Dynamic Mechanical Properties and Thermal Stability of Poly(lactic acid) and Poly(butylene succinate) Blends Composites

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Abstract

The blend of poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) were prepared and extruded with various compositions and their molded properties were examined. Thermogravimetric analysis showed that thermal stability of the blends was higher than that of pure PLA and the weight loss of PLA/PBS (40/60 wt%) was lower than neat polymers. Differential scanning calorimetry thermograms of blends indicated that the thermal properties of PLA did not change noticeably when blended with PBS. The tensile strength and modulus of blends decreased with the increasing PBS content. But impact strength has improved about two times compared to pure PLA. Rheological results revealed that the addition of 10% and 20% of PBS increased the storage modulus, loss modulus and viscosity of the blend at nearly all frequencies, and decreased viscosity with increasing shear stress. Dynamic mechanical properties results showed the lowering of storage modulus of all blended PLA which indicated the increase of molecular mobility by adding PBS due to lower glass transition.

Keywords: PLA/PBS Blends; Thermal Stability; Dynamic Mechanical Properties

1 Introduction

In past few decades, a lot of attention has been focused on biomass based polyester derived from renewable resource [1]. Among a few commercially available biobased or partially biobased thermoplastic polymers, poly(lactic acid) (PLA) has been investigated extensively [2, 3]. It is a linear aliphatic thermoplastic polyester, produced from renewable resources with good biocompatibility, non-toxic byproducts, excellent transparency, and high strength and modulus [4-8]. Biodegradable PLA is perhaps the most important polyester in biomedical applications [9, 10]. PLA has attracted an increasing interest in various markets, such as packaging, textile [11-15], and automotive industries [16, 17]. It can be processed using injection-molding, compression-molding, extrusion, and thermoforming etc. Several drawbacks tended to limit its widespread applicability such as high cost, brittleness, toughness, and low heat distortion temperature. Thus
in order to broaden the applications of PLA, material properties and processability has to be improved.

Modification of PLA by copolymerization or physical blending is a useful way to decrease the brittleness, toughness, and heat distortion temperature. Various additives such as plasticizers, toughening agents, reinforcing fillers and compatibilizers have been incorporated into PLA [18-23]. Many reports about blending of PLA with ductile polymers are available [24-26]. On the other hand, poly(butylene succinate) (PBS) is commercially available aliphatic polyester with high flexibility, good toughness, high elongation at break and lower glass transition temperature, and has a good biodegradability. But the low molecular weight PBS, with low melting point (114°C), low stiffness and strength, greatly limits its potential applications. Although many reports about PLA/PBS blends are reported in literature [27-31], the results have shown that the PLA/PBS blends that with 20 wt% of PBS has good compatibility. Liu et al., discussed the properties of biocompatible fibers obtained by blending the cellulose nanowhiskers and the cellulose matrix, and latter the characteristics of wool/keratin hydroxyapatite were also investigated [32, 33]. Morphology and the mechanical properties of electrospun PA 6/66 nanofibers and the electric field analysis of spinneret design for needleless electrospinning of nanofibers were also investigated [34, 35]. In this study, PLA/PBS was blended with various compositions and was prepared by using a twin-screw extruder. Thermal, dynamic mechanical analysis, rheological, and mechanical properties in these blend systems were examined and studied by different characterization techniques. The thermal stability of the PLA/PBS blends and their rheological properties were used to understand the effect of the addition of PBS in the PLA to decrease the brittleness and increase elongation.

2 Experimental Methods

2.1 Materials

PLA polymer (4032D-grade, melting point of 170°C) in pellet form produced by Unic Technology (Suzhou) Co., LTD was used in this study. PBS Polymer (Molecular Weight 8000, melting point of 109°C) in pellet produced by Anqing Hexing chemical co., LTD was used to blend with PLA.

2.2 Blend Preparation and Injection Molding

The pellets of both PLA and PBS were initially dried in a vacuum oven at a temperature of 80°C for 12 h to remove water before processing through the extruder. Blends of various compositions were prepared as shown in Table 1. Measured quantities of each polymer were first mixed in a container before they were blended in a twin-screw extruder. The extruder was operated at 145-175°C at 80-100 rpm screw speed, then again placed in the oven at 60°C. Specimens of blended samples were obtained by injection molding into the standard test after drying at 60°C for at least 12 h under vacuum. The injection molding process parameters are as follows: Temperature at 160-195°C, injection pressure 1 MPa, dwell time: 9 sec and mold temperature of 40°C.
Table 1: Compositions of PLA/PBS blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>PLA content (wt%)</th>
<th>PBS content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

3 Characterization

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere using a TGA Q5000 IR (TA Instruments-waters LLC) with a heating ramp of 10°C/min from 0-600°C. Differential Scanning Calorimetry (DSC) characterization of the blends was performed with DSC Q20 (TA Instrument-waters LLC). To eliminate the thermal history, all the samples were heated up to 180°C, and then rapidly cooled to −50°C. The actual measurements reported here were performed during a second heating cycle from −50 – 200°C at a heating rate of 10°C/min. Dynamic Mechanical Analysis (DMA) were performed using a DMA Q800, TA Instrument. The dimension of rectangular specimens was 60 × 7.5 × 2.5 mm. The measurements were performed at a frequency of 1 Hz and a strain rate of 0.1% by dual cantilever method with a heating rate of 3°C/min, and the temperature ranges from 24-120°C. Rheological properties were measured using ARES-RFS, TA Instrument. The frequency range was set at 0.1–100 rad/sec. Before the measurement, the samples were prepared using injection molder at 190°C. The tensile test was carried according to ASTM D638-08 with a universal testing machine (UTM, Zwick Co.) at a crosshead speed of 50 mm/min and a temperature of 25°C. Impact testing was done using an impact tester (Ceast Model 6545) according to ASTM D256 at 25°C. All the reported results are an average of at least five measurements for each blending system.

4 Results and Discussion

4.1 Thermal Properties of PLA/PBS Blends

TGA curves of the neat PLA, PBS, and PLA/PBS blends are given in Fig. 1 (a), have revealed the thermal stability of these blends. The thermal degradation of PLA, PBS, and PLA/PBS took place in two step processes from 360-450°C, approximately. All of the samples displayed single-step degradation process, and PBS has shown more resistant at thermal degradation than PLA. The initial decomposition temperature of PBS is 396°C, and the temperature ascribed to the maximum rate of thermal degradation is 455°C, while the initial decomposition temperature of PLA is 375°C, and the temperature ascribed to the maximum rate of thermal degradation is 411°C. The thermal stability of PLA/PBS blend is higher compared to the neat PLA, 60 wt% and 40 wt% of PBS in blend show higher thermal stability as shown in Table 2. The weight
loss of PLA/PBS (40/60 wt%) was lower than neat polymers due to its difference of morphology. This indicates that the PLA/PBS blends have an effect on the thermal stability and this may be regarded to the thermal stability of PBS. Finally, the weight loss of all the specimens was very little varying from 0-330° C. This means that there was no affect by the weight loss during manufacturing process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(PLA/PBS) content wt%</th>
<th>T_{onset} °C</th>
<th>T_{endset} °C</th>
<th>Weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/0</td>
<td>375±2</td>
<td>411±3</td>
<td>98.5</td>
</tr>
<tr>
<td>2</td>
<td>90/10</td>
<td>373±1</td>
<td>416±2</td>
<td>97.5</td>
</tr>
<tr>
<td>3</td>
<td>80/20</td>
<td>370±2</td>
<td>424±1</td>
<td>98.3</td>
</tr>
<tr>
<td>4</td>
<td>60/40</td>
<td>366±1</td>
<td>436±1</td>
<td>97.6</td>
</tr>
<tr>
<td>5</td>
<td>40/60</td>
<td>361±3</td>
<td>447±2</td>
<td>96.9</td>
</tr>
<tr>
<td>6</td>
<td>20/80</td>
<td>383±2</td>
<td>450±1</td>
<td>97.5</td>
</tr>
<tr>
<td>7</td>
<td>0/100</td>
<td>396±2</td>
<td>455±3</td>
<td>98.2</td>
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</table>

The results of DSC heating scans for the PLA/PBS blends are presented in Fig. 1 (b). The Tg of the PBS and the PLA were about −44.3°C and about 63.9°C, respectively. The Tg for the blends with content > 20 wt% of PBS were shifted to a low temperature with a minor difference of 2°C-3°C. On the other hand, the Tg of the blend showed slightly higher value than that of pure PBS. The melting temperature of PLA was around 152°C but that in the blend decreased up to 149.6°C.

The crystallinity was calculated by using the equation as shown below:

\[
X_c\% = \left( \frac{\Delta H_m}{\Delta H_0^m} \right) \times 100
\]

where \( \Delta H_m \) was the experimental melting enthalpy (J/g) of polymer blend and \( \Delta H_0^m \) was the melting enthalpy for 100% crystalline polymer taken from the literature [PLA (93.7 J/g) and PBS (110.3 J/g)]. From Table 3, it could be seen that the crystallinity \( (X_c, \%)\) of blends first improved about 8% due to the nucleation effect, and then decreased by increasing the PBS
content. Conversely, the crystallization of PBS per unit mass of PBS decreased. This indicates that the degree of crystallinity of the blends decreased with the addition of PLA that is due to the slow movement of PLA chain with higher Tg. Fig. 1 (b) also showed the exothermic peaks which are attributed to the crystallite reorganization during heating. The re-crystallization temperature of PLA increased with increasing PBS content.

Table 3: Thermal properties of PLA/PBS blends

<table>
<thead>
<tr>
<th>PLA/PBS (wt%)</th>
<th>PLA</th>
<th>PBS</th>
<th>T&lt;sub&gt;rc&lt;/sub&gt;</th>
<th>ΔH&lt;sub&gt;m&lt;/sub&gt;</th>
<th>X&lt;sub&gt;a&lt;/sub&gt;</th>
<th>X&lt;sub&gt;b&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Tg (°C)</td>
<td>Tm (°C)</td>
<td>Tg (°C)</td>
<td>Tm (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>63.9</td>
<td>152</td>
<td>-</td>
<td>-</td>
<td>14.88</td>
<td>15.9</td>
</tr>
<tr>
<td>90/10</td>
<td>63.2</td>
<td>149.5</td>
<td>-</td>
<td>108.23</td>
<td>120.6</td>
<td>22.28</td>
</tr>
<tr>
<td>80/20</td>
<td>63.9</td>
<td>150.1</td>
<td>-</td>
<td>108.58</td>
<td>119.5</td>
<td>19.00</td>
</tr>
<tr>
<td>60/40</td>
<td>61.2</td>
<td>150.3</td>
<td>-</td>
<td>109.1</td>
<td>124.64</td>
<td>17</td>
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<tr>
<td>40/60</td>
<td>60.9</td>
<td>150.7</td>
<td>-</td>
<td>109.5</td>
<td>126.86</td>
<td>-</td>
</tr>
<tr>
<td>20/80</td>
<td>-</td>
<td>149.6</td>
<td>-</td>
<td>109.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0/100</td>
<td>-</td>
<td>-</td>
<td>-44.3</td>
<td>109</td>
<td>-</td>
<td>49</td>
</tr>
</tbody>
</table>

X<sub>a</sub> and X<sub>b</sub>: Crystallinity for neat PLA and PBS.

4.2 Viscoelastic Behavior of PLA/PBS Blends

DMA helps to study the polymer miscibility in polymer blends and also measure the (Tg) of the polymers. Moreover, we can obtain an idea about the storage (dynamic) modulus, loss modulus and damping behavior. The curves of the storage modulus as a function of temperature were shown in Fig. 2 (a). The storage modulus showed that all blended PLA exhibited lower values than PLA which indicated the increase of molecular mobility of PBS due to low Tg, and the entire blends indicated significant fall in the regions between 55°C to 65°C except for PBS. The Tg of PLA was 60°C and 10 wt% of PBS blend has decreased Tg to 57°C, which indicated that the PLA and PBS have partial miscibility, and Tg decreased when content of PBS increased.

Fig. 2: Storage modulus (a) and tan delta (b) of PLA/PBS blends
The tan delta as a function of temperature was shown in Fig. 2 (b). The intensity of the tan delta peaks for the blends and decreased observably compared to that of the neat PLA, which indicates that the presence and somewhat good dispersion of the PBS retarded the segmental motions of the polymer matrix during the transition. Tan delta peaks of all types were remarkably observed in the region between 55 to 80°C except for PBS. As the temperature increases, damping goes through a maximum near Tg in the transition region, and then a minimum in the rubbery region. The Tg shifting to low temperature was only between 1-2°C on the all blends due to the low Tg of PBS. But again temperature shifting to high than that of PLA when content of PBS was 60 wt% and 80 wt%, is due to the increase in the crystallinity.

4.3 Rheological Properties PLA/PBS Blends

The rheological properties of polymeric materials are important for optimizing the processing conditions such as extrusion, injection moulding and melt spinning, which is highly dependent on temperature, molecular weight and shear rate [36]. It can give important information about the flow behaviour of the melts. The storage modulus (G’) and loss modulus (G’’) versus the frequency for PLA, PBS and PLA/PBS blends with different composition of PBS are shown in Fig. 3 (a) and 3 (b). All the samples are featured by prominent typical increase in G’ and G’’ with increasing frequency. PLA/PBS (60/40 wt%) showed almost same behaviour like PLA. The addition of PBS with (10 and 20 wt%) resulted in the gradual increase in the G’ and G’’ which indicated a further increased entanglement density. But the blends with 40/60 wt% and 20/80 wt% (PLA/PBS) concentration decreased compared to the neat PLA, and falls between the neat polymers. At high frequencies, the values of G’ of PBS and PLA/PBS (20/80 wt%) are practically unaffected by the frequency. The lower G’ of the blends is supposed to be originated from the decrease in molecular entanglements in the blends [37]. These results are important since they indicated that the optimal processing conditions for shaping operations of the blends could be quite different as compared to those for shaping operations of pure PLA. It should thus be possible to significantly reduce the processing temperature in shaping operations with increase content of PBS. From rheological results, it is clear that the optimal processing conditions for shaping operations of the blends could be quite different as compared to those for shaping operations of pure PLA. The viscosities of blend clearly increased when PBS increased up to 20 wt% compare to neat PLA. This increased in viscosities was good to produce PLA/PBS blend fibres.

The dynamic viscosities of the neat polymers and their blends as a function of frequency at

![Fig. 3: The storage modulus (a), loss modulus (b), and viscosities (c) of PLA/PBS blends](image-url)
180°C are shown in Fig. 3 (c). The high viscosity at a low shear rate provided the integrity of the product during extrusion, and the low viscosity at a high shear rate enables low injection pressure, high injection speed and less time of the injection cycle [38]. PLA/PBS blend of 90/10 and 80/20% wt% showed a shear thinning behavior at low frequencies. The polymers, PLA, PBS and PLA/PBS (40/60 wt% and 20/80 wt%) exhibited almost Newtonian behavior in the investigated frequency range. The PBS showed lower viscosity and PLA/PBS (60/40 wt%) showed almost same behavior as PLA. The viscosities of blend clearly increased when PBS increased up to 20 wt% compare to neat PLA, while (40/60 wt% and 20/80 wt%) PBS content blend composition showed viscosities between the neat polymers. The decreased melt viscosity of the blend can be related to an increased free volume due to the plasticization by PBS.

4.4 Mechanical Properties

Fig. 4 (a) showed tensile strength of various PLA/PBS blend compositions. Among these compositions, neat PLA has a higher value (about 61.6 MPa) of the tensile strength. With the increase of PBS content, the tensile strength was decreased slowly up to 20wt%, and then decreased fast due to the poor stress transfer across the phase of each polymer. Fig. 4 (b) exhibited elongation at break for various PLA/PBS blend compositions. Elongation was increased with increased PBS content; this may be attributed to the more elastic characteristic of the neat PBS matrix. Pure PBS demonstrated an amazing value of elongation (about 224%). Fracture behavior in the tensile test changed from the brittle fracture of neat PLA to the ductile fracture of the blend during the test.

Impact strength of PLA/PBS blends with PBS contents was shown in Fig. 4 (c). Impact strength of the blends was higher than neat PLA. We could observe that by increasing PBS content, the impact strength had also improved. Like a typical rubber toughening system, a remarkable improvement of about two times of pure PLA in impact strength can be realized by using 60 wt% PBS in PLA and again decreased by using 80 wt% PBS in PLA. Improvement in impact strength might be due to high flexibility of PBS. Thus, the effect of polymer blends was exhibited in the impact performance.

![Graphs showing tensile strength, elongation, and impact strength](image)

Fig. 4: Tensile strength (a), elongation (b), and impact strength (c) of PLA/PBS blends
5 Conclusion

The blends of PLA and PBS were prepared with various compositions. The blends were extruded and their molded properties were examined. The thermal stability of PLA/PBS (60 wt% / 40 wt%) blend is higher compared to the neat PLA. The weight loss of PLA/PBS 40/60 wt% was lower than neat polymers due to its difference of morphology. This indicates that the PLA/PBS blends have an effect on the thermal stability and this may be due to the thermal stability of PBS. DSC thermograms of blends indicated that the thermal properties of PLA did not change noticeably when blended with PBS. However the crystallinity of blends improved. Rheological results showed that the addition of PBS with (10 and 20 wt%) resulted in the gradual increase in the $G'$ and $G''$ which indicates a further increased entanglement density. But the blends with 40/60 wt% and 20/80 wt% (PLA/PBS) concentration decreased compared to neat PLA. Viscosities of blend clear increased when PBS increased up to 20 wt% compare with neat PLA, while (40/60 wt% and 20/80 wt%) PBS content blends composition showed viscosities between the neat polymers. Dynamic mechanical analysis showed that the storage modulus of all blends PLA exhibited lower than PLA. And the glass transition of PLA was 60°C and 10 wt% of PBS Tg decreased to 57°C indicated that PLA and PBS have partial miscibility. The tensile strength and modulus of blends decreased with the increasing PBS content but impact strength has improved about two times than pure PLA. The above results are analyzed to understand the effect of addition of PBS in the PLA to decrease the brittleness and elongation properties of the blends. It is clear that the addition of up to 20 wt% of PBS in the PLA/PBS blend was appropriate to be used as fibers and the 60 wt% of PBS in the blends would be suitable for packaging applications.

References


