Low density polyethylene/poly(butylene adipate-co-terephthalate) films: Effect of a compatibilizer on morphology and properties

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Abstract. Low density polyethylene (LDPE)/poly(butylene) adipate-co-terephthalate (PBAT) blend films were fabricated using a cast film extruder with different content of PBAT (0, 10, 20 and 30 wt%). Polyethylene-graft-maleic anhydride (PE-g-MA) was used as a compatibilizer for the LDPE/PBAT blends. Morphology, mechanical properties, thermal properties, water vapour and oxygen permeability properties of the LDPE/PBAT films with and without adding the compatibilizer were investigated. Scanning electron microscopic (SEM) results revealed that the LDPE/PBAT/PE-g-MA films showed better compatibility and homogeneity between LDPE matrix and PBAT phase. Young’s modulus and tensile strength of the LDPE/PBAT/PE-g-MA films were higher than those of the LDPE/PBAT films. The PBAT content and incorporating PE-g-MA did not affect on melting temperature (T_m) of the LDPE/PBAT blends. On the other hand, melting enthalpies (ΔH_m) of the polymer blends decrease as increase in PBAT concentration and at same content of the PBAT, the melting enthalpies (ΔH_m) of the LDPE/PBAT/PE-g-MA films were higher than those of LDPE/PBAT films. Water vapor transmission rate (WVTR) of the blend films increased but oxygen permeability (OP) decreased when the PBAT content increased. Compared with uncompatibilized LDPE/PBAT films at the same PBAT loading, the compatibilized LDPE/PBAT films provided a lower water vapor barrier whereas the LDPE/PBAT/PE-g-MA films showed a better oxygen barrier.

1. Introduction
Polyethylene (PE) is petroleum-based polyolefin and commonly used in a variety of applications such as packaging, automotive, electrical and agriculture. The PE has many advantages compared with other polyolefins, for examples, high crystallinity, good mechanical properties, water barrier, good oxygen permeability and low price. Nevertheless, the main drawback of PE is non-biodegradable leading to the critical environmental problems from plastic wastes. In the recent year, eco-friendly biodegradable polymer such as poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), polyhydroxybutyrates (PHB), polybutylene succinate (PBS) and poly(butylene adipate-co-terephthalate) (PBAT) etc. have received attention to replace the conventional polyethylene. However, these biodegradable polymers are more expensive than the PE. Thus, blending the PE and biodegradable polymers is one attractive approach not only to reduce cost for industrial applications, but also decrease an extensive use of the non-biodegradable PE. The poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable and compostable aromatic-aliphatic copolyester with higher
flexibility and elongation than PLA and PBS [1]. Moreover, PBAT has a similar properties like low density polyethylene (LDPE) [2] and PBAT also has good water vapor transmission rate (WVTR), oxygen barrier and fully biodegradable property. Thus, the PBAT are suitable for various packaging and agricultural applications [3]. However, polarity of LDPE and PBAT is significantly different, leading to immiscibility of the LDPE/PBAT blend. Thus, in this research, polyethylene-grafted maleic anhydride (PE-g-MA) was used as a compatibilizer and incorporated into the LDPE/PBAT blends in order to enhance interfacial adhesion between LDPE matrix and PBAT phase. The effect of incorporation of the PE-g-MA compatibilizer and the PBAT content on morphology, mechanical and thermal properties as well as water vapor and oxygen barrier properties of the LDPE/PBAT and LDPE/PBAT/PE-g-MA were studies.

2. Experimental
2.1 Materials
Low density polyethylene, LDPE, (InnoPlus LD2426K) with melt flow index (MI) of 3.9 g/10 min was obtained from PTT Global Chemical Company Limited, Thailand. Poly(butylene adipate-co-terephthalate), PBAT, (Ecoflex® F Blend C1200) with MFI of 3.8 g/10 min was supplied by BASF Corporation. Linear low density polyethylene-graft-maleic anhydride, LLDPE-g-MA, (Fusabond® E226) with MFI of 1.5 g/10 min was purchased from Dow Chemical Company as a compatibilizer agent for LDPE/PBAT blends.

2.2 Preparation of LDPE/PBAT and LDPE/PBAT/PE-g-MA blend films
The LDPE, PBAT and PE-g-MA pellets were dried in an oven at 60°C for 8 hours to remove the moisture prior to cast film processing. The LDPE/PBAT and LDPE/PBAT/PE-g-MA blends were prepared at different PBAT contents of 10, 20 and 30 wt% of LDPE with an addition of 10 wt% of PE-g-MA as the compatibilizer in a cast film extruder (Lab Tech Engineering, Thailand). The temperature profile of the cast film extruder was 150, 160, 170, 180 °C with screw speed of 60 rpm and 55°C at chill-roll. The casted film thickness was between 150-200 microns.

2.3 Characterization Methods

Scanning electron microscopy (SEM) analysis
Cryo-fractured surface morphologies of uncompatibilized LDPE/PBAT and compatibilized LDPE/PBAT/PE-g-MA blends were investigated by a Scanning Electron microscope (TM3030, Hitachi, Japan). The fractures surfaces of all films were platinum coated to avoid electrostatic charging prior to analysis.

Tensile properties
Tensile testing of LDPE, PBAT as well as LDPE/PBAT and LDPE/PBAT/PE-g-MA blends was performed by Universal testing machine (Instron 5969, Instron, USA.) according to ASTM D882: Standard Test Method for Tensile Properties of Thin Plastic Sheeting using a load cell of 5kN with initial distance between the grips of 50 mm and speed rate of 500 mm/min. At least 15 replicates of all blends were tested and Young’s modulus, maximum tensile strength and elongation at break were recorded.

Differential scanning calorimetry analysis
Thermal properties of LDPE, PBAT, LDPE/PBAT and LDPE/PBAT/PE-g-MA films were performed by using Differential Scanning Calorimeter (DSC; DSC 1 STAR System, Mettler Toledo Co., Ltd.). The heating and cooling cycles of the samples were operated between -80 to 170 °C with scanning rate of 10 °C/min under nitrogen atmosphere.

Water vapor transmission rate (WVTR)
The WVTR of the sample films were determined according to ASTM E96: Standard Test Methods for Water Vapor Transmission of Materials with the method A (dry cup method). Glass bottles with a diameter of 3.0 cm containing silica gel (0% RH) were covered with the films (thickness of 0.24 mm),
sealed with a parafilm tape and then kept inside a chamber in which relative humidity of 50 ± 3 °C at room temperature. The glass bottles covered with the film were weighted at certain times until 24 days. Weight changes of the glass bottles were plotted vs. times and then slopes of the plot in each sample films were calculated in unit of g/h. The WVTR in unit of g/m²h was defined as the slope divided by test area (m²) of the films. Three replicates of each film formulation were examined to determine the WVTR.

**Oxygen permeability**

Oxygen permeability of all films were measured by Gas permeability tester (GDP-C, Brugger Co., Ltd.) based on an ASTM D1434.

### 3. Results and discussion

**Morphology characterization.**

Effect of the PE-g-MA compatibilizer on phase morphology of LDPE/PBAT blends was study by SEM technique. The cryo-fractured surface morphologies of the LDPE/PBAT and LDPE/PBAT/PE-g-MA blends with different PBAT contents of 10, 20 and 30 wt% is presented in Figure 1. For uncompatibilized LDPE/PBAT blends as shown in Fig. 1(a)-(c), phase separation between the LDPE matrix and PBAT phase was clearly observed and the minor PBAT phase formed in spherical particles dispersed in the matrix. Furthermore, the uncompatibilized blends in all PBAT contents showed some cavities from pull-out of PBAT particles indicating poor adhesion between LDPE and PBAT phases.

However, in the case of the compatibilized LDPE/PBAT blends, incorporation of the PE-g-MA compatibilizer could dramatically reduce the particle size of the PBAT phase and the PBAT particles became very fine particles embedded in the LDPE matrix, which were not clearly visible observed at magnification of 3000x. Besides, there was no appearance of pull-out of PBAT particles from the matrix. These results confirmed that the addition of PE-g-MA compatibilizer could enhance the interfacial adhesion between LDPE matrix and PBAT phase leading a better compatibility of two polymers in the blend, thereby more homogeneous dispersion of PBAT in the LDPE/PBAT blends.

![Figure 1. SEM micrographs of cryo-fractured surfaces of (a) LDPE/PBAT (90/10), (b) LDPE/PBAT (80/20), (c) LDPE/PBAT (70/30), (d) LDPE/PBAT/PE-g-MA (90/10/10), (e) LDPE/PBAT/PE-g-MA (80/20/10) and (f) LDPE/PBAT/PE-g-MA (70/30/10) films at magnification of 3000x.](image)

**Mechanical properties.**

The Young’s modulus, maximum tensile strength and elongation at break of neat LDPE, neat PBAT, uncompatibilized and compatibilized LDPE/PBAT are illustrated in Figure 2 (a)-(c), respectively.
**Figure 2.** Mechanical properties of LDPE, PBAT, uncompatibilized LDPE/PBAT and compatibilized LDPE/PBAT films at various ratios: (a) Young’s Modulus, (b) Maximum tensile strength and (c) Elongation at break.

As seen in Fig. 2, the PBAT showed a lower modulus (72 MPa) with a higher elongation at break (1206 %) when compared to LDPE with modulus and elongation at break of 124 MPa and 837 %, respectively. This is because the PBAT is a random block copolymer with a small degree of crystallization in the polymer structure, thus leading to a low elastic modulus, high flexibility and toughness with respect to the LDPE. However, maximum tensile strength of the PBAT (25 MPa) was higher than that of LDPE (14 MPa), likely due to a presence of aromatic terephthalate groups in PBAT structure, resulting in high tensile strength [4]. In the LDPE/PBAT films with and without compatibilizer, modulus tended to decrease whereas tensile strength and elongation at break became higher as an increase in PBAT content. Compared with the uncompatibilized blend films at same PBAT concentration, it was clearly seen that the compatibilized LDPE/PBAT films provided greater modulus and tensile strength; in contrast, a lower elongation at break was observed. These results indicated that incorporation of the PE-g-MA compatibilizer enhanced interfacial adhesion between LDPE matrix and PBAT phase, resulting from a formation of physical entanglement between PE chains in PE-g-MA and LDPE matrix chains and chemical reaction of MA groups on PE-g-MA with hydroxyl and carboxyl groups of PBAT. This led to improvement of mechanical properties of the compatibilized LDPE/PBAT films.
Differential scanning calorimetry analysis

DSC results including melting temperatures \((T_m)\) and melting enthalpies \((\Delta H_m)\) of LDPE, PBAT, uncompatibilized and compatibilized LDPE/PBAT films are represented in Table 1. The \(T_m\) of neat LDPE and PBAT appeared at 110.62 and 123.41 °C, respectively and the \(\Delta H_m\) of LDPE (121.24 J/g) was higher than that of PBAT (15.65 J/g), indicating higher crystallinity in LDPE compared with PBAT. In all polymer blend films, there was a presence of a single peak of \(T_m\) around 110-111°C, corresponding to the \(T_m\) peak of LDPE phase in the polymer blends and no observation of \(T_m\) peak of PBAT because intensity of the \(T_m\) peak of PBAT was quite low and overlapped with the \(T_m\) peak of LDPE. Moreover, the DSC results revealed that the \(T_m\) of LDPE in all polymer blends did not change when the PBAT content increased. Besides, the \(\Delta H_m\) of the polymer blends decreased as the PBAT concentration, which was probably because the PBAT chains containing bulky aromatic terephthalate groups in the PBAT structure could restrict LDPE crystallization, thus a reduction of \(\Delta H_m\) of the polymer blends. Comparing to the uncompatibilized LDPE/PBAT films at the same content of PBAT, the films containing PE-g-MA compatibilizer gave the higher \(\Delta H_m\) which inferred more crystallinity content in the polymer blends. This result suggested that the compatibilizer improved interfacial interaction and compatibility between LDPE and PBAT phases, thus promoting crystallization formation in the polymer blends.

| Sample           | Compatibilizer content (%) | \(T_m\) (°C) | \(\Delta H_m\) (J/g) |
|------------------|----------------------------|--------------|----------------------|
| LDPE             | -                          | 110.62       | 121.24               |
| 90/10            | 0                          | 110.14       | 94.69                |
| 80/20            | 0                          | 110.35       | 92.69                |
| 70/30            | 0                          | 110.19       | 86.32                |
| 90/10            | 10                         | 110.40       | 105.23               |
| 80/20            | 10                         | 111.06       | 101.4                |
| 70/30            | 10                         | 110.56       | 92.35                |
| PBAT             | -                          | 123.41       | 15.65                |

Water vapor transmission rate (WVTR)

The Water vapor transmission rate results of neat LDPE, neat PBAT, LDPE/PBAT films with and without the PE-g-MA compatibilizer at different the PBAT contents are displayed in Figure 3. Among all films, the PBAT film showed the highest WVTR value indicating poor water vapor barrier property of the PBAT films. This was due to more hydrophilic characteristic of polar functional groups in the PBAT chains such as ester, hydroxyl and carboxyl groups forming intermolecular bonding with water vapor molecules via hydrogen bonding and dipole-dipole interaction. In the case of the LDPE/PBAT films with and without incorporating the PE-g-MA compatibilizer, the WVTR significantly increased as an increasing PBAT content in the films. In addition, it was clearly observed that the WVTR of the compatibilized LDPE/PBAT films was higher than that of the uncompatibilized films at the same PBAT concentration. This may be because the addition of the PE-g-MA compatibilizer led to an increase in polarity of the polymer blend system due to possessing maleic anhydride group in the PE-g-MA chains, resulting in a higher degree of WVTR of the LDPE/PBAT films containing the PE-g-MA.
Figure 3. The Water vapor transmission rate of neat LDPE, neat PBAT, LDPE/PBAT and LDPE/PBAT/PE-g-MA films at ratios of 90/10, 80/20 and 70/30.

Oxygen permeability study

Comparison of the oxygen permeability of neat LDPE, neat PBAT, LDPE/PBAT and LDPE/PBAT/PE-g-MA films was present in Figure 4. The LDPE film exhibited higher oxygen permeability value than that of PBAT film. This result could be explained by considering that solubility parameter ($\delta$) of LDPE ($\delta = 3.1$ MPa$^{1/2}$) [5] is closed to that of O$_2$ gas ($\delta = 6.7$ MPa$^{1/2}$) [6] compared with solubility parameter of PBAT ($\delta = 18.9$ MPa$^{1/2}$) [7], resulting in increment of dissolution of oxygen gas in LDPE film and more penetration of O$_2$ molecules through the LDPE film with respect to PBAT film. Considering the polymer blend films, it was found that the oxygen permeability of the LDPE/PBAT and LDPE/PBAT/PE-g-MA films was lower than the pure LDPE films and decreased proportionally with the increasing order of the PBAT contents. This is possibly because a presence of the PBAT droplets dispersed in the LDPE phase as shown in the SEM images could hinder diffusion path of O$_2$ molecules and prolong the permeation of O$_2$ molecules through the polymer blend films. Besides, it was seen that the compatibilized LDPE/PBAT films provided lower oxygen permeability value, indicating a better barrier property, compared with the uncompatibilized films at the same PBAT loading. These results were be attributed to more homogeneous dispersion of the fine PBAT particles in the LDPE matrix and the better interfacial adhesion between LDPE and PBAT phases which restricted diffusion path of O$_2$ molecules and created longer and more tortuous paths, resulting in a reduction of oxygen permeation through the compatibilized films.

Figure 4. The oxygen permeability of neat LDPE, neat PBAT, LDPE/PBAT and LDPE/PBAT/PE-g-MA films at ratios of 90/10, 80/20 and 70/30.
4. Conclusions
The SEM results showed more homogeneous in morphologies and better compatibility in the LDPE/PBAT with addition of the PE-g-MA compatibilizer. Moreover, it was found that the compatibilized LDPE/PBAT films exhibited superior mechanical properties to those the LDPE/PBAT films without the PE-g-MA, resulting in a greater interfacial adhesion between LDPE and PBAT polymers. Incorporating PE-g-MA compatibilizer into the LDPE/PBAT blends enhanced crystallization ability in the blends and also promoted the oxygen barrier property as well as slightly increased the WVTR with respect to uncompatibilized LDPE/PBAT blends.

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