Physical and rheological properties of plasticized linear and branched PLA

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Abstract

Extrusion of Poly(lactic acid) (PLA) is difficult to carry out due to the brittleness and low melt strength of PLA. In this investigation, linear Poly(lactic acid) (L-PLA) and branched (B-PLA) were plasticized with poly(ethylene glycol) (PEG) having $M_w$ of 1,000 g/mol in various PEG concentrations (0, 5, 10, 15 and 20 wt%). In addition rheological, thermal and mechanical properties were also investigated in this study. In relation to the plasticizer content, dynamic rheological studies showed that the plasticized linear and branched PLA with higher PEG loading have lower viscosity and elastic properties than that of pure PLA. Storage modulus decreased with PEG loading at all frequencies and exhibited weak frequency dependence with increasing PEG content. As expected, plasticizing both linear and branched PLA lowered the glass transition temperature and modified the crystallization characteristics. Moreover, the toughness was increased by plasticizing up to 15 wt% of B-PLA and up to 10 wt% of L-PLA. However, there was decreasing in toughness due to phase separation of PEG phase in the PLA matrix at 20 wt% and 15–20 wt% of B-PLA and L-PLA, respectively. Therefore, the combination usage of branching and plasticizing showed the better properties both the melt stability and the ability to plastic deformation of PLA to meet the requirements for further.

Keywords: linear poly(lactic acid), branched poly(lactic acid), plasticization

1. Introduction

Poly(lactic acid) (PLA) is currently receiving attention because of its production from renewable, rather than from petrochemical sources (Henton \textit{et al.}, 2005). It is likely to become competitive with lower-priced commodity polymers in near future. PLA is a thermoplastic with a glass transition temperature around 65°C, a melting point around 175°C and a degree of crystallization around 70%. PLA possesses good mechanical properties, with elastic modulus and tensile strength in the range of 3.2–3.7 GPa and 55–60 MPa, respectively (Baiardo \textit{et al.}, 2003). PLA uses in film packaging applications would be highly desirable due to its environmentally friendly nature. However, this requires film extrusion of PLA to be performed. As known, linear PLA have a low degree of crystallization and very low melt viscosity, which give a comparative brittleness and fabric ability (Martin and Averous, 2001; Kim \textit{et al.}, 2004). So it is necessary to modify the physical properties of the polymer by changing in structure.

Two routes may be considered. The first one is to introduce branched structure to stabilize the melt viscosity and mechanical properties. A second possibility is to add a plasticizer which weakens the intermolecular force between polymer chains. Consequently, there is a change in free volume that causes reduction of glass transition temperature ($T_g$) and increase in flexibility in the system. Many studies have attempted to improve mechanical and rheological properties by modifying chain architecture (Ouchi \textit{et al.}, 2006) or blending between linear and branched PLA (Lehermeier, 2001). The study of chain architecture modification carried out by Ouchi \textit{et al.} (2006) reported that the branched PLA film exhibited a lower $T_g$, melting temperature ($T_m$), crystallinity, Young’s modulus and a higher strain at break than that of the corresponding linear PLA film. Whilst, the rheology of blends of linear and branched PLA architectures has been carried out by Lehermeier \textit{et al.} (2001). The authors found that both the zero shear viscosity and the elasticity increased with increasing branched content. The second route towards increased ductility is the addition of a plasticizer to increase free volume and enhance chain mobility. Possible plasticizers for PLA include oligomeric lactic acid, lactide, (Sinclair, 1993) polyethylene glycol (PEG) (Sheth \textit{et al.}, 1997) and low molecular weight esters such as citrates (Ljungberg and Wesslen, 2002). These blends have been shown to improve the flexibility of PLA. The selection of a plasticizer to be used in a specific PLA composition requires the consid-
eration of many criteria: compatibility, low volatility, resistance to migration, extraction during service life, lack of toxicity, etc. (Hansen, 2004).

Low molecular weight PEG is the most suitable material to be classed as an impact modifier for PLA due to its miscibility, biodegradability and food contactable applications (Jacobsen and Fritz, 1999; Baiardo et al., 2003; Kulinski and Piorkowska, 2005; Pillin et al., 2006). Recent studies (Baiardo et al., 2003; Pillin et al., 2006) of PLA plasticized with PEG in various contents have shown a limit of miscibility of polymer blends. The PLA blended to PEGs became very brittle as a function of plasticizer content and molecular weight. The plasticizing efficiency increased with decreasing molecular weight of PEG. In contrast, at the same molecular weight of PEG, material became brittle at higher content because of a lack of cohesion between the separate phases.

In this research, PEG, as a plasticizer, will be blended with linear and branched PLA to investigate and compare the effect on the thermal, mechanical and rheological properties on both structures of PLAs while at the same time retaining its biodegradability and food contact status. Surprisingly, there is very little literature examining the combined effects of branching and plasticization on the mechanical and rheological properties of PLA. Combining branching and plasticizers could have higher melt viscosity and more flexible polymer, due to increase in chain entanglement and the enhanced chain mobility.

2. Experimental

2.1. Materials

The Linear Poly(lactic acid, L-PLA) (4032D-grade) from NatureWorks produced by Cargill Dow LLC, used in this study, comprised of 2% D-LA content. Branched PLA (B-PLA) was produced directly from L-PLA by reactive extrusion. Polyethylene glycol (molecular weight 1000 g/mol), a food-contact approved grade from Sigma–Aldrich, was chosen as a plasticizer for both PLAs. The materials used and their properties are listed in Table 1.

![Fig. 1. Reactive extrusion process diagram.](image-url)

Table 1. Properties of PLAs and plasticizer used in this study

<table>
<thead>
<tr>
<th>Materials</th>
<th>$M_w$ (g/mol)</th>
<th>$M_n$ (g/mol)</th>
<th>$T_m$ (°C)</th>
<th>$T_g$ (°C)</th>
<th>MFI (g/10 min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Linear Poly(lactic acid) NatureWorks 4032 D (L-PLA)</td>
<td>155,000a</td>
<td>93,200a</td>
<td>169</td>
<td>61</td>
<td>7.72</td>
</tr>
<tr>
<td>2. Branched Poly(lactic acid) (B-PLA)</td>
<td>193,600°</td>
<td>64,100°</td>
<td>169</td>
<td>63</td>
<td>5.60</td>
</tr>
<tr>
<td>3. Poly(ethylene glycol) (PEG)</td>
<td>1,000b</td>
<td>-</td>
<td>40</td>
<td>-70</td>
<td>-</td>
</tr>
</tbody>
</table>

* Determined by Gel Permeation Chromatography (GPC) versus polystyrene standards.
* As stated by the manufacturer.
* Determined by Differential Scanning Calorimetry (DSC).
* Determined by Melt Flow Indexer.
were preliminarily heated to 200°C and cooled to -20°C. The samples were then set from -20°C to 190°C at 10°C/min before a second heating scan from -20°C to 200°C at 10°C/min scan rate was carried out. During the second heating scan the glass transition, cold crystallization and melting temperature of the material could be determined; whilst the crystallization temperature was determined from the cooling scan. The degree of crystallinity of all samples were calculated by equation (1).

\[
\text{Crystallinity(\%)} = \frac{\Delta H_m - \Delta H_{cc}/\Phi_{PLA}}{93.6} \times 100
\]  

Most commonly, an enthalpy of fusion of 93.6 J/g is used for a 100% crystalline Poly(L-lactic acid), PLLA or Poly(D-lactic acid), PDLA homopolymers (Fisher et al., 1973), where \(\Delta H_m\) is the measured heat of fusion and \(\Delta H_{cc}\) is the heat of cold crystallization. This value is used throughout the PLA literature. \(\Phi_{PLA}\) is the PLA content in the component.

2.3. Blending conditions

Both PLA pellets were dried in an oven under vacuum at 50°C overnight (12–15 hrs) prior to blending. Drying was necessary to minimize the hydrolytic degradation of the polymers during melt processing in the extruder. Both PLA and PEG were melt-blended using a Brabender twin-screw extruder in the ratio of 100/0, 95/5, 90/10, 85/15 and 80/20 where the first and second number represent L-PLA or B-PLA and PEG by weight percentage, respectively. For better comparison, the pure PLA sample was also processed in the same twin screw extruder and processing conditions to ensure identical thermal history with those of PLA/PEG blends. Dry-mixing of each polymer was first carried out in a zip-lock bag before blending. The twin screw extruder had a screw diameter of 17.8 mm and an L/D ratio of 40. The extruder had three controlled temperature zones which were set from 180°C (next to the feeding segment), 190°C (Compression zone) and 200°C (die adaptor). The screw speed was maintained at 30 rpm for all runs. Subsequently, plasticized L-PLA and B-PLA pellets were dried again under vacuum at 50°C overnight prior to sample preparation by injection and compression molding.

2.4. Differential scanning calorimetry

Differential scanning calorimetry (DSC) study was carried out with a DSC TA instrument 2920. The samples were preliminarily heated to 200°C to discard any anterior thermal history and held at that temperature for 5 min. It was then cooled to -20°C at a rate of 10°C/min and kept at -20°C for 5 min before a second heating scan from -20 to 200°C at 10°C/min scan rate was carried out. During the first and second number represent L-PLA or B-PLA and PEG by weight percentage, respectively.
behaviour of these L-PLA/PEG and B-PLA/PEG blends with varying PEG concentration was necessary.

Fig. 2 shows a direct comparison of the rheological properties for the linear and branched of PLA at 180°C. Unprocessed branched PLA did not show a clear Newtonian region in the measured region of frequency. In contrast, unprocessed linear PLA exhibited a Newtonian plateau at low frequency and seemed to be shear-thinning at high frequency. As expected, behaviour for a material with long branches is evident with high η' and G' but at higher frequency branched PLA shear thinned stronger than the linear material. Branching is often introduced to modify the flow properties of polymeric materials for specific forming operations. The general effects associated with branching are reasonably well understood (Dealy and Wissbrun, 1990) when the branch length exceeds some critical value that the branches themselves entangle and lead to an increase in the viscosity for a comparable molecular weight.

According to Fig. 3, plasticizing of both PLA with PEG showed the rheological behaviour are pseudoplastic and exhibit shear thinning behaviour. However, both plasticized B-PLA and L-PLA showed slightly Newtonian-like behavior at higher PEG content as decreasing in slope over the shear thinning region values. Considerably, plasticized L-PLA and B-PLA also showed a decrease in zero-shear viscosity with PEG concentration increase as shown in Tables 3 and 4. In view of the fact that the increase of PEG content further promotes the disentanglement of chains due to the plasticization effect of PEG.

The zero-shear viscosity was calculated by the modified Cross model as follows (Dealy and Wissbrun, 1990):

\[ \eta = \frac{\eta_0}{[1 + (\tau_0/\gamma)^m]} \]  

(2)

where \( \eta_0 \) represents the zero shear rate viscosity (Pa.s), \( \tau_0 \) represents the characteristic relaxation time (s), \( m \) characterizes the slope of the line over the pseudoplastic region in the logarithmic plot and \( r^2 \) refers to the correlation coefficient of the equation.

Moreover, the degradation in PLA during processing in the presence of plasticizers with ester groups could also be due to potential transesterification reactions leading to a decrease of PLA molecular weights (Murariu et al., 2008) and resulted in a decrease in PLA viscosity.

The corresponding storage modulus for these blends is shown in Fig. 4. Storage modulus of linear and branched PLA/PEG blends were decreased with increasing PEG concentration at all frequency. However, at low-frequency G' of all blends presented lower frequency dependency. This is accepted to be attributed to the change of the shape of the discrete phase in the polymer matrix during the oscillatory shear deformation, namely shape relaxation (Ferry, 1980; Bousmina et al., 1995).

In this investigation, at medium to low frequency region the storage modulus exhibited weak frequency dependency with increasing PEG content. However it illustrated the discrete phase as well in the matrix if the plasticizer saturation point was reached. As seen in Fig. 4, the slopes of
log $G'$ vs. log $\omega$ for the pure L-PLA and B-PLA were close to 2 and 1, respectively, similar to the behaviour of thermorheologically simple polymer in the terminal regime. In contrast, the slopes of the storage moduli, in the terminal region of low frequencies (0.1–1 rad/s), for plasticized L-PLA and B-PLA were much smaller than 1 (in fact close to 0.5), especially for L-PLA/PEG blends at 15 wt% and 20 wt% and B-PLA/PEG blend at 20 wt%. Lee et al. (2003) reported that the experimental values of the slope for $G'$ obtained from either phase separated or degraded polymer blends varied between 0.5 and 1. Therefore, the small values of these exponents suggested that the high concentration of PEG may have contributed to the phase separation in these blends as can be verified presently in the thermal and mechanical characterization.

### 3.2. Thermal properties

DSC experiments were carried out to investigate the thermal properties of the blended materials. Figs. 5 and 6 show DSC traces comparing B-PLA and L-PLA with different contents of PEG blends, respectively. The curves display crystallization, glass transition, cold crystallization, and melting peaks. The thermal characteristics are summarized in Tables 5 and 6. As expected, the un-processed B-PLA and L-PLA exhibited no crystallization peak upon cooling rate at 10°C/min but the peak has become slightly visible when extruded. According to a number of observations (Jacobsen and Fritz, 1999; Di Lorenzo, 2005; Kulinski and Piorkowska, 2005; Li and Huneault, 2007), even at high L-LA content, PLA crystallization is typically too slow to develop significant crystallinity unless the crystallization is induced by strain from processes used to produce biaxially oriented films or bottles. Therefore, as the PEG content was increased up to 20%, a sharp crystallization peak upon cooling appears with a peak temperature range 91–100°C as shown in Table 5 (B-PLA) and Table 6 (L-PLA). The addition of a plasticizer would increase the polymer chain mobility and would enhance the crystallization rate by reducing the energy required during crystallization for the chain folding process.

However, there was an irregular characteristic of crystallization temperature, $T_c$, in both plasticizing B-PLA and L-PLA which showed sudden decrease in the presence of a small amount of plasticizer of 5 wt% PEG. This can be explained that during the formation of PLA crystals at higher temperature than the formation of PEG crystals. Some amounts of PEG probably could be trapped in the intra-spherulitic region of PLA and led to hindering the crystallization of PLA. Nevertheless, addition more wt% of PEG would be able to enhance the crystallization rate of both B-PLA and L-PLA as seen in Tables 5 and 6.

On subsequent heating, thermograms showed the glass transition, $T_g$, cold crystallization, $T_c$, and melting tem-

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**Table 3. Rheology characterization of plasticized B-PLA melts**

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 wt% PEG</th>
<th>5 wt% PEG</th>
<th>10 wt% PEG</th>
<th>15 wt% PEG</th>
<th>20 wt% PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$</td>
<td>1996</td>
<td>856</td>
<td>297</td>
<td>242</td>
<td>199</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>0.049</td>
<td>0.059</td>
<td>0.010</td>
<td>0.004</td>
<td>0.001</td>
</tr>
<tr>
<td>$m$</td>
<td>0.25</td>
<td>0.17</td>
<td>0.11</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.994</td>
<td>0.918</td>
<td>0.932</td>
<td>0.925</td>
<td>0.925</td>
</tr>
</tbody>
</table>

**Table 4. Rheology characterization of plasticized L-PLA melts**

<table>
<thead>
<tr>
<th>Sample</th>
<th>0 wt% PEG</th>
<th>5 wt% PEG</th>
<th>10 wt% PEG</th>
<th>15 wt% PEG</th>
<th>20 wt% PEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$</td>
<td>834</td>
<td>474</td>
<td>301</td>
<td>204</td>
<td>117</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>0.005</td>
<td>0.009</td>
<td>0.002</td>
<td>0.001</td>
<td>0.0005</td>
</tr>
<tr>
<td>$m$</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>$r^2$</td>
<td>0.889</td>
<td>0.903</td>
<td>0.845</td>
<td>0.899</td>
<td>0.919</td>
</tr>
</tbody>
</table>

**Fig. 4.** Comparison of the storage modulus for plasticized (a) branched and (b) linear of PLA at 180°C.
temperature, $T_m$, of each blend. The $T_g$ of both unplasticized L-PLA and B-PLA was around 60°C. As the content of plasticizers increased up to 20 wt%, the glass transition temperature dropped to approximately between 48°C to 33°C. Moreover, the incorporation of PEG decreased cold crystallization temperature by approximately 20°C and narrowed the peak width as shown in Fig. 5(b) and Fig. 6(b), indicating an enhanced crystallization of PLAs. For samples containing higher PEG content, cold crystallization was no longer visible, suggesting that unprocessed B-PLA and L-PLA did not have the ability to complete the crystallization process at cooling stage and hence displayed very low crystallinity. Therefore, it could be concluded that the addition of PEG greatly increased the crystallization rate of both B-PLA and PLA.

The subsequent melting temperature of PLAs shifts slightly to lower temperature with blend composition. It clearly appears that PEG induced a decrease in both PLAs’ melting point as already noticed by Younes and Cohn (1988). The significant explanation was a lower capacity of the short chains of PEG have to crystallize and their high mobility, which are powerful enough to plasticize PLA chains. Tables 5 and 6 also show the crystallinity of the blends which were determined from Eq. (1). PLA is expected to crystallize up to a maximum level of 40–45% which corresponds to 37–42 J/g endothermal peaks (using 93 J/g as the theoretical value for the heat of fusion of PLA crystals (Fisher et al., 1973)). In this investigation, the plasticized B-PLA showed crystallinity between 29 and 41% for all the four different PEG contents examined while the higher crystallinity could be seen in plasticized L-PLA at the same PEG content. On the other hand, Figs. 5(b) and 6(b) have shown the small melting peak of PEG at high plasticizer content that probably was the phase-separation of pure PEG in these blends.

Moreover, there is a double peak of melting peak at 0 wt% PEG in Fig. 5(b). There are two reasons why double peaks were observed. Firstly, few authors (Nijenhuis et al., 1996) had reported this behaviour as a result of lamellar rearrangement during crystallization of PLA: low-temperature peak or shoulder was formed on the melting endotherm of the original crystallites, and the high-temperature peak was formed on the melting endotherm of the recrystal crystallites. In another case, the two melting peaks may be a result of the difference of crystalline structure that can exist in PLA as described by Cartier et al. (2004).

| Table 5. Results from DSC for the B-PLA/PEG Blends |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| PEG content (wt%) | Cooling | Subsequent heating |
|                 | $T_g$ (°C) | $\Delta H$ (J g$^{-1}$) | $T_g$ (°C) | $\Delta H$ (J g$^{-1}$) | $T_m$ (°C) | $\Delta H$ (J g$^{-1}$) | $X_c$ (%) |
| Unprocessed B-PLA | - | - | 63 | 117 | 17 | 170 | 21 | 4 |
| 0 | 98 | 2 | 63 | 114 | 15 | 170 | 24 | 9 |
| 5 | 91 | 9 | 49 | 97 | 6 | 170 | 32 | 29 |
| 10 | 94 | 26 | 35 | 91 | 1 | 168 | 29 | 34 |
| 15 | 97 | 26 | 34 | - | - | 168 | 30 | 38 |
| 20 | 100 | 27 | 33 | - | - | 167 | 31 | 41 |

| Table 6. Results from DSC for the L-PLA/PEG Blends |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| PEG Content (wt%) | Cooling | Subsequent Heating |
|                 | $T_g$ (°C) | $\Delta H$ (J g$^{-1}$) | $T_g$ (°C) | $\Delta H$ (J g$^{-1}$) | $T_m$ (°C) | $\Delta H$ (J g$^{-1}$) | $X_c$ (%) |
| Unprocessed L-PLA | - | - | 61 | - | - | 169 | 12 | 13 |
| 0 | 96 | 12 | 62 | 100 | 12 | 171 | 38 | 27 |
| 5 | 90 | 13 | 46 | 92 | 7 | 170 | 39 | 36 |
| 10 | 95 | 21 | 38 | 90 | 1 | 170 | 34 | 40 |
| 15 | 98 | 30 | 33 | - | - | 168 | 30 | 39 |
| 20 | 102 | 30 | 33 | - | - | 167 | 33 | 44 |
Physical and rheological properties of plasticized linear and branched PLA

It was also found that the endotherm of the low-temperature peak of melting suddenly disappeared after PEG addition. This behaviour indicated that plasticizer made crystallization of PLA more easier and complete. This result was in agreement with the disappearance of cold crystallization peak.

Similarly, linear PLA/PEG and branched PLA/PEG blends showed that glass transition, cold crystallization and melting temperatures were decreased while crystallization peak and % crystallinity were increased. Additionally, the presence of small melting peak and crystallization peak of PEG persistently occurred at high plasticizer content as a result of PEG phase separation. This behaviour could be observed at plasticized B-PLA with 20 wt% PEG whereas phase segregation in linear PLA/PEG blends was found at plasticizer at 15~20 wt%. In this investigation the phase separation was obviously driven by an increase of plasticizer content in the amorphous phase. Another evidence of the phase separation in this investigation was also found by SEM micrograph as shown in Figs. 7(e), (i) and (j).

### 3.3. Impact properties

The concept of improving the impact strength of PLA by introducing plasticizers in the matrix was examined. Clearly, it could be seen that the presence of PEG in PLAs enhanced the toughness of branched and linear PLA by increasing the impact strength. As shown in Fig. 8, the impact strength of plasticized B-PLA exhibited the higher values up to 34 J/m for 15 wt% PEG and showed values higher than the plasticized L-PLA at all PEG content, even though, there was a decrease in impact strength at 20 wt% PEG of B-PLA and 15~20 wt% of L-PLA. As supposed the decrease in impact strength would be observed at higher PEG content as a result of phase separation of PEG.

This behaviour was supported by SEM micrographs of the impact-fractured surfaces in Fig. 7. The SEM micrographs showed rather brittle fracture of pure PLA with little amount of plastic deformation with lateral contraction of the examined bar. When both PLAs were plasticized with increasing PEG loading, the fractured surface has shown more plastic deformation as a ductile material. In addition, the formation of more fibrils could be seen on the...
surface at higher PEG content in both PLA. However, there were the distribution of white round shape and also a smooth fractured surface at PEG loading of 20 wt% of B-PLA and 15–20 wt% of L-PLA. This was probably caused by the accumulation of PEG during phase separation that can be also proved with thermal characterization.

4. Conclusions

This paper demonstrated that plasticizing of B-PLA and L-PLA with PEG could produce a more flexible and higher melt viscosity material with different rheological and mechanical properties. It was found that the plasticized linear and branched PLA with higher PEG loading produced lower viscosity and elastic properties compared pure PLA. Storage modulus decreased with PEG loading at all frequencies and exhibited weak frequency dependence with increasing PEG content. Definitely, the introduction of branching into PLA chain has the ability to modify the melt viscosity of PLA. When branch length exceeds some critical value and the branches themselves entangle it will lead to an increase in viscosity for a comparable molecular weight of the linear polymer.

Moreover, plasticized PLA in both chain structures lowered the glass transition temperature and modified the crystallization characteristics. The toughness of the blends could be confirmed by the increase in impact strength values and the evidences from SEM micrographs.

B-PLA and L-PLA blended with PEG became very brittle at higher plasticizer content due to phase separation of PEG phase as evidences from SEM micrographs and thermal characteristic. It clearly appeared that the blends were miscible at 5 wt% and 10 wt% PEG content for L-PLA/PEG blends and at 5, 10 and 15 wt% PEG content for B-PLA/PEG blends.

Eventually, plasticized branched PLA showed higher melt viscosity and flexibility compared to the plasticizing linear PLA.
References

Younes, H. and D. Cohn, 1988, European Polymer Journal 24, 765.