Role of lubricant with a plasticizer to change the glass transition temperature as a result improving the mechanical properties of poly (lactic acid) PLLA

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Abstract

Poly (lactic acid) (PLLA) is the best important bioplastics derived from renewable resources like blackstrap molasses (sugar beet, date palm and sugar cane). PLLA is brittle and has a low elongation at break, which hinders its applications in the industry. One method to solve this problem is to improve its mechanical properties by adding plasticizers. The PLLA blends were prepared at first by solution blending as a solvent casting method and then melting using a hydraulic hot press. PLLA was blended with a plasticizer (GMS/TA) to obtain a higher ductile of PLLA. The addition of lubricant and plasticizer (GMS/TA) leads to reduce the glass transition temperature (Tg), melting point (Tm), and the cold crystallization temperature (Tc) in PLLA blends. The mechanical properties of PLLA have been investigated. The results indicated compatibility between PLLA and additives. The elongation at the break of the PLLA blend is stretched 270% with a tensile strength of 16 MPa. The addition of lubricant with the plasticizer leads to sliding the chain of PLLA, which causes to increase the strain. The physical blending has been demonstrated to be an effective technique to obtain an environmentally friendly PLLA blend with good mechanical properties, therefore it can be used in the food packaging sector.

1. Introduction

Above the past years, the use of plastics has developed the most important material because of its low cost, ease of manufacture, lightness, and good physical and mechanical properties compared to other materials [1]. The thermal stability and durability of these materials from petrochemicals have been improved, allowing them to resist corrosion in the environment and not biodegradable. In the last 10 years, the demand for bioplastics has increased. However, the market portion is very small in total plastic production due to its poor physical properties and high price. Many consumers do not view biodegradation as a new function to solve pollution problems. The introduction of these new bioplastics contributes to sustainable development to reduce the negative impact on the environment. The first use of polymeric materials in food packaging was in 1960 to overcome the high prices of other materials used in packaging such as paper, glass, and metal, as the plastic is low cost, good mechanical properties, lightweight and better chemical resistance, as well as ease of casting and processing. Most plastic products are currently manufactured from petrochemical products, where plastics production consumes 7% [2] of total world oil production. This evaluation may increase in the coming days due to increasing yearly in plastic production and consumption. During the past years, petrochemical polymers have been used in many applications in different fields, especially in the food packaging industry. In fact, plastics have many desired properties, but their negative impact on the environment and human health is unsafe. Environmental pollution and food safety problems have raised concerns about plastics produced by petrochemicals, where bioplastics are reflected better food packaging materials to solve the problem of
environmentally caused by polymers from petrochemicals. Bio-plastics are normally biodegradable, but efforts should be made at the industry level to develop less expensive and high-performance products compared to plastics from petrochemicals, to preserve the environment.

Poly (lactic acid) (PLLA) is a bio-polymer with a promising future that is able to replace petrochemical polymers, it can be used in industrial applications. PLLA is a linear aliphatic polyester thermoplastic. It is produced by fermentation of renewable agricultural resources like sugar, corn, potatoes, and beets. The main disadvantage of PLLA is the higher glass transition Tg at 60 °C and low crystallization rate, therefore its applications in the industry is limited. In order to solve these problems and contribute to sustainable development in the future, biodegradable polymers are used for plastics production. PLLA blend can be used in the food packaging for the short-term instead of non-degradable polymers like polyethylene, polypropylene, and polystyrene. Polymer blending is a physical blend of two or more homogeneous polymers, which interact with each other as physical blends such as hydrogen bonding. Physical polymer blends are an economical method to become new materials with certain properties without needing to prepare a new monomer and then a polymerization, which requires energy i.e. expensive in the industry and takes a long time. In the industry, different techniques are used to melt extrusion or solution blending. Polymer blends can be classified mainly as homogeneous mixtures. In which the components can be miscible and obtained a single glass transition Tg, and heterogeneous mixtures, in which the components are not miscible, and obtain more than the glass transition temperature Tg, resulting in poor adhesion between them, therefore poor mechanical properties. Most polymer blends cannot be good mixed because of the positive enthalpy change of the mixtures. Several efforts are made to reduce the glass transition temperature of PLLA by mixing PLLA with plasticizers [3–5], PLLA, with nucleation agent [6]. Natural plasticizers can be combined into the PLLA matrix to overcome this brittleness and improve their mechanical properties to use in food packaging. It is well-known that the plasticizers are the main character for improving the physical properties of polymers and manufacturing processes where plasticizers reduce the melt flow index, Tg and Tm. As a result of the addition of plasticizers to PLLA lead to reduce tensile strength and increase the elongation at break significantly. There is a physical interaction between the PLLA and plasticizers as polar interactions. In our previous study, TBC and PHB were with CNC selected as additives to improve the elongation at break of the PLLA [7]. Many scientists have been focused on studying the effect of plasticizers and other bio-polymer materials on the mechanical properties of PLLA like poly (glycolic acid) and amorphous poly (D,L-lactic acid) (PGA and PDLLA) blend [8], Poly (propylene carbonate) PPC [9, 10], poly (butylene adipate) (BAT) [11], starch and PCL [12], Poly (Butylene Succinate-Co-Adipate) [13].

The aim of this research is to overcome the brittleness of PLLA by using different concentrations of lubricant and natural plasticizer (GMS/TA) using the cast solution method, then melting and study the behavior of thermal analysis and mechanical properties of PLLA. This plasticizer must be non-toxic as well as the lack of migration.

2. Experimental

2.1. Material
Poly lactic acid (PLLA) as granules with average Mn = 40,000 and Poly ((R)-3-hydroxybutyric acid) PHB as a white powder (CAS 29435–48–1) were provided by Sigma-Aldrich Chemie GmbH, Germany. Glycerol monostearate (GMS) in the form powder as plasticizer and lubricant from Trigon Chemie. Triacetin (TA) as plasticizer from Sigma Aldrich.

2.2. Sample preparation
The casting of PLLA blends was prepared by dissolving all components in dichloromethane (DCM), then poured in a petri dish, after evaporating the solvent, the obtained films were dried in an oven at 60 °C for 24 h. The samples of PLLA/PHB (GMS/TA) with a ratio (25%: 75% weight) blends were prepared with different weight ratios as follows in table 1.

2.3. Methods
2.3.1. Differential scanning calorimetry (DSC)
DSC was shown from –50 °C to 190 °C with rate of heating 10 °C min⁻¹, and rate of cooling of 20 °C min⁻¹, by Shimadzu-DSC 50, Japan. The weight of the samples (0.5 μg) was put in pans from aluminum and dry nitrogen atmosphere is used. The curves DSC was approved from the first heating run, second heating run and cooling run. It can be determined the Tg, the Tm, and the Tcc.
Table 1. To explain the content of PLLA blends.

| Blend   | PLLA | PHB | GMS/TA (25%: 75%) |
|---------|------|-----|-------------------|
| 1 Blend | 75   | 10  | 15                |
| 2 Blend | 70   | 10  | 20                |
| 3 Blend | 65   | 10  | 25                |
| 4 Blend | 60   | 10  | 30                |

Table 2. Thermal properties of PLLA and its blends at different concentrations.

|         | Pure PLLA | Blend 1 | Blend 2 | Blend 3 | Blend 4 |
|---------|-----------|---------|---------|---------|---------|
| $T_m$ (°C) | 61       | 40      | 30      | 27      | 23      |
| $T_C$ (°C) | 135      | 105     | 99      | 93      | 86      |
| $T_g$ (°C) | 168      | 166     | 161     | 160     | 158     |
| $\Delta H_m$ (J g$^{-1}$) | 7.1      | 36      | 34      | 35      | 35      |
| $\Delta H_c$ (J g$^{-1}$) | —       | 23      | 17      | 20      | 13      |
| $X$ (%)   | 8        | 19      | 26      | 25      | 39      |

2.3.2. Thermogravimetric analysis (TGA)

TGA is used to investigate the thermal stability by TGA (Q500) for pure PLLA and its blends. The Weight of samples from 15 mg were heated under the air flow (80 ml min$^{-1}$) from 25 °C to 600 °C with the rate of heating of 10 °C min$^{-1}$.

2.3.3. Mechanical properties

The elongation at break and tensile strength determined by the issue ASTM-D412-80 testing. The universal testing machine (Shimadzu) is used to study the stress-strain curves with the rate of 10 mm min$^{-1}$ at used temperature. Tensile test samples were prepared like dog-bone shape of the stainless steel die (DUMBELL Co. Ltd, Saitama-Ken, Japan) with dimension (4.8 mm, 22.25 mm, 20–75 μm). In the end, the fracture surface of the PLLA film samples was studied by SEM.

2.3.4. Scanning electron microscopy (SEM)

The broken surfaces after the tensile tester of the PLLA blends was observed using a scanning electron microscope (JSM-6360LA, JEOL Co., Japan) at an accelerating voltage of 10 KV. The fracture surface of samples 2 and 4 were investigated by SEM, after sputter-coated with gold using a sputter coater (EMITECH K550X, England).

3. Discussion and results

3.1. DSC analysis

DSC is a technique for determining thermal properties by heating a sample and measuring the heat flow. DSC can be studied the thermal properties by plotting the heat flow (mW) versus the sample temperature (°C). It gives information about the glass transition temperature $T_g$, the ratio of crystalline ($X_c$) and the melting temperature $T_m$. GMS/TA is lubricating and non-toxic plasticizing, and it reduces the aging process in PLLA film during storing at use temperature, therefore it can be used in the food packaging sector. The $T_g$ is typical of the amorphous portion of the polymers. The addition of plasticizers and lubricants makes a significant change in the movement of the polymer chain, i.e. leads to change in $T_g$ which helps to improve the physical and mechanical properties of the PLLA.

The glass transition temperature ($T_g$), the ratio of crystalline ($X_c$), cold crystallization temperature ($T_{cc}$), and the melting temperature ($T_m$), melting— and cold enthalpy are calculated by DSC in table 2.

Figures 1(a)–(c) shows the DSC thermograms of the PLLA blend films with different additives. It was detected that pure PLLA has $T_m$ at 171 °C and $T_g$ at 62 °C. It presented that pure PLLA has a very small peak at $T_{cc}$, this means that the PLLA remains in an amorphous state or very slow crystallization. Pure PLLA is amorphous due to the absence of crystallization peak through the cooling run. The addition of PHB to the PLLA matrix helped the crystallization kinetics [14]. When adding (GTS/TA) alone, no cold crystallization temperature ($T_{cc}$) appears, i.e. the PLLA sample remains on the surface of the metal for a long time during manufacture, and this is not desirable in the industry. When adding PHB alone, there is no decrease in the glass transition temperature ($T_g$). But when adding both together in PLLA matrix, the change in physical properties is shown. Adding the plasticizer (GMS/TA) with different concentrations to pure PLLA leads to reduce $T_g$ of pure PLLA. It was observed that the higher concentration of (GMS/TA), lead to the lower $T_g$ of the PLLA. In addition, the melting point ($T_m$) for pure PLLA to
a lower temperature when (GMS/TA) was added. This shift was detected to be more obvious when (GMS/TA) content was increased. It is known that the addition of PHB to the PLLA matrix in small quantity of 10% helped the crystallization kinetics. More than 10% of PHB in blends lead to phase separation in PLLA matrix with poor mechanical properties. PHB was added to increase the process of crystallization and fast the temperature of crystallization \((T_{cc})\) of PLLA, consequently, increase the melting enthalpy content \((\Delta H_{m})\) resulting in more strong melting peaks for PLLA blends. PLLA blend does not contain melt crystallization \((T_c)\) during rapid cooling, but crystallize well during the second heating process. The aim of the rapid cooling process is to show \(T_g\). The presence of cold crystallization peak \(T_{cc}\) around 105 °C for blend 1, 99 °C for blend 2, 93 °C for blend 3 and 86 °C respectively. It was detected in table 2 that the melting enthalpy \((\Delta H_m)\) of pure PLLA is 7.1 J g\(^{-1}\) and the degree of crystallinity for pure PLLA = 8%, blend 1 = 19%, blend 2 = 26%, blend 3 = 25% and blend 4 = 39%, blend 4 was the highest compared to the other blends. This behavior has clearly affected the mechanical properties of PLLA/PHB/(GMS/TA) blends. Increasing the crystallization percentage in the PLLA blends due to the effect of the plasticizer (GMS/TA), caused in reduced \(T_g\), which helped to increase the chain movement, as well as PHB helped to form a higher crystallization temperature \((T_{cc})\). The decreasing in \(T_{cc}\) is related to an increase in (GMS/TA) content in the PLLA matrix. This behavior is due to adding of PHB to PLLA makes it freer crystallized at low temperatures due to increased movement of PLLA chains when plasticizers are added. The ratio of the crystallinity \((X%)\) of PLLA and its blends was calculated by equation (1): 

\[
X(%) = \frac{\Delta H_{cc}}{\Delta H_{m} \times (1 - \text{ wt filler})} 
\]

where \(\Delta H_{cc}\) is the cold crystallization enthalpy of the sample or \(\Delta H = \Delta H_m- \Delta H_{cc}\) (for second heating curves, as \(\Delta H_m\) is the melting enthalpy of the sample), \(\Delta H_{m}^{PBLA}\) is the melting enthalpy of the 100% crystalline polymer matrix (93 J g\(^{-1}\)) for PLLA [15] and % wt filler is the total weight percentage of PHB in PLLA matrix.

Figure 1(c) shows the characteristics of the melting for PLLA blends from the second heating run. The pure PLLA demonstrations the melting point \(T_m\) at 168 °C and crystallization point \(T_{cc}\) at 135 °C. The melting temperature \((T_m)\) of PLLA blends reduced with an increase in (GMS/TA) content. It is known that below \(T_g\), of amorphous polymer becomes glassy and it is affected by the aging process. But above \(T_g\) in the semi-crystalline polymer, a portion of the polymer is amorphous and remains glass. Therefore, for such materials, the aging process at room temperature will be studied. It is known that the behavior of PLLA aging at room temperature changes in amorphous areas, leading to an increase in the brittleness of PLLA [5, 16].
The values of $T_g$, $T_{cc}$, and $T_m$ temperatures, and melting—and cold enthalpy calculated by a DSC second heating run.

Physical aging leads to changes in the physical properties of the polymer in the amorphous region because the date of polymer preparation did not leave it in a thermodynamic equilibrium state, and thus the polymer attempts to reach equilibrium. Polymer molecules move slowly and try to fill amorphous areas over time as a result of reduced free energy and free volume of the system. Most of the aging effects that occur in crystalline thermoplastics are associated with reduced amorphous part and reduced the free volume of the amorphous phase. In figure 1(d) show PLLA 4 with one glass transition at around 23 °C. The Tg of PLLA blend 4 shows no change in entropy relaxation with aging time, i.e. PLLA blends are stable. It can control that the effect of bio-additives value on the Tg and Tcc of PLLA was investigated by DSC in detail. The Tcc of all PLLA blend can be observed, indicating that they are all crystalline. The Tcc decreases with increasing plasticizers value and disappears by rapid cooling and appears only for PLLA blends in the second heating run.

3.2. Thermal stability by TGA
Thermal thermogravimetric analysis (TGA) is a method for determining the thermal degradation of polymers at high temperatures during manufacture, in which changes in physical properties are measured, i.e. the substance does evaporation during manufacture as a function of time and temperature with constant heating rate.

Figures 2(a) and (b) shows TGA of PLLA and its blends after heating in the temperature range between 30 ºC–900 ºC with a constant heating rate of 10 ºC min⁻¹ under nitrogen. It calculates the part of unstable components by checking the sample mass loss as a function of temperature. From the TG curves of pure PLLA and PLLA blends, we can see that the thermal degradation of PLLA blends could be divided into two-steps thermal
degradation process above 350 °C. The first-stage degradation at around 300–400 °C could be typically ascribed to the decomposition of the main chain of plasticizer (GMS/TA). The second stage at above 400 °C is attributed to PLLA and the splitting of chains. The PLLA blend is found to be stable up to 300 °C with weight loss of about 1%–3%, indicating these PLLA blends show good thermal stability. From figure 2(b) it can be seen that the main mass loss is detected in approximately 80–90 weight% in between 200 °C–350 °C for all PLLA blend which correspond to the breakdown of (GMS/TA). The pure PLLA has higher thermal stability than that of PLLA blend. The first derivative of TGA curves as shown in figure 2(b), the mass loss of the PLLA blend is moved to a lesser temperature related to pure PLLA. The thermal decomposition of the PLLA blend shifted slightly toward lower temperatures compared to PLLA. With an increasing PHB (10%) and GUS/TA 80 (15%–30%) content in the PLLA matrix, the initial weight loss temperature decreases slightly. The temperature at a 30% weight loss of the blends shifts from 250 to 400 °C. The degradation temperature at about 415 °C, which was moved to lesser temperatures, around 320 °C, to (GMS/TA), close to the peak decomposition of PHB. Lubricants are used to improve the polymer manufacturing process. This is considered as external lubrication between polymer chains, thus reducing the interactive force. The addition of lubricants to plastics protects the chain from the heat during manufacture. GMS/TA were used as a lubricant to protect of PLLA from thermal degradation. These are clear from TGA measurements. It can be said that the addition of plasticizers to the PLLA matrix improves the thermal degradation during manufacture and reduces Tg. It is clear from TGA measurements, the manufacture
of the PLLA blend lies between the temperatures 200 °C to 250 °C. GMS/TA was used as a lubricant to protect of PLLA from thermal degradation and reduce Tg.

3.3. Tensile behavior analysis
The values of elongation at break, the yield stress of PLLA blends are studied and plotted in figure 3. The elongation at break pure PLLA about 7% and the stress above 19 MPa, i.e. poor mechanical properties. Figure 3 is shown the elongation at break for PLLA blends with different (GMS/TA) ratios. It caused a reduction in the stress and an increased elongation at break in all PLLA blend. The elongation at break of blend 4 reached more than 270% compared to pure PLLA. As the GUS/TA content in the blends increased, the elongation increased gradually, it was observed that the elongation at break improved 40 times, demonstrating that the stiffness of the material had improved significantly. Therefore, it showed that additives have a clear effect on improving the brittleness of the PLLA. When the (GMS/TA) content was 30% by weight, the PLLA blends kept good elongation at breakage and high tensile strength and had better mechanical properties.

3.4. Scanning electron microscope (SEM)
The morphology was demonstrated by SEM for the broken surfaces after the tensile tester to study the microstructure of PLLA blends. In figures 4(a)–(d) is shown the fracture surface of blend 2 and compare it with the blend 4. When the plasticizer was added and reacted with PLLA to improve the mechanical properties, the shape of the broken surface was significantly changed in blend 2 and 4. Instead of pure PLLA surface with cracks [16], the fracture surface of the blend 4 showed no cracks a smooth and elastic surface (figures 4(c) and (d)). The microstructure of the PLLA blends is another indication that PLLA with plasticizer makes it very flexible. As shown in figure 3, the blend 3 reaches greater values of both elongation at break and stress, while blend 4 reaches the maximum value of elongation at break. In figure 4(e) is showing the pure PLLA exhibits typical brittle behavior without whitening distortion. In contrast, the PLLA blends show the formation of the neck whitening deformation. This indicates that the plasticizer makes whitening in the stress zone, therefore PLLA blends are ductile, this is due to the presence of more characters formed during the crazing deformation mechanism, this means more elongation and strength. There were changes in elongation and tensile strength with plasticizer content and it was observed no aging process by DSC. The two different blends show good behavior as flexible and ductile polymer material in food packing applications. The addition of lubricants with the plasticizer lead to sliding the chain of PLLA, which causes to increase the strain.

4. Conclusion
PLLA can be used in the food packaging sector, after improving its mechanical properties. It is observed that the elongation at break of the PLLA blends is improved by additions of PHB and (GMS/TA) compared to the pure PLLA. When the content of (GMS/TA) is 30 wt%, the elongation at break was increased by 140 times. DSC demonstrates that the Tg, Tc, and Tm of PLLA blends have been affected by the adding of additives. Increasing the plasticizers (GUS/TA) leads to change the Tg, the Tm, the Tc, this means improving the brittleness of PLLA. For this reason, we applied these physical blends to obtain an environmentally friendly PLLA blend with good mechanical properties. PLLA can be applied to PLLA in the food packaging industry.

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