Research Progress in the Synthesis and Modification of Polylactic Acid

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Abstract. Polylactic acid (PLA) has garnered significant attention due to its advantages of excellent biodegradability, biocompatibility, and renewable raw materials. This article begins by briefly introducing the research progress in the synthesis and modification of PLA, as well as its specific applications such as medical sutures and textiles, and the pros and cons of PLA itself. It then provides a detailed overview of the direct polymerization methods of PLA, including melt condensation and solution polymerization, and ring-opening polymerization methods such as cationic, anionic, and coordination. The process mechanisms, advantages, and disadvantages of each method are discussed, along with their suitability for practical industrial production and current limitations. Several specific modification methods of PLA are also discussed, such as low-temperature plasma modification and blending modification, highlighting the advantages, disadvantages, and specific research examples. These modifications aim to improve the deficiencies of PLA in areas such as mechanical strength or biological activity, allowing PLA to be applied in specific fields. Ultimately, the goal is for PLA to replace petroleum-based plastics and achieve widespread application in order to reduce environmental impact.

Keywords: Polylactic acid, synthesis, modification, polymerization methods.

1. Introduction

Polylactic acid (PLA) is a green, functional polymer material that can be synthesized by the fermentation of biomass raw materials (such as corn starch, wheat starch, sweet potato starch, and natural fibers) into small molecules of lactic acid. It possesses excellent biocompatibility and biodegradability [1] and can completely degrade into water and carbon dioxide through the process of photosynthesis in plants [2, 3]. Compared to petroleum-based plastics, PLA is more in line with the concepts of circular economy and sustainable development. Not only is it easily degradable without causing environmental pollution, but it also addresses the rising costs associated with the depletion of petroleum resources and the management of environmental pollution.

In the history of PLA synthesis, Pelouze obtained lactate dimer for the first time using a dehydration esterification reaction [4]. Subsequently, Nef confirmed that lactic acid oligomers could be obtained through dehydration reactions at lower pressure and higher temperatures. Lowe further improved the process for synthesizing high molecular weight PLA. After the 1960s, PLA and its copolymers began to be applied in the field of biomedicine. Around 1970, the American company Ethicon used PLA and its copolymers to produce surgical sutures. In the 1980s and 1990s, researchers such as Kricheldorf studied the synthesis and molecular characteristics of lactate homopolymers and copolymers, while Pennings researched the crystallization and physical properties of PLLA fibers produced by spinning and stretching. Ikada conducted research on the medical and pharmaceutical applications of PLA and its copolymers. In 2001, Shuhui Kang analyzed the crystalline state of PLA chains. In 2006, J.R. Dorgan reviewed the applications, degradability, and environmental performance of PLA. In 2007, Takahiko Kawai studied the influence of crystallization temperature on the crystalline structure and thermal behavior of PLA. In 2010, Tingting Lin researched the elastic crystals of PLA, demonstrating that PLA crystallization exhibits mechanical anisotropy. These studies provide various theoretical and experimental foundations for further applications of PLA.

The advantages of PLA include moderate mechanical strength, flexibility, and good biocompatibility. As a result, with deeper research, PLA products have been widely used in various fields such as medicine (surgical sutures, orthopedic fixation devices, surgical adhesives, artificial blood vessels, various biological scaffolds, drug delivery carriers, tissue engineering), packaging materials, textiles, daily necessities, and industrial products [4]. PLA also possesses good processability and can be thermally molded in different ways. However, due to its inferior mechanical strength, impact resistance, and elongation at break compared to traditional plastics such as polyethylene (PE) and polypropylene (PP), it exhibits characteristics of being hard and brittle at room temperature. This hinders its application in industries that demand high material toughness, such as the automotive industry and household appliance packaging. Additionally, PLA's thermal and gas barrier properties are poor, posing challenges for its application in the packaging industry.

Currently, there have been numerous studies in the academic community on the modification of PLA aimed at addressing these issues. PLA is also considered the most promising material for replacing traditional plastics. This article introduces various synthetic methods of PLA and discusses the advantages and disadvantages of each method. It also presents research results on several modification cases that overcome the inherent property flaws of PLA.

2. Synthetic methods of PLA

Currently, there are two main methods for synthesizing PLA, i.e., direct polymerization and ring-opening polymerization of lactide. Each method has its own advantages and limitations. The direct polymerization method has a shorter production process and lower cost, but the resulting PLA has lower molecular weight and inferior mechanical properties. However, it degrades faster, making it suitable for medical applications such as oral capsules for controlled drug release. On the other hand, the ring-opening polymerization of lactide can produce PLA with higher molecular weight and better mechanical properties, but the production process is more complicated and costly compared to direct polymerization. PLA produced using this method is suitable for applications such as plastics and textiles that require higher strength. The details of these two synthesis methods are as follows.

2.1. Direct polymerization method

Due to the higher reactivity of the hydroxyl and carboxyl groups at both ends of lactic acid, it can undergo self-condensation to form PLA through a dehydration condensation reaction, as shown in Figure 1. This method has a shorter process and lower cost. However, as the reaction progresses, the molecular weight of the system gradually increases, leading to an increase in viscosity and difficulties in removing the by-product water, resulting in a reverse reaction. To increase the molecular weight of PLA, methods such as increasing vacuum and temperature are commonly employed. However, this may also result in depolymerization and coloration reactions to some extent, leading to inferior product properties. To address this issue, researchers have developed two different direct polymerization methods.

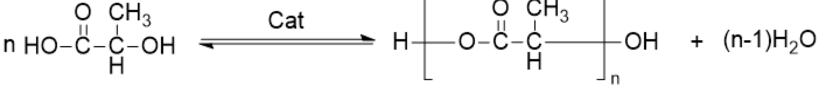

Figure 1. Direct polymerization of lactic acid

2.1.1 Melt-solid polycondensation Method

In this method, low molecular weight oligomers formed by melt polycondensation are further polymerized to obtain PLA with higher molecular weight by undergoing granulation and crystallization drying steps at a temperature between the T_g (glass transition temperature) and T_m (melting point) [5]. Moon et al. have successfully synthesized PLA with a molecular weight exceeding 670,000 using a binary catalyst system $SnCl_2 \cdot 2H_2O$/TSA (p-tolulenesulfonic acid monohydrate) through the melt-solid polycondensation method [6].

Although this method significantly improves the molecular weight of PLA, it requires a vacuum level. Additionally, it takes several tens of hours to obtain high molecular weight PLA [7], which limits its wide-scale industrial application.

2.1.2 Solution polymerization method

The principle of the solution polymerization method is to use high-boiling solvents (such as toluene, xylene, etc.) that can form an azeotrope with water. These solvents can dissolve the polymer but do not participate in the reaction. Through this process, water is removed by reflux, and the resulting PLA is brought back into the reaction system to avoid its decomposition, thereby achieving the preparation of high molecular weight PLA. In this method, the better the water removal effect is, the higher the molecular weight of the product will be, so it is necessary to choose suitable solvents. This method is also known as azeotropic distillation and was proposed by Japanese scholar Ajioka in 1995. By using lactic acid as the monomer and diphenyl ether as the solvent, PLA with a molecular weight exceeding 300,000 was successfully obtained through azeotropic distillation [7].

However, the low solubility of high polymers leads to the consumption of a large amount of solvent in the solution polymerization method, causing significant environmental harm. Moreover, the requirement for high-boiling solvents in this process makes the process more complex and increases the cost of equipment. The high boiling point also makes the purification of the product more difficult and energy-consuming, resulting in some residual organic solvents in the final product.

2.2. Propylene glycol opening ring polymerization

The propylene glycol opening ring polymerization method is a widely studied approach in the academic community, which has the advantage of using impure lactic acid as a raw material to synthesize high molecular weight PLA. The opening ring polymerization method mainly includes three steps: propylene glycol synthesis, purification, and ring-opening polymerization.

2.2.1 Synthesis of propylene glycol

The synthesis mechanism of propylene glycol involves the dehydration condensation of lactic acid to form a cyclic dimer, and the cyclic dimer is then depolymerized under high temperature, high pressure, high vacuum, and catalysis to obtain propylene glycol. The preparation of propylene glycol can be divided into the atmospheric gas flow method and the reduced pressure gas flow method. Both methods involve extracting the product propylene glycol from the reaction system using inert gas in order to reduce side reactions. The inert gas also removes oxygen from the reaction system, thus improving the purity of the propylene glycol product [8].

2.2.2 Purification of propylene glycol

The purification of propylene glycol is a crucial step in the whole ring-opening polymerization process. Only when the purity of propylene glycol is sufficiently high can it be used to synthesize high molecular weight and good physical properties PLA. Currently, distillation is the most commonly used method for industrial purification of propylene glycol, while extraction and recrystallization methods are often used in laboratory settings.

2.2.3 Mechanism of propylene glycol opening ring polymerization

According to the different initiators, catalyst reaction conditions, and reaction mechanisms used, the overall reaction equations for propylene glycol ring-opening polymerization are shown in Figure 2. There are three methods for propylene glycol ring-opening polymerization: cationic ring-opening polymerization, anionic ring-opening polymerization, and coordination ring-opening polymerization.

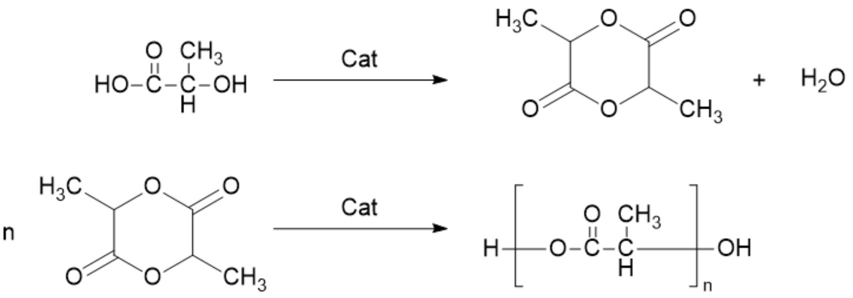

Figure 2. The reaction equation of lactide ring-opening polymerization

2.2.3.1 Cationic ring-opening polymerization

In cationic ring-opening polymerization, the cation generated by the initiator reacts with the oxygen atom in the non-carbonyl oxygen of lactide, generating oxonium ions. Under the action of oxonium ion intermediates, the carbonyl oxy bond in propylene glycol breaks, promoting monomer chain growth and forming PLA chains. The mechanism is shown in Figure 3.

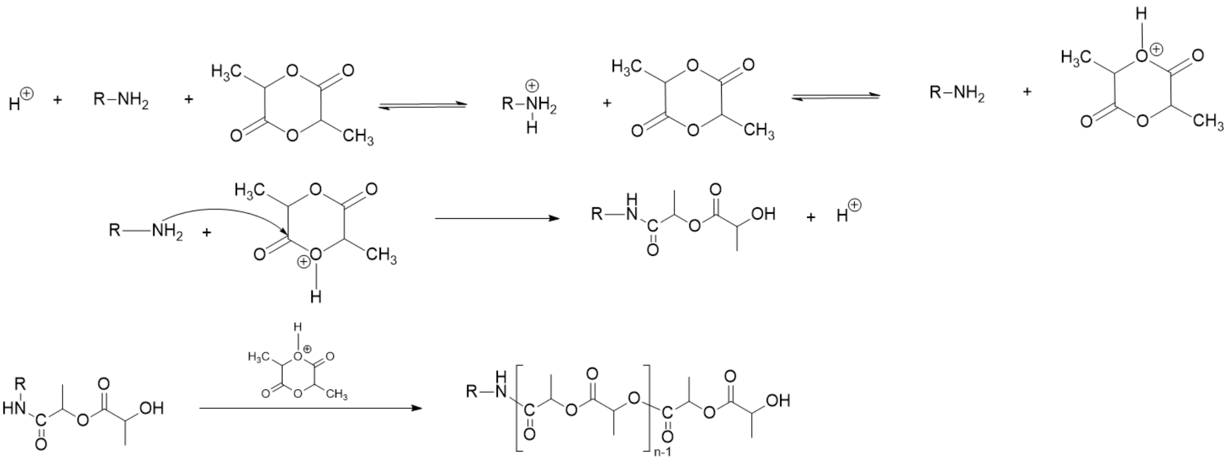

Figure 3. Mechanism of cationic ring-opening polymerization

The commonly used initiators in cationic ring-opening polymerization include Lewis’s acids (such as BF_3), protonic acids (such as HCl), and alkylating agents (such as CF_3SO_3Me) [1]. Among these initiators, stannous chloride is considered the most effective catalyst. However, this method has lower reactivity, unstable product properties, and insufficient optical purity, resulting in low molecular weight of the obtained product.

2.2.3.2 Anionic ring-opening polymerization

In anionic ring-opening polymerization, the nucleophilic oxygen anion of the initiator attacks the carbonyl bond in the propylene glycol, causing a chemical bond cleavage between the carbonyl and epoxy bonds. The result of the reaction is the formation of a new nucleophilic oxygen anion, which further attacks the propylene glycol to achieve chain growth and form long chains of PLA. The mechanism is shown in Figure 4.

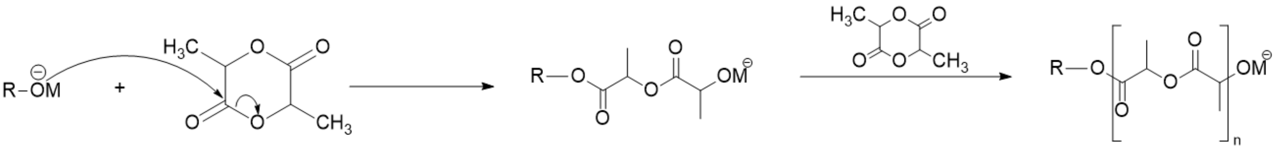

Figure 4. Mechanism of anionic ring-opening polymerization

The initiators commonly used in anionic ring-opening polymerization are strong bases, among which potassium tert-butoxide and sodium phenoxide have been found to be effective. In the study conducted by Kricheldorf et al. [9], anionic ring-opening polymerization was employed using lactic acid as the raw material, potassium tert-butoxide as the initiator, and toluene as the solvent. PLA was obtained with a yield of up to 92% at room temperature. Therefore, the anionic ring-opening polymerization method has the advantages of high reaction activity and fast reaction rate. However, its drawback is the difficulty in obtaining high molecular weight PLA due to unavoidable side reactions and racemization of the active chain end caused by the base, resulting in a decrease in the degree of polymerization. Therefore, this method is currently difficult to apply in industry.

2.2.3.3 Coordination ring-opening polymerization

Coordination ring-opening polymerization is currently the most extensively studied and widely used method for the production of high molecular weight PLA in both academic research and industrial applications. The high molecular weight PLA produced by this method finds wide application in specific industries such as textiles and plastics.

The mechanism involves the coordination reaction between the carbonyl oxygen in the propylene carbonate and the initiator. The initiators used in this method are typically metal salts or carboxylic acid salts that possess free p orbitals or d orbitals, such as Sn, Ti, Al, Zn, or rare earth metal alkoxides. They form covalent bonds between the metal and oxygen atoms, catalyzing the ring-opening polymerization of propylene carbonate and ultimately producing high molecular weight PLA chains. Wang et al. used iron alkoxide ($Fe(OEt)_3$) as an initiator, achieving an average viscosity-average molecular weight (M_v) of 7.28×10^4 and a conversion rate of 90% under suitable conditions [10]. The mechanism of coordination ring-opening polymerization is illustrated in Figure 5.

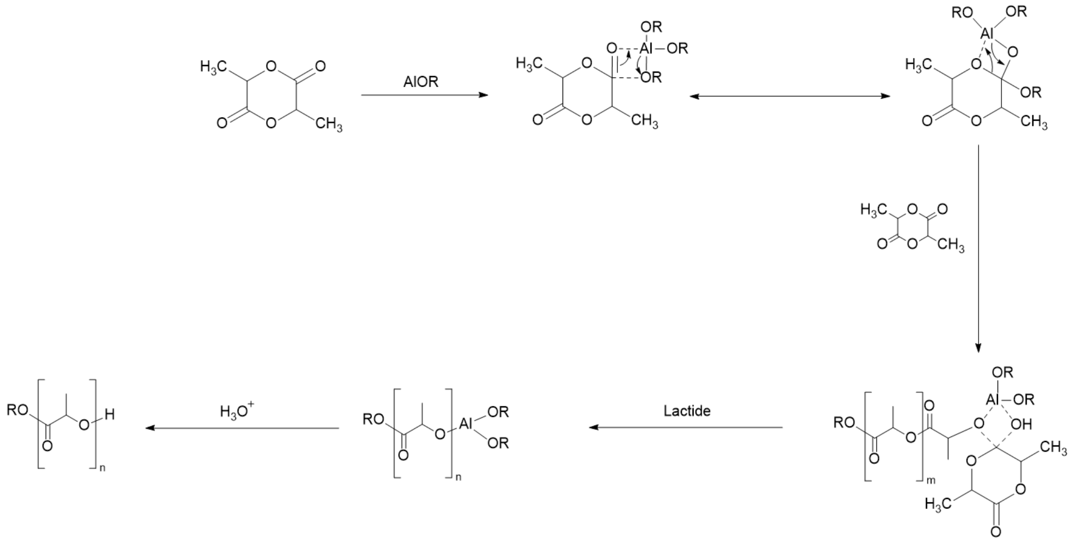

Figure 5. Coordination ring-opening polymerization mechanism

The selection of catalysts for coordination ring-opening polymerization mainly includes metal salts, oxides, compounds, as well as tin-based and rare earth-based compounds. Although the use of such catalysts and initiators incurs higher costs, coordination ring-opening polymerization remains a feasible industrial method for the production of high molecular weight PLA with stable chemical structures and good mechanical properties.

3. Modification of PLA

As mentioned earlier, although PLA possesses advantages such as high biocompatibility, processability, and degradability, it also has some drawbacks including brittleness at room temperature, poor impact toughness, and relatively high cost, which limit its applications and promotion in areas such as structural engineering and biomedicine. Therefore, it is necessary to modify PLA to meet the required performance in different fields. Currently, there have been extensive studies in academia on this topic, and modification methods mainly include chemical modification (such as copolymer modification), physical modification (such as blending modification), and physicochemical modification involving plasma modification.

3.1. Low-temperature plasma surface modification of PLA

The bulk properties of polymers, such as mechanical, thermal, and electrical characteristics, as well as biocompatibility and biodegradability, are closely related to their surface properties [11]. In the case of medical implant applications, the lack of specific functional groups on the surface of PLA, such as carboxyl groups, nitrogen-containing groups, and other functional groups that interact with biological media, results in potential tissue inflammation or unnecessary immune responses when implanted in the human body [11]. Therefore, in order to graft the desired functional groups onto the polymer surface, a low-temperature plasma flow method is used to establish a sufficient concentration of carboxyl groups on the surface of the polymer for subsequent fixation of the desired functional groups.

Plasma modification technology has incomparable advantages compared to other modification technologies, such as fast reaction time, high modification efficiency, no waste or byproduct generation, no additional pollution, and high versatility. With low ionization degree, plasma modification only occurs on the surface of materials at the nanometer and micrometer scale, without damaging the overall properties of the substrate. It is an effective technique for improving surface energy, polarity, permeability, wettability, and adhesion of different types of materials [12]. Low-temperature plasma treatment can significantly improve the structure and physicochemical characteristics of PLA scaffolds for biomedical applications. During the plasma treatment of PLA, the surface free energy increases, which facilitates cell growth and vitality on the material [13].

The studies by Laput et al. have shown that surface treatment of PLA using low-temperature argon plasma can reduce the contact angle of PLA from 118.1° to 41°, significantly enhancing its hydrophilicity. At the same time, the surface energy increases from 6.44 to 201.44 mN/m [11, 13]. The changes in chemical composition caused by plasma surface modification are parallel processes of polymer chain scission and crosslinking, accompanied by the formation of oxygen-containing functional groups and the generation of nitrogen-containing groups.

3.2. Nucleating agent modification for toughening PLA

Due to the slow crystallization rate of PLA and the rapid cooling during the actual processing, the crystal structure of PLA is mostly amorphous, resulting in poor toughness. Nucleating agents are substances that promote nucleation and can help improve the crystallinity and crystallization rate of PLA. There have been studies on adding nanomaterials or amide compounds as nucleating agents to PLA, and the results have shown significant improvements in the toughness of PLA.

Xue et al. used decanedioic acid bis(p-phenylhydrazide) (TMC-300) as a nucleating agent for PLA and prepared PLA/TMC-300 composite materials using melt blending method [14]. The results showed that the addition of TMC-300 improved the thermal stability, heat resistance, impact strength, and tensile strength of PLA. Specifically, when 0.5% TMC-300 was added and the sample was heat-treated at 120℃ for 5 minutes, the crystallinity of PLA increased from 6.00% to 41.27%, and the impact strength increased by 49.78%.

3.3. Blending modification of PLA

Blending, as the simplest means of polymer modification, involves mixing two or more materials without chemical reactions. It allows the chemical structures of the substances to remain fundamentally unchanged, thus retaining their inherent properties, while the properties of the resulting product are a combination of the properties of the original materials. Therefore, blending PLA with different materials can improve its heat resistance, toughness, and mechanical strength.

In the study conducted by Ceren and Yunus [15], a blend film was prepared by blending a natural rubber derivative containing acetate pendant groups (ANR) with PLA. The research results showed that the blend exhibited the best compatibility with PLA when the ANR content was 25wt%. The tensile strength, elastic modulus, and yield strength of the blend film were measured as 11.6 MPa, 397.3 MPa, and 6.9 MPa, respectively. In contrast, the pure PLA film had a tensile strength, elastic modulus, and yield strength of 7.9 MPa, 162.5 MPa, and 1.97 MPa, respectively.

4. Conclusion

This article summarizes the synthetic methods of PLA and their advantages and disadvantages. The direct polymerization method includes the solution polymerization method, which has mild reaction conditions but faces challenges in purification. The melt condensation method can produce PLA of higher molecular weight but requires expensive equipment. In the ring-opening polymerization of lactide, the cationic method produces unstable products, while the anionic method struggles to suppress side reactions. The coordination polymerization method can achieve high molecular weight but has high catalyst requirements and costs. The article also provides examples of PLA modification, such as surface modification for improved hydrophilicity and the addition of nucleating agents or blending for increased toughness. However, during modification, it is important to be cautious about reducing PLA's biodegradability excessively.

Currently, research on PLA still faces many challenges. In addition to issues related to mechanical properties, practical applications of PLA encounter difficulties such as high production costs, processing challenges, and excessive degradation rates in certain environments, hindering its large-scale use. Going forward, efforts should focus on finding efficient catalysts, optimizing production processes, and developing PLA synthesis and modification methods that are practical for large-scale production. This will enable control over PLA's molecular weight, molecular weight distribution, mechanical properties, degradation characteristics, and weatherability, meeting the requirements in industries such as manufacturing and medicine.

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