability (P) values of gases in PLA is as the following order: PCO<sub>2</sub> > PHe > PO<sub>2</sub> > PH<sub>2</sub> > PN<sub>2</sub> > PCH<sub>4</sub>.<sup>[81]</sup> Figure 9

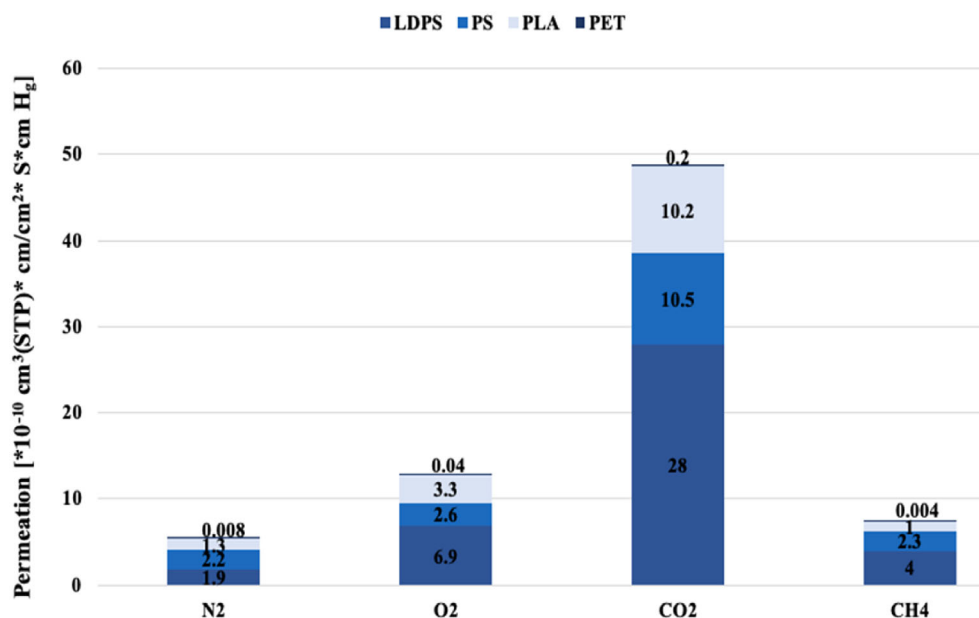
shows PLA (L:D ratio 96:4) gas permeability on N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub>.<sup>[73]</sup>

In high crystallinity of biaxially oriented film, for instance, CH<sub>4</sub> permeation is 4.5 times fewer than in films with a linear and branched structure. Nanocomposite PLA films can decrease PLA permeability. Some inorganic fillers such as talc can be used during PLA polymerization to increase nucleation density, decrease crystallization half time, and crystallization processing time.<sup>[28,76,82]</sup>

### 3.4 | Compostability and biodegradation properties

A polymer can be degradable without being biodegradable since it might disintegrate into pieces or even an invisible powder, but not be assimilated by microorganisms. In addition, the polymer can be degradable or even biodegradable without being compostable since it might biodegrade at a rate that is too slow to be considered compostable.<sup>[83–85]</sup> Composting is above all an aerobic procedure and can be considered a nature's way of recycling.<sup>[86]</sup>

PLA like most synthetic polymers is rarely utilized alone by itself and some characteristics need to be



**FIGURE 9** The permeability properties comparison between poly(lactic acid) (PLA) with low-density polyethylene, polyethylene terephthalate, and polystyrene at 30°C, reprinted from Hamed.<sup>[73]</sup>

improved by the inclusion of additives.<sup>[87]</sup> When these polymers are recuperated through recycling or composting they can reach their potential environmental profits.<sup>[86]</sup> The materials such as PLA and PLA-based composite can be biodegraded in biological milieus as soil and compost.<sup>[88]</sup> Even if recycling could be energetically a better opportunity than composting for these polymers, it may not be practical because of excessive sorting and cleaning supplies.<sup>[88]</sup>

Biodegradability is an end-of-life possibility that exploits the power of microorganisms present in the disposal milieu to eliminate polymer produces intended for biodegradability from the environment via the microbial food time chain in a timely, safe, and efficient way.<sup>[89]</sup> Specific polymer materials are biodegraded depending on their chemical structure, the number of additive compounds, and the environmental situations.<sup>[89]</sup> Particular conditions for microorganisms' growth like as control of humidity (around 50–60%), oxygen concentration (over 5%), C/N ratio (range 20:1–40:1), and the temperature (up to 60°C) must be set up, whereas in home composting places this is not accessible.<sup>[89]</sup>

Biodegradation of PLA follows two steps of hydrolytic degradation and microbial assimilation.<sup>[90–92]</sup> While hydrolytic degradation happens, water molecules decrease the molar mass. As a consequence, this procedure causes low molecular chain formation throughout random chain scission.<sup>[93]</sup>

Microbial digestion requires low molecular weight polymer chains, while microbes assimilate these intermediates for energy and they decompose into several compounds like CO<sub>2</sub> and H<sub>2</sub>O.<sup>[94]</sup> PLA is stated to facily biodegrade under composting environments and to require more time to decompose under soil conditions.<sup>[95,96]</sup> The carbon dioxide evolution measurement is a critical means

to measure biodegradation since it aids to monitor kinetic parameters throughout biodegradation.<sup>[97–99]</sup>

The procedure of biodegradation comprises two important aspects; the first one is abiotic degradation which is associated with the action of physicochemical factors. The second procedure contains microbial activity meaning biotic degradation.<sup>[3]</sup> Temperature is one of the most significant factors when it concerns biodegradation in compost.<sup>[83]</sup> The biodegradation process is eased when the temperature is nearby to the glass transition temperature of the PLA (around 60°C). PLA is decomposed up to 90% into CO<sub>2</sub> in compost at 70°C after 180 days. In addition, composting process occurs under anaerobic conditions.<sup>[83]</sup> Besides, PLA takes years to be decomposed under an unmanaged natural soil environment<sup>[93]</sup> and it is compostable under industrial composting environments which can biodegrade entirely in 180 days.<sup>[90,100,101]</sup>

Life cycle assessment (LCA) is a valuable means for assessing and quantifying the energy and ecological consequences related to a product, procedure, or service.<sup>[102]</sup> Even though LCA is an established approach, results may vary according to the scope, system boundary, country, and time. Many studies have shown that a biopolymer (such as PLA) engenders fewer carbon and lower fossil energy consumption than fossil-based polymers such as PET, PS, and polypropylene.<sup>[103,104]</sup>

PLA is an ecological alternative to traditional polymers as the lactides can be obtained by the microbial fermentation of agricultural by-products, mostly carbohydrate rich resources.<sup>[105]</sup> The latest progress shows that lactic acid can be transformed into PLA through two principal ways: first, the indirect route utilizing lactide, and second, direct polymerization by polycondensation, generating PLA.<sup>[106]</sup>

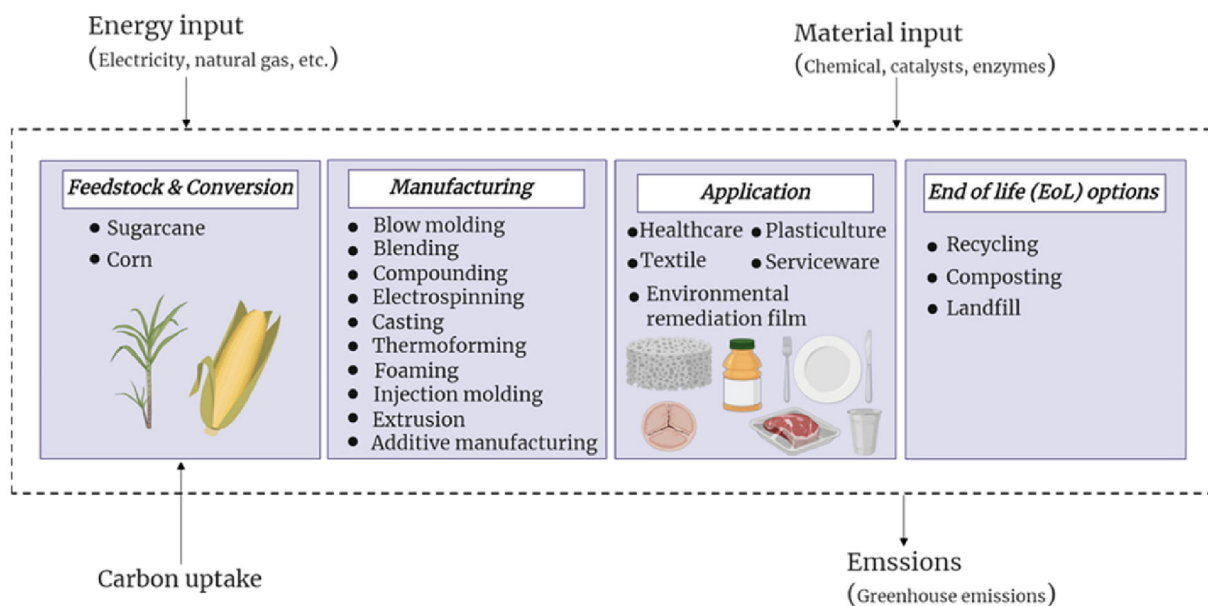


FIGURE 10 Polymeric acid life cycle with potential emissions at diverse steps reprinted from Rezvani.<sup>[107]</sup>

The lifecycle of PLA is argued through its waste management steps to define the principal drivers affecting its ecological aspects.<sup>[107]</sup> The system boundary of PLA fabrication direction concerning energy, materials, and emissions flow has been presented in Figure 10.

The first phase of the lifecycle of PLA is feedstock gathering and conversion, (Figure 10). PLA elaboration consists of three principal stages. First of all, bio-based materials such as corn should be accumulated and transported to the herb. Then, the feedstock is transformed into lactic acid through the fermentation procedure of starch. This is the furthest common producing technique of lactic acid as it is chemical, cost-effective, and leads to produce pure lactic acid. One of the principal factors influencing the crystallization behavior and natural degradation of PLA is the optical purity of the lactic acid, hence determining a low concentration of impurities matters. Consequently, it is important to consider that during the downstream processing of lactic acid, the fermentation broth comprises significant quantities of impurities. The identification and separation of the impurities is a critical phase that defines the final characteristics of PLA.

## 4 | PLA APPLICATIONS

PLA, a compostable, and biodegradable polymer has versatile applications in food packaging,<sup>[23,24,41,56,57,63,108–112]</sup> biomedical industry,<sup>[113–122]</sup> drug delivery,<sup>[108,123–141]</sup> tissue engineering,<sup>[142–147]</sup> bio composites,<sup>[41,95,109,112,142,148–151]</sup> and AM.<sup>[15,41,49,52,53,69,115,120,122,139,152–156]</sup> Besides, compared to commodity petrochemical-based plastics

the application request of PLA as a biodegradable and cost-effective alternative polymer increases. The following part summarizes the applications of PLA in biomedical, food packaging, composites, automotive, AM, the challenges, and requirements for related applications.

### 4.1 | Biomedical

PLA monomers extract from nontoxic renewable sources. In addition, this polymer has ease of degradation and reabsorbing through the metabolic pathway. Thus, PLA has a widespread application in biomedical industry,<sup>[31,41,139,152,155,157–159,113–115–120]</sup> drug delivery,<sup>[73,108,123–127,131–134,136,139–141,152,160–163]</sup> and tissue engineering.<sup>[41,115,139,142,145,146,148,160,163–167]</sup>

Polymeric drug release occurs in one of three ways: erosion, diffusion, and swelling. It is important to notice that the polymer properties can modify the drug release profile.<sup>[31]</sup> In terms of biodegradable polyesters, the drug release occurs followed by penetration of water into the device, thus monomer degradation. Copolymer composition and unit arrangement along the polymer chains, stereoregularity, molecular weight and polydispersity, chain end groups and branching or cross-linking structures, blending with other polymers or small molecules (i.e., drugs), and surface area are the effective parameters on mechanical and physical properties.<sup>[73,168]</sup> Comonomer or blending agents with higher molecular weight, degree of crystallinity, and hydrophobicity have slower polymer degradation, thus a slower drug release rate.<sup>[168]</sup>

TABLE 4 Utilization of PLA in the biomedical fields obtained by innovative techniques

Reference	Materials used	Processing techniques	Output
[113]	PCL polymer	ITOP	3D printing technology has been used to realize human-scale mandible bone, ear-shaped cartilage, and organized skeletal muscle
[114]	PCL	Multi-head tissue/organ building printer (MtoBS)	3D printing technology has been used to regenerate the auricular cartilage and fat tissue.
[116]	PVA-PLA nanofibers	Single nozzle	Core-shell-structured (PVA)-PLA nanofibers combining the hydrophilic trait of PVA were produced using coaxial electrospinning.
[117]	NFC-Alginate	3D bioprinter discovery (regenHU)	3D bioprinting human chondrocytes with nanocellulose-alginate bioink for cartilage tissue engineering applications
[118]	Alginate and fibrin hydrogel materials	3D inkjet droplets technique	Direct 3D cell printing systems using inkjet droplets have been used to construct 3D structures with multiple types of cells.
[119]	HEPG2 hepatoma cells	3D printing (Z printer)	Liver cells mixed with an UV cross-linkable hydrogel solution are introduced into parallel channels of a sealed microfluidic device and photopatterned to produce stable tissue constructs in situ.
[120]	Poly(L-lactic acid) and poly(D,L-lactic acid)	MDM technique	Bone tissue engineering scaffolds with different properties were fabricated by a tri-nozzle deposition process, in the MDM system.
[132]	PLA, PLGA, CS	Cell printing	The uptake of rodamine-NPs by OECs was time dependent and was influenced by the carrier charge.

Abbreviations: CS, chitosan; ITOP, integrated tissue-organ printer; MDM, multi-nozzle deposition manufacturing; NFC, nanofibrillated cellulose; NOs, nanoparticles; OECs, olfactory ensheathing cells; PLA, poly(lactic acid); PLC, poly( $\epsilon$ -caprolactone); PLGA, poly-lactic-co-glycolic acid; PVA, polyvinyl alcohol.

PLA and their copolymers were used most frequently in tissue engineering as well as orthopedic devices. Although PLA has drawbacks of low impact toughness, brittle nature, and low elongation-at-break.<sup>[169]</sup> It is worth mentioning that the polymer scaffold must retain the appropriate mechanical, geometrical, and permeability properties over time.<sup>[139]</sup> It is noticeable that different techniques such as blending, composites, forming, and copolymerization require to overcome the poor mechanical properties of PLA. PLA polymer is applicable to fabricate absorbable screws and pins where high mechanical stiffness or strength was not required.<sup>[73]</sup> As it was mentioned before, blending PLA with other polymers can enhance the mechanical properties of PLA polymer. Besides, based on the material content, as well as blend morphology blending polymers can also modify the degradation profile.<sup>[169]</sup> The previous study has reported the manufacturing of PLA/PEG-based scaffolds via the 3D printer technique. The 3D-printed scaffold had well defined structure, enhanced hydrophilicity, elastic modulus, as well as tuned degradation.<sup>[170]</sup> Tables 4 and 5 represent PLA applications in biomedical fields obtained by innovative (Table 4) and conventional techniques (Table 5).

Wang et al.<sup>[167]</sup> have developed vastly permeable 3D interconnected scaffolds through surface cohesion of

cotton-type nonwoven fibers using  $\text{CHCl}_3$  (Figure 11). Their results revealed that bonding for 90 minutes with a fiber density of  $0.15 \text{ g cm}^{-3}$  could ease satisfied porosity, and supportive mechanical characteristics as well as 3D spatial microstructure for cell development. They exposed that fibers coating with gelatin induced greatly efficient bone formation and restoration of rabbit radius bone defect.

PLA can be blended with other polymers like PCL,<sup>[171]</sup> and PEG to modify PLA properties.<sup>[172-174]</sup> Tailored PLA structure is applicable to optimize drug delivery.<sup>[173,175-177]</sup> For instance, blended PLA with PCL decreases the local acidification followed by decreasing the inflammatory response.<sup>[31]</sup> Polylactic-co-glycolic acid (PLGA) copolymers are widely employed for encapsulation of sustained drug delivery, and vaccine antigens like proteins, peptides, and DNA.<sup>[139]</sup> PLA-PLGA microsphere containing bioactive agents can apply in the design and development of therapeutic applications.<sup>[160]</sup>

To have more flexibility, and greater impact resistance, it is essential to utilize plasticizers. The plasticizer employed for PLA should be biodegradable and nontoxic. So far, PEG is the greatest common plasticizer and hydrophilic polymer used to increase the hydrophobicity of PLA, thus forming amphiphilic PLA-PEG copolymer.<sup>[41,172-174]</sup>

**TABLE 5** Utilization of PLA in the biomedical fields obtained by conventional processes

Reference	Materials used	Processing techniques	Output
[115]	Reinforced PLLA nanofibers	The cold compression molding process	Dual-porosity scaffold structure was developed for a facile transport of metabolic nutrients
[124]	Poly(D, L-lactic acid)	Emulsification solvent diffusion	Improve the therapeutic antitumor efficacy of ORI by encapsulation in NPs
[108]	AM PLA films	Solvent-casting method	The developed AM PLA films had similar or superior mechanical properties and gas permeability characteristics compared to pure PLA films.
[125]	PLGA nanoparticles	Human dendritic cells were generated by conventional in vitro differentiation	PLGA NPs encapsulation of tumor-derived lysate protein antigens is an efficient methodology allowing to increase cell responses to ovarian cancer TAA (tumor-associated Ags)
[126]	PLGA nanoparticles	Cell culture	Developer the NPs (PLGA NPs) to deliver hydrophobic payloads to intracranial glioma.
[127]	PLA nanoparticles	Solvent evaporation method	The action of TMZ against C6 glioma is sustained when loaded into nanoparticles.
[131]	PLA	Injection molding	Starch provided a biological fuel for the growth of microorganisms in the soil which accelerated the degradation rate of PLA more obviously than wood-flour.
[133]	Poly(DL-lactic acid), Poly(D,L-lactide-co-glycolide)	Emulsification and solvent evaporation	Particle size range could promote the passive targeting of the nanoparticles to tumor cells based on the EPR effect.
[134]	Poly(D,L-lactic acid) (PLA), PVA	Modified spontaneous nanoprecipitation	The tumor size in was significantly reduced ( $p < .001$ ) by treating tamoxifen (Tmx) NPs as compared to pure Tmx
[136]	PLGA, PLA-PEG-PLA	Emulsion solvent extraction/evaporation technique	The presence of PEG on the surface of PLA-PEG-PLA microspheres could improve their biocompatibility.
[140]	PLGA	Nanoprecipitation technique	Nano-CUR6 [optimized curcumin nano-formulation] improved anticancer potential in cell proliferation and clonogenic assays compared to free curcumin.
[141]	Monomethoxy poly(ethylene glycol)-PLA	Ring-opening polymerization	MPEG-PLA copolymer was successfully synthesized and processed into nanoparticle to load honokiol.
[164]	Absorbable PLA	The experimental protocol	The absorbable PLA suture anchor construct, tested in an in vivo, intra-articular model, had similar strength over a 12-week period of implantation with a comparable metal anchor construct.
[145]	Poly[(rac-lactide)-co-glycolide]	Co-oligomer synthesis	Networks based on poly[(rac-lactide)-co-glycolide] showed reduced material switching temperature (Tsw) and enabled SME at room temperature as well as in 37°C water.
[167]	PLA, gelatin/PLA	Centrifugal melt-spinning technique	Biofunctionalized fibrous scaffolds could bionically represent topographic nanofeatures and biological composition for cell binding affinities similar with that of natural ECM.
[142]	PLGA nanofibers, PLA MY	Electrospinning setup	Combination of Tβ4 with the PLGA/PLA HY promotes tenogenesis of adult stem cells for tendon tissue engineering.
[146]	PLA and PGA	Injection molding (specific mold)	It was concluded that purified canine myoblasts were able to promote meniscal fibrocartilage healing by regenerating fibrocartilage-like tissue.

Abbreviations: AM, antimicrobial; ECM, extracellular matrix; EPR, enhanced permeability and retention; HY, hybrid yarns; MY, microfiber yarns; NPs, nanoparticles; ORI, oridonin; PGA, polyglycolic acid; PLA, poly(lactic acid); PLGA, poly-lactic-co-glycolic acid; PVA, Poly(vinyl alcohol); SME, shape-memory effect; Tβ4, thymosin beta-4; TMZ, temozolomide.

## 4.2 | Additive manufacturing

The growing use of AM is one of the main disruptive technologies in the fourth industrial revolution. This rapid technique allows the manufacture of a three-dimensional element using a virtual model and the successive addition of material layer by layer.<sup>[49,178–181]</sup> 3D printing is increasingly used in industry in the aerospace, automotive, healthcare, construction, casting, and energy sectors.<sup>[182–188]</sup> Three types of materials are formerly used for 3D printing: polymers, metals, and more slightly, ceramics. Polymers are the most broadly utilized materials for AM in the industry.

Usually, thermoplastic polymer filaments which have a low melting point have been proposed for the AM technique.<sup>[49]</sup> Nevertheless, innovative composite filaments permitting improved characteristics have been suggested in recent times.<sup>[189,190]</sup> The neat thermoplastic pieces printed by the AM technique, do not have sufficient resistance to be used as fully functional parts. AM of polymer matrix composites purposes to get over limited mechanical characteristics and functionalities of neat thermoplastic pieces.<sup>[191–194]</sup> Among them, PLA, ABS, and PCL have the most applications in AM techniques due to their simple and easy processes.<sup>[195,196]</sup>

Previously, the effects of isothermal treatment of PLA 3D printed specimens, and final mechanical properties at different crystallization temperatures have been investigated. The heat-treated were ranged from 80 to 119°C. It was determined that annealing can tune the mechanical PLA properties. Increasing the annealing temperature enhanced the bond between the layer, thus the mechanical properties. The fastest crystallization kinetics have been observed for the annealing temperature of 100–119°C. Hence, flexural strength, and Young's modulus could improve by 34–47% and 26–51%, respectively. Figure 12 shows the morphology and size of the spherulites analyzed by a polarized light microscope (MOLP). While it can be assumed there is a correlation between the spherulite size and the mechanical properties improvement, there is no spherulites have been detected on the printed specimens before annealing.<sup>[52]</sup>

The application of synthetic and natural materials to develop reinforced filament for the AM method has been suggested recently.<sup>[197,198]</sup> In reinforced polymer composites, the fiber could be used to sustain the force. At the same time, the polymeric matrix has the role of associating and ensuring the fibers and transmitting the force to the reinforcing fibers.<sup>[199–202]</sup> Natural fibers are becoming an appreciated alternative in reinforced polymer composites, as a result of the energy-intensive processing needed to produce synthetic fibers. Natural fibers are not only renewable and

biodegradable but also possess excellent mechanical characteristics.

Matsuzaki et al.<sup>[203]</sup> have utilized jute fibers to reinforce PLA filaments for AM. The mechanical behavior of these composites demonstrated higher tensile characteristics than those of neat PLA. Besides, they have found that the presence of the natural fibers had favorable effects on the dimensional stability of the filament during the extrusion process, which is an important advantage for its application in the fused deposition modeling technique. The presence of natural fibers improves compostability and accelerates the degradation mechanism of 3D-printed PLA-based parts.

Graphene nanoplatelets, with a good mechanical, electrical and thermal performance are known as promising method to improve the working condition during the AM process. The effect of graphene nanoplatelets additive on texture, mechanical properties, dimensional accuracy, and surface texture of 3D printed PLA has been evaluated by Caminero et al.<sup>[204]</sup> The results determined that the PLA–graphene composite specimens had the best performance in terms of tensile and flexure stress, specifically in upright orientation, and the highest interlaminar shear strength. Although the results obtained that the addition of graphene nanoparticles reduced the impact strength of the PLA–graphene composite samples, with no effect on the dimensional accuracy. Indeed, it was obtained that PLA–graphene composite samples have the best performance in terms of texture.

## 4.3 | Food packaging

PLA, a “green” alternative has unlimited applications for food packaging.<sup>[109]</sup> The PLA film inhibiting microbial growth limits migration into foods, and its resistance to supporting bacterial and fungal growth. Thus, it has the potential to be used for covering the shelf life of a wide range of perishable food products, antimicrobial packaging, and coating.<sup>[23,63,108,109]</sup> For an instance, PLA can be used as fruits, vegetables, and biscuits containers or films, yogurt cups, trays, bowls for fast food, and a plate for hot food.<sup>[109]</sup> Although in food packaging application, PLA is appropriate for fresh goods and those whose quality is not affected by PLA oxygen permeability.<sup>[109,205]</sup> PLA functional properties for packaging are grouped in Table 6.

To enhance PLA barrier characteristics, several methods are available. These approaches are evocated as follows<sup>[41,111]</sup>:

- PLA coating with constituents to modulate the hydrophobicity of packaging material.
- Lamination with other biopolymers (coextrusion).

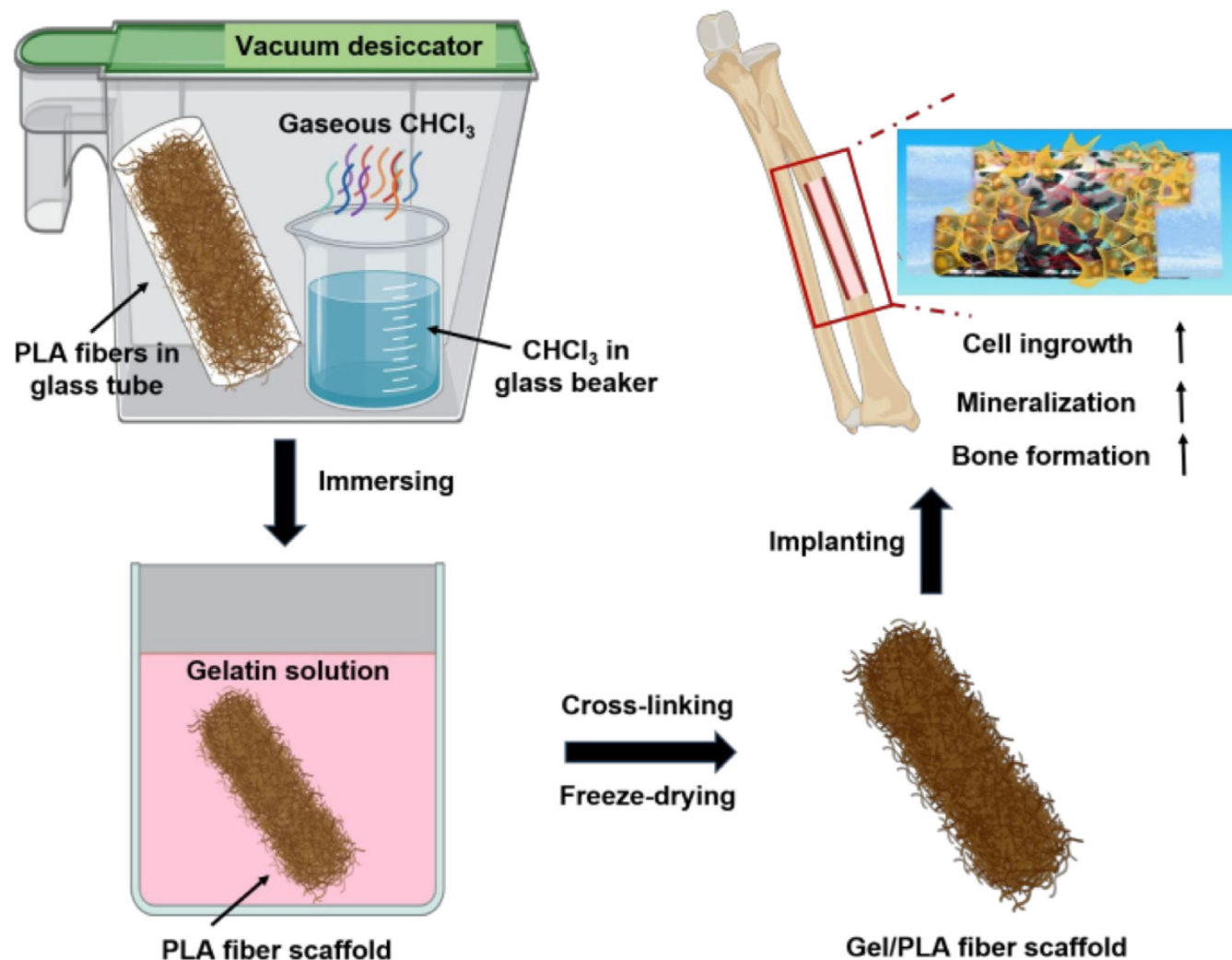


FIGURE 11 The schematic diagram illustrates the gel/poly(lactic acid) (PLA) fiber scaffolds modified by gaseous  $\text{CHCl}_3$  cohesion and gelatin-coating. The figure also presents the in vivo implantation for efficient cell ingrowth, and bone repair, courtesy of Wang.<sup>[167]</sup>

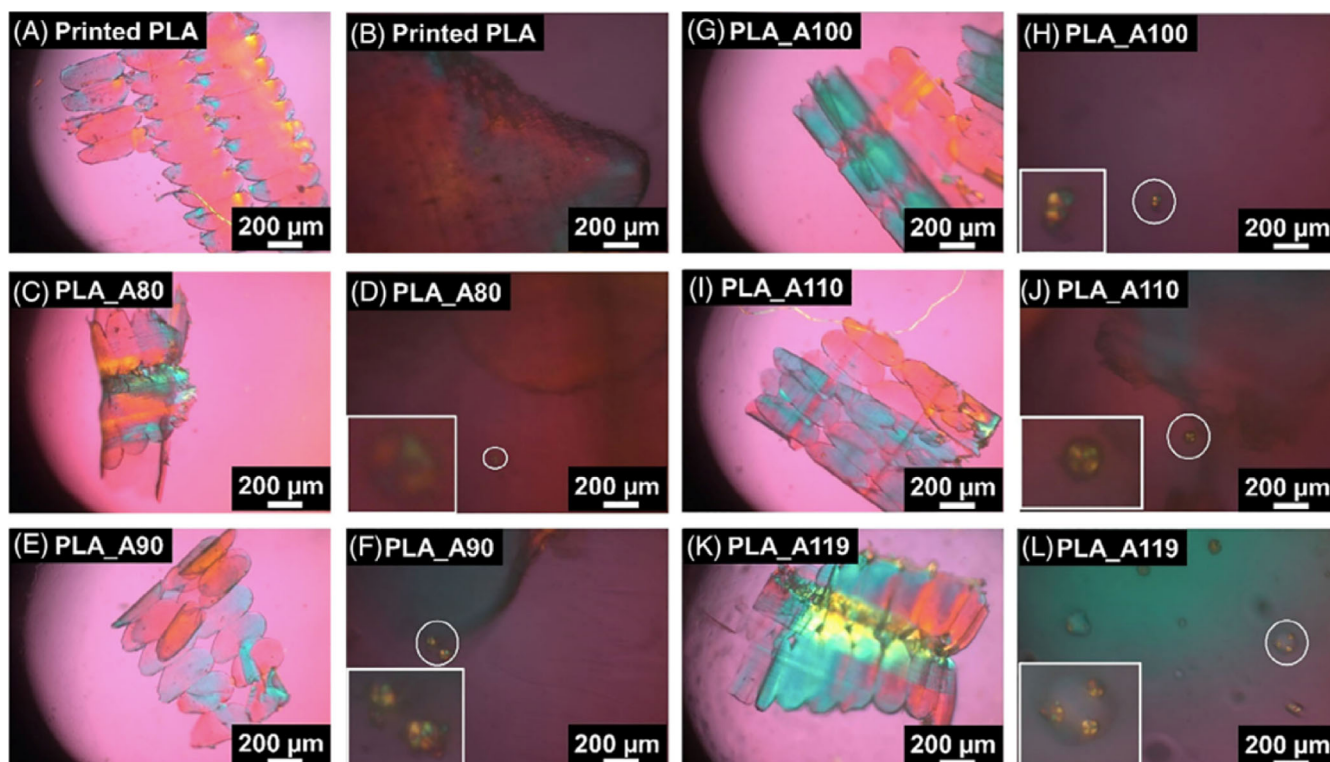
- Employing an edible coating with required barrier characteristics for the food application as primary packaging.
- Enhancing PLA properties by blending it with various biopolymers such as PLA/PEG, PLA/PHA, and PLA/PCL blends.
- Chemical and/or physical variation of biopolymers.
- Improvement of microcomposite and nanocomposite based on biopolymers.

#### 4.4 | Composites

The biodegradation of composite is an essential issue for plastics with a short life cycle considering environmental effects and a decrease in the quantity of plastic waste disposal.<sup>[148]</sup> So far, the furthest considered

biodegradable nanocomposites appropriate for packaging applications are starch and derivatives, PLA, poly(butylene succinate), polyhydroxybutyrate, and aliphatic polyester as PCL.<sup>[112]</sup> Based on the microstructural properties, PLA segregates during 10 months to 4 years period of time.<sup>[41]</sup> The molecular weight, crystallinity, chain flexibility, dimension, and form are of main importance to control the degradation rate.<sup>[148]</sup>

For furthest composite applications, PLA can be synthesized. In this process, a star-shaped PLA polymer structure is functionalized with carbon-carbon double connections and sustains crosslinking reactions by the free radical initiator. Synthesized PLA reduces melt viscosity, increases reproduction into the fiber reinforcement, and improves the composite's mechanical characteristics.<sup>[70]</sup> Kale et al.<sup>[95]</sup> compared the degradation of PLA bottles and PLA deli containers with different



**FIGURE 12** Micrographs detected from polarized light microscope (MOLP). (A, B) Printed samples before annealing and (C–K) annealed samples with different temperatures. Annealed pieces presented an increase in spherulite (white circles) size. The spherulites zoom were represented in white rectangles, reprinted from Reis.<sup>[52]</sup>

crystallinity of 96 and 94% of L-lactide, respectively. Reported data showed that the faster degradation rate of the container was associated with the high crystallinity of the bottle. Nevertheless, some additives have also can accelerate the degradation process. Petinkas et al.<sup>[149]</sup> have investigated the effect of additives on the degradation and decomposition of PLA-based materials. They slightly tune the PLA degradation by adding hydrophilic fillers (starch and wood-flour). Nieddu et al.<sup>[206]</sup> have determined the influence of nano-clay on biodegradation and discovered that the clay accelerated the biodegradation of PLA. Navarro et al.<sup>[207]</sup> revealed that the incorporation of phosphate glass particles into PLA considerably accelerated its degradation and generated the formation of calcium phosphate precipitates at the composite surface. Shinoda et al.<sup>[208]</sup> had research on melt-blended PLA with a small quantity of poly aspartic acid-*co*-lactide (PAL) or poly sodium aspartate-*co*-lactide (PALNa) and acquired homogeneous press films. The results proved that PAL and PALNa additives can be used for accelerating the hydrolysis of PLA. Some additives that can accelerate the degradation process of PLA are grouped in Table 7.

Nanoparticles are good delegates to improve PLA biodegradation.<sup>[134,148]</sup> In tissue engineering nanoparticles

with a range of 10–1000 nm can be carried out as dispersed or solid particles along with bioactive molecules, within can be dissolved, entrapped, encapsulated, or attached to the matrix of the nanoparticle itself.<sup>[148]</sup> Nanocomposite PLA films can reduce PLA permeability. Inorganic fillers such as talc can increase nucleation density, decreasing crystallization half-time, and crystallization processing time.<sup>[28,76,82]</sup> With nanotechnology improvement and the safety of PLA nanocomposites, PLA weakness can be improved compared to petrochemical-based polymers. The presence of clay in PLA/clay nanocomposites can enhance the hydrophobicity of the PLA nanocomposites.<sup>[148,150]</sup> Previous studies have incorporated nanoparticles/fibers into PLA to improve PLA properties (Table 8).

#### 4.5 | Automotive

In the automotive industry, progressively restrictive regulations have been applied in terms of CO<sub>2</sub> emissions.<sup>[217]</sup> For this reason, automobile manufacturers and suppliers are making significant efforts to reduce the mass of vehicles, fuel consumption, and emissions. In terms of materials, this is reflected in the increasing use of polymers. In



**TABLE 6** PLA feasible characteristics for packaging applications<sup>[109]</sup>

Functional characteristic	Packaging improvement	Comment
Dead fold, twist, and crimp <sup>a</sup>	Better folding and sealing	OPLA has excellent dead fold and twist retention
High gloss, and clarity	Package esthetics	Comparable with PET and cellophane, 3 times more than nylon and PP, 10 times more than LDPE
Barrier properties	Grease and oil resistance	Good resistance to oils and terpenes
Renewable resource	Made from CO <sub>2</sub> and H <sub>2</sub> O	
Low-temperature heat seal	Stronger seals at inferior temperatures	PLA can offer an “easy-open” package
Low coefficient of friction, polarity	Printability	Excellent printability, metallizable, antifogging capability
GRAS status	Food contact permitted	

Abbreviations: LDPE, low-density poly(ethylene); PET, polyethylene terephthalate; PLA, poly(lactic acid); PP, polypropylene.

<sup>a</sup>The capacity to hold a fold, or the capability to keep a twist that is imparted with the intention of near the edges of the film around a small body.

particular, thermoplastic materials can be applied to replace metallic parts.<sup>[38]</sup> These polymer materials are usually reinforced with the intention of thermomechanical characteristics, compatible with extreme mechanical stresses, and under a wide temperature range of automotive applications. All at once, regulations set increasingly high objectives in terms of the number of materials from renewable resources in vehicles.

Among the bio-based polymers available for industrial applications, PLA has considerably advantageous characteristics, such as high tensile strength, stiffness, and easy shaping at an affordable cost.<sup>[35,43]</sup> As an advantage, PLA is compostable and biodegradable. Thus, degradation of this polymer occurs by hydrolysis, and fragmentation, followed by the breaking of the ester bond in the macromolecular chain.

Toyota was the first manufacturer to use PLA charged with natural fibers (kenaf) to produce a spare wheel cover in 2003, fitted to the Toyota Raum.<sup>[36]</sup> This company has its unit of PLA production acquired in 2004, with a capacity of 1000 t/year. Bouzouita et al.<sup>[34]</sup> proposed a vastly tough poly(L-lactide)-based ternary blend for automotive applications. Their contribution intentions at designing rubber-toughened PLA/PMMA-based formulation with increased

**TABLE 7** Some additives can accelerate the degradation process of PLA

Additive	Polymer	Reference
Starch and wood-flour	PLA	Petinkas et al. <sup>[149]</sup>
Nano-clay	PLA	Nieddu et al. <sup>[206]</sup>
Phosphate glass	PLA	Navarro et al. <sup>[207]</sup>
Poly aspartic acid-co-lactide, poly sodium aspartate-co-lactide	PLA	Shinoda et al. <sup>[208]</sup>

Abbreviation: PLA, poly(lactic acid).

**TABLE 8** Some studies that incorporated nanoparticles/fibers into PLA

Nanoparticles/fibers	Polymer	Reference
Phormium tenax fibers	PLA	[209]
Talc, sodium stearate, calcium lactate	PLA	[76,82]
Nano clay	PLA	[150]
CNCs	PLA	[210]
Polyester-grafted-cellulose nanocrystals	PLA/PCL	[211]
Graphene particles	PLA	[212]
HAp	PLA	[213]
HAp	PLA/PCL	[214]
Nanocellulose	PLA, PBS	[215]
Nanocellulose	PLA(PLA-g-MA)	[216]

Abbreviations: CNCs, cellulose nanocrystals; HAp, hydroxyapatite; PBS, polybutylene succinate; PLC, poly( $\epsilon$ -caprolactone); PLA, poly(lactic acid).

heat deflection temperature appropriate for injection-molding technique through the addition of a commercially accessible impact modifier. Kumar et al.<sup>[38]</sup> successfully manufactured PLA biocomposites reinforced by nettle fibers in dissimilar mass quantities. This process is followed by compression-molding techniques and assesses their static and dynamic mechanical characteristics, with an intention of automotive dashboard panel use.

## 5 | CONCLUSION AND PERSPECTIVES

PLA-based polymers have been widely studied in the literature. Among the bio-based materials progressed to date, PLA polymers are at the forefront of their applied use and production. Although the inadequate characteristics and lack of functionality of PLA have constrained broader

applications. Thus, by interoperating a better comprehension of the PLA characteristics and different key parameters to modulate these properties, PLA can fit with worldwide applications.

Numerous speciality derivatives demonstrating flexibility and functionality can broaden the practical application of PLA polymers. The molecular mass, copolymer configuration, and functionalities should be considered to optimize PLA characterization. Depending on the stereochemistry and thermal history, in the solid state, PLA can be in the amorphous phase or semicrystalline. Overall, optical composition, main structure, thermal history, and molecular weight have a strong effect on  $T_g$  and  $T_m$ . PLA morphologies can be modified by several combinations of L and D monomers. By increasing the D level, PLA tunes to be more amorphous while PLA with a higher amount of L-content is (semi) crystalline. The innovative progress in order to determine PLA with high melting temperature as well as high glassy temperature includes unit modification and polymer blending. PLA has low gas barrier properties with a slow crystallinity rate. The crystalline phase of polymer is known to be impermeable; hence, to improve PLA barrier properties, it is significant to optimize its crystallization condition.

PLA synthesis is multiple processes beginning with the fabrication of lactic acid and finishing with polymerization. Lactic acid condensation, azeotropic dehydration, and condensation ROP of lactide are three methods for PLA polymerization. During the polymerization process, the solvent, catalyst, reaction temperature, and quantity of impurities are the effective parameters for the degree of polymerization and final molecular weight. Both biodegradable and non-biodegradable plasticizers can be applied to enhance the  $T_g$ , increasing ductility, and improving processability.

PLA demand is increasing due to its natural availability, biodegradability, and its customization, accomplished by incorporating multiple fillers, fibers, and nanoparticles. PLA can be easily reinforced with various natural fibers and fillers. This polymer is compatible with synthetic reinforcements as well as interfacial adhesions such as natural fibers (cellulosic). The physical and mechanical properties of PLA can be tuned by incorporating different blends. The processing of PLA has become appropriate with the progress of research in bio-based production. Nevertheless, the cost of this process remains the essential subject to be approached from a commercial point of view.

- It would be more appropriate to find inexpensive substrates and high-performance microorganisms to enhance the manufacturing efficiency of lactic acid and acquire economical and high-quality PLA.
- In order to reduce the production cost of PLA and progress its mechanical properties, new copolymers can be utilized as blending polymers with PLA.

- Certain nanoparticles (MgO, ZnO, TiO<sub>2</sub>, ...) that can confer considerable strength to the PLA can be used during the manufacturing phase. The latter can be utilized in a hybrid formula with natural reinforcements to guarantee the stability of the PLA.


## CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

## DATA AVAILABILITY STATEMENT

This article is a review article and the mentioned information synthesizes previously published research studies.

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