

# Synthesis, Modification and Application of Polylactic Acid

Jintian Xue\*

Department of Chemical Engineering, Tianjin University, Tianjin, China

\* Corresponding Author Email: 3021207195@tju.edu.cn

**Abstract.** The massive use of petroleum-based plastics has caused tremendous damage to the world's environment, so it has become increasingly urgent to develop biodegradable materials represented like polylactic acid (PLA). PLA is a non-polluting, completely degradable and renewable polymer material with high strength, high modulus and good biocompatibility. However, the disadvantages of conventional PLA, such as poor heat resistance and limited flexibility, limit its application. Therefore, its modification is needed. This article summarizes the structure and properties of PLA and describes the synthesis methods based on direct polymerization, ring-opening polymerization and enzyme-catalyzed polymerization. The article also reviews the methods of PLA modification, including physical modification by adding fibrous materials, nucleating agents, and compound modification, and chemical methods such as copolymerization and cross-graft modification. Moreover, the article presents the applications of PLA in packaging and medical materials. At the end of this article, future research and development directions of PLA are discussed.

**Keywords:** Polylactic acid; biopolymer; synthesis; modification.

## 1. Introduction

Since the 19th century, a variety of polymeric plastic products derived from petroleum have been used in people's lives and industrial production. With the continuous exploration of polymers, petroleum-based plastics have become an integral part of industry and life. However, these plastics are produced from non-renewable petroleum resources and are not inexhaustible. At the same time, as plastic products are used, the disposal of waste plastics becomes more and more important. Plastics derived from petroleum have a very low degradation rate. Typically, it takes hundreds of years to complete the degradation process. Over the next hundred years, a large number of plastic products have been buried and burned, which not only damages the quality of soil, pollutes air and rivers, but also poses a major threat to the survival of wildlife and the entire earth's ecosystem. Therefore, there is an urgent need for a new environmentally friendly polymer that can be obtained in large quantities from natural resources to replace the use of traditional plastics. Biodegradation is the core of the process, which mainly refers to the ability of waste materials to transform their physicochemical properties through changes in chemical structure and composition in natural environment, and to be further broken down into other compounds such as water, carbon dioxide or biological humus. Polylactic acid (PLA) is a new type of polyester material based on lactic acid, which is renewable and highly biocompatible. It can be directly derived from corn and other agricultural crops and degrades to produce water and carbon dioxide. Its emergence is of great significance for environmental protection and sustainability. Therefore, it is used in packaging, 3D printing and medical applications. At the same time, pure PLA has some defects in mechanical properties such as heat resistance and extensibility. In order to make PLA more widely used, a series of modification operations are needed to improve its defects. This paper reviews the research and progress of PLA synthesis and modification in recent years, focusing on direct polymerization, ring-opening polymerization and enzyme-catalyzed polymerization, as well as physical and chemical modification methods, and summarizes the application of PLA in packaging and biomedical applications.

## 2. Structure and Properties of PLA

### 2.1. PLA Structure

The two spin isomers of PLA: poly-L-lactic acid (PLLA) and poly-D-lactic acid (PDLA) are obtained by the polymerization of their corresponding monomers L-lactic acid and D-lactic acid, separately. The physical and chemical properties of these two monomers are very similar and the properties of the corresponding polymers are also very similar. However, D-lactic acid does not participate in the metabolism of most organisms and may even cause toxicity when used in excessive amounts. Therefore, PLLA, which is made by the polymerization of L-lactic acid, has been used on a large scale. It is a thermoplastic crystalline polymer with a melting point between 170 °C and 175 °C, a glass transition temperature of about 58 °C, and a 7% breaking elongation and 60% crystallinity. There is another polymer, PDLA, which is an irregular polymer with no crystallinity.

PLA has three lattice structures:  $\alpha$ ,  $\beta$  and  $\gamma$  crystal systems, which match their respective helical conformation and unit symmetry.  $\alpha$  crystal system is the most common one and can be transformed into  $\beta$  crystal system under high temperature and high stretching rate, which is a pseudo-rhombohedral crystal, while  $\beta$  and  $\gamma$  crystal systems are triangular and rhombohedral crystals [1].

### 2.2. PLA Properties

PLA is mainly derived from biomaterials such as corn, wheat and barley, which makes it highly biodegradable and environmentally friendly. The large number of ester groups on the main chain and the methyl groups on the side chains of PLA make it less susceptible by enzymes produced by natural bacteria, and therefore it is stable under natural conditions. However, it is easily degraded to water and carbon dioxide under high humidity and high temperature conditions. This makes it a recyclable biomaterial that can be recovered and processed. In addition, PLA has a high degree of biocompatibility. When PLA material enters the human body, it does not cause local tissue inflammation or rejection. It also does not affect tissue recovery because PLA degrades into small molecules such as non-toxic water and carbon dioxide in the body and then is excreted with metabolism. This is why it is widely used in the biomedical field.

## 3. PLA Synthesis

There are mainly three types of PLA synthesis: direct polymerization, ring-opening polymerization and polymerization by biological means.

### 3.1. Direct Polymerization

Direct polymerization is the simplest and most economical one of the three methods. The principle of this method is to grow PLA chains by the esterification between highly reactive hydroxyl and carboxyl groups on lactic acid monomers or lactic acid oligomers. Since this is an equilibrium reaction, various efficient dehydrating agents are usually added to the reaction for isolating the water from the reaction system so that the equilibrium proceeds forward. Nevertheless, as the reaction proceeds and the PLA chain grows, the dehydration process becomes increasingly difficult. Therefore, it produces PLA with rather low average molecular weight. Direct synthesis methods can be divided into three main categories as follows.

#### 3.1.1. Melt Polymerization

Melt polymerization is the condensation reaction between the lactic acid monomers in the reaction system and the resulting PLA under molten conditions reaction system has a temperature above the PLA melting point and does not contain any medium. Therefore, this method can produce PLA with high purity. However, as the reaction proceeds, the viscosity of the reaction system increases, leading to difficulties in removing small molecules like water produced during the reaction. Therefore, it produces PLA with low molecular weight.

### 3.1.2. Solid-Phase Melt Polymerization

Solid-phase melt polymerization is a process in which lactic acid monomers are added to the system at low pressure to have intramolecular dehydration and condensation to produce polylactic acid with lower molecular weight. These oligomers undergo a granulation and crystallization drying process. Finally, the polycondensation reaction is carried out again at a temperature between its glass transition temperature and melting point to produce PLA with higher molecular weight. During the reaction, the heat transfer between the dried particles is uniform, and the water generated by the reaction can be removed by the introduction of an inert gas into the system, which facilitates the production of high molecular weight PLA. Because the catalyst and the small molecule monomer will be repelled in the amorphous region without crystallization, additional energy can be obtained to promote the reaction to proceed completely. In addition, due to the lower reaction temperature, fewer side reactions such as racemization and thermal oxidation will occur during the reaction. This will all enhance the purity of the product.

### 3.1.3. Solution Azeotropic Polymerization

The solution azeotropic polymerization method uses azeotropic reaction between the water produced in the polycondensation reaction and the organic solvent to remove the water from the reaction system. Therefore, the reaction proceeds in the positive direction. This kind of reaction can occur at a relatively low temperature, but a large amount of organic solvent needs to be put into the production process. Although these solvents can be reclaimed, the risk of using this method to produce PLA is greater than the other two methods. At the same time, like other direct reaction methods, the higher amount of water is removed during the reaction process, the higher the molecular weight of the PLA product can be produced. Therefore, this method requires the selection of appropriate solvents to achieve better reaction results. There is research that compared the molecular weights of products obtained with different catalysts using diphenyl ether as azeotropic solvent. The results revealed that high molecular weight products could be obtained at only 130 °C when using stannous compounds as catalysts [2]. Nevertheless, the current difficulties in recovering the solvent after the reaction and the harsh reaction conditions make it less used in industrial production.

## 3.2. Ring-Opening Polymerization

Ring-opening polymerization is a common method for producing high molecular weight PLA. This method uses the dehydration reaction between the hydroxyl and carboxyl groups of the lactic acid molecule to produce lactide and further synthesize PLA. This method is widely used in the industrial production of PLA because of its ability to produce high molecular weight PLA in a short period of time. However, the catalyst and reaction initiator added to the reaction system can greatly affect the reaction mechanism. Therefore, depending on the added initiator and the type of reaction mechanism, such reactions can be divided into the following types.

### 3.2.1. Cationic Polymerization

The mechanism of the cationic polymerization reaction is to add cationic initiator as an electrophilic reagent. The initiator forms ions with the oxygen atoms in the propylene glyceride molecule, thereby breaking the acyl-oxygen bond and triggering the ring-opening reaction of the propylene glyceride. Finally, the acyl positive ion generated by the ring-opening reaction starts the chain growth reaction. The initiators commonly used for this reaction include zinc tetrachloride and boron trifluoride. Protonic acids such as hydrochloric acid and hydrogen fluoride, Lewis's acids such as aluminum chloride and tin chloride with alkylating reagents are also often used as initiators. Also, protonic acids can act as cationic catalysts in the reaction, so amino acids can potentially be used to catalyze propylene glycolate polymerization reactions.

### 3.2.2. Anionic Polymerization

There are two types of mechanism for anionic polymerization reactions, mainly distinguished by the basicity of the initiating system. In a strongly basic initiation system, the negative ion in the

catalyst would react with the propylene glyceride's acyl group and form an active central lactone anion. Then, the active anion formed in the previous reaction will attack another propylene glyceride molecule and insert into the main chain to trigger the chain growth of the propylene glyceride. In systems with weak basic conditions, the initiator will directly trigger the ring-opening polymerization of the propylene glyceride. The catalysts and initiators for such reactions are usually alkali metals or alkali metal alcohol oxidizers. The most representative ones are sodium alkoxide and potassium alcohols. Meanwhile, anionic polymerization can also be carried out in solution. Liu et al. proposed that sodium alcohol can be added to the mixed solution of propyl cross ester and benzene as an initiator. This reaction system can be reached at a temperature of about 70 °C for 11 hours [3]. Finally, protonic acid was added at the end of the reaction to terminate the reaction, and then the protonic acid and sodium alcohol were filtered out of the reaction system. They also used different monomers to carry out the reaction. They found that the chance of synthesizing polymers with the addition of ethylene glycolate was several times higher than that of the pure propylene glycolate system. When the reaction initiator was octylene and isocline, the chance of polymer synthesis was up to 25 times that of the pure propylidene system. From this, it can be discovered that the type of initiator, the type of monomer and the environment of the reaction system can affect the polymerization products.

### 3.2.3. Coordination Polymerization

Coordination polymerization is the most commonly used method for the synthesis of PLA nowadays, and it is the most studied method by researchers worldwide. This method makes it easy to synthesize PLA products with very high molecular weights. Therefore, PLAs made by this method can be widely used in industries that require very high molecular weight polymers, such as plastic synthesis or textiles. The ligand polymerization method uses metal initiators. The mechanism of the propylene glycolate coordination reaction is that: The carbonyl group on the propylene glycolate monomer undergoes a coordination reaction with the metal initiator, resulting in the formation of an activated coordination complex. Subsequently, the coordination compound is inserted into the metal-carbon bond, which generates a high molecular weight polymer. The metal initiator atoms contain empty p- or d-orbitals. Covalent bonds can be formed between through these orbitals of the metal and p orbitals of oxygen atoms, and thus the ring-opening polymerization of propylene glycolate can be catalyzed to produce poly lactic acid chains with a high degree of polymerization. Therefore, various high molecular weight polylactic acid derivatives can be obtained. Salts, oxides and organic compounds of transition metals and lanthanides mainly constitute initiators for coordination polymerization reactions. The common initiators are metal oxides, carboxylates, alkyl and alkoxyl metals [4]. Nevertheless, although this method is easier to obtain large molecular weight PLA compared with other methods, it has high requirements for catalysts. This leads to the high cost of PLA prepared by this method in the market nowadays. Also, uncontrollable side reactions occur in the later stages of the reaction of coordination polymerization, so this method needs to be further researched and improved [5].

### 3.3. Enzyme-Catalyzed Polymerization

The bio enzyme-catalyzed synthesis of PLA is also being researched extensively as a green and non-polluting synthesis method. Compared with other inorganic and organic catalysts, enzymes are extremely active catalysts. Also, when using enzyme for catalysis, the reaction temperature is lower compared to conventional methods, and the reaction conditions are milder with side reactions. Therefore, the synthesis cost and the separation cost of the products are lower when PLA is synthesized by this method. More importantly, this is a completely green and clean catalytic synthesis method. It is more environmentally friendly than other methods. Rahmayetty et al. used rosmarinic lipase to catalyze the ring-opening reaction of lactide in their experiments [6]. It was shown that the enzyme catalyzed the generation of PLA with high output and product molecular weight at 90°C and 2% mass fraction. Some other studies have shown that lactyl-CoA can also be used for the direct synthesis of PLA from glucose [7].

## 4. PLA Modification

Due to the limitations of PLA's own properties, there are some defects in PLA for practical applications. For example, PLA has poor heat resistance, poor toughness, poor fluidity and hydrophilicity, and slow degradation rate, etc. These defects can limit its use in industrial production, 3D printing and daily applications such as packaging and medical supplies. Therefore, it is very important to improve the properties of PLA by adopting some physical and chemical means.

### 4.1. Physical Modification

Currently, the main method of physical modification of PLA is to blend PLA with several other polymers by mechanical co-blending. This method can improve the deficiencies of PLA in mechanical properties, biodegradability and compatibility. At the same time, it does not affect its original excellent properties. Compared with other modification methods, this method is more cost-effective. The physical modification of PLA can be divided into plant fiber modification, nucleating agent modification and composite modification depending on the type of material added in the modification process.

#### 4.1.1. Plant Fiber Modification

The addition of degradable plant fibers to PLA is the main method of plant fiber modification. On the one hand, this method can well maintain the biodegradability and biocompatibility of the modified product. On the other hand, it can also improve the weaknesses of PLA like increasing the mechanical properties and glass transition temperature of PLA. Also, the use of this method can effectively reduce the cost of the final product due to the wide source of plant fibers. For example, Jamaluddin et al. used cellulose nanofibers (CNFs) as a filler to incorporate into PLA [8]. The hydroxyl group of cellulose was also modified to acyl group by adding acid anhydride, which led to the improvement of the compatibility of PLA with CNF. It was shown that all PLAs with the addition of acetylated cellulose nanofibers (ACNFs), propionylated cellulose nanofibers (PCNFs) and butylated cellulose nanofibers (BCNFs) fillers, respectively, developed better mechanical properties. The surface smoothness and transparency of PLAs were also improved.

Other biocomposites were prepared by R. Scaffaro et al. by melting grinded cactus powder into PLA [9]. The effect on the improvement of PLA properties varied considerably between different sizes of cactus powder. Among them, when the particle size of cactus powder is between 150  $\mu\text{m}$  and 300 $\mu\text{m}$  and the content is 20%, the tensile elastic modulus of the composite can be increased by 135% compared to pure PLA, reaching 2450 MPa. It was shown that the increase in tensile modulus of the modified PLA was positively correlated with the particle size, and that the increase in the content of cactus particles could significantly increase the viscosity of the composites under a certain particle size.

#### 4.1.2. Nucleating Agent Modification

Nucleating agent modification mainly involves adding nucleating agents to PLA to increase the number of crystallizable nucleation sites in the polymer chain, thereby increasing the proportion of the crystalline part in the whole PLA chain. This can effectively promote the crystallization of PLA chains by reducing their mobility, which in turn increases the melting enthalpy and reduces the melting entropy of PLA, resulting in enhanced heat resistance of PLA. At the same time, the addition of nucleating agent can shorten the crystallization time significantly and shorten the period of PLA crystallization. When a small amount of nucleating agent is added to PLA, the nucleating effect can be excellent. The nucleating agent is well dispersed in PLA, and its decomposition temperature is higher than the melting temperature of PLA. The amount of nucleating agent has a decisive influence not only on the size of the crystallized grains, but also on the size and number of PLA pellets. Commonly used PLA nucleating agents include inorganic substances such as talc, barium sulfate and calcium carbonate, and also some organic substances like Phenylphosphonate metal salts.

Talc, as a common inorganic nucleating agent can effectively improve the crystallinity of the composite while lowering its crystallization temperature. Meanwhile, the crystallization of PLA and the particle size of talc powder are closely related. In comparison, smaller talc particles can promote the crystallization of PLA more efficiently [10].

Yanping Hao investigated the effects of substituting aryl phosphate analogues (TMP-6) into PLA [11]. Experimentally, melted TMP-6 was blended with PLA to prepare its blends with PLLA and PDLA. It was shown that this nucleating agent can be used for significant reduction in the T<sub>g</sub> of the composites. When 0.5 unit of nucleating agent was used, the T<sub>g</sub> of the blends could be reduced by 12.5%. At the same time, the addition of nucleating agent can also promote the formation of single crystal (sc) -PLA.

In addition, a combination of inorganic nucleating agent and organic nucleating agent can be applied. Since inorganic nucleating agents have lower thermal conductivity, they can lower the crystallization temperature and increase the crystallinity of PLA, thus improving the heat resistance of PLA. The addition of inorganic and organic nucleating agents can also improve the tensile and mechanical strength of composites compared to pure PLA.

#### 4.1.3. Composition Modification

Composition modification is mainly achieved by adding polar or rigid particles to PLA, creating physical crosslinks between the filler and PLA molecules. The inter-chain interaction between the blends is thus enhanced, resulting in enhanced mechanical strength and higher temperature resistance. The nanomaterials are the main materials used for the composite modification because of their better bulk, structural and surface effects.

Zuo investigated the properties of PLA composite modified materials with the addition of nano-silica [12]. With the constructed PLA-grafted bamboo fiber/poly(lactic acid) composite structure, nano-silica can promote the crystallization and nucleation process of PLA. It was shown that the amount of nano-silica used was positively correlated with the initial decomposition temperature of the composites. The polymeric material had the maximum crystallinity and the best thermal stability when the nano-silica was added at a rate of 1.5%.

F. S. Senatov et al. chose nano-hydroxyapatite modified reinforced PLA [13]. the added nanoparticles can form the center of additional stationary phase in PLA chains, which can change the friction between the molecular chains of the composite, thus controlling the structure memory properties of its molecular chains. This phenomenon starts to appear significantly when the incorporated nano-hydroxyapatite content reaches 15%. When the composite possesses 20% of material deformation, the recovery stress of the blended material can reach 156% of the pure PLA polymer at a temperature of 64 °C.

#### 4.2. Chemical Modification

Chemical modification improves the properties of PLA by changing the surface structure and molecular chains of it. Chemical modification can reduce the regularity and crystallinity of PLA macromolecular chains, and enhance the hydrophilicity and degradability of PLA. According to the modifying method, chemical modification can be divided into copolymer modification and cross-linking modification.

##### 4.2.1. Copolymerization Modification

Copolymerization modification is a method which inserts other small molecule monomers or multimolecular chains into the main chain of PLA by copolymerization reaction. PLA can be effectively modified by adjusting the type and ratio of inserted groups, or by introducing copolymer monomers with special groups. For example, by inserting a molecular chain with good flexibility into the PLA molecular chain through copolymerization reaction, the regularity of PLA chain could be broken, and the intermolecular force could be reduced. This can lower the crystallization temperature and melting point of the copolymer, and also lower the glass transition temperature, thus improving the performance of PLA. In addition, pure PLA has poor hydrophilicity and large fragility. The

copolymerization modification can copolymerize PLA with monomers with hydrophilic groups, which can improve the hydrophilicity and crystallization ability of the composite at the same time. Meanwhile, the tensile properties of the copolymer can also be improved. The degradation rate can be improved by appropriately adjusting the total molecular mass of the composite and the mass ratio of the different chain segments.

There are two main types of copolymerization modifications: graft copolymerization and block copolymerization. Graft copolymerization requires inserting different monomers into the PLA molecule by polymerization. By this method, side chains with different groups such as hydroxyl, carboxyl or amino groups can be introduced into a single PLA chain. Zhou et al. found that the content of the main chain and the grafting density of the branch chain on the main chain in the composites had a decisive effect on the crystalline properties of the composites through the copolymerization modification of poly ( $\beta$ -laurane) main chain and PLLA branch chain [14]. It was also shown that linear comb copolymers have a lower breaking elongation compared to star comb copolymers.

The mechanism of block copolymerization is to link PLA chains to the ends of other monomers to synthesize composites with different blocks. Gu Liang Liang et al. used block copolymerization to modify PLA by linking poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymers (PEO-PPO-PEO) to the PLA backbone [15]. It has been shown that the ductility of the composite can be significantly improved at the content of 5% triblock copolymer. In this case, the polymer with high PPO content and large molecular weight forms droplets in PLA and the viscosity of the composite is reduced as well.

#### 4.2.2. Cross-Linking Modification

Creating chemical bonds between different PLA macromolecular chains to produce a net-like structure polymer is the approach used for cross-linking modification. The monomers are cross-linked with PLA by cross-linking agents and radiation, resulting in a mutually cross-linked mesh structure. The cross-linking modification usually uses electron radiation or  $\gamma$ -ray radiation to promote the reaction of monomers with PLA chains. However, PLA chains can be broken by radiation, which reduces the molecular mass and mechanical properties of the composites. Therefore, a cross-linking agent which consists of multifunctional substances is added to protect the PLA molecular chains while radiation is applied. The type of crosslinker added in the reaction depends on the type of radiation, but usually polyfunctional anhydride or isostere anhydride is chosen.

Liu et al. researched the reaction of anhydride with epoxy [16]. It was shown that the long chain branched structure in the PLA-poly (propylene-co-caprolactone) block copolymer improved the viscoelasticity and tensile ratio of the composite. This is due to the strong molecular entanglement and stress-hardening behavior of the composite.

## 5. Applications

### 5.1. Food Packaging

Due to the harmlessness of PLA to human body and its degradability, it has become the most promising packaging material nowadays. Compared to the degradation time of hundreds of years required for other polymers, the degradation time of PLA packaging under natural conditions is only 2 to 6 months. Studies have shown that the degradation rate of PLA composites can be increased compared to pure PLA after melt blending modification, and it does not cause any pollution after degradation. PLA can be made into film materials with high transparency and the ability of oxygen resistance. When this material is used for food packaging, it can inhibit the growth of bacteria and prevent food from becoming moldy. In addition, when vegetables and fruits are packaged in PLA, the high carbon dioxide environment created by this packaging material can also inhibit their respiration. As a result, the loss of organic matter and water of vegetables and fruits is significantly reduced when they are stored, thus improving their taste and storage time [17].

## 5.2. Medical Use

PLA material has good biocompatibility and mechanical properties, so it is widely used in medical fields such as surgical sutures, bone fixation materials and drug carriers. PLA sutures and filler materials are not biotoxic and are highly biocompatible and biodegradable. Compared with conventional materials, the probability of wound infection and ulceration is significantly reduced after use, and the potential for secondary surgery is eliminated. At the same time, the copolymers of PLA can be used as drug carriers, allowing the full release of active drug components in the organism. The glucose-PLA copolymer synthesized by Tao Yadong et al. can play a slow-release role in the process of drug release, which helps in the control and release of the drug [18].

## 6. Conclusion

Bio-based materials are the key research direction for sustainable polymer composites, and the development of PLA is one of the effective solutions to the current environmental and resource problems in the world. The excellent biocompatibility and biodegradability of PLA make it an outstanding choice for packaging and biomedical applications. The modified PLA can be adjusted according to the specific needs of its mechanical properties and microstructure, which also drives PLA to further market and application. Overall, the development of PLA, research and applications are very promising. However, the various modification methods currently available for PLA can only improve one of its properties, but not its overall performance in a comprehensive manner. More in-depth research can be conducted accordingly in the future. At the same time, the overall production capacity of PLA is still small and the technical barriers to production are still high. Research is still needed to reduce its production cost and technical barriers so that it can replace petroleum-based plastics on a larger scale in the future and enhance the protection of the environment.

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