

Modification and Application of Polylactic Acid

Siyuan Yin¹, Juzheng Zhang², and Mingyu Zhang^{3*}

¹Reading academy, Nanjing University of Information Science and Technology, Nanjing, 210044, China

²Tianjin Farragut School, Tianjin, 300000, China

³Chemistry, Sun Yat-sen University, Guangzhou, 510000, China

Abstract. Polylactic acid (PLA) is a biobased product and compostable polymer material. As awareness of plastic pollution grows, PLA, as a biodegradable plastic, is regarded as a key material to replace traditional plastics. In recent years, PLA has been studied for a variety of applications. However, the inherent drawbacks of pure PLA, such as poor heat resistance, low degradation rate, brittleness, and poor toughness, make it difficult to meet practical production and application requirements. Therefore, effective modification strategies for PLA have received significant attention. This paper reviews the main modification strategies for PLA polymers in recent years, including copolymerization, blending, and the use of plasticizers, as well as the applications of modified PLA in packaging, 3D printing, and biomedical fields. The study finds that PLA has been widely studied and applied in various fields, but there are still challenges remain, such as the high cost of PLA, especially in the medical field. There are also limitations in mechanical properties, and constraints in precision and functionality in 3D printing applications.

1 Introduction

Plastic pollution is one of the most pressing environmental challenges facing the world today. Traditional petroleum-based plastics degrade slowly in natural environments, leading to increasingly severe "white pollution." In this context, the development of biodegradable green materials has become a global consensus and polylactic acid (PLA), as the most promising bio-based biodegradable material, is receiving wide attention [1].

As one of the most comprehensively developed and best-performing bio-based biodegradable materials, the related research and application of PLA become more and more. PLA stands out among many biodegradable materials because of its multiple advantages: good processability, allowing it to be shaped using conventional plastic processing methods; excellent biodegradability, capable of decomposing into carbon dioxide and water under appropriate conditions; and outstanding biocompatibility, granting it unique advantages in the medical field [2, 3]. Although the synthesis methods for PLA are quite mature, its inherent performance limitations still restrict its broader application. PLA suffers from deficiencies such as high brittleness, poor toughness, low heat deflection temperature, and slow

* Corresponding author: zhangmy225@mail2.sysu.edu.cn

degradation rates, making pure PLA unsuitable for high-end application scenarios. To overcome these limitations, targeted modification of PLA has become a key approach to expanding its application scope. Currently, common modification methods include chemical modification (e.g., copolymerization, crosslinking) and physical modification (e.g., blending, plasticization). These methods can significantly enhance PLA's melt strength, improve its toughness, and adjust its bioactivity and degradation rate. This review aims to systematically summarize the latest research progress in PLA modification technologies and analyze the performance of modified PLA in various application fields. The article will delve into how different modification strategies address PLA's inherent limitations and the practical effectiveness of these materials in diverse application scenarios

2 Polylactic acid

Poly(lactic acid) (PLA), also known as polylactide, is a biodegradable thermoplastic polymer. Lactic acid monomer (LA) is produced by fermentation of sugars from renewable resources such as corn, wheat, sugarcane, and rice, or by chemical synthesis of acetaldehyde and hydrogen cyanide and then polymerized to form linear bio-based polyester chains. Polymerization methods include direct polycondensation, azeotropic dehydration polymerization, and ring-opening polymerization (ROP). The PLA synthesized through direct polycondensation typically has small molecular weight and limited properties, and it often needs the assistance of chain extenders. The azeotropic dehydration condensation method involves solvents and complex post-processing, so it is always along with the high costs. Therefore, although ROC has complex steps, it is the mainstream synthesis method of PLA, due to the high molecular weight and controllable structure of the synthesized PLA.

The ROP process can be divided into three main steps: pre-condensation, depolymerization and cyclization, and ring-opening polymerization. First, LA is synthesized by pre-condensation, and then depolymerized and cyclized to form its cyclodimer, lactide. After the purification of lactide, by adding initiator as catalyst, the high molecular weight PLA was synthesized. The proportional order of D-LA and L-LA units can be controlled by changing the reaction temperature and time, as well as the type and concentration of catalysts.

Besides PLA, there are other commonly used synthetic biodegradable polymers including poly(glycolic acid) (PGA), polycaprolactone (PCL), polyhydroxybutyrate (PHB), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). PGA often degrades too rapidly because of its hydrophilic nature, which would lead to premature loss of mechanical strength when using. PCL has a relatively low melting point about 60 degree, which limits its applicable temperature range. PHB and PHBV have high production costs and less outstanding overall properties. Therefore, PLA has been considered as the most promising biodegradable polymer. It is noteworthy that although the properties of other degradable materials may be limited, single materials themselves often struggle to meet complex application requirements. Utilizing these polymers for modifying PLA, such as blending, could sometimes receive unexpectedly beneficial results.

3 Modification

3.1 Copolymerization

Copolymerization changes PLA's chain structure through chemical bonds, which allow to adjust PLA's properties to meet diverse application requirements. Therefore, it is a good way to modify PLA. There are two main methods to synthesize PLA copolymers. One way is the condensation polymerization of lactic acid with other monomers (or polymer segments).

Another way is the ring-opening polymerization of lactide with other cyclic monomers (or polymer segments).

Polyethylene glycol (PEG) is a polyether. It has good elasticity and hydrophilicity and it also degrades faster than PLA. Through synthesizing PLA-PEG-PLA triblock copolymers, it improves PLA's degradation rate and hydrophilicity and also enhances biocompatibility of PLA. Because of these unique properties, such copolymers are highly promising for drug delivery [4]. In addition, glycolic acid can be used to adjust hydrophilicity and degradation rate, too. It is copolymerizing LA and glycolic acid that could synthesize the random copolymer poly (lactic-co-glycolic acid) (PLGA).

Polycaprolactone (PCL) is a biodegradable polyester. It is very flexible and biocompatible. PCL segments are soft, while PLA segments are hard, so combining them could effectively toughen the material. Designing block or random copolymers of caprolactone and lactic acid (PLA/PCL) improves the polymer's flexibility and strength. Especially triblock structures (like PLA-PCL-PLA) are considered as perform well as excellent compatibilizers for PLA/PCL blends. They strengthen the interface between components, creating a more unified system [5].

Besides block and random copolymerization, graft copolymerization of PLA is also a topic of frequent discussion. PLA can form graft copolymers with materials like lignin, starch, or natural rubber. This method greatly improves impact strength and elongation at break. More importantly, such copolymers work as effective compatibilizers in physical blends. What's more, using natural substances in copolymerization helps improve the biocompatibility of PLA.

3.2 Positioning

Polymer blending represents a more economical and easier approach compared to synthesizing new polymers. This method mixes different polymers to get combined benefits. The two main methods are solution blending and melt blending. In the industry, melt blending is more common. It avoids pollution from solvents. It also does not need steps to remove solvents. However, melt blending uses high heat. This can be a problem for some natural polymers, which may break down or react badly with PLA at high temperatures.

To achieve toughening modification, PLA can be compounded with some flexible polyesters. Common examples include PCL, PBS, and PBAT. These polyesters act like elastic plastics. They have low glass transition temperatures (T_g), which means their chains can move easily at room temperature and they are much more flexible. However, mixing PLA with these polymers is not as simple as expected. This is because they do not mix well naturally, so in actual operation, compatibilizers need to be considered more often than not [6, 7]. Compatibilizers do not fully mix the polymers fully mix. Instead, their job is to better connect the different phases. They strengthen the bond at the interface, thereby making the blended material behave more uniformly.

What's more, PLA can also be blended with agricultural polymers such as starch, chitin, cellulose, proteins etc. This strategy cannot only lower the cost of PLA materials but also improve the biodegradability. Unlike copolymer synthesis, blending is low-cost and more suitable for large-scale production in industry. In actual manufacture, blending and copolymerization exist side by side and play a part together. Most of time, a small amount of copolymer would be added as a compatibilizer during blending, which can significantly improve product quality.

3.3 Plasticizers

Adding oligomeric or small-molecule plasticizers into the gaps between PLA chains can reduce intermolecular forces, which would make the chains move more easily. As a result, the material becomes more flexible and stretchable. Its glass transition temperature (T_g) also drops which means the temperature range for processing PLA would become wider.

Citrate esters, such as acetyl tributyl citrate, are the most common plasticizers for PLA in practical production. Studies have indicated they are non-toxic and have better compatibility with PLA [8]. Polyethylene glycol (PEG) is another choice. But its molecular weight plays an important role in the plasticization process. Low molecular weight PEG plasticizes very well, but it migrates a lot. This sometimes would lead the sticky surface. On the other hand, high molecular weight PEG does not plasticize as effectively.

Plant-based plasticizers, like epoxidized soybean oil and acetylated monoglycerides, have also gotten more attention in current research. They work well as plasticizers and are stable under heat. However, they are generally not as effective as citrate esters yet [9].

4 Application

4.1 Packaging

Poly(lactic Acid) (PLA) has emerged as an ideal alternative to traditional petroleum-based plastics due to its biodegradability, excellent transparency, and mechanical properties. Therefore, PLA has been widely used in the packaging industry. Commercial production of PLA-based products such as films, containers, beverage cups, and food trays has been realized. The U.S. Food and Drug Administration (FDA) has approved PLA for use in food-contact materials, particularly for packaging short-shelf-life foods like fruits and vegetables [10]. In addition, PLA is utilized in shrink wraps, foam cushioning materials, and shopping bags. It can rapidly degrade under industrial composting conditions which means it can significantly reduce environmental pollution of plastic waste.

4.2 3D printing

PLA is one of the most popular materials in Fused Deposition Modeling (FDM). It is because of its low printing temperature, minimal warping tendency, availability in a variety of colors, and mild odor. It is suitable for a broad range of 3D printing applications. It ranges from prototyping to functional parts, including housings for household appliances, educational models, customized tools, and artistic designs. In recent years, by incorporating fillers such as graphene and carbon nanotubes, PLA composites become more functional. Its conductivity, mechanical strength, and flame retardancy can be purposively adjusted, which broadens its applications in more high-grade, precision and advanced fields such as electronic enclosures and structural components [11].

4.3 Medical domain

4.3.1 Tissue engineering

PLA and its composites are extensively utilized in bone tissue engineering. They generally fabricate porous scaffolds that support cell attachment, proliferation, and differentiation. Adding materials like hydroxyapatite (HA) or bioactive glass (BG) can improve the bioactivity and osteogenic properties of PLA scaffolds. For instance, PLA/HA composites

have been confirmed that it can help bone-forming cells grow and create new bone [12]. Furthermore, PLA is also applied in skin regeneration. PLA/cellulose acetate (CA) electrospun fiber membrane can be used as wound dressing. It can promote healing and has antibacterial properties [13, 14].

4.3.2 Surgical sutures

PLA can be used to make absorbable sutures. These stitches slowly break down into lactic acid inside the body. The body then metabolizes this into carbon dioxide and water. This means patients do not need a second surgery to remove the stitches. PLA has good strength and it is compatible with the body. Furthermore, its breakdown rate can be controlled by modification, such as being copolymerized with PEG, which makes it very suitable for stitching internal organs and deep tissues

4.3.3 Drug Delivery

PLA and its copolymers (like PLGA) are common materials used for drug carriers such as microspheres, nanoparticles, implants, and fibrous membranes. By adjusting PLA's molecular weight, crystallinity, or copolymer mix, how a drug is released can be control, which means the release can be slow, targeted, or precisely managed. For example: Anticancer drugs (like doxorubicin) can be loaded into PLA/chitosan nanofibers to enable targeted release at tumor sites and achieve high cell mortality. Antibiotics (like vancomycin) loaded onto PLA coatings can be applied to orthopedic implants to prevent postoperative infections. Protein and peptide drugs (like insulin-like growth factor-1, rhIGF-1) can achieve sustained release for up to 180 days through PLA/HA bilayer microspheres [15].

4.4 Future Development

PLA currently enjoys a wide range of applications, yet there remains significant room for improvement. In future research, enhancements can be made by modifying its structure, such as constructing hierarchical architectures spanning from the nano- to the macro-scale, to create novel materials that combine high strength, toughness, and excellent elasticity. This approach offers a new direction for the development of advanced PLA composite surgical sutures. Presently, the cost of PLA materials remains higher compared to traditional alternatives. This issue could be addressed by optimizing direct polycondensation methods, discovering novel catalysts, or exploring new reaction conditions. As one of the most commonly used materials in Fused Deposition Modelling (FDM) technology, the application of PLA is gradually expanding to include more 3D printing processes such as Direct Ink Writing (DIW), Digital Light Processing (DLP), and Selective Laser Sintering (SLS). This expansion necessitates the development of corresponding new PLA-based composite materials (e.g., photosensitive resins, high-performance powders) to meet the demands of different scenarios for precision, speed, and complex structural fabrication.

5 Conclusion

In summary, through modification approaches such as copolymerization, blending, and plasticization, the performance of polylactic acid (PLA) can be targeted to improve one or more of its properties, transforming it into a category of "engineering-grade" high-performance materials that can meet various complex practical demands. Without modification, the applications of PLA would be limited to very basic fields.

Future research focus will continue to be centered on the development of efficient and green modification methods, particularly addressing the compatibility issues among multi-component systems, and further exploring the innovative applications of modified PLA in cutting-edge fields such as high-end medical care, intelligent packaging, and advanced manufacturing. Ultimately, with continuous breakthroughs in modification technologies, PLA is expected to play a more central role in replacing traditional plastics and promoting sustainable development.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

References

1. S. Nizamuddin, A.J. Baloch, C. Chen, M. Arif, N.M. Mubarak, Bio-based plastics, biodegradable plastics, and compostable plastics: biodegradation mechanism, biodegradability standards and environmental stratagem. *Int. Biodeterior. Biodegrad.* **195**, 105887 (2024).
2. N. Shekhar, A. Mondal, Synthesis, properties, environmental degradation, processing, and applications of Polylactic Acid (PLA): an overview. *Polym. Bull.* **81**, 11421–11457 (2024).
3. N.G. Khouri, J.O. Bahú C. Blanco-Llamero, P. Severino, V.O.C. Concha, E.B. Souto, Polylactic acid (PLA): Properties, synthesis, and biomedical applications – A review of the literature. *J. Mol. Struct.* **1309**, 138243 (2024).
4. N. Rostami, F. Faridghiasi, A. Ghebleh, H. Noei, M. Samadzadeh, M.M. Gomari, A. Tajiki, M. Abdouss, A. Aminoroaya, M. Kumari, et al., Design, Synthesis, and Comparison of PLA-PEG-PLA and PEG-PLA-PEG Copolymers for Curcumin Delivery to Cancer Cells. *Polymers* **15**, 3133 (2023).
5. O. Prasitnok, K. Prasitnok, Architectural Effects of Biodegradable Block Copolymers on Enhancing PLA/PCL Blend Compatibility: Molecular Dynamics Simulations. *Macromolecules* **58**, 4103–4111 (2025).
6. Y. Yu, W. Liu, Q. Yue, Q. Shi, M. He, X. Liu, X. He, B. Wen, N. Liu, T. Ge, Effects of Butylene Adipate-Lactate-Butylene Terephthalate Copolyester on the Properties of PLA/PBS Blends. *J. Appl. Polym. Sci.* **142**, e57684 (2025).
7. A. Altınbay, C. Özsaltık, D. Jahani, M. Nofar, Reactivity of Joncryl chain extender in PLA/PBAT blends: Effects of processing temperature and PBAT aging on blend performance. *Int. J. Biol. Macromol.* **303**, 140703 (2025).
8. P. Brdlík, J. Novák, M. Borůvka, L. Běhálek, P. Lenfeld, The Influence of Plasticizers and Accelerated Ageing on Biodegradation of PLA under Controlled Composting Conditions. *Polymers* **15**, 140 (2023).
9. D. Bajwa, M. Eichers, J. Shojaeiarani, A. Kallmeyer, Influence of biobased plasticizers on 3D printed polylactic acid composites filled with sustainable biofiller. *Ind. Crops Prod.* **173**, 114132 (2021).
10. S. Ubeda, M. Aznar, P. Alfaro, C. Nerón, Migration of oligomers from a food contact biopolymer based on polylactic acid (PLA) and polyester. *Anal. Bioanal. Chem.* **411**, 3521–3532 (2019).
11. B.N. Teixeira, P. Aprile, R.H. Mendonça, D.J. Kelly, R.M.d.S.M. Thiré Evaluation of bone marrow stem cell response to PLA scaffolds manufactured by 3D printing and

- coated with polydopamine and type I collagen. *J. Biomed. Mater. Res., Part B* **107**, 37 - 49 (2019).
12. Y. Zhang, M. Fang, J. Zhu, T. Li, N. Li, B. Su, G.-D. Sun, L. Li, C. Zhou, Exosome-loaded hyaluronic acid hydrogel composite with oxygen-producing 3D printed polylactic acid scaffolds for bone tissue repair and regeneration. *Int. J. Biol. Macromol.* **274**, 132970 (2024).
 13. L.R. Jaidev, K. Chatterjee, Surface functionalization of 3D printed polymer scaffolds to augment stem cell response. *Mater. Des.* **161**, 44–54 (2019).
 14. Z.A. Alhulaybi, Fabrication and Characterization of Poly (lactic acid)-Based Biopolymer for Surgical Sutures. *Chem. Eng.* **7**, (2023).
 15. N. Varga, V. Hornok, L. Janovák, I. Dékány, E. Csapó, The effect of synthesis conditions and tunable hydrophilicity on the drug encapsulation capability of PLA and PLGA nanoparticles. *Colloids Surf., B* **176**, 212–218 (2019).