

Modification and Applications of Polylactic Acid

Jiatong Wang

Faculty of Art and Science, Queen's University, Kingston K7L 3N8, Canada

21jw27@queensu.ca

Abstract. Polylactic Acid (PLA) is a biodegradable and bioactive polyester derived from renewable sources such as corn and sugar cane. Because PLA is eco-friendly, researchers have recently tried to make PLA replace other polymers that cause greenhouse gases and other pollution. However, for many industries, PLA has limitations of unsatisfactory toughness, heat resistance, etc. In this case, it is necessary to invest in the modification of PLA, which can offer PLA desired traits to adapt to different situations. This review focuses on the recent modifications that successfully improve PLA to fit the aims, as well as the advantages and disadvantages of each method that is used for modification. There is no doubt that these methods provide a path to expand the use of PLA in different fields, such as packaging, medicine, agriculture, and textiles. The paper concludes by emphasizing the need for continued research and technological development to fully release PLA's potential in promoting a sustainable and eco-friendly future.

Keywords: Polylactic acid, renewable sources, biodegradability, modification.

1. Introduction

Currently, the pollution caused by the mass production of plastic has been a crucial concern for a few years [1]. Therefore, the development of degradable and renewable polymers is of great significance. PLA is a biodegradable hydrolysable aliphatic semicrystalline polyester and has attracted wide attention [2]. It has become a focal point in scientific research and industrial applications due to its unique features. PLA is usually derived from corn or other organic products. PLA has good mechanical and chemical properties, as well as lower greenhouse gas emissions. Thus, PLA is widely used in packaging, agriculture, and biomedical industries.

Polylactic acid is composed of multiple lactic acids as monomers. Each lactic acid is carboxylic acid which has an OH group on each end of the molecule. The lactic acid undergoes a direct condensation process where water is produced as a side product and removed by azeotropic distillation. This is a common method of producing PLA [3]. Another method is ring-opening polymerization (ROP). This method allows lactide to form PLA. In this method, there is no need to remove water. [4] According to stereochemistry, the structure of PLA can be categorized into four different types, isotactic, syndiotactic, heterotactic, and isotactic stereo block. As shown in Figure 1, the isotactic structure is either L or D for the repeated structure, while the heterotactic structure has regions of L or D. The syndiotactic structure has alternating L and D for the repeated units.

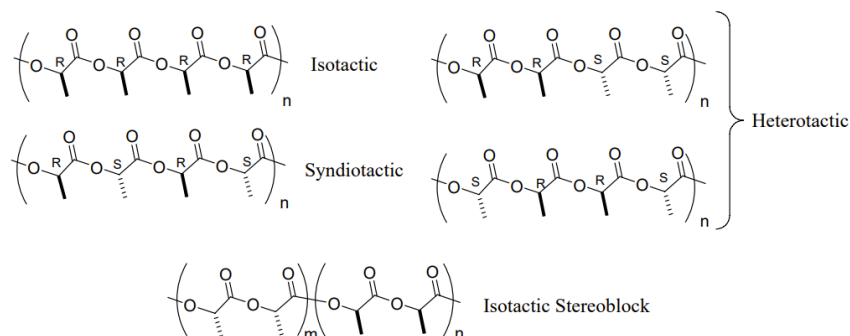


Figure 1. Different structures of PLA [4]

Indeed, the advantage of PLA makes it a valuable material. However, there are still limitations such as its relatively low heat resistance and high brittleness, which limits its applications in certain domains. Thus, in the past few years, large efforts are being put into the modification of PLA to

overcome such limitations. Many of them achieved their goal in modifications to PLA's structure. In the future, as more research is done, PLA can be adapted to more situations.

This paper explores many aspects of PLA, including the structure and production, and more importantly, the medications and some case studies. The goal is to explain the potential of PLA in creating a more sustainable environment in the future.

2. Modification of PLA

PLA is one of the most widely used biodegradable and renewable polyesters. It has the potential to replace conventional petrochemical-based polymers [5]. PLA-based technologies are aimed at altering chemical, mechanical, and biological properties. To achieve the intended goals, both chemical and physical modification is applied.

2.1. Blending

One of the most common methods of PLA modification is by blending it with other polymers to improve material properties. For example, polycaprolactone (PCL), poly(butylene adipate-co-terephthalate) (PBAT), or poly(butylene succinate) (PBS) are common polymers that blend to PLA to enhance its toughness [6]. According to Su's review, he states that the simple blending of PLA with PBS could achieve a combination of the desirable properties of each component and form a potential matrix for preparing composites without losing biodegradable behavior [6]. Another example is the blending of the PLA and Acrylonitrile Butadiene Styrene (ABS). It is a common combination used in additive manufacturing [7]. The surfaces of the blending polymers are treated with inductively coupled plasma (ICP) and coated with Cystic Fibrosis (CF) materials to modify the surface hydrophobicity. Then, the reduction of the water resistance on the surface not only improves the surface protection of the printing product but also increases the toughness of the product. The blending of PLA with other polymers that are stronger and have higher heat resistance can improve the properties of PLA and allow them to adapt to different situations.

2.2. Copolymerization

Copolymerization is commonly used to modify the properties of plastics. Thus, this method could also apply to PLA as a solution to modify its property. It is more a chemical way that allows PLA to have a better adaptation to biomedical usage. Degradable PLA polymers in the PLA family can bear functional groups that serve as intermediates for further chemical modifications [8]. In this case, copolymerization is appropriate to apply to PLA. For example, copolymerizing lactic acid and glycolic acid can generate useful biomedical materials [9]. In this example, the product provides a higher degradation rate, making it useful for applications such as medical sutures where this type of modification is desirable. The advantage of copolymerization is that it can modify the properties of the polymer by changing the type and ratio of the monomers used. However, the overall process is hard to manage. It depends on factors such as temperature, catalysts, and monomer ratio.

2.3. Plasticization

Plasticizers are often added to PLA to increase its toughness and flexibility. PLA as an eco-friendly material always is considered by scientists for its application in the packaging industry. However, due to its brittleness, low stiffness, and incompatibility, PLA is hard to be considered a proper material for plastic bags [10]. For example, poly(butylene adipate-co-terephthalate) (PBAT) is derived from petroleum, which has a high elongation and good ductility. PBAT usually has inferior properties, such as tensile strength, which can limit its applications where high strength is required. Thus, by blending PBAT and PLA, the weakness of each polymer can be compensated and form a material that suites better for packaging.

2.4. Physical treatments

Physical treatments are methods that are using physical changes to modify the properties of PLA. For example, in 3-D printing, researchers tried to use heat treatment to modify the properties of PLA. Heat treatments can influence the porosity of the specimen structure. At the same time, there is also improvements in the crystallinity. The experiment also suggests that heat treatment is appropriate for PLA application in 3-D printing [11].

2.5. Nanocomposition

Incorporating nanoparticles into PLA can also improve its property. The implantation of nanoparticles derived from reinforcing inorganic oxide, graphite, and silica-based particles can improve tensile strength, crystallinity, glass transition temperature, and so on [12].

There are some of the methods used to modify PLA and expand its range of applications in industry. They all share similar drawbacks, such as it is hard to manage since almost every method requires precise control of factors and amount of materials. However, the advantage is by modification, scientists can manually improve the desired properties of PLA. Combining PLA's own advantage, it shows great potential in the future where PLA can be adapted into more industries.

3. Application

3.1. PLA application in additive manufacturing

Additive manufacturing is a revolutionary technique that has many advantages compared to traditional 3-D printing [13]. One of the most significant advantages is design freedom. It allows porous structures, and it also does not need assembly or expensive tooling. Originally PLA has a low melting point, and a glass transition temperature (T_g) of 60-65°C [14]. Particularly to PLA, a lower T_g is preferred. The product of additive manufacturing is in the state that materials are successively bonded to each layer. With a lower T_g , the required temperature of the print bed could be lower. However, if T_g is higher than the print bed, the material may become too soft and lose its shape, leading to deformation. To address these limitations, researchers and manufacturers have explored various PLA modifications to enhance their properties. A common process of heat treatment includes placing samples in a vacuum oven at 50°C for 24 hours and then treating them to a temperature of 160-210°C for an hour [15]. After this process, the T_g value changes which results in improving the surface of the finished product.

3.2. PLA in the packaging industry

Plastic products, prevalent in the packaging industry, are causing environmental problems such as microplastic pollution. To address this issue, research has been conducted on modifying PLA for packaging use. Since PLA's natural rigidity is a challenge, various high-molecular and low-molecular compounds were introduced as plasticizers to enhance its deformability. Key plasticizers like di-2-ethylhexyl adipate (ADO) and di-2-ethylhexyl sebacate (SDO) were particularly effective, shifting the glass transition temperature to lower values and increasing elongation at break without degrading the polymer. In the experiment done, the selected plasticizers also showed potential for use in PLA food films, exhibiting advantages over traditional citrate plasticizers. The study's findings support the notion that these modifications to PLA can contribute to greener packaging technologies in line with the principles of a circular economy [16].

3.3. PLA in medical science

PLA, due to its biocompatibility, biodegradability, mechanical strength, and processability, is increasingly being used for various biomedical applications such as drug delivery, implants, sutures, and tissue engineering. However, challenges with PLA include a slow degradation rate, hydrophobicity, and low impact toughness [17]. To overcome these, PLA is often blended with other

polymers to enhance its properties or to create new PLA polymers for specific applications. For example, fabricating biointerfaces is suitable for cellular physiological environments, particularly those with micro-structured surfaces for applications in the biomedical field. Specifically, self-assembled PLA with micro-structured surfaces can be applied in areas like tissue engineering scaffolds, controlled drug release, and tumor therapy. Several self-assembly methods including breath figure, phase separation, electrospinning, and foaming are potential ways to fabricate PLA with the desired topography for biomedical uses. However, the methods have limitations. PLA scaffolds created through phase separation have small pores that can hinder cell penetration, and those created via electrospinning have low thermal stability [18].

4. Conclusion

This paper summarizes the modification and applications of PLA. PLA has great potential in the future due to its renewable sources and biodegradability. However, challenges remain in terms of production cost, the lack of mechanical properties, and degradation rates. In addition, for massive production in industries, cost and efficiency must be considered. Nowadays, PLA production techniques are hard to balance between increasing efficiency and reducing cost, which is a key factor for PLA when compared with other traditional materials. Technological advances in the modification of PLA in recent years have been popular in various fields. These improvements in properties and production processes will drive the border of adaptation into various industries. As environmental protection becomes the concern of all human, the demand for bioplastics like PLA modification will undoubtedly grow. In fact, the use of PLA is expected to grow across various sectors, including medical, and textile. Whereas in the current stage, it needs more research and development to fully realize the potential of PLA. According to the current state of PLA, future research and development will likely focus on improving PLA's inherent characteristics, such as toughness, flexibility, and heat resistance, making it more versatile and suitable for a wider range of applications.

References

- [1] Ghomi, E. R., Khosravi, F., Ardaheai, A. S., et al. 2021 *Polymers* 13 1854.
- [2] R. Hagen (2012) *Poly lactide, Poly lactide - an overview* | ScienceDirect Topics. Available at: <https://www.sciencedirect.com/topics/materials-science/poly lactide> (Accessed: 29 July 2023).
- [3] Ghomi, E. R., Khosravi, F., Ardaheai, A. S., et al. 2021 *Polymers* 13 1854
- [4] Porter, K. A. (2006, March 2). Ring Opening Polymerization of Lactide for The synthesis of Poly (Lactic Acid). https://chemistry.illinois.edu/system/files/inline-files/06_Porter.pdf.
- [5] Rasal, R. M., Janorkar, A. V., & Hirt, D. E. 2010 *Progress in polymer science* 35(3), 338–356.
- [6] Su, S., Kopitzky, R., Tolga, S., & Kabasci, S. 2019 *Polymers* 11(7) 1193.
- [7] Lovinčić Milovanović, V., Guyon, C., Grčić, I., Tatoulian, et al. 2020 *Materials* 13 (23) 5578.
- [8] Saulnier, B., Ponsart, S., Coudane, J., Garreau, H., & Vert, M. 2004 *Macromolecular Bioscience* 4 (3) 232–237.
- [9] Lassalle, V., Galland, G. B., & Ferreira, M. L. 2008 *Bioprocess and Biosystems Engineering* 31 (5) 499–508.
- [10] Kim, D. Y., Lee, J. B., Lee, D. Y., & Seo, K. H. 2020 *Polymers* 12 (9) 1904.
- [11] Shbanah, M., Jordanov, M., Nyikes, Z., Tóth, L., & Kovács, T. A. 2023 *Polymers* 15 (6) 1587.
- [12] Mulla, M. Z., Rahman, M. R., Marcos, B., et al. 2021 *Molecules* 26 (7) 1967.
- [13] Brancewicz-Steinmetz, E., & Sawicki, J. 2022 *Materials* 15 (16) 1.
- [14] Gzyra-Jagięła, K., Sulak, K., Draczyński, Z., et al. 2021 *Polymers* 13 (21) 3651
- [15] Ribeiro, M., Sousa Carneiro, O., & Ferreira da Silva, A. 2019 *Rapid Prototyping Journal* 25 (1) 38–46.
- [16] Gzyra-Jagięła, K., Sulak, K., Draczyński, Z., et al. 2021 *Polymers* 13 (21) 3651.

- [17] Singhvi, M. S., Zinjarde, S. S., & Gokhale, D. V. 2019 Journal of applied microbiology 127 (6) 1612–1626.
- [18] Chen, Tianyu et al. 2023 Frontiers in chemistry 10 1107620.