Synthesis, Modification and Application of Polylactic Acid

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Abstract. Due to the increasing shortage of environmental resources, the idea of sustainable development increases the attention to the biodegradable substances. Polylactic acid (PLA) possesses outstanding mechanical and processing properties, and its products can be rapidly degraded in various ways after use. The synthesis and use of PLA have received more and more attention. Lactide, the intermediate to synthesize PLA, is challenging to produce and purify. As a result, the application cost of PLA is high, and it is hard to employ on a wide scale. Carbon dioxide (CO_2) can be used for the synthesis and modification of PLA through a cell factory. It offers a wide range of potential applications and can successfully address the lactide production and purification issue. Additionally, we talked about the significance of supercritical carbon dioxide (sc-CO_2) in the creation of PLA products and the viability of producing PLA directly utilizing sc-CO_2 as a medium. Furthermore, we discussed how sc-CO_2 affects the properties of PLA as well as the application of PLA products.

Keywords: Polylactic Acid, Synthesis, Modification, Application.

1. Introduction

No matter in our daily life or industry production, plastic plays an important role attributed to its cheap price, low weight, easy shaping, and stable chemical properties. Its production has expanded significantly throughout the years, going from 1.5 million tons in the 1950s to around 400 million tons in 2018. By 2050, it is anticipated that production will amount to 1800 million tons. However, petroleum-based plastic is hard to recycle. There are amounts of plastic is buried under the ground, affecting the soil structure. Besides, plastic pollution endangers the safety of marine life. To address this issue, bio-based plastics as an alternative to petroleum-based plastics has been widely used in a diverse of different fields. Bio-based plastics like polylactic acid (PLA) have outstanding biocompatibility and improved durability [1]. Because of its properties, PLA has been used in many fields, such as packing, biomedicine, 3D printing, and so on.

Direct condensation polymerization and lactide ring-opening polymerization are the two main processes used to create PLA. PLA has two configurations, including L-lactic acid and D-lactic acid. All of them contain –OH and –COOH groups. As a result, polymerization can occur immediately through self-condensation. Direct condensation includes solution and melt polymerization. PLA is dissolved in the organic solvent. And after removing water, the mixture is refluxed, leading to high molecular weight. Different from solution polymerization, melt polycondensation doesn’t need the organic solvent and PLA can be generated in a shorter time, but the temperature should be higher than Tm. However, it still has problems to solve. The other method is opening polymerization, which is more commonly used. The reactant can obtain by dimerization of the lactic acid. Under a vacuum or an inert environment, PLA is obtained by using the catalyst. Through the changing of time and temperature, D- and L-lactic acid with different ratios can be obtained. Researchers all over the world are interested in the process since catalysts play a crucial part in it [2].

Though PLA can get from renewable resources, it breaks down to CO_2 and H_2O. As a result, the use of PLA emits CO_2, which in turn contributes to the greenhouse effect. Global warming leads to the rise of sea level, it also destroys biodiversity, affects marine ecology and accelerates ocean acidification. According to a recent research, PLA can be synthesized by using CO_2 directly. This method solves the problem of plastic pollution as well as global warming. It can also skip the propylene ester for direct synthesis, which can help reduce cost [3].

This research will focus on the role of CO_2 in the synthesis of PLA and the direct synthesis of PLA from CO_2. Then we focus on the effect of CO_2 on the properties of PLA products. Ultimately, we discuss the possibility of using supercritical carbon dioxide (sc-CO_2) as a medium for the direct synthesis of PLA.

2. Synthesis of PLA and its composites with different methods

2.1. Biological method

So far, PLA is mainly directly polymerized by lactide or lactic acid. However, the production methods of lactic acid and lactide require sugar-based materials, resulting in resource competition between PLA production and food supply. As a result, it is necessary to explore non-edible materials which are used as raw materials to product PLA. Tan et al. used cyanobacteria cells to convert CO_2 into PLA directly. They use LED lamp to provide controllable light and concentration of CO_2 from the waste gas as carbon source of cyanobacterial bacteria to achieve high-density culture of cyanobacterial cells (HDC), which significantly improves the productivity of the HDC. They also optimized expression of two pivotal enzymes in cyanobacteria: PCT and PHA. Then they knock out four genes. The carbon flux was directed to PLA biosynthesis by sRNA which were added artificially. This combination of HDC and metabolic engineering significantly increased the yield of PLA [3], as shown in Figure 1.

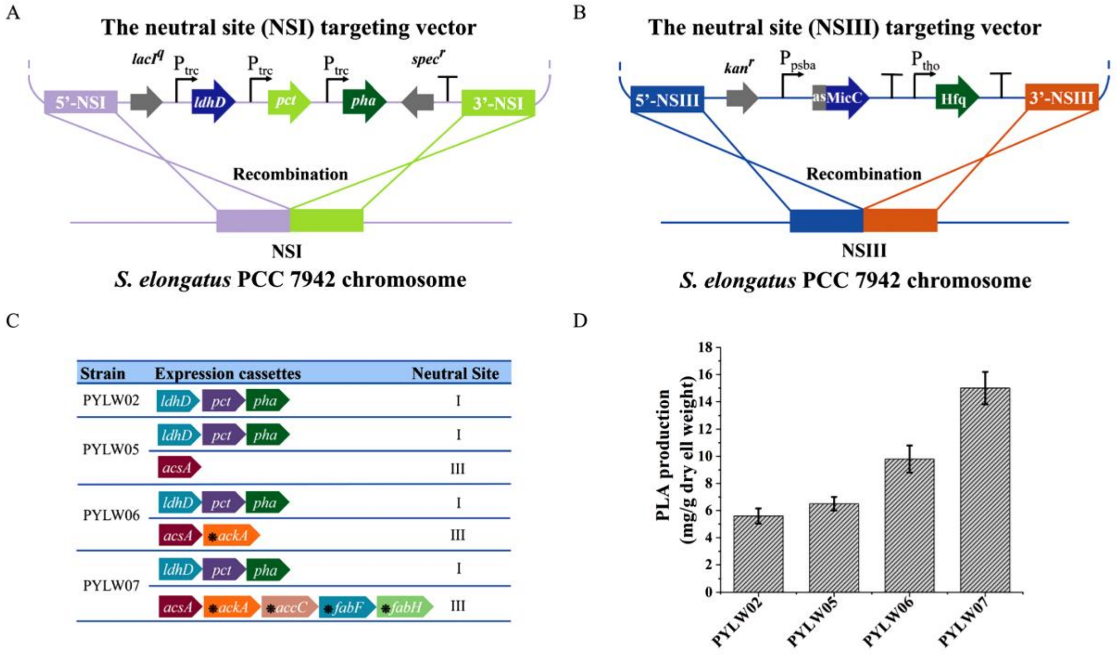

Figure 1. The PLA production by optimizing experimental conditions [3]

2.2. Foaming method

In addition to direct conversion, sc-CO_2 can also be used to replace traditional foaming agents, such as chlorofluorocarbons, to prepare of porous plasticser. Buzmakov et al. used sc-CO_2 as a plasticizer in the initial stage and a foamer in the main step to form a Nanoscale PLA co-glycolic acid scaffold [4]. In the initial stage, sc-CO_2 was gradually uniformly spread in the sample. The polymer swelled, and the intermolecular bond weakened. Then, sc-CO_2 was further foaming as a foaming agent in the decompression stage. After the connectivity analysis of the samples, it was found that almost all the holes are open and attached. The volume percent of closed pores is only 0.38 %. Huang et al. used sc-CO_2 as a foam beater to obtain PLA foam with bimodal porosity structure [5]. Oluwabunmi et al. used PLA and microcellulose fiber to prepare biodegradable plastic foams by using sc-CO_2 physical foaming method [6]. Foaming experiment adopts two-step CO_2 decompression process. The original foam beater, such as CFC, provided adequate vapor pressure for expansion of foam. Since chlorofluorocarbons are now considered one of the most important ozone depleter, the use of CO_2 is more conducive to environmental protection. At the temperature of 70 °C and the pressure of 11.72 MPa, CO_2 was released into the container for soaking the sample for 5 h to assurance that the gas was completely dissolved in the polymer. At the end of time, the system temperature decreased sharply to 58 °C. At this temperature, the pressure was rapidly reduced to 3.45 MPa for 10 min, which provides a driving power for cell nucleating to promote the growth of foams. Then in the second stage, it can be to decompress the pressure, while cooling the pressure vessel to ambient temperature. This method also ensures that there are no volatile organic compounds in the foam.

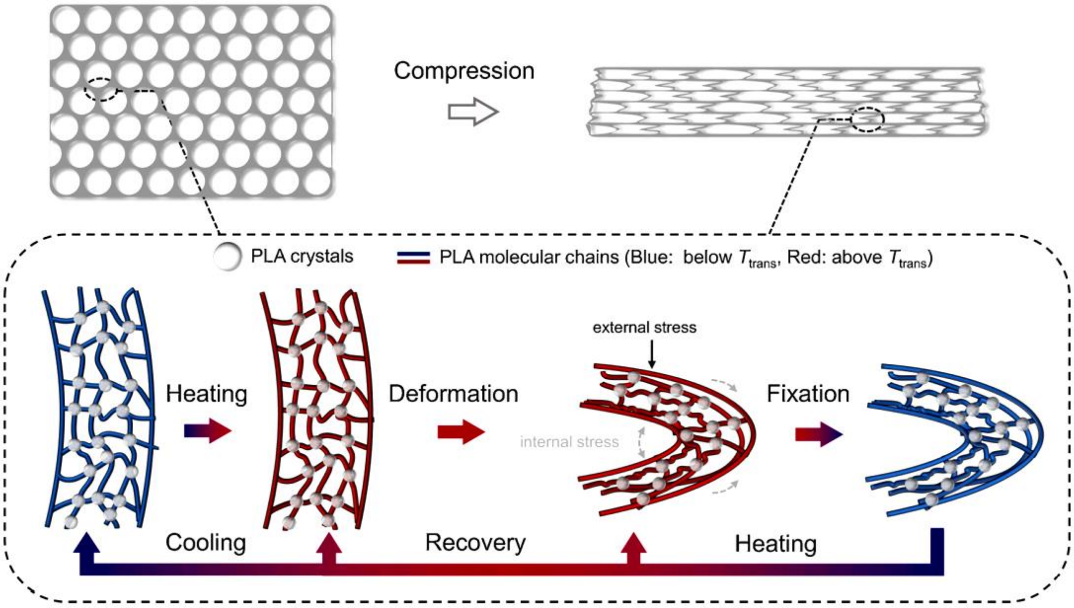

Figure 2. Schematic diagram of the mechanism of shape memory [7]

Recently, porous shape memory polymers have attracted much attention due to their broad application prospects. Chai et al. adopted a new and flexible two-step CO_2 microcellular foaming method to prepare bio-friendly PLA/PMMA shape memory foams [7], as shown in Figure 2. After the blending of PLA and PMMA, the sample was put into CO_2, and the temperature was maintained at 25 °C. The pressure was maintained at 2 MPa for 24 h, and then maintained at 3.5 MPa for 6 h. Finally, the temperature of the foam rapidly decreased to 0 °C. The sample was taken out from the container and quickly put in boiling water for 60 seconds to carry on the foam blowing. Finally, the sample was moved to ice bath again to make the porous structure stable. This provides a new idea for the preparation of PLA-based composites.

2.3. Drying method

After measuring the glass transition temperature (Tg) and crystallinity of PLA, Bueno et al. used the corresponding ternary phase diagram to determine the proportion of the gelled polymer/solvent/anti-solvent. And then the PLA aerogel was prepared by sc-CO_2 drying method [8]. What should be noticed is that the temperature should not exceed Tg of PLA. The use of sc-CO_2 drying can avoid the damage of gel mesoporous structure caused by volume shrinkage during evaporation drying. Salerno et al. used EL as a nontoxic resolvent for PLA and sc-CO_2 as a clean desiccant. Then researchers used thermal-induced phase separation to prepare porous PLA aerogels with tissue engineering potential [9]. After dissolving PLA with EL to form isotrope solution, the temperature was reduced to below the gel point of the solution, and the solvent exchange was carried out to generate the gel. After the gel was sealed to the reactor, the temperature was increased to 39 °C and the pressure was increased to 19 MPa to ensure the supercritical condition.

2.4. Application of High-pressure CO2

The mechanical properties of PLA depend on its crystallinity and crystal structure. Chai et al. used in-situ nanofibrillation technology and High-pressure (HP)-CO_2 treatment to prepare PLA, which enhances the strength, ductility and heat tolerance of PLA [10]. They first prepared amorphous PLA/PTFE samples, then placed them at ordinary temperature for two weeks for physical aging. After heat treatment, the sample was placed in a sealed container containing 3.5 MPa CO_2 and kept it at ordinary temperature for 4 hours. Then it was cooled the container to 0 °C and decompressed CO_2. The CO_2 treatment used in this experiment is a new strategy, where the HP-CO_2 is used as a elasticizer to induce the crystallization of PLA, thereby enhancing and toughening the PLA by increasing degree of crystallization and refining crystallographic structure.

2.5. Possibility of direct polymerization under sc-CO2

Direct polymerization is a method for generating PLA. It has the benefits of a straightforward production process, high yield, and inexpensive production costs. However, the disadvantage is that as the reaction progresses, the viscosity of the reaction solution increases, the water product is difficult to remove, and depolymerization is easy to occur. Additionally, the result of this process has a lower molecular weight. Under sc-CO_2, it is easy to purify the product, and sc-CO_2 has a good swelling effect on the polymer, which can reduce the viscosity of the solution to a certain extent. According to the principle of similar compatibility, some non-organic solvent small molecules and polymers have good solubility in supercritical CO_2 because CO_2 is a non-polar molecule. For most polymers, even if sc-CO_2 cannot dissolve them, but it still has a good swelling effect. In addition, sc-CO_2 has good safety and stability, which can inhibit the occurrence of chain transfer reactions. At the same time, adding a small amount of polar co-solvent can improve the solubility of sc-CO_2 and the swelling effect on the polymer. Second, increasing the pressure of the sc-CO_2 system facilitates the reaction. Supercritical CO_2 overcomes the residual problem of the solvent. The raw components are still dissolved in the supercritical CO_2 after the reaction and are released together with the CO_2, which serves to purify the product. This can not only take advantage of the low cost and high yield of direct polymerization, but also hinder polymer depolymerization to a certain extent. Many current studies primarily concentrate on how sc-CO_2 affects the foaming of PLA products.

3. Modification of PLA

3.1. Crystallization

Under the influence of the sc-CO_2, PLA may be induced to form four distinct crystal structures: ring-shaped spherulites, transition spherulites, mixed spherulites and conventional spherulites. Ring-shaped spherulites with alternating concentric ridges and concentric troughs are more likely to form under low temperature and high pressure. At high temperatures (130 °C), it tends to generate spherulites that are radially dispersed. At moderate temperatures (100 °C or 120 °C), mixed spherulites are likely to form, with conventional spherulites at the core surrounded by ring-shaped spherulites. In the meanwhile, when isothermal crystallization temperature and immersion pressure increased, the crystallinity of PLA isothermal crystallization produced by the sc-CO_2 decreased. During spherulite development, the mutual transition between conventional and ring-shaped spherulites occurs to varying degrees, which may contribute to the process of the production of three specific crystal forms. The study of PLA cell structure revealed that foaming (16 MPa, 80 °C) induced the formation of ring-shaped and transition spherulites, resulting in radially elongated cell structures. In addition, raising the immersion pressure is advantageous for enhancing foamability, decreasing cell size and cell density, and developing a partly open-cell structure. Under various foaming conditions, the compressive strength displayed an early rise followed by a decline [11].

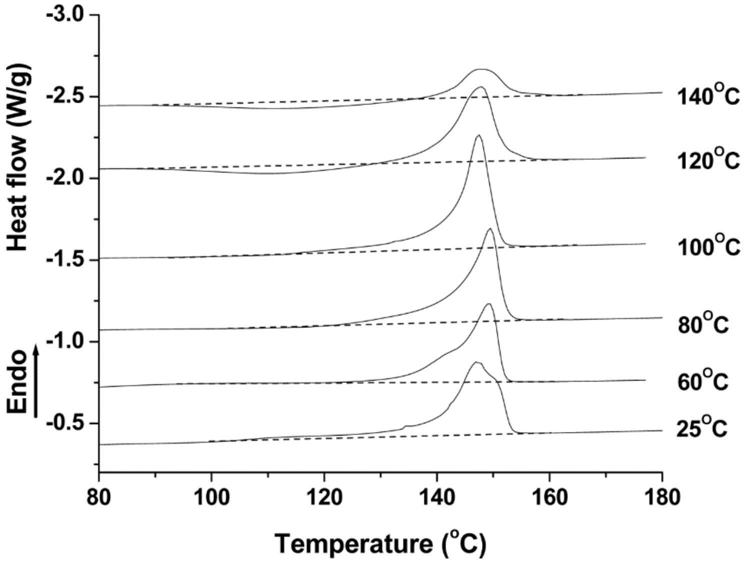

Figure 3. DSC curves of the prepared PLA samples [12]

The crystallinity of PLA may reach 27.4% at a temperature as low as 25 °C and form after just 1 minute of CO_2 treatment at 100 °C. In addition, the crystallization equilibration time was drastically shortened to 20-40 minutes, and the strong plasticizing impact of compressed CO_2 effectively boosted the polymer mobility chain, hence speeding the crystallization rate of PLA and expanding its crystallization window. 100°C and 6.89 MPa are the optimal crystallization temperature for PLA. Due of its poor chain mobility, linear PLA crystallizes at a relatively slow pace under atmospheric pressure, requiring around 10 hours to induce its isothermal crystallization at 120 °C. At lower temperatures, a rise in temperature tended to increase the PLA's crystallinity, but at higher temperatures, the converse was true. The DSC curve revealed that when crystallinity increased, the tendency for crystals to diminish and vanish increased, as shown in Figure 3. Changes in treatment conditions had no effect on the crystals, and hence had no effect on the crystallization of PLA during the lamellar thickening of the crystal domains [12].

3.2. Morphology and structure

Effectively promoting the production of homogenous cell structure, the combination of chain extender and talc. We looked at how basalt fiber and cellulose reinforcing affected the mechanical, form, and foaming properties of the PLA foam. The nucleation of cell was increased by the addition of 5% natural fiber, however, the distribution of the size of cell was uneven because of micropores brought on by local fiber-matrix debonding. The PLA foam material reinforced by basalt fiber had a 40 kPa compressive strength. Acting as an environmentally substitute for petroleum-based polymer foam, the properties of fiber-reinforced PLA foam were studied. Supercritical CO_2-assisted extrusion was used to produce microcellular PLA foams with high porosity. Epoxy-functional chain extenders were used to address the problem of the low melt strength of PLA, and talc was introduced to enhance its crystallization kinetics, both of which promoted homogeneous cellular structures [13].

Melt blending, gas foaming, and particle leaching of PLA/PEG/NaCl mixes were used to produce scaffolds with high porosity and interoperability. The miscibility and dispersibility of NaCl and PEG inside PLA matrixes were enhanced by using homemade three-screw compounding extruders. The microcellular foaming technique employing supercritical CO_2 as the physical foaming ingredient was investigated. NaCl was introduced as porogen agent to make PLA scaffolds more porous. Concurrently, the impacts of PEG and NaCl on the structure and characteristics of PLA-based blends was further analyzed, as well as the porosity, pore size, connectivity, and hydrophilicity of the porous scaffolds. NaCl and PEG significantly sped up PLA's crystallization process while lowering its viscoelastic characteristics. Moreover, the scaffold of the PLA/PEG/NaCl mix systems has linked bimodal porous structures with around 86% open-pore contents and about 80% maximum porosities.

PEG's addition improved the amount of NaCl that could be removed from PLA/NaCl composites during the leaching process, which enhance interconnectivity [14], as shown in Figure 4.

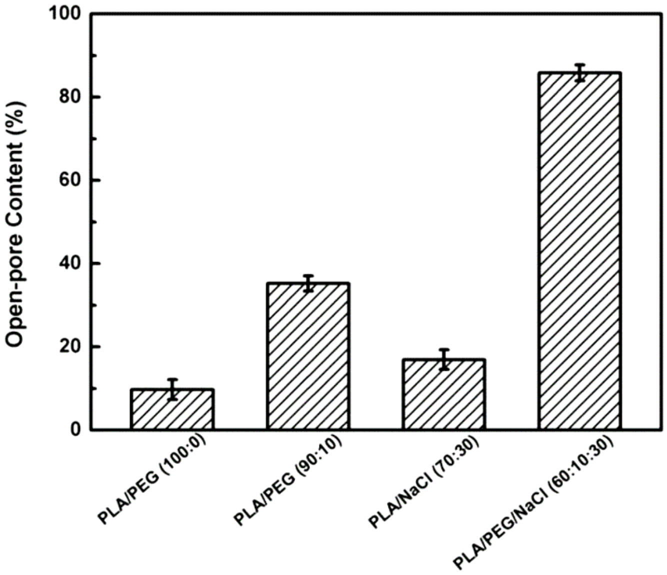

Figure 4. Open-pore content of the PLA-based composites [14]

3.3. Wettability

Due to the potential use in circumstances requiring the conversion of two opposing features, bio-inspired and switchable honeycomb-like porous films have become a popular area of research in recent years. In this research, the authors implemented CO_2-responsive ON/OFF wettability switching into biocompatible PLA honeycomb porous films [15]. By adjusting the PLA/MET ratio, hydrophilic CO_2-sensitive groups can be precisely distributed on the inner surface of the pores and/or the outer surface of the films. Highly ordered porous films with pore structures were created using complexes of non-responsive PLA and a CO_2-sensitive melamine derivative. This process, known as CO_2-responsive ON/OFF wettability switching, occurs when groups on the inner surface of pores act as switches when activated by CO_2 gas. Honeycomb films are most sensitive at a water contact angle of 35 degrees, and a change from hydrophobic to hydrophilic was clearly visible for water contact angles between 100 and 65 degrees. Due to the increased surface wettability, the contact between the cell and the honeycomb film surface was boosted, resulting in enhanced cell attachment. Future biomedical and bioengineering applications of these films will be illuminated by the wettability-related features of the biocompatible polymer and the biological gas trigger.

4. Applications of the PLA

4.1. Biomedicine

The application of PLA in biomedicine is mainly concentrated in tissue engineering, drug delivery, fracture internal fixation material and ophthalmic implant materials, due to its good biocompatibility and biodegradability. Endothelial grafts made of PLA can degrade to provide suitable mechanical support. The degradation of PLA endothelial grafts can offer proper mechanical support. Although gradually absorbed, it can still offer mechanical support, which makes the cell grow [16]. For tissue engineering, a tissue engineering scaffold refers to a three-dimensional porous scaffold that transports nutrients for cell growth and excretes metabolites in tissue engineering. Through necessary production methods and control methods, medical materials wrapped with fibers or various sponges can be produced, which can be combined with living tissue cells and implanted in organisms, so that effectively meet the requirements of tissue engineering scaffolds [17]. Artificial blood is one of the most important research topics. For instance, PEG-PLA can be utilized to make nanocapsules. As a result, these homogeneous particles have good antioxidant activity and good dispersion [18]. Epithelial cells can also be renewed with PLA. For example, PLA can relieve the symptom of myocardial infarctions. Copolymers of PLA and chitosan electrospun have the potential to promote the development of cardiomyocytes.

For drug delivery, PLA can guarantee drugs released at a constant pace over a set period. The biodegradable polymer is gradually degraded in the patient's body and its structure changes from compact to dense. This property can be used to achieve long-term constant drug release [17]. PLA can be degraded in the human body to LA. PLA-based microspheres contain paclitaxel, which is prepared by PLA copolymers. It has a uniform size and porous structure that facilitates drug release inside, lengthening the time that drugs work in our body. It has many advantages, such as avoiding a high concentration of drug for a certain period and reducing side effects [19,20]. In the treatment process, the targeted drug system is worthy to study.

For fracture internal fixation material, PLA has good biocompatibility, which can effectively adapt to the fracture of patients and will not produce rejection in the body. Compared with traditional fracture fixation materials, PLA can fully fit the patient's bone growth. In addition, in the fracture made of PLA, after the fixation material is implanted into the human body, the degradation rate of the material can be adjusted according to the specific situation, avoiding the need for a second operation. The patient can metabolize the internal fixation material for the fracture through its own metabolism [21]. For ophthalmic implant materials, with good biodegradability and biocompatibility, PLA can meet the application requirements of ophthalmic implant materials and solve the rejection problem that other traditional materials can't. PLA has good thermal stability and solvent resistance, so it has good resistance and stability in complex surgery situations. In addition, the application of PLA materials can also solve ophthalmic diseases such as cataracts and glaucoma [22].

4.2. Packaging and 3D printing

For packaging, PLA can get from renewable resources and it is biodegradable. Adjusting the polymer structure can alter physical and mechanical properties. For example, PLA foam is also biodegradable and can be used to produce disposable tableware and cushioning packaging. Compared with traditional materials, PLA is more easily processed and has a greater melting point. Some properties and their corresponding applications are shown in Table 1 [23].

Table 1. The properties of PLA and its applications

Properties	Applications
Isolate the smell and antibacterial	Antibacterial food packaging
Breathability, oxygen permeability and CO_2 permeability	Fresh-keeping packaging materials (Extend shelf life and reduce packaging waste)
Outstanding gloss and transparency	Biaxially oriented films, thermoplastic containers and blow molded bottle

For 3D printing, ABS is the most commonly used 3D printing material before PLA. Compared to ABS, PLA is more environmentally friendly and has excellent mechanical properties, resulting in a series of products. It does not emit harmful gases and has a low shrinkage rate. Because PLA does not warp or crack, it can print large-sized models. FDM printing is the most widely used technique right now. On the basis of PLA and PBBSI, the brand-new TPV material with the proper hardness and fluidity can be prepared, which not only satisfies the flowability requirements of FDM printing but also offers great elasticity [24]. The corners are not easy to lift when heated. Besides, PLA has a low shrinkage rate, performing well when printing large-sized models [25].

5. Conclusions

This research mainly introduces the synthesis, modification and application of PLA. In biopreparation, PLA can be synthesized directly from cyanobacterial cells using CO_2 as a feedstock.

The sc-CO_2 and HP-CO_2 has also been used to prepare PLA and its composites. Further, we discuss the effect of sc-CO_2 on the properties of PLA products. PLA is a novel bio-based substance that is frequently utilized. In China, the PLA industry is still in its infancy and the main production route is still the ring-opening polymerization of lactide. The new research tells us that cyanobacterial cell factory can directly use CO_2 as raw material to synthesize PLA, which is expected to solve the potential problems of competing with people for food and land with food in the production of PLA. With the development of production and economy, sustainable development has become the main theme, environmental protection has been put on the national development agenda, and the ban on plastics has been proposed. Because it is environmentally friendly and biodegradable, PLA will become increasingly popular.

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