

# Performance Modification and Application Of Poly (Lactic Acid)-Based Biodegradable Biomaterials

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**Abstract.** As new type of biodegradable material, polylactic acid (PLA) is synthesized by plant resources. This material features high mechanical properties, biocompatibility and biodegradability. It is mainly used in agriculture, medicine, biology, environmental protection, engineering and other fields. With the progress of science and technology, new requirements and applications have been put forward for the properties of PLA material, thus it must be modified to improve its processing and application properties. Only higher performance polylactic acid based materials can meet the growing needs of production and life. This review summarizes the research progress of PLA performance improvement from both physical modification and chemical modification, involving blending modification, plasticizing and toughening modification, composite modification as well as copolymerization modification, cross-linking modification and other modification methods, and introduces the research progress in the fields of agriculture, food, engineering. Furthermore, it is aimed at providing certain references for the broadening of PLA application market and discusses the future development trends of PLA.

**Keywords:** Polylactic acid; Degradable; Modification.

## 1. Introduction

Poly(lactic acid) (PLA) is an important lactic acid derivative, which is a thermoplastic biodegradable polymer material formed by the polycondensation of lactic acid monomer [1]. During production, people can extract it from recyclable resources such as corn starch or sugarcane. Because of its degradability, excellent biological compatibility and mechanical performance, and ability to be easily processed, it is considered to be promising biologically degradable materials, and it is the only biodegradable plastic with excellent antimicrobial and antifungal properties. In biomedical application, PLA is used in biodegradable surgical sutures, slow-release drug carriers, medical wound dressings, 3D porous PLA scaffolds, artificial skin and oral fixation materials, ophthalmic materials, etc [2]. PLA can be manufactured into a wide variety of plastic items ranging from industrial to household applications, which include food packaging, fast food cartons, non-woven fabrics, and industrial and household fabrics [3][4]. PLA can also be processed into agricultural mulch film to address the shortcomings of traditional, fragile, non-degradable mulch films and improve farmland hydrothermal properties [5]. Additionally, it can be used for automobile spare parts and engineering materials, construction ropes, and slow-release materials for pesticides and fertilizers [6].

Because polymer is inherently non-biodegradable, it can remain in the environment and pose serious environmental and health hazards. Most plastics and other petrochemical polymers are considered difficult to degrade because of their resistance to corrosion [7]. PLA is a biodegradable material that absorbs carbon dioxide from the air and degrades faster than conventional plastics. With excellent durability, physical strength and transparency compared to other biodegradable products, PLA is one of the first choices for biodegradable materials. However, PLA has the disadvantages of bad toughness, stiff and fragile texture, lack of flexibility and resilience, poor processability, lack of thermal resistance, limited strength and modulus, high price, and uncontrollable degradation cycle. A pure PLA can no longer meet the needs of all parties [8]. Thus, modifying PLA has become an essential area of investigation and development. In order to remedy the defects of PLA materials and to broaden its applications, many researchers have tried to modify PLA by physical and chemical

methods such as copolymerization, blending, molecular modification, etc., and have achieved new results in synthetic methods and modification studies.

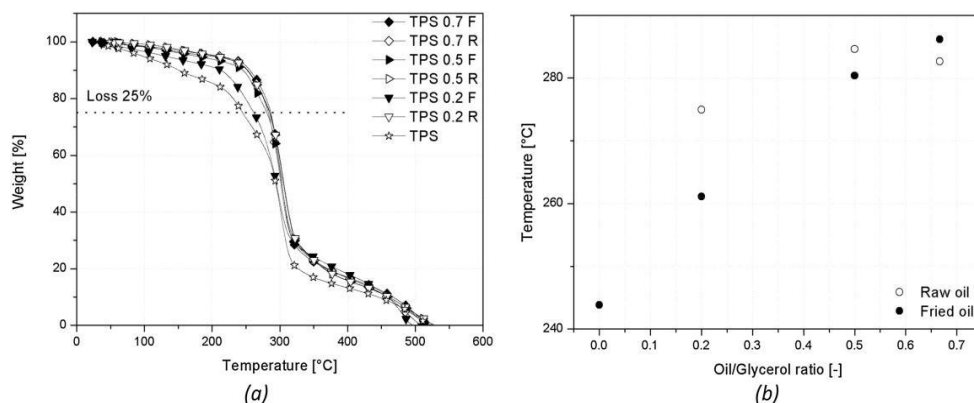
## 2. Biodegradable biomaterials

### 2.1. Physical Modificatio

Ali Khanjari et al. pour glycerol as a plasticizer into PLA film solution with different concentrations of cinnamon essential oil (CVEO). This PLA film was characterized by microbiological analysis, chemical analysis, sensory evaluation and statistical analysis. The results showed that CVEO binds very thoroughly to the PLA film. In the *in vitro* antimicrobial evaluation, it was able to diffuse out of the active film. The researchers stored samples that are wrapped with PLA films and contain different concentrations of CVEO for 12 days. The results showed a remarkable decline in the number of *E. coli* and *L. monocytogenes* compared to the pure PLA films. It demonstrates that it is a novel approach to pack food with little changes in sensory properties [9].

Stoll et al. researched the application of acetyltributyl citrate (ATBC) as a PLA film plasticizer. Although the plasticizer ATBC reduced the barrier properties to oxygen of the film, it has a significant positive impact on the kinetics of the release of bixin in food simulants. As an ingredient in PLA, bixin can be used in the packaging of light-sensitive products to prolong the quality of lipids, vitamins and biologically active compounds in food products by protecting them from light exposure. Besides UV protection, the emission of bixin also prevents perishable items from undergoing oxidative reactions [10].

In a starch plasticization process, V. Volpe et al. replaced a portion of the thermoplastic starch (TPS) with sunflower oil from the frying process of a fast food restaurant for reducing the cost of glycerol while reusing the waste product. The plasticized TPS is then blended with PLA. Replacing a proportion of glycerol with fried sunflower oil as a starch plasticizer will not alter the characteristics of the PLA/TPS mixture and can improve the material properties of TPS. As shown in Figure 1, the thermogravimetric analysis leads to the conclusion that the stability of starch plasticized with oil at elevated temperatures is better than that of the starch plasticized with glycerol only. From the evaluation of the modulus of elasticity and utmost stress, it is found that the modulus of TPS containing just glycerin is less than that of TPS containing oil. In addition, oil positively impacts the overall heat stability of PLA/TPS mixtures. It shows that the oil/glycerol ratio increases while the thermal degradation temperature rises. The tensile test proved that the maximum stress value is the highest for PLA/PPS mixtures with an oil/glycerin ratio of 0.5 [11].

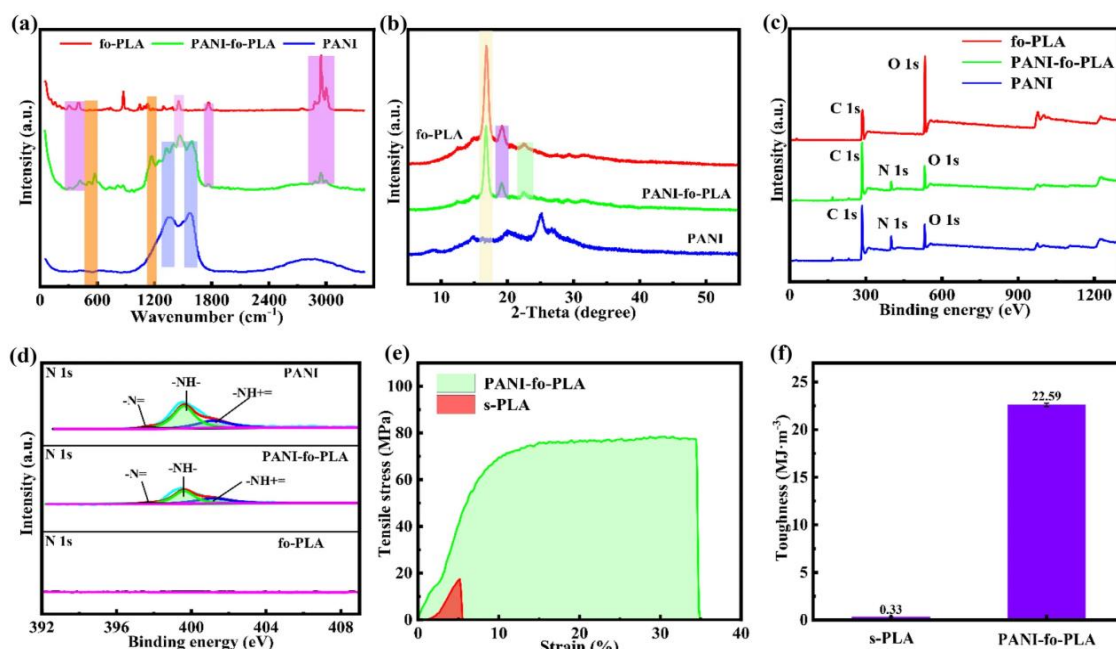


**Figure 1.** TGA of the starch/glycerol/sunflower oil blends (a); temperature corresponding to a weight loss of 25% of the TPS blends with raw and fried oil at all the oil/glycerol ratios (b) [11].

Cristian Jean da Silva Pens et al. incorporate ethylene-butyl acrylate-glycidyl methacrylate (E-BA-GMA) as compatibilizing agent to enhance the recoverability of polyethylene terephthalate (PET) and PLA blended wastes. The tension test result shows that with the addition of compatibilizers,

tensile strength is reduced, the maximum force elongation gradually decreases, and the blends become tougher. Scanning electron microscope micrographs showed that the diameter of the dispersed particles are reduced and the particle size distribution is more refined due to the inclusion of the compatibilizer into the mixture. Furthermore, the thermal stability of the mixture is improved by the use of compatibilizers [12].

Guixing Li et al. prepare flexible and robust polyaniline-coated foamed PLA (PANI-fo-PLA) electrodes by a nonsolvent-induced-phase-separation (NIPS) method. Specifically, researchers performed direct polymerization of aniline monomers on porous foamed polylactic acid (fo-PLA). As shown in Figure 2, owing to the presence of PLA foam, PANI-fo-PLA electrodes have excellent pliability and high mechanical strength, considerably superior to solvent-cast PLA membranes. In addition, the porous structure furnished abundant spots for the formation of PANI, so that it notably augments the loading of the electroactive material as well as promotes ion transport in the energy storage process. When using PVA/H<sub>2</sub>SO<sub>4</sub> as a gel electrolyte, the equal area capacitance of the symmetric PANI-fo-PLA//PANI-fo-PLA SC delivers is very much higher than the SC of the PANI electrodes on nonporous PLA films. Moreover, in alkaline solutions, PANI-PLA can be degraded in a short time under the presence of ultrasound [13].



**Figure 2.** Raman (a), XRD (b), XPS(c), N 1 s XPS of PANI, fo-PLA, and PANI-fo-PLA (d). Stress–strain curves (e) and the corresponding toughness of s-PLA and PANI-fo-PLA (f) [13].

A series of magnetic composites are prepared by Itziar Galarreta-Rodriguez et al. through solution casting method. The authors combined Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) with a mixture made of PLA and polycaprolactone (PCL). Compared to pure PCL, this polymer blend improves structural strength and maintains the fusing temperature at around 328 K. This advantage makes it possible to manufacture flexible filaments as material for fused deposition modeling 3-D printing. At lower concentrations of NPs, the filaments show a regular and compact configuration. Whereas, as filler elements multiply, the filaments become rough and the porosity increases. The experimental results show that the addition of magnetic NPs to the polymer blends results in magnetically responsive composites, and the saturation magnetization of such materials is positively correlated with the concentration of NPs [14].

## 2.2. Chemical Modification

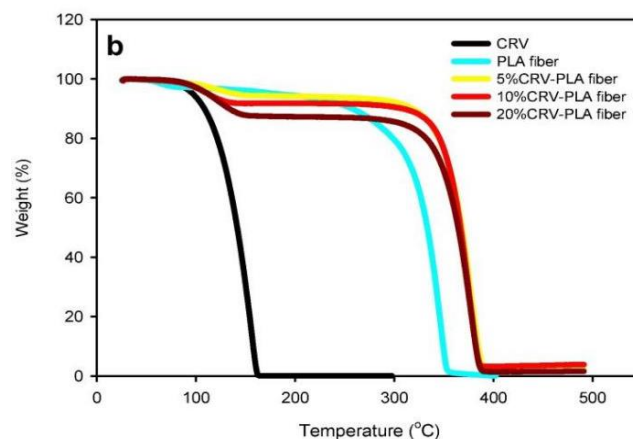
Tairong Kuang et al. prepare high performance PLA composites by using nucleating agents. They add a self-assembling nucleating agent (TMC-306) to PLA particles and melt-mixed the dried particles and powders at a certain mass ratio. The nucleating agent originally forms random "shish-

kebab" crystal structures in PLA material during the process of structural treatment. After adding self-assembling nucleating agent, fibers are first formed in substrate, then fast nucleating on fibers, and finally "shish-kebab" crystal structure is formed. In this process, this nucleating agent plays the role of the "shish" structure. A compression injection molding (CIM) process was subsequently employed in order to obtain chain-like interlaced "shish-kebab" crystal structures with gradients in length and thickness. Characterization results show the product has excellent tensile strength, enhanced toughness and high elongation at break. Compared to pure PLA, this material exhibits a lower heat distortion variable and a higher Vicat softening temperature. This material has considerable potential use in the field of commodity and engineering plastics [15].

I.A. Kurzina et al. artificially altered the surface properties of PLA by using ion implantation. X-ray photoelectron spectroscopy shows alternating bond ratios in PLA. This result suggests that different chemical processes depend on the type of implanted ions. X-ray diffraction analysis showed a reduction in crystallinity for all ion types, which leads to a reduction in microhardness and modulus of elasticity. Atomic force microscopy showed that the surface roughness of PLA declined with increasing irradiation dosage, leading to an increase in hydrophilicity. The enhancement in hydrophilicity depends on the increase in concentration of adsorbed oxygen and surface roughness. A preliminary cytotoxicity assessment of macrophages of two donors showed that the dose of material processed by the ion beam did not negatively affect the cells of the immune system. This conclusion is expected to have applications in the biomedical field [16].

Makri et al. modify PLA by introducing lignin. The experimental results showed that lignin has a highly branched structure and the carboxyl groups of PLA can interact with the hydroxyl groups of lignin to form hydrogen bonds. In addition, the interfacial adhesion is increased due to the  $\pi$ - $\pi$  interactions between the functional groups in lignin and the carbonyl groups of PLA. Due to the high specific surface area and enhanced dispersing ability of lignin, its size reduction from micrometer to submicrometer contributes to improve reactivity and compatibility with PLA, which allows it to obtain more effective attachment to PLA matrix. The performance of PLA-nanolignin composite films is usually superior to that of PLA-lignin composite films due to the much finer distribution of nanolignin throughout the PLA matrix. Both lignin and nanolignin reduce the UV transmittance of PLA. And the antioxidant activity of PLA is also enhanced by the additives [17].

Aylin Altan et al. added carvacrol to electrospun corn protein and PLA fibers. As shown in Figure 3, owing to the interaction of PLA chains with carvacrol molecules through hydrogen bonding, the decomposition temperature of carvacrol-added PLA fibers is above pure ones. Therefore, carvacrol is an effective additive that can be used to improve thermal stability of PLA fibers. Meanwhile, the electrospun fibers with carvacryl phenol have antioxidant and antimicrobial properties. This fiber can be applied as an electrospun fiber in food applications, which can effectively extend the shelf life of fresh food and can be manufactured into antioxidant fibers for packing [18].



**Figure 3.** TGA thermograms of carvacrol, electrospun fibers from PLA with different carvacrol content [18].

### 3. Conclusion

With the development of green chemistry demand, biodegradable materials will become an important part of future scientific research. Meanwhile, bioplastics are environmentally-friendly alternatives to conventional petroleum-based plastics. PLA is of great significance in the field of research and development as it is the only biodegradable polymer material with excellent bacteriostatic and mold-resistant properties. In terms of production process there are PLA has a variety of processes such as extrusion, injection molding and thermoforming, so it has a great attraction in the field of biomedical, engineering, agriculture and other manufacturing industries. As these industries continue to grow, the market for the production of PLA and bioplastics is also expanding. The combination of the engineering properties and commercial potential of the materials allows for a great deal of research and development of industrial applications for PLA, such as in biodegradable food packaging, biocompatible pharmaceutical materials, and lightweight automotive parts. However, PLA is in fact very fragile and exhibits very little elongation at break. Its relatively high tensile strength and modulus of elasticity do not compensate for deficiencies in toughness, which limits its employment in high stress level applications. The incorporation of chemical reagents substantially improves the properties of PLA, which increases its hydrophilicity and toughness of PLA material and slows down the degradation cycle. The addition of natural components preserves the biodegradability of PLA, which has the advantage of lower cost and greenness. Although the modification of single addition of natural substances is not as strong as that of chemical substances, this paper can improve PLA by mixing multifunctional systems for natural substances with different characteristics, so that all the shortcomings of PLA can be solved to a certain extent. While the current modification methods have improved the toughness of PLA, they still have disadvantages including high cost, low thermal properties, and poor compatibility. Therefore, the direction of future research will revolve around the development of green modified methods, cost reduction, and the search for compatible and biodegradable modified monomers.

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