Morphologies and Properties of Linear Low Density Polyethylene/Poly(butylene adipate-co-terephthalate) Films

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Abstract:

The aim of this research is to prepare polymer blends of linear-low density polyethylene (LLDPE) and poly(butylene adipate-co-terephthalate) (PBAT) at the ratio of LLDPE/PBAT 100/0, 90/10, 80/20, 70/30 and 0/100 by cast film extrusion with adding low density polyethylene-graft-maleic anhydride (LDPE-g-MA) as a compatibilizer which is varied from 0, 5, 10 and 15 wt%. The scanning electron (SEM) micrographs of LLDPE/PBAT films showed large particle size of PBAT dispersed in LLDPE phase when PBAT content increased. Miscibility between LLDPE and PBAT phases were improved by incorporation of LDPE-g-MA. As an increase in PBAT concentration, modulus and tensile strength decreased. The mechanical properties, especially tensile strength of LLDPE/PBAT/LDPE-g-MA films were higher than those of LLDPE/PBAT films. Thermal analysis result revealed that incorporation of PBAT and LDPE-g-MA into LLDPE did not affect a change of melting temperature of the polymer blends.

1. Introduction

The advantages of polyethylene (PE) are high crystallinity, good mechanical properties, water barrier, good oxygen permeability and low cost. PE has a variety of applications such as packaging, automotive, electrical and plastic culture. However, the polyolefin is non-biodegradable and plastic wastes produced from the PE are the critical environmental problems. To solve this problem, it could be replaced non-biodegradable polymers with biodegradable polymers such as poly(lactic acid) (PLA), polybutylene succinate (PBS) and poly(butylene adipate-co-terephthalate) (PBAT). Moreover, cost of the biodegradable polymers is higher than that petroleum-based polyolefins. The blending polyolefins and biodegradable polymers is one attractive approach to reduce cost for industrial applications.

In this research, PBAT is selected to blend with linear low-density polyethylene (LLDPE) because PBAT processes mechanical properties similar to LDPE. Moreover, PBAT has higher elongation at break, good water vapor transmission rate (WVTR), oxygen barrier and fully biodegradable property. However, polarity of LLDPE and PBAT are different, leading to immiscibility of LLDPE/PBAT blend. In order to improve miscibility between the polyolefin and PBAT, incorporation of compatibilizer can reduce interface tension and also enhance interfacial adhesion between PBAT and LLDPE phases.

There are many research that use polyethylene-grafted maleic anhydride (PE-g-MA) as a compatibilizer in order to enhance interfacial adhesion between two immiscible polymers, for example in polymer blends of LDPE/PLA² and HDPE/PBS³.

Thus, in this present work, polymer films between LLDPE and PBAT (LLDPE/PBAT) blend were prepared by cast extrusion machine with LDPE-g-MA as a compatibilizer. The effects of LLDPE/PBAT ratios and compatibilizer content on morphology, mechanical properties, thermal properties and oxygen permeability of the films were investigated.
2. Materials and Methods

2.1. Materials

Linear low density polyethylene (LLDPE) film grade (InnoPlus LL7420A). Poly(butylene adipate-co-terephthalate) (PBAT; ecoflex © F Blend C1200). Compatibilizer is low density polyethylene-graft-maleic anhydride (LDPE-g-MA; DuPont™ Fusabond® E226).

2.2. Preparation of polymer blend films

The LLDPE, PBAT and LDPE-g-MA were dried in a vacuum oven at 50° C for 18 hours to remove the moisture before processing. The LLDPE/PBAT blends were prepared at different ratios of 100/0, 90/10, 80/20, 70/30 and 0/100 wt% with adding LDPE-g-MA as the compatibilizer varied from 0, 5, 10 and 15 wt% in a twin screw extruder. The temperature at feed zone and die section of the twin screw extruder was 110 and 150° C, respectively with screw speed of 80 rpm. The extrudates were cooled down and cut into pellets and fed them into a cast film extruder. The temperature profile of the cast film extruder was 150° C at feed zone, 180° C at die and 55° C. The casted film thickness was between 70-90 microns.

2.3 Characterization

2.3.1 Morphology study

Fractured surface morphologies of the uncompatibilized and compatibilized LLDPE/PBAT films were observed by using Field emission scanning electron microscopy (FESEM; TESCAN MIRA3, TESCAN Company) at an acceleration voltage of 15 kV. The specimens were cryo-fractured under liquid nitrogen and soaked in dichloromethane at room temperature for 6 hours to extract the PBAT phase in the polymer blends. The etched surfaces of LLDPE/PBAT films were platinum-coated before observation.

2.3.2 Mechanical testing

The LLDPE/PBAT films with and without LDPE-g-MA were tested by Universal Testing Machine (3300, Instron Co., Ltd.) according to ASTM D882. Initial distance between the grips of 50 mm with rate of 500 mm/min was used for testing. At least 10 replicates of each blend were tested.

2.3.3 Thermal testing

Thermal properties of the polymer blend films were tested on Differential Scanning Calorimeter (DSC; DSC 1 STAR System, Mettler Toledo Co., Ltd.) from -80 to 170 °C at heating and cooling rates of 10 °C/min under nitrogen atmosphere.

2.3.4 Oxygen barrier properties

Oxygen permeability of LLDPE, PBAT and LLDPE/PBAT films was determined by Gas permeability tester (GDP-C, Brugger Co., Ltd.) according to ASTM D1434. The Oxygen permeability of each film was calculated by multiplying the solubility by the diffusion coefficient. At least 3 replicates of each blend were tested.

3. Results & Discussion

3.1 Morphology analysis

Morphology and compatibility of the LLDPE/PBAT films with and without the LDPE-g-MA compatibilizer were observed by scanning electron microscopy (SEM). In this research, the etching method was used to investigate dispersion and size distribution of PBAT in LLDPE matrix. Figure 1 illustrates the etched surface morphologies of uncompatibilized LLDPE/PBAT films at ratios of 90/10, 80/20 and 70/30 at x10,000 magnifications. It can be clearly seen that all blends exhibited typical immiscible blend morphologies that is there was a presence of phase separation between hydrophobic LLDPE phase and hydrophilic PBAT phase, which was formed in particles and unevenly dispersed in the LLDPE matrix. The size of PBAT dispersed in LLDPE phase became larger when PBAT content increased. Figure 2 shows the etched surface morphologies of the LLDPE/PBAT films containing the compatibilizer at higher magnification of
Figure 1 Dichloromethane etched SEM micrographs of uncompatibilized LLDPE/PBAT films at magnifications of x10,000 at various ratios of (a) 90/10, (b) 80/20 and (c) 70/30.

Figure 2 SEM micrographs of the etched surface of uncompatibilized and compatibilized LLDPE/PBAT films at magnifications of x30,000 at various ratios of LLDPE/PBAT with different compatibilizer content.

3.2 Mechanical properties

Mechanical properties of neat LLDPE and PBAT, LLDPE/PBAT and LLDPE/PBAT/PE-g-MA films are presented in Table 1 Young’s modulus of both uncompatibilized and compatibilized blends was lower than that of LLDPE but higher than that of PBAT. Compared with the uncompatibilized blends, the...
blends with PE-g-MA and a random copolymer of ethylene and glycidyl methacrylate as a compatibilizer.

3.3 Differential Scanning Calorimetry analysis

DSC results of neat LLDPE, PBAT and LLDPE/PBAT films with and without compatibilizer are shown in Table 2 Melting temperatures (T_m) of neat LLDPE and PBAT appeared at 120.9 and 121.7 °C, respectively whereas melting enthalpies (∆H_m) of LLDPE and PBAT were around 106.8 and 16.1 J/g, respectively. The higher ∆H_m value in the melting peak indicated possessing a high degree of crystallinity in the blend. This revealed that LLDPE has higher crystallinity than PBAT. In all polymer blends, it was found that there is no two separated melting temperatures of LLDPE and PBAT but a single melting peak around 120-122 °C was observed, corresponding to the T_m of the polymer blend because of overlapping T_m peaks of LLDPE and PBAT. From the DSC result, an increase in PBAT or compatibilizer contents did not significantly change T_m of the binary blend between LLDPE and PBAT. However, the blending PBAT into LLDPE and adding LDPE-g-MA compatibilizer into the blends significantly affected a change in ∆H_m of the blends. The lower ∆H_m (lower crystallization ability) of the binary blends was observed when PBAT content increased. This could attribute that PBAT chains restrained LLDPE crystallization. Similar result was reported by Trongsatitkul et al. for a decrease in crystallinity of LDPE as increasing PLA content. Considering in the LLDPE/PBAT films at the same ratio, the ∆H_m of the blend tended to reduce with an increase in the compatibilizer loading. This result suggested that compatibilizer addition into the blends enhanced interaction between LLDPE and PBAT phases, thus leading to a higher degree of hindering the formation of crystallization in LLDPE. Similar result in reduction of the melting enthalpies for HDPE in HDPE/PLA binary blends with higher compatibilizer content has been reported.

3.4 Oxygen Permeability

The oxygen permeability (OP) of LLDPE, PBAT and the binary blend films

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**Table 1** Mechanical properties of LLDPE/PBAT and LLDPE/PBAT/PE-g-MA films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength* (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
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<tbody>
<tr>
<td>LLDPE</td>
<td>146.85±16.24</td>
<td>25.41±1.11</td>
<td>984.92±34.14</td>
</tr>
<tr>
<td>PBAT</td>
<td>64.88±2.12</td>
<td>17.93±0.53</td>
<td>625.04±30.93</td>
</tr>
<tr>
<td>90-10</td>
<td>115.34±6.69</td>
<td>22.24±0.85</td>
<td>874.63±113.34</td>
</tr>
<tr>
<td>90-10(5)</td>
<td>119.05±2.26</td>
<td>24.75±2.17</td>
<td>960.94±89.27</td>
</tr>
<tr>
<td>90-10(10)</td>
<td>137.81±2.61</td>
<td>24.85±1.33</td>
<td>1094.01±38.96</td>
</tr>
<tr>
<td>90-10(15)</td>
<td>152.79±4.78</td>
<td>26.40±0.87</td>
<td>1006.57±35.2</td>
</tr>
<tr>
<td>80-20</td>
<td>108.61±0.94</td>
<td>20.92±0.98</td>
<td>981.07±37.14</td>
</tr>
<tr>
<td>80-20(5)</td>
<td>107.94±1.09</td>
<td>25.59±1.64</td>
<td>915.70±147.91</td>
</tr>
<tr>
<td>80-20(10)</td>
<td>109.33±4.75</td>
<td>25.72±1.74</td>
<td>993.72±55.01</td>
</tr>
<tr>
<td>80-20(15)</td>
<td>105.40±1.73</td>
<td>25.58±0.61</td>
<td>935.39±23.54</td>
</tr>
<tr>
<td>70-30</td>
<td>98.02±2.05</td>
<td>19.69±1.24</td>
<td>929.93±67.42</td>
</tr>
<tr>
<td>70-30(5)</td>
<td>101.13±5.25</td>
<td>24.26±0.23</td>
<td>915.24±16.65</td>
</tr>
<tr>
<td>70-30(10)</td>
<td>105.41±1.79</td>
<td>25.58±0.61</td>
<td>974.36±17.64</td>
</tr>
<tr>
<td>70-30(15)</td>
<td>111.22±3.08</td>
<td>26.32±2.4</td>
<td>900.04±80.73</td>
</tr>
</tbody>
</table>

*Maximum tensile strength

**Note**: The number in parentheses represents PE-g-MA content in the blends.

**Table 2** Thermal properties of neat polymer and blend films: melting peak temperature (T_m) and melting enthalpy (∆H_m).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ratios</th>
<th>Compatibilizer content</th>
<th>T_m (°C)</th>
<th>∆H_m (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE</td>
<td>120.90</td>
<td>106.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE-g-MA</td>
<td>119.19</td>
<td>110.60</td>
<td></td>
<td></td>
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<tr>
<td>PBAT</td>
<td>121.7</td>
<td>16.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| LLDPE/PBAT | 121.91 | 97.40 | 120.85 | 92.68 |
| 10  | 121.16 | 88.20 | 120.03 | 84.32 |
| 15  | 121.56 | 82.80 | 120.74 | 75.24 |
| 10  | 120.74 | 70.51 | 120.10 | 68.17 |
| 15  | 121.47 | 60.78 | 120.59 | 60.53 |

**3.4 Oxygen Permeability**

The oxygen permeability (OP) of LLDPE, PBAT and the binary blend films
with various ratios of the PE-g-MA content is illustrated in Figure 3. The OP of the neat LLDPE was higher than that of PBAT. This could be explained by solubility parameters (δ) of PBAT, LLDPE, and O₂ gas, which are 18.97, 3.1 and 6.7 (MPa)⁰.⁷ respectively. That is, the solubility parameter of LLDPE is closed to that of oxygen gas than that of PBAT so oxygen gas is likely to be soluble and permeable in the LLDPE phase compared to the PBAT phase. In the case of uncompatibilized LLDPE/PBAT films, the oxygen barrier property increased as an increase in PBAT concentration in the films. A presence of dispersed particles of PBAT phase in the LLDPE matrix led to more indirect and longer diffusion pathways for oxygen molecules through the binary films. According to the SEM result as shown in Figure 1, amount of dispersed PBAT in the blend at higher ratio (70/30) is much greater than the blends with lower PBAT contents (80/20 and 90/10). Therefore, higher particulate content of PBAT provided the increased tortuous paths of the gas molecules. Considering to compatibilizer LLDPE/PBAT films at the same ratio of PBAT, the film containing high quantity of PE-g-MA compatibilizer presented lower oxygen permeability because of possessing the good dispersion of PBAT as well as a greater number of smaller PBAT particles dispersed in the LLDPE phase as represented in the SEM images in Figure 2, leading to increased tortuosity in the films as shown in Figure 4.

![Oxygen permeability of the LLDPE/PBAT films with adding LDPE-g-MA varied from 0, 5, 10 and 15 wt%](image)

**Figure 3** Oxygen permeability of the LLDPE/PBAT films with adding LDPE-g-MA varied from 0, 5, 10 and 15 wt%.

![Oxygen pathways across the LLDPE, LLDPE/PBAT-g-MA and LLDPE/PBAT films.](image)

**Figure 4** Oxygen pathways across the LLDPE, LLDPE/PBAT-g-MA and LLDPE/PBAT films.
4. Conclusion

The SEM results revealed LLDPE/PBAT blends showed immiscibility morphologies with PBAT particles dispersed in the LLDPE matrix. Incorporation of PE-g-MA compatibilizer into the blends can improve interfacial adhesion of the binary blend between LLDPE and PBAT leading to better dispersion and smaller size of PBAT particles in the blends compared the blends without compatibilizer. Moreover, the mechanical properties of the compatibilized LLDPE/PBAT films were higher than those of uncompatibilized LLDPE/PBAT films. The DSC result showed adding PBAT and LDPE-g-MA into LLDPE did not affect a change of melting temperature of the blends. On the contrary, incorporating higher PBAT or compatibilizer contents resulted in a decrease in the melting enthalpies of the blends. The dispersed PBAT particles in the blends could reduce oxygen permeability in the films due to generating tortuous pathways of oxygen across the films. Furthermore, the compatibilized blend containing high content of PE-g-MA provided an enhancement of oxygen barrier property in the LLDPE/PBAT films.

Acknowledgements

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References