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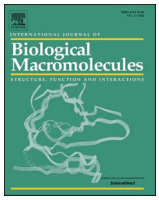

# A natural butter glyceride as a plasticizer for improving thermal, mechanical, and biodegradable properties of poly(lactide acid)

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ABSTRACT

Polylactic acid (PLA) is a biobased and biodegradable thermoplastic polyester with great potential to replace petroleum-based plastics. However, its poor toughness and slow biodegradation rate affect broad applications of PLA in many areas. In this study, a glycerol triester existing in natural butter, glycerol tributyrate, was creatively explored and compared with previously investigated triacetin and tributyl citrate, as potential plasticizers of PLA for achieving improved mechanical and biodegradation performances. The compatibilities of these agents with PLA were assessed quantitively via the Hansen solubility parameter (HSP) and measured by using different testing methods. The incorporation of these compounds with varied contents ranging from 1 to 30 % in PLA altered thermal, mechanical, and biodegradation properties consistently, and the relationship and impacts of chemical structures and properties of these agents were systematically investigated. The results demonstrated that glycerol tributyrate is a novel excellent plasticizer for PLA and the addition of this triester not only effectively reduced the glass transition, cold crystallization, and melting temperatures and Young's modulus, but also led to a significant improvement in the enzymatic degradation rate of the plasticized PLA. This study paves a way for the development of sustainable and eco-friendly food grade plasticized PLA products.

## 1. Introduction

Polylactic acid (PLA) is a linear aliphatic thermoplastic polyester and has attracted considerable attention due to its renewability, biocompatibility, and thermal processability [1,2]. PLA is considered to have great potential to replace conventional petroleum-based polymers as it is usually manufactured by ring-opening polymerization of lactides, products of fermentation of renewable carbohydrate products. For these reasons, it has been widely used in a great number of fields, such as the biomedical industry, food packaging, textile, agricultural production, and transportation [3,4]. However, its inherent brittleness and low elongation at break affect the ductility of the materials, and its slow degradation rate in regular environmental settings reduces its rating as compostable (biodegradable) materials according to the industry standard of ASTM D6400 [5]. The properties of brittleness, rigidity and slow biodegradation rate may all relate to the chemical and morphological structures of PLA, especially the molecular weight and crystallinity [6].

To overcome these drawbacks, many efforts to modify these properties of PLA have been conducted, including copolymerization, blending and compositing [2]. Among these procedures, blending PLA directly with another polymer or chemical agent in extruders is a simple and cost-effective method of modifying polymer properties and has been widely employed by many researchers [7]. Biobased and biodegradable polymers, including thermoplastic starch (TPS) [8–10], poly (butylene succinate) (PBS) [11,12], poly (ε-caprolactone) (PCL) [13,14] and poly (hydroxybutyrate) (PHB) [15,16] could be blended with PLA to achieve improved biodegradability and mechanical properties in products. The miscibility of these polymers with PLA is a determining factor that could affect some properties of the blended products, such as strength and elongation at break. Phase separation of immiscible polymers is the main drawback of blended products. Different from these polymers, low molecular weight compounds such as plasticizers have been widely employed in improving the processability, ductility and flexibility of commodity polymers and also have found applications in modifying properties of PLA ([17]; Yong [18]). Some typical plasticizers that have been employed in blending with PLA include citrate esters, poly (ethylene glycol) (PEG), oligomeric lactic acid (OLA) and partial fatty acid esters [19–21]. These plasticizers can drastically lower the glass transition temperature and improve the elongation at break of the PLA blends, thus generating homogeneous and flexible materials [22].

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Besides, several vegetal oils (triglycerides) have been investigated to act as more eco-friendly plasticizers, such as jojoba oil, karanja oil, epoxidized soybean oil and car-doon oil [23–26]. However, most of these plasticizers still exhibit poor compatibility with and phase separation from PLA at a plasticizer concentration of 20 wt% or more, thereby limiting their potential applications [18].

Glycerol is a common additive in the processing of bio-based polymers and biopolymers and was employed in mixing with PLA but exhibited poor miscibility [27]. Many glycerol triesters are biobased, biodegradable and biocompatible compounds, containing aliphatic ester groups similar to PLA, and are potential plasticizers for the biopolymers [28]. Among them, glycerol tributyrate (tributyrin), an oil naturally present in butter and a food additive, possesses proper thermal stability for potential melt processing. The use of glycerol tributyrate as an edible plasticizer for the thermoplastic PLA has not been reported, though glycerol triacetate (triacetin) has been studied as a potential plasticizer for PLA in a previous study [20]. More importantly, glycerol tributyrate is a natural and biodegradable compound. Its extensive use will not exacerbate any growing pressure on the dwindling petroleum resources and pose fewer environmental concerns.

In this study, the natural butter component, glycerol tributyrate (GT), was evaluated and compared with other two biobased triester plasticizers, triacetin (TA) and tributyl citrate (TC), in performances of compatibility with PLA and improving mechanical and biodegradable properties of the products. Hansen solubility parameters (HSP) were utilized to quantify the compatibility of these agents with PLA. All chemicals were blended with virgin PLA in a melt mixer in varied ratios, ranging in additives from 1 % to 30 %. The plasticized PLA mixtures were heat-pressed to obtain homogeneous films. The influences of three plasticizers with varied contents on the crystallization, thermal, mechanical and degradation properties of the PLA films were evaluated in detail. The results of using these biobased triesters as PLA plasticizers may open the applications of the plasticized PLA.

## 2. Materials and methods

### 2.1. Chemicals

Poly(lactide acid) (PLA, 3051D) was made by NatureWorks LLC (Minnetonka, USA). Triacetin (TA, 99 %) was analytical grade and obtained from TGI AMERICA (Portland, USA). Glycerol tributyrate (GT, 97 %), triethyl citrate (TC, 99 %) and proteinase K were purchased from Thermo Scientific Inc. (Ward Hill, USA). The chemical structures of three selected plasticizers are shown in Fig. 1. Hydrochloric acid (HCl, 36.5 %) and Tris-HCI buffer (1 mol/L, pH = 8.0) were provided by Sigma-Aldrich Corporation (Louis, USA) and Invitrogen (New York, USA), respectively. All reagents were used directly.

### 2.2. PLA blending

Before blending, PLA was dried at 60 °C for 8 h in a vacuum oven. Different contents of three plasticizers were mixed with PLA in a beaker for 5 min in varied compositions shown in Table 1. Then, the mixture of PLA and a plasticizer was added into a 3-piece compounding mixer (Brabender Plasti-Corder ATR, C. W. Brabender) and blended at 170 °C and 50 rpm for 5 min. Nitrogen gas was purged into the mixing chamber to prevent oxidation during the blending.

**Table 1**
Sample name and composition of PLA films.

| Samples | PLA (g) | TA (g) | TC (g) | GT (g) |
|---|---|---|---|---|
| PLA-0 | 20 | | | |
| PLA-TA-1 | 20 | 0.2 | | |
| PLA-TA-3 | 20 | 0.6 | | |
| PLA-TA-5 | 20 | 1 | | |
| PLA-TA-10 | 20 | 2 | | |
| PLA-TA-20 | 20 | 4 | | |
| PLA-TA-30 | 20 | 6 | | |
| PLA-TC-1 | 20 | | 0.2 | |
| PLA-TC-3 | 20 | | 0.6 | |
| PLA-TC-5 | 20 | | 1 | |
| PLA-TC-10 | 20 | | 2 | |
| PLA-TC-20 | 20 | | 4 | |
| PLA-TC-30 | 20 | | 6 | |
| PLA-GT-1 | 20 | | | 0.2 |
| PLA-GT-3 | 20 | | | 0.6 |
| PLA-GT-5 | 20 | | | 1 |
| PLA-GT-10 | 20 | | | 2 |
| PLA-GT-20 | 20 | | | 4 |
| PLA-GT-30 | 20 | | | 6 |

### 2.3. PLA film extrusion

Films of neat PLA and PLA plasticized with TA, GT and TC were prepared using a Portable Manual Heat Press Machine CK220 (Karlsruhe, Germany). The temperature and time for the film formation were 160 °C and 35 s, respectively. The prepared films were stored in zipped plastic bags at ambient temperature and are labeled and summarized in Table 1.

### 2.4. Characterizations

#### 2.4.1. Differential scanning calorimetry (DSC)

DSC analysis of neat and plasticized PLA films was carried out using a DSC-60 instrument (SHIMADZU). Polymer samples (4– 7 mg) were placed in aluminum pans and heated from 30 to 200 °C at a 10 °C/min heating rate under a nitrogen flow of 30 mL/min. The glass transition temperature ($T_g$), cold crystallization temperature ($T_c$), melting temperature ($T_m$), and the enthalpy values of the cold crystallization process ($\Delta H_c$) and melting process ($\Delta H_m$) were determined using the software of TA-60WS (SHIMADZU). The degree of crystallinity ($\chi_c$) was calculated according to Eq. (1), where $\Delta H_m^o$=93 J/g is the reported melting heat of pure crystalline PLA. $W_{PLA}$ is the proportion of PLA in the blended polymer [10,23,29].

$$\chi_c\ (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 1 \Big/ W_{PLA} \times 100 \quad (1)$$

After the initial heating to 200 °C, the samples were cooled down to 30 °C under the nitrogen protection in the DCS device without cooling temperature control. Afterward, the samples were heated again from

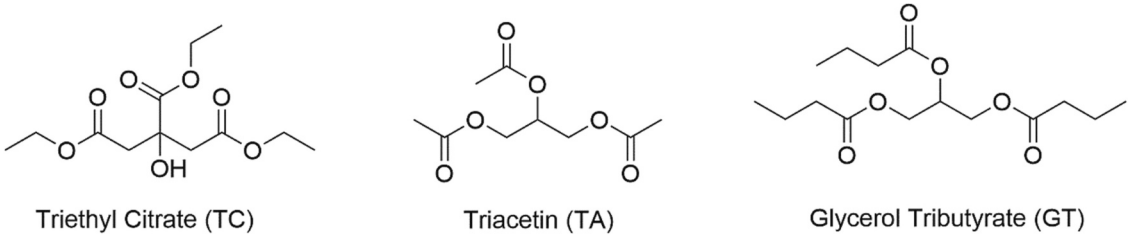


**Fig. 1.** Chemical structures of three triesters.

30 °C to 200 °C under the same heating conditions.

#### 2.4.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the polymers was performed on a TGA-50 instrument (SHIMADZU) to investigate the thermal decomposition behavior of the materials. The samples (5– 10 mg) were placed in a platinum pan and heated from 30 to 500 °C at a heating rate of 10 °C/min under a nitrogen flow of 30 mL/min.

### 2.5. Properties of PLA blends

#### 2.5.1. Exudation behavior (heat release of plasticizers)

The exudation property of plasticizers in the PLA films was investigated by placing a plasticized PLA film (~20 mg, 20 mm × 20 mm × 1 mm) between two pieces of filter paper. Then, the system was placed in an oven for 24 and 48 h at 60 °C, respectively. The weight loss of the plasticized PLA film was obtained according to Eq. (2) [30].

$$\text{Weight loss } (\%) = \frac{m_0 - m_1}{m_0} \times 100 \quad (2)$$

where $m_o$ and $m_1$ are the original or final weights of the PLA before and after the heating or biodegradation.

#### 2.5.2. Tensile test

The mechanical properties of neat and plasticized PLA films were measured on an Instron 4502 tensile tester (Norwood, USA) following a testing method of ASTM D 882 – Tensile Testing of Thin Plastic Sheeting. The dimensions in the straight region of the samples were 60.0 mm in length, 30.0 mm in width and ~0.15 mm in thickness. The drawing speed was set at 5 mm/min. Five specimens of each sample were tested and the mean values of Young's modulus (MPa), tensile strength (MPa) and elongation at break (%) were recorded.

#### 2.5.3. Enzymatic degradation

Three replicate samples of PLA-GT, PLA-TC and PLA-TA films (2 × 2 cm, ~15 mg) were placed into capped vials containing 2 mL Tris-HCI buffer (0.05 mol/L, pH = 8.0) and 0.5 mL proteinase K solution with a concentration of 1 mg/mL [31–33]. Then these vials were incubated at a constant temperature of 37.5 °C. After the incubation, the films were thoroughly washed with deionized water and vacuum dried. The weight loss was used to evaluate the enzymatic degradation rate and was calculated in percentage according to Eq. (2).

## 3. Results and discussion

### 3.1. Miscibility of plasticizers and PLA

Hansen solubility parameters (HSP) have been widely used to predict compatibility between two materials in many different areas, such as solvent and additive selection, permeation rates, and swelling properties of polymers [34–36]. Based on the idea of "like dissolves like", each molecule is given three Hansen parameters: dispersion forces ($\delta_d$), polar forces ($\delta_p$) and hydrogen bonding forces ($\delta_h$) [37,38]. Besides, the affinity between two substances can be quantitatively evaluated by using the HSP distance (R), which is calculated using Eq. (3).

$$R = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \quad (3)$$

The smaller the R-value, the closer of two substrates in HSP and the more likely they are compatible and have more affinity for each other [39]. Compatibility of the plasticizers to PLA is very important for the functional modification of the properties of PLA through physical blending. The corresponding R results are summarized in Table 2, together with that of glycerol and PEG-400, other commonly studied plasticizers of PLA. All three triesters have pretty close dispersion forces ($\delta_d$) and hydrogen bonding forces ($\delta_h$) but different polar forces ($\delta_p$) values to that of PLA. As a result, the HSP distance (R) values are in a small range of 8.30–9.30 for three triesters with triacetin (TA) exhibiting the smallest HSP distance with a value of 8.35, followed by glycerol tributyrate (GT) of 9.04, and finally triethyl citrate (TC) of 9.26. TA and TC were proven having good miscibility with PLA [20]. Although GT shows a slightly larger R-value of 9.04, its difference between TA and TC is not obvious, suggesting that GT have good compatibility with PLA. In comparison, glycerol and PEG-400 have also been reported as plasticizers to blend with PLA, but their HSP distance (R) values (23.32 and 22.76 for glycerol and PEG-400, respectively) are much higher than that of three biobased triesters, indicating their poor compatibility with PLA, which is consistent to the literature results [40]. Thus, both glycerol and PEG 400 were not utilized in the following experiments.

**Table 2**
Characteristics and mutual HSP distances of different plasticizers for PLA.

| Samples | Molecular Weight (g/mol) | Boiling Point (°C) | $\delta_d$ (MPa) | $\delta_p$ (MPa) | $\delta_h$ (MPa) | R |
|---|---|---|---|---|---|---|
| PLA | – | – | 16.1 | 13.1 | 4.9 | 0 |
| GT | 302.4 | 288 | 16.2 | 4.1 | 5.7 | 9.04 |
| TC | 360.4 | 325 | 16.9 | 4.3 | 7.3 | 9.26 |
| TA | 218.2 | 260 | 16.8 | 5.8 | 8.7 | 8.35 |
| Glycerol | 92.1 | 290 | 18.3 | 12.7 | 27.8 | 23.32 |
| PEG-400 | 400 | 250 | 17.8 | 13.5 | 27.4 | 22.76 |

In addition, plasticizers play a "lubricating" role and usually decrease melt viscosity and improve the processibility of PLA [41]. The evolution of mechanical torque during the melt mixing process could provide primary rheological information on the mixing process of plasticizers in PLA. During the melt mixing process, the torque values of the Brabender mixer were recorded as a function of time. The melt mixing torque evolutions of neat PLA (PLA-0), PLA with 30 % of GT (PLA-GT-30), TC (PLA-TC-30) and TA (PLA-TA-30) were recorded, with plots of the torque changes versus time of the mixing processes shown in Fig. S1 and characteristic data summarized in Table 3. As the pure PLA (PLA-0) was added to the mixer, the torque increased sharply to 13.3 Nm at 34 s, then eventually decreased and leveled out to 3.2 Nm, the end torque which is considered the formation of homogeneous melt. The plasticizer addition dramatically decreased the torque values or melt viscosities of PLA blends and even generated different torque curves. Meanwhile, with the increase of plasticizer amounts, the torque values decreased more obviously and rapidly. The loading peaks and end torques of PLA-GT-30, PLA-TC-30 and PLA-TA-30 were 1.9 and 1.1, 1.0 and 1.1, and 1.4 and 0.9 Nm, respectively, which are significantly low and even below the accurate measurement range of the mixer. These results indicate that GT, TC and TA have a good miscibility with PLA and functioned as good plasticizers.

After melt blending, these plasticized PLA mixtures were hot-pressed into uniform and transparent films, as shown in Fig. S2a. Besides, the FT-IR spectra (Fig. S2b) of PLA-0, PLA-GT-30, PLA-TC-30 and PLA-TA-30 showed characteristic peaks, corresponding to its groups, such as C—H stretching vibration at 3000 and 2940 $cm^{-1}$, C═O stretching vibration at 1740 $cm^{-1}$, C—H bending vibration at 1450 and 1360 $cm^{-1}$ and C—O stretching vibration at 1180 and 1080 $cm^{-1}$, due to similar structures.

**Table 3**
The torque data (Nm) of PLA with different plasticizers during melt blending.

| Samples | Loading Peak | Minimum | Inflection Point | Maximum | End |
|---|---|---|---|---|---|
| PLA-0 | 13.3 | 3.0 | 3.1 | 3.2 | 3.2 |
| PLA-GT-30 | 1.9 | 0.7 | 1.0 | 1.5 | 1.1 |
| PLA-TC-30 | 1.0 | 0.1 | 0.6 | 1.1 | 1.1 |
| PLA-TA-30 | 1.4 | 0.6 | 0.9 | 1.2 | 0.9 |

### 3.2. Properties of plasticized PLA films

The melt blended PLA samples were subjected to thermal characterization by using Differential Scanning Calorimetry (DSC). Typical DSC spectra of PLA-0, PLA-GT, PLA-TC, and PLA-TA are shown in Fig. 2, and their key thermal characteristic data are summarized in Table 4. Pure PLA exhibits a typical glass transition temperature ($T_g$) of 62 °C, a cold crystallization temperature ($T_c$) of 126 °C, and a melting temperature ($T_m$) of 153 °C, consistent with the literature [42]. Glass transition temperatures of the blended polymers decreased consistently and almost linearly with the increase of the plasticizer contents, shown in Fig. 3a, an indicator of the effective plasticization of the polymer by the agents. The PLA films three plasticizers (GT, TC and TA) exhibited unique single glass transition temperatures in DSC, suggesting good miscibility and compatibility of the chemicals with PLA. When the contents of GT, TC and TA were increased from 1 to 30 % in the blends, the $T_g$ values of the plasticized PLA films decreased to 23– 26 °C from 62 °C, >36– 39 °C drop and more effective in comparison to the literature of using other plasticizers [23,26]. The performance of GT in lowering the $T_g$ of plasticized PLA films was as good as TA and TC, due to the small molecular sizes and similar structures of all three agents, as well as close HSP distances to PLA. In fact, GT revealed a better plasticizing effect than the other two agents in the PLA films with high concentrations of the plasticizers, possibly due to the very close dispersion force ($\delta_d$) values or hydrophobicity of GT and PLA (Table 2). Small molecules with good compatibility to PLA are easier to move into the polymer to greatly improve the free volumes of the molecular chains, thus increasing the chain mobility and leading to the obvious decrease in $T_g$. This phenomenon is a good indication that these plasticizers have good compatibility and plasticizing effect with PLA. The results are not only in good agreement with previous investigations [20,21] but consistent with the HSP analyses.

**Table 4**
DSC data and crystallinity of plasticized PLA.

| Samples | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta H_c$ (J/g) | $\Delta H_m$ (J/g) | $\chi_c$ (%) |
|---|---|---|---|---|---|---|
| PLA-0 | 62 | 126 | 153 | 1.81 | −2.03 | 0.24 |
| PLA-GT-1 | 58 | 127 | 150 | 3.35 | −3.87 | 0.56 |
| PLA-GT-3 | 56 | 125 | 150 | 4.46 | −5.92 | 1.62 |
| PLA-GT-5 | 54 | 123 | 149 | 4.54 | −7.42 | 3.26 |
| PLA-GT-10 | 44 | 99 | 150 | 14.30 | −18.36 | 4.85 |
| PLA-GT-20 | 38 | 76 | 147 | 11.24 | −16.35 | 6.87 |
| PLA-GT-30 | 23 | 68 | 145 | 12.18 | −19.75 | 11.6 |
| PLA-TC-1 | 59 | 128 | 149 | 4.12 | −5.79 | 1.81 |
| PLA-TC-3 | 56 | 126 | 148 | 2.86 | −3.67 | 0.90 |
| PLA-TC-5 | 54 | 125 | 147 | 1.67 | −2.24 | 0.65 |
| PLA-TC-10 | 47 | 113 | 150 | 10.40 | −14.67 | 4.85 |
| PLA-TC-20 | 39 | 97 | 147 | 12.69 | −18.61 | 7.60 |
| PLA-TC-30 | 26 | 67 | 142 | 13.63 | −21.84 | 12.6 |
| PLA-TA-1 | 59 | 130 | 149 | 1.83 | −1.32 | 0.55 |
| PLA-TA-3 | 55 | 127 | 148 | 1.95 | −2.69 | 0.82 |
| PLA-TA-5 | 53 | 125 | 148 | 1.14 | −3.32 | 2.47 |
| PLA-TA-10 | 49 | 123 | 147 | 7.88 | −11.95 | 4.86 |
| PLA-TA-20 | 36 | 99 | 145 | 5.92 | −12.51 | 8.86 |
| PLA-TA-30 | 25 | 66 | 142 | 10.06 | −18.05 | 12.3 |

Cold crystallization is a common phenomenon of polymers and is responsible for the growth of polymer crystalline from smaller spherulite sizes of linear polymers. Reduced cold crystallization temperatures ($T_c$) represent the lubrication effects of the plasticizers, improving polymer chain movements and alignment into ordered zones. At low contents of plasticizers (below 5 %) in the PLA films, the addition of these plasticizers caused minimum changes to $T_c$, and in some cases, minor increases in some samples, such as PLA-GT-1, PLA-TC-1, PLA-TA-1 and PLA-TC-3. However, when the contents were higher than 10 %, these three plasticizers were able to significantly decrease the cold crystallization temperature of the corresponding PLA films (Fig. 3b). For

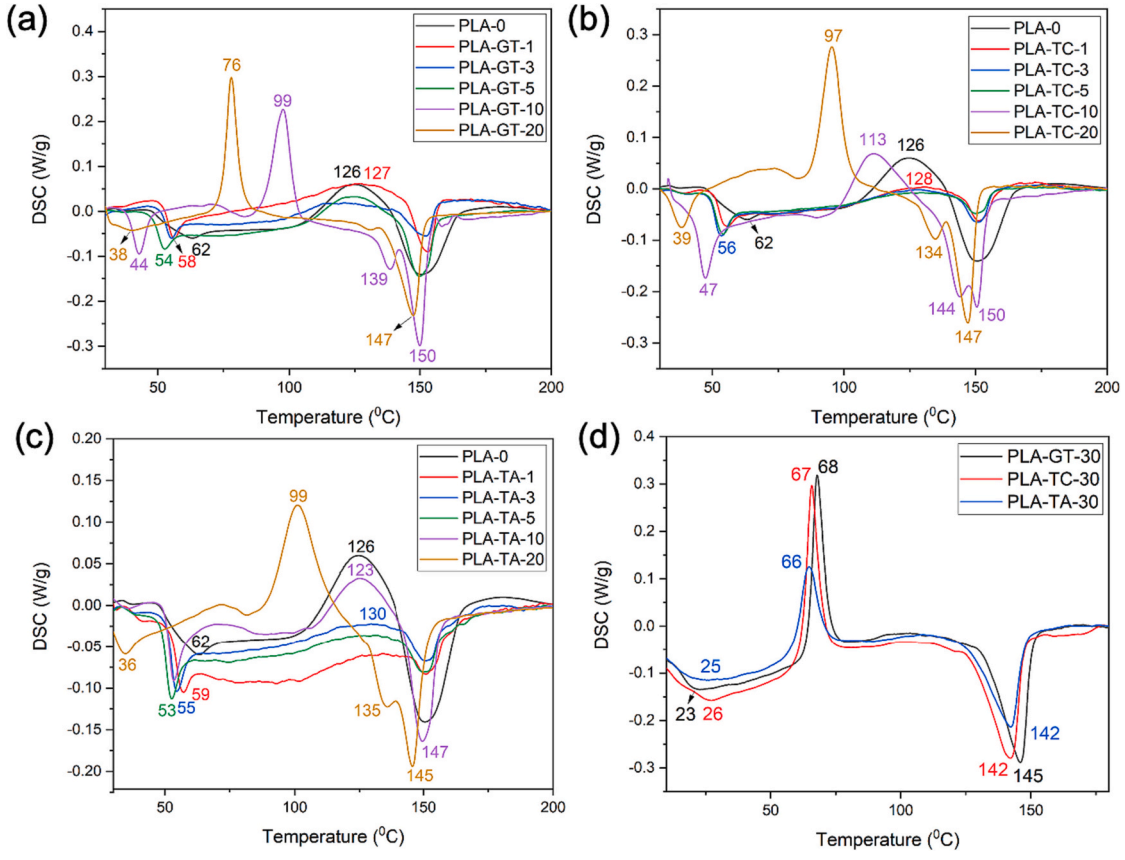


**Fig. 2.** DSC curves of plasticized PLA films (a) PLA-GT-1∼20 (b) PLA-TC-1∼20 (c) PLA-TA-1∼20 (d) PLA-GT-TC-TA-30.

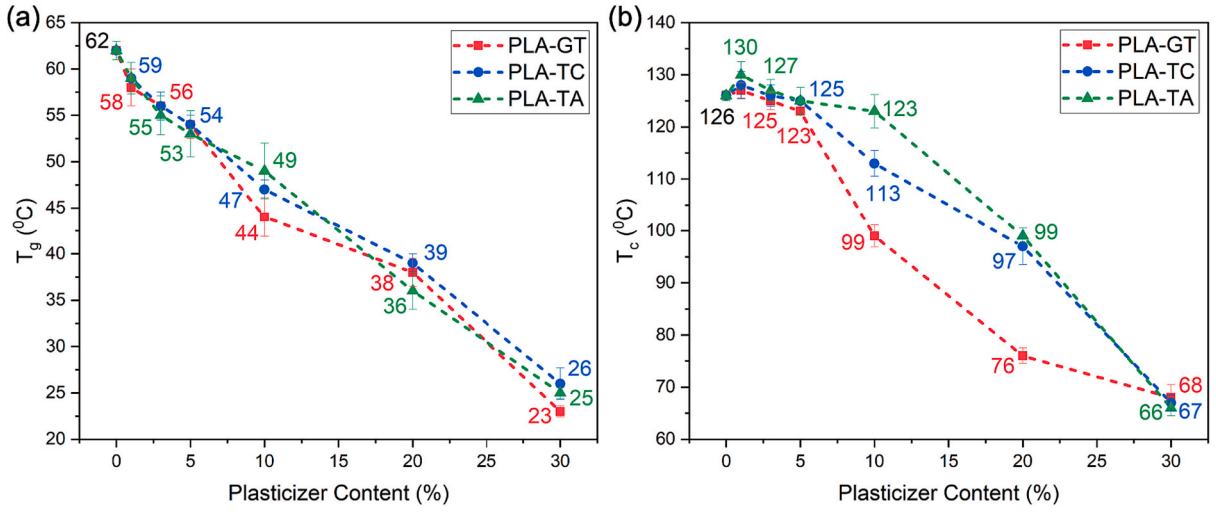


**Fig. 3.** Effect of plasticizer content on (a) $T_g$ (b) $T_c$ of plasticized PLA films.

instance, the $T_c$ values of the plasticized PLA films decreased from 126 °C to 68, 67 and 66 °C for PLA-GT-30, PLA-TC-30 and PLA-TA-30, respectively, thus further confirming the good compatibility and plasticizing functions of the triesters with PLA. Noteworthy, GT was more effective than the other two in lowering the $T_c$ of the PLA films when the content of the plasticizer was over 5 %. $T_c$ values of PLA-GT-10 (99 °C) and PLA-GT-20 (76 °C) were much lower than those of PLA-TC-10 (113 °C), PLA-TC-20 (97 °C) and PLA-TA-10 (121 °C), PLA-TA-20 (99 °C), respectively.

In addition, it was found that the melting points ($T_m$) gradually fell with the increasing content of the plasticizers, although the reduction is not as great as $T_g$ and $T_c$ (Table 4). The GT-caused decrease of $T_m$ of the

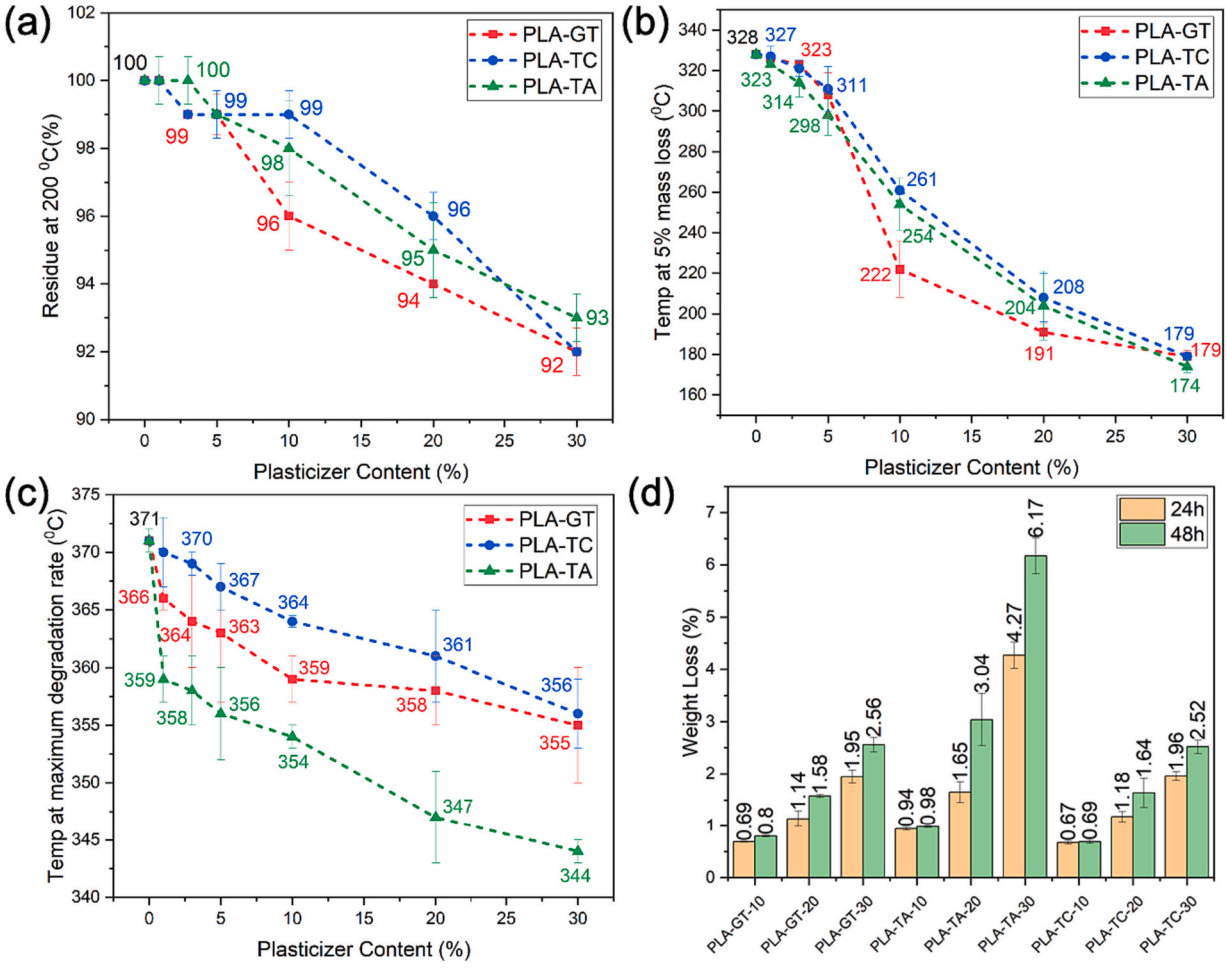


**Fig. 4.** Thermal stability of plasticized PLA films (a) Residual weights at 200 °C (b) Temperature at 5 % mass loss (c) Temperature at maximum degradation rate (d) Exudation test.

PLA film was not as significant as that caused by the other two plasticizers, changing from 155 °C to 145, 143 and 142 °C for PLA-GT-30, PLA-TC-30 and PLA-TA-30, respectively. Interestingly, some plasticized PLA samples exhibited two distinct endothermic peaks, especially for PLA-GT-10, PLA-TC-10, PLA-TC-20, and PLA-TA-20 (Fig. 2). This behavior was observed by other researchers in using TC and TA as PLA plasticizers, which was attributed to a lamellar rearrangement during the crystallization of PLA [21,40]. Because such a phenomenon only exists in certain plasticizer concentration ranges not throughout all plasticized PLA films, the explanation is reasonable. More interestingly, when these PLA films were heated in second cycles, the lamellar structure disappeared (Fig. S3), indicating the existence of the crystal structure in the composition and further development into a more stable crystal structure during repeated or extended heating.

The addition of the plasticizers not only lowered the $T_c$ and $T_m$ of the PLA films but also facilitated the crystallization of PLA, evidenced by the increased heats of cold crystallization ($\Delta H_c$) and crystallinity ($\chi_c$). More plasticizers lead to increased crystallinity in the PLA films. GT demonstrated comparable results with the other two plasticizers.

### 3.3. Thermal stability properties of plasticizers in PLA

The thermal stability of the materials is very important affecting their processing and applications under elevated temperatures. The effect of the three plasticizers on the thermal properties of PLA films was investigated by using thermogravimetric analysis (TGA). The corresponding TGA curves are shown in Fig. S4, and key thermal performance parameters, including PLA residues at 200 °C, temperatures at 5 % weight loss ($T_{5\%}$), and temperatures at maximum weight loss rate ($T_{max}$), are shown in Fig. 4, respectively. As shown in Fig. 4a, the addition of the plasticizers did not lead to significant weight losses in the PLA films at 200 °C with all exhibiting high retention (>90 %) of the original weights. However, the different contents of the plasticizers generated an obvious influence on both temperatures at 5 % mass loss ($T_{5\%}$) (Fig. 4b) and maximum degradation rate ($T_{max}$) (Fig. 4c). It can be clearly seen from Fig. 4b that the PLA films with low-contents of the plasticizers (from 1 to 5 %) showed a small downward trend in the $T_{5\%}$, whereas the high-content plasticizer (from 10 to 30 %) resulted in a significant decrease in degradation temperatures. The $T_{5\%}$ values of PLA decreased from 328 °C to 179, 179, and 174 °C for PLA-GT-30, PLA-TC-30 and PLA-TA-30, respectively. This observation could be attributed to the vaporization of the plasticizers during the heating process. All three triesters have boiling points above 260 °C. However, as shown in Fig. S5, the initial loss ($T_{5\%}$) of GT, TC and TA began at 168, 160 and 135 °C, respectively, and reached a maximum weight loss rate at 236, 249 and 203 °C, respectively, which could be caused by phase change of the chemicals. The initial losses of the plasticizers could be due to evaporations, while the lower $T_{max}$ values from TGA than the reported $T_b$ values of the compounds could be caused by differences in testing methods. The low $T_{5\%}$ of these plasticizers significantly reduced the $T_{5\%}$ of PLA films with high contents. This phenomenon was in line with the reported results of using PEG, OLA and citrate esters as plasticizers of PLA [43,44]. Meanwhile, $T_{max}$ values of the plasticized PLA films also exhibited a reduction with increased plasticizer addition from 1 to 30 %, especially over 5 %. It is worth noticing that PLA-TA showed the maximum reduction in $T_{max}$ with the value of 344 °C, followed by PLA-GT of 355 °C and PLA-TC of 356 °C, consistent with the thermal stability of these agents. Again, the thermal stability of GT is better than TA and similar to TC, further proving its potential as a plasticizer for PLA.

Small molecule plasticizers are prone to diffusion and migration in the films under elevated temperatures, resulting in loss of the improved mechanical properties and potential contamination to other materials in contact under prolonged or repeated heating [30]. An exudation experiment was adopted to evaluate the stability of the plasticizers in the plasticized PLA products. Weight losses of PLA films to two layers of filter papers were measured for prolonged times at 60 °C. The plasticized PLA films containing <10 % of the plasticizers did not show obvious weight loss, even after 48 h of contact time. However, the higher plasticizer content in the PLA films led to a significant increase in weight loss (Fig. 4d). The percentage weight loss values of PLA-GT-30, PLA-TC-30 and PLA-TA-30 were tripled than those containing 10 % of the plasticizers after 48 h of heating, respectively. The three plasticizers exhibited different exudation resistance properties in plasticized PLA films. Under identical plasticizer concentrations and heating durations, PLA-TC and PLA-GT demonstrated similar mass losses, whereas PLA-TA showed a significantly higher loss. This was particularly evident at a 30 % concentration level of PLA-TA, with a 4.27 % loss over 24 h and a 6.17 % loss over 48 h. This phenomenon is primarily attributed to the smaller molecular weight of TA (218 g/mol), compared to GT (302 g/mol) and TC (360 g/mol), resulting in weaker intermolecular interactions with the polymer chains of PLA. As the diffusion of the plasticizer molecules is related to their interactions with the polymers, which are affected by the molecular sizes of the compounds, the exudation properties of these plasticizers show the impact of intermolecular interactions between plasticizers and PLA [45]. These results prove that GT could be a good plasticizer with proper exudation properties in PLA blends.

### 3.4. Mechanical properties of plasticized PLA film

Pure PLA has a high elastic modulus and a very low elongation at break, typical mechanical properties of brittle polymers. One of the main purposes of plasticizing PLA is to improve flexibility, toughness and elongation at break of the polymer. Tensile properties of the plasticized PLA films were measured, and the mechanical properties, including Young's modulus (MPa), tensile strength (MPa) and elongation at break (%) are summarized in Table S1. As shown in Fig. 5, pure PLA (PLA-0) exhibited a high Young's modulus of 2752 MPa, a tensile strength of 52 MPa and a low elongation at break of 2.3 %. When the contents of these plasticizers were increased from 1 to 10 %, Young's moduli of PLA-GT, PLA-TC and PLA-TA showed a decrease from 2658, 2690 and 2482 MPa to 2032, 1590 and 1976 MPa, respectively. However, the addition of the plasticizers in low ratios had little effect on the elongation at break of the PLA films. When the plasticizer content was increased over 10 %, a significant decrease in Young's modulus and a great increase in elongation at break were observed for the films. The highest elongations at break of PLA-GT-30, PLA-TC-30 and PLA-TA-30 were achieved at 202.7 %, 290.7 % and 305.3 %, respectively. The addition of these plasticizers is beneficial to facilitating polymer chain movements and improving the elongation at break. Meanwhile, the corresponding values of Young's modulus and stress at break significantly decreased from 2752 and 52 MPa to 10 and 7, 8 and 6, and 5 and 10 MPa for PLA-GT-30, PLA-TC-30 and PLA-TA-30, respectively. The films become easy to be stretched without much resistance. Again, PLA-GT films performed similarly to PLA-TC and PLA-TA films. It is worth of noting that PLA-GT-20 showed a very high elongation at break with 155.3 % and a low Young's modulus with 789 MPa, which was far superior to those of PLA-TC-20 and PLA-TA-20. The phenomenon was attributed to the lower $T_c$ of PLA-GT-20, which was beneficial in improving the tensile properties.

### 3.5. Degradation properties of plasticized PLA film

Although PLA is a biobased and biodegradable polymer, the biodegradation rate is slow, which affects its wide applications [46]. Improving the biodegradation rate of PLA has been a challenge and was also another main objective of the plasticization with the addition of GT as a comparable plasticizer. The addition of these triester plasticizers could accelerate the biodegradation process of PLA due to their good miscibility and small molecules. Biodegradation of PLA may involve hydrolysis and enzymatic degradation processes, and the crystallinity of the polymers may affect the degradation rate as well. Enzymatic degradation is frequently undertaken as a standard laboratory test method to understand and evaluate the degradation processes [47].

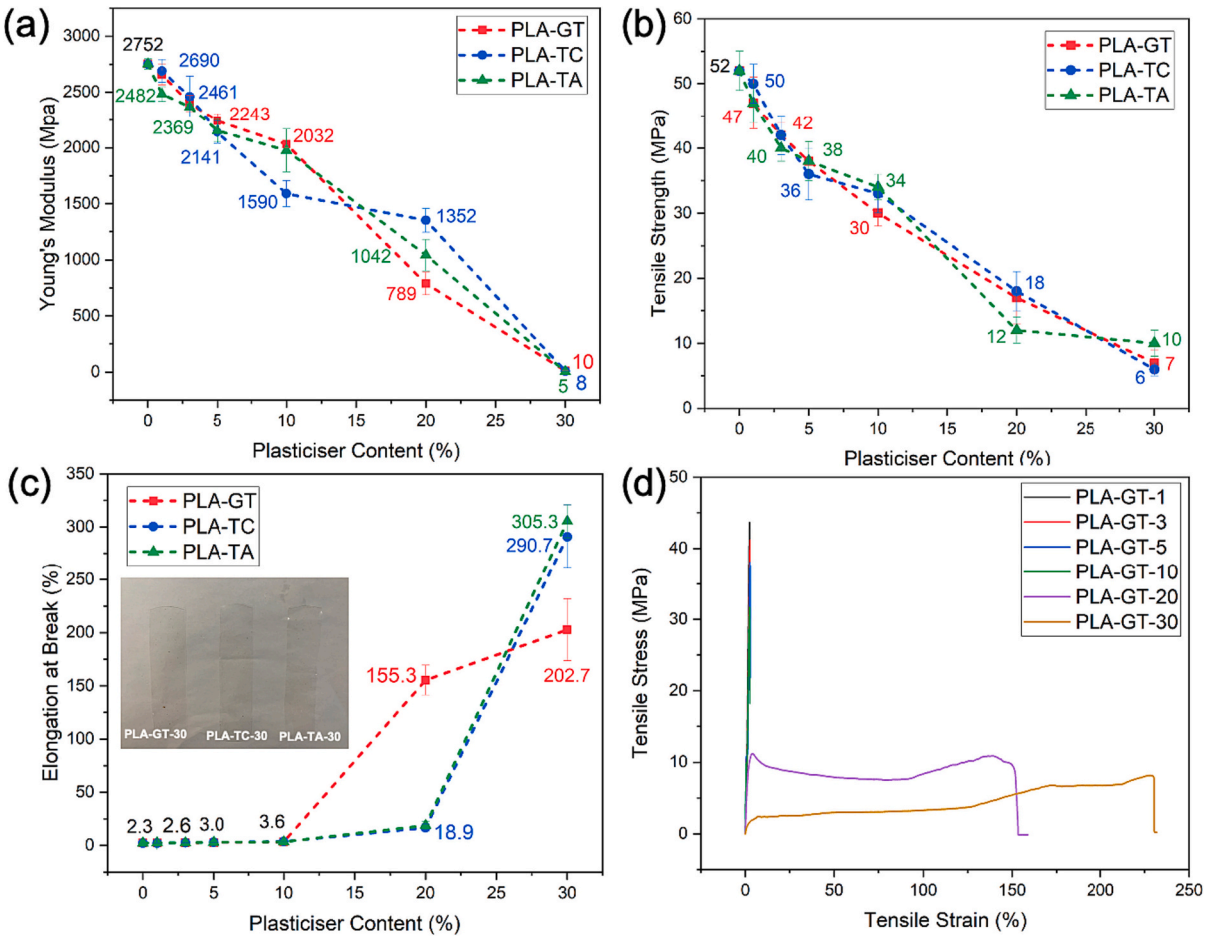


**Fig. 5.** Tensile properties of plasticized PLA films (a) Young's Modulus (b) Tensile strength (c) Elongation at break (d) Strain-stress curves of PLA-GT.

Many studies have demonstrated that the proteinase K from the *Tritirachium album* has a high ability to degrade PLA [31,32]. The results of weight losses of PLA-GT, PLA-TC and PLA-TA films treated with proteinase K are presented in Fig. 6. In general, the addition of the plasticizers significantly improved the degradation rate of the PLA films. However, the different contents and different plasticizers may bring in varied degradation rates. When the plasticizer content was increased from 1 to 5 %, both PLA-GT and PLA-TA showed slight decreases, while PLA-TC exhibited a gradual increase in weight losses. PLA-GT-1 demonstrated the fastest degradation rate with a value of 16.6 % at 72 h, followed by PLA-TA-1 at 13.7 % and PLA-TC-5 at 13.4 %. The interesting phenomenon could be attributed to the differences in the plasticized PLA films in crystallinity. When the plasticizer content increased from 1 to 5 %, PLA-GT and PLA-TA both exhibited an upward trend in crystallinity (Table 4), while the crystallinity of PLA-TC decreased. Crystalline regions are more resistant to enzymatic hydrolysis and degradation of the polymer, leading to a slow degradation rate. When the content increased from 10 to 30 %, there was an obvious upward trend in weight loss of these PLA films containing three plasticizers. The highest total weight losses of the plasticized PLA films were achieved for PLA-GT-30, PLA-TC-30 and PLA-TA-30 with values of 18.9 %, 14.6 % and 14.9 %, respectively, after 72 h of biodegradation. Compared to the low content of plasticizers, the high content of plasticizers did not demonstrate a significant improvement in weight loss, which is a concern. However, the initial impact of GT on the increased biodegradation rate of PLA was encouraging, which could lead to continuous investigation of using more practical biodegradation approaches in evaluating the performance.

## 4. Conclusions

According to HSP distance values, glycerol tributyrate (GT), similar to triacetin (TA) and tributyl acetate (TC), has good compatibility with PLA and could serve as a plasticizer of the polymer. The melt mixing of PLA with all three chemicals proved the speculation. The addition of the plasticizers has a significant effect on the thermal, mechanical and degradation properties of PLA films, and GT was effective in decreasing the glass transition, cold crystallization, melting temperatures and improving the elongation at break, as well as the degradation rate of the plasticized PLA. The content of the plasticizer also played an important role in these properties, similar to both TA and TC. At a low content from 1 to 5 %, these plasticizers mainly functioned at the reduction of glass transition temperature with little effect on the cold crystallization, melting temperatures and tensile properties. GT plasticizer in high contents in the PLA films (from 10 to 30 %) presented drastic plasticizing effects on PLA, similar to TA and TC, reducing glass transition and cold crystallization temperatures, and increasing the elongation at break at the cost of Young's modulus and tensile strength. The enzymatic degradation rates of plasticized PLA films were significantly increased due to the addition of GT, TA and TC as plasticizers. However, the degradation rates were not linearly increased with higher contents of plasticizers. Compared with PLA-TC and PLA-TA, PLA-GT showed faster and better degradability.

## Author statement

The manuscript reports original research that has not been published previously and is not under consideration for publication elsewhere, in

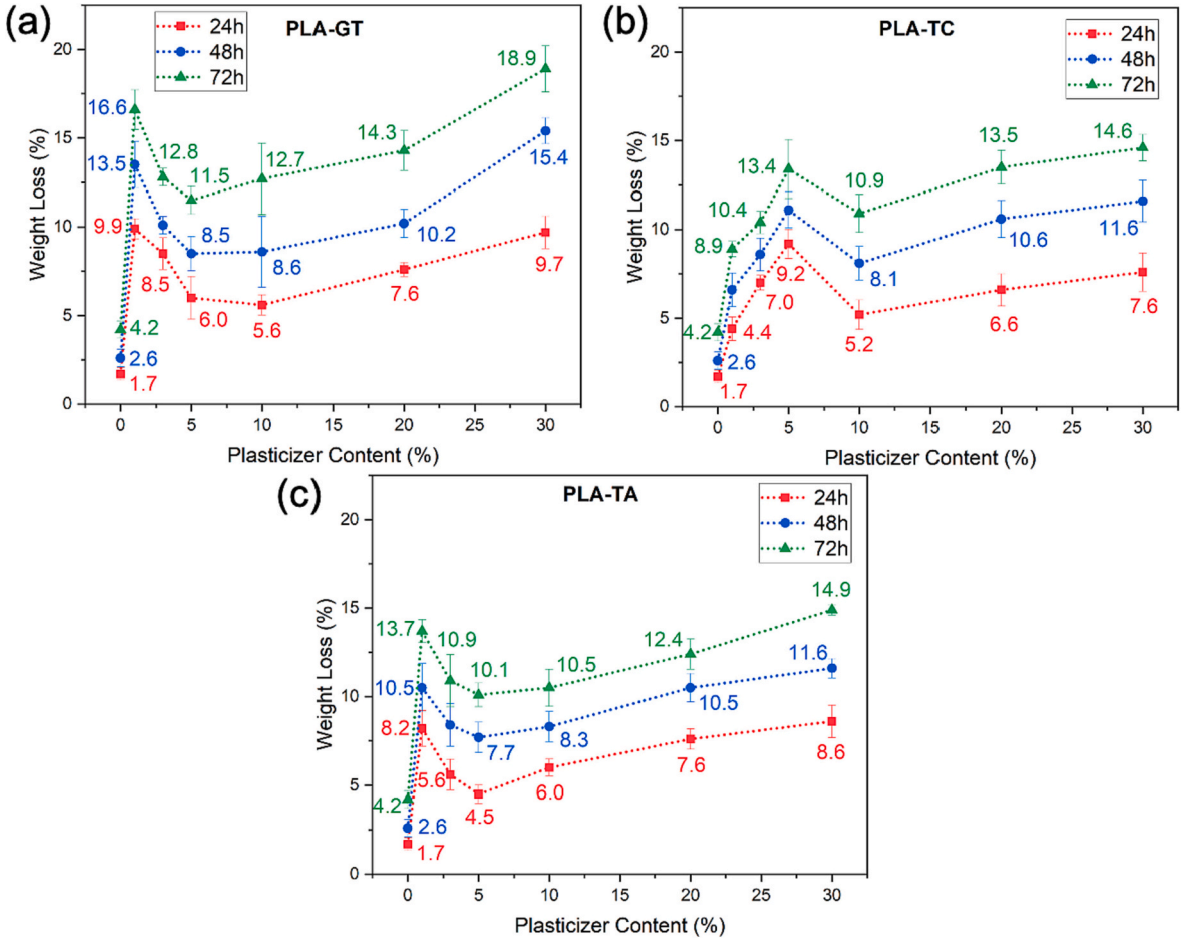


**Fig. 6.** Enzymatic degradation of plasticized PLA films at different times.

whole or in part. No conflict of interest exists regarding the submission of this manuscript, and the manuscript has been approved by all authors for publication.

## CRediT authorship contribution statement

**Yufa Sun:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Gang Sun:** Writing – review & editing, Supervision, Funding acquisition, Data curation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijbiomac.2024.130366.

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# A natural butter glyceride as a plasticizer for improving thermal, mechanical, and biodegradable properties of poly(lactide acid)

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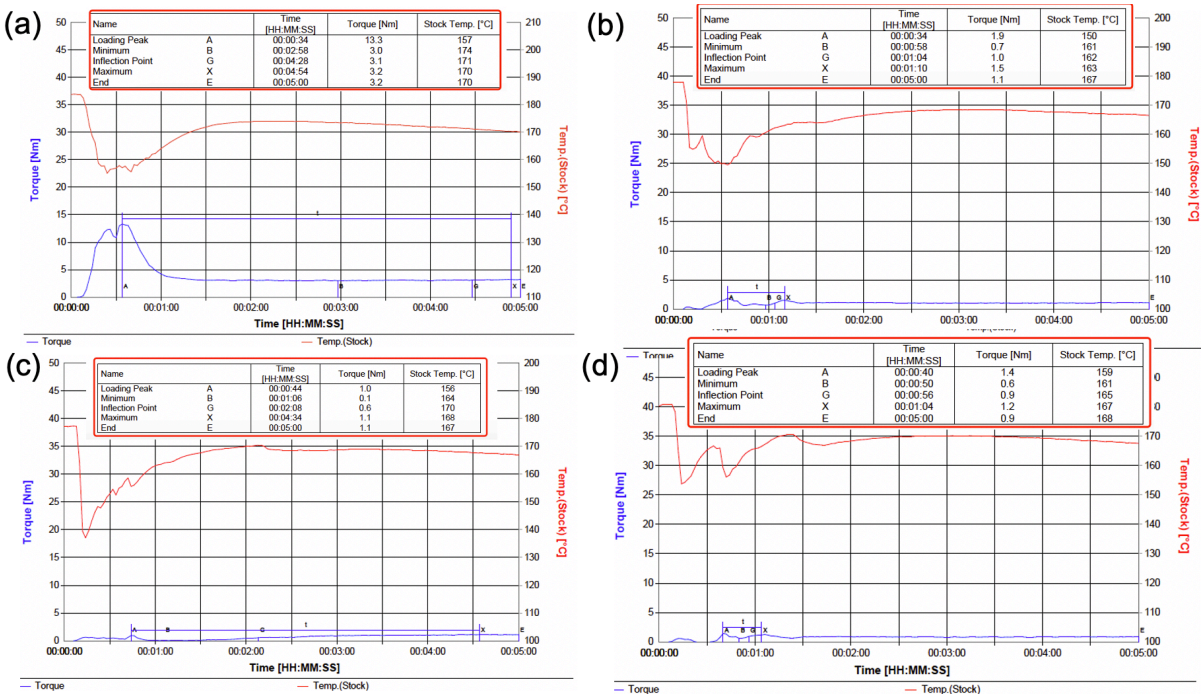


**Figure S1**. Evolution of torque during melt blending of PLA (a) PLA-0 (b) PLA-GT-30 (c) PLA-TC-30 (d) PLA-TA-30

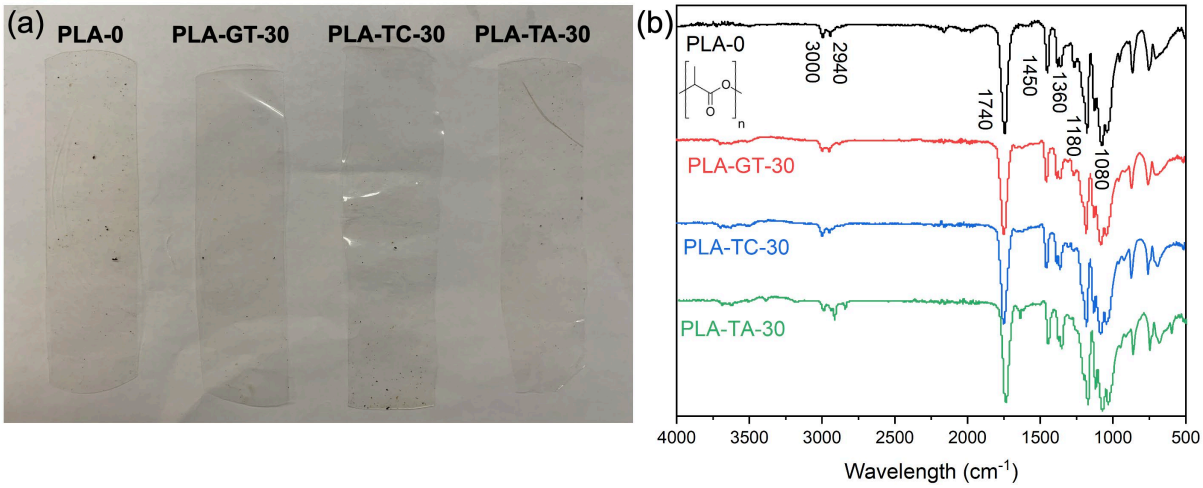


**Figure S2**. (a) Optical images (b) FT-IR spectra of PLA and plasticized PLA films

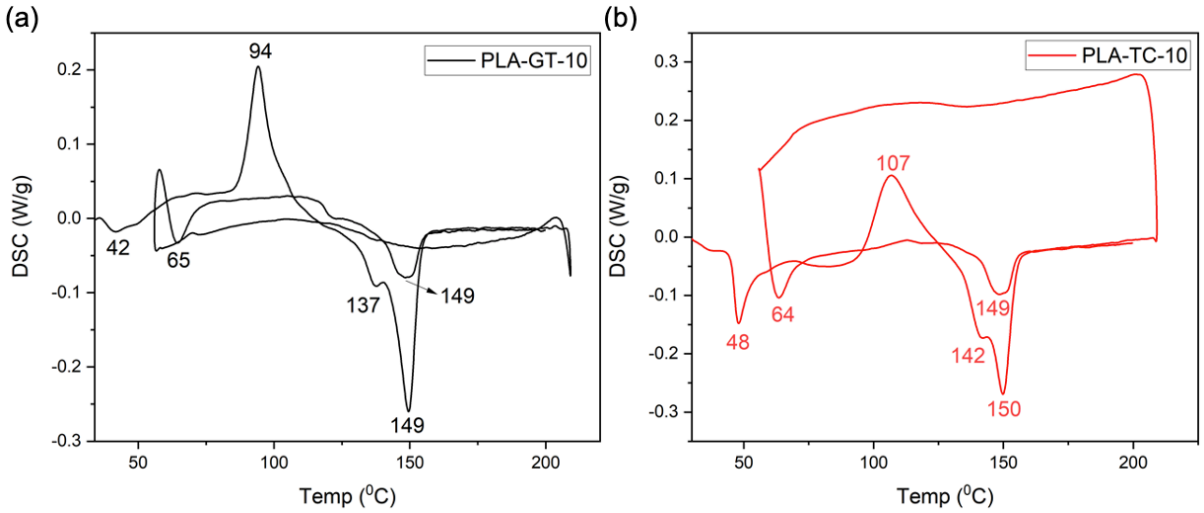


**Figure S3**. DSC curves with second heating of plasticized PLA films (a) PLA-GT-10 (b) PLA-TC-10

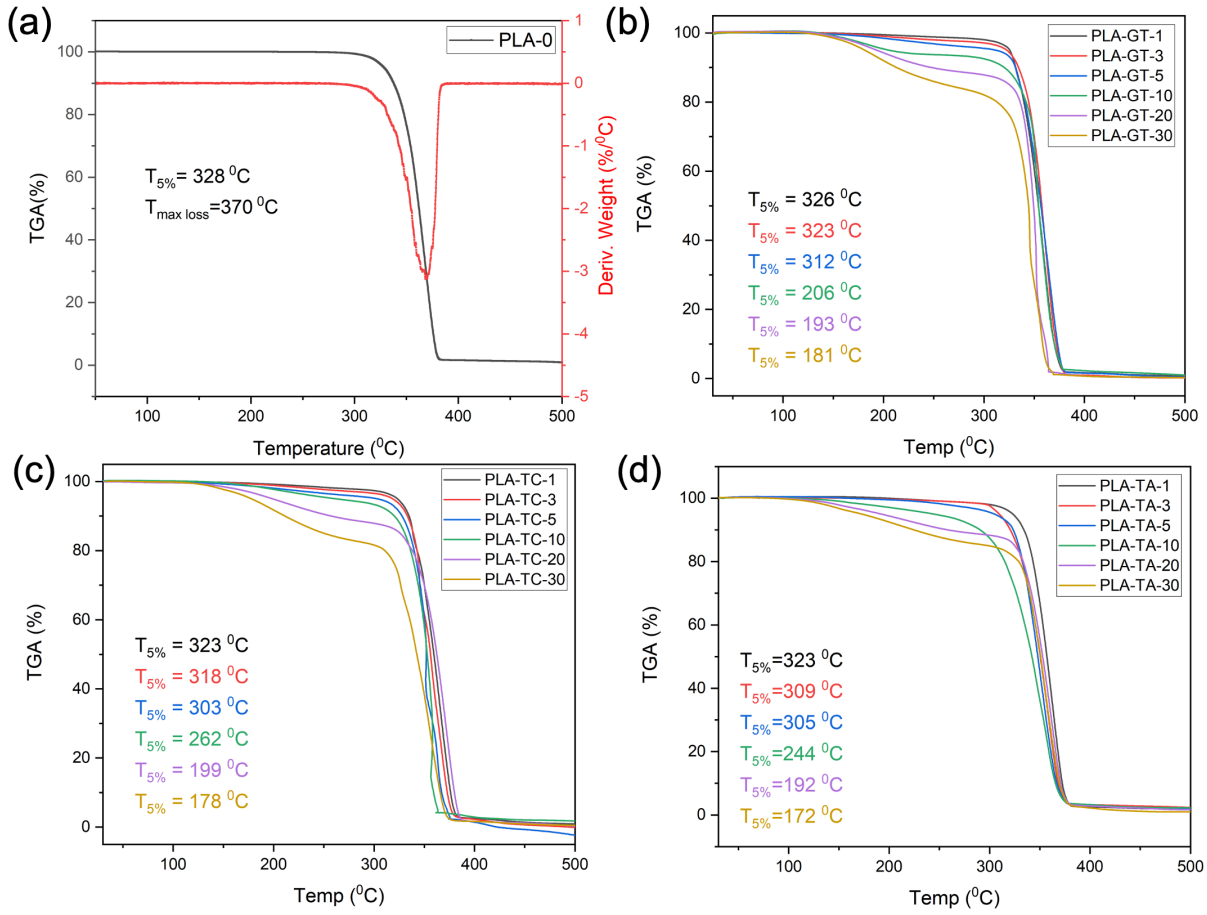


**Figure S4**. TG curves of (a) PLA-0 (b) PLA-GT (c) PLA-TC (d) PLA-TA

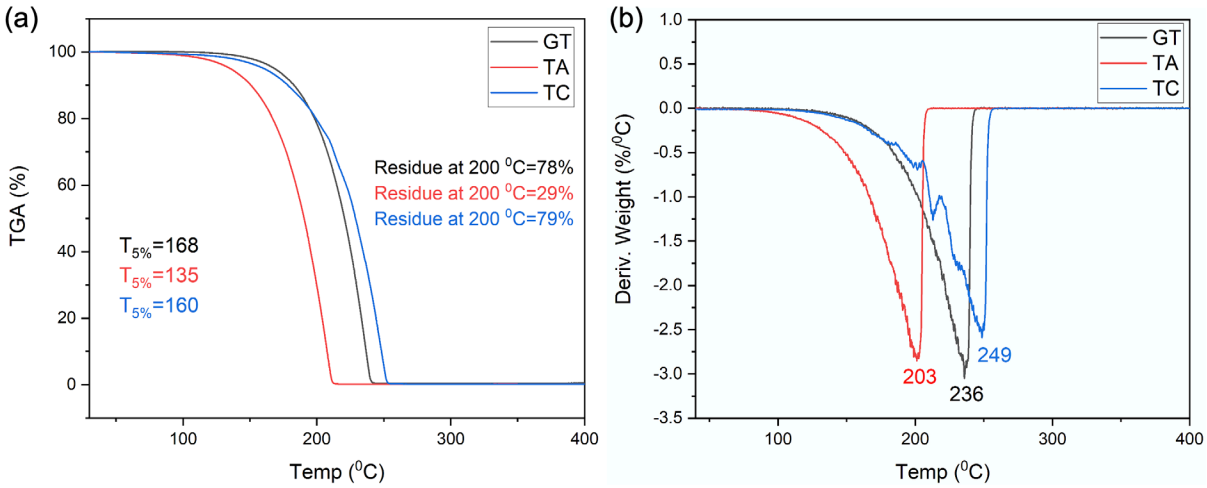


**Figure S5**. (a) TG curves (b) DTG curves of GT, TA and TC

**Table S1**. Mechanical properties of plasticized PLA films

| Samples | Young's modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|
| **PLA-0** | 2752 ± 45 | 52 ± 3 | 2.3 ± 0.1 |
| **PLA-GT-1** | 2658 ± 91 | 47 ± 4 | 2.4 ± 0.2 |
| **PLA-GT-3** | 2398 ± 76 | 42 ± 2 | 2.53 ± 0.15 |
| **PLA-GT-5** | 2243 ± 61 | 38 ± 3 | 2.77 ± 0.12 |
| **PLA-GT-10** | 2032 ± 35 | 30 ± 2 | 3.37 ± 0.15 |
| **PLA-GT-20** | 789 ± 101 | 17 ± 4 | 155.33 ± 14 |
| **PLA-GT-30** | 10 ± 2 | 7 ± 2 | 202.67 ± 29 |
| **PLA-TC-1** | 2690 ± 102 | 50 ± 3 | 2.3 ± 0.2 |
| **PLA-TC-3** | 2461 ± 183 | 42 ± 3 | 2.63 ± 0.2 |
| **PLA-TC-5** | 2141 ± 99 | 36 ± 4 | 3.0 ± 0.1 |
| **PLA-TC-10** | 1590 ± 116 | 33 ± 3 | 3.63 ± 0.25 |
| **PLA-TC-20** | 1352 ± 107 | 18 ± 3 | 16.67 ± 3.6 |
| **PLA-TC-30** | 8 ± 1 | 6 ± 1 | 290.67 ± 29.94 |
| **PLA-TA-1** | 2482 ± 65 | 47 ± 3 | 2.47 ± 0.06 |
| **PLA-TA-3** | 2369 ± 26 | 40 ± 2 | 2.57 ± 0.12 |
| **PLA-TA-5** | 2155 ± 103 | 38 ± 2 | 3.0 ± 0.3 |
| **PLA-TA-10** | 1976 ± 193 | 34 ± 2 | 3.47 ± 0.25 |
| **PLA-TA-20** | 1042 ± 140 | 12 ± 2 | 18.87 ± 3.78 |
| **PLA-TA-30** | 5 ± 2 | 10 ± 2 | 305.33 ± 15.57 |