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Compatibilization of Immiscible Poly(*l*-lactide) and Low Density Polyethylene Blends

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Abstract: Blends of poly(*l*-lactide) (PLA) and low density polyethylene (LDPE) were prepared by melt mixing in order to improve the brittleness of PLA. A reactive compatibilizer with glycidyl methacrylate (GMA), PE-GMA, was required as a compatibilizer due to the immiscibility between PLA and LDPE. It contributes to reduce the domain size of dispersed phase and enhance the tensile properties of PLA/LDPE blends, especially for PLA matrix blends. A reaction product between PLA and PE-GMA, which was formed during melt-mixing and considered to act as a reactive compatibilizer, was characterized using ^{1}H-NMR spectroscopy.

Keywords: Poly(*l*-lactide), Low density polyethylene, Polymer blend, Compatibilization

Introduction

Aliphatic polyesters as biodegradable polymers have been widely investigated in recent years because they are environmentally-friendly and also bio-compatible [1,2]. Among those, poly(*l*-lactide) (PLA) is very attractive from a viewpoint of mass production [3]. However, PLA is brittle at room temperature and hydrolyze easily. Therefore, such disadvantages should be overcome for a wide application of PLA.

Polymer blends has been used as an effective approach to modify the disadvantages of neat polymers [4]. Although an increasing number of miscible blends have been reported in literature [5], most polymer pairs are immiscible because the entropy of mixing in polymer blends is negligibly small. Without special treatment, such blends can not be commercialized due to poor mechanical properties. Even not miscible at molecular level, immiscible polymer blends can be compatibilized by adding a polymeric compatibilizer, which can improve the dispersion and the adhesion of phases and stabilize the morphology [6]. Such compatibilizers can be introduced by adding a premade block or graft copolymer, or by in situ reactive formation during melt processing. Since the former is expensive and is not available for most cases, the latter is generally used for commercial applications.

In this study, we prepare polymer blends of PLA and low density polyethylene (LDPE) by melt-mixing and investigate the effect of reactive compatibilizer on their morphology and tensile properties. LDPE has chosen as a counterpart of PLA due to its superior mechanical properties and major use for packaging. Blends of PLA and LDPE may be a candidate for excellent biodegradable packaging materials.

Experimental

Materials

PLA used in this study was LACTY 9031 obtained from Shimadzu Co., Japan and has the molecular weight of 143,000 g/mol. LDPE was LDPE 751 manufactured by Dow Chem. Three olefinic copolymers were chosen as reactive compatibilizers: EAA, PE-GMA8, and PE-GMA25. EAA and PE-GMA have acrylic acid (AA) and glycidyl methacrylate (GMA) as functional groups, respectively. The number following PE-GMA indicates the weight percent of GMA units in PE-GMA. All polymers were vacuum-dried at 50 °C before use. The characteristics of the polymers used in this study was summarized in Table 1.

Preparation of Polymer Blends

PLA/LDPE blends with and without reactive compatibilizers were prepared by melt-mixing with a Haake batch mixer, operated at 210 °C and the rotor speed of 50 rpm for 10 min, except mentioned. Sample amount per batch was fixed at 50 g and 0.2 wt% thermal stabilizer, Irganox IR225 from Ciba Specialty Chemicals, was added. After mixing, blends were quenched in iced water and then thoroughly vacuum-dried.

Table 1. Characteristics of the polymers used in this study

Polymers	Source	Characteristics	Remarks
PLA	Shimadzu	57 °C (T_g), 169 °C (T_m)	-
LDPE	Dow Chem.	MI = 6.4 g/10 min; 113 °C (T_m)	LDPE751
EAA	Dow Chem.	95 °C (T_m)	Primacor3460[a]
PE-GMA8	Elf-Atochem	-	8 wt% GMA
PE-GMA25	Elf-Atochem	-	25 wt% GMA

[a]AA content = 9.54 %.

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Characterization

Thermal properties of blends were measured using a differential scanning calorimeter (DSC2920 from TA Instruments). After maintaining samples at 210 °C for 3 min to remove thermal history and then quenching rapidly to 10 °C, they were heated with the rate of 20 °C/min. During scanning, melting temperatures (T_m) of PLA and LDPE and cold crystallization temperature (T_c) of PLA were determined.

Morphology of blends was investigated using a field-emission scanning electron microscopy (S-4700, Hitachi) at an acceleration voltage of 5 kV. Samples were fractured at liquid nitrogen temperature and the surface was gold-coated.

^{1}H-NMR spectra were obtained using a 300 MHz ^{1}H-NMR spectrometer (Bruker, AMX-R300) to confirm the formation of reaction products between PLA and PE-GMA during mixing at melt state. 80/20/5 PLA/LDPE/PE-GMA8 blend was subjected to extraction with chloroform ($CHCl_3$) for 24 hr in a Soxhlet. PLA is completely soluble in $CHCl_3$ whereas LDPE and PE-GMA8 insoluble. The $CHCl_3$ soluble fraction was filtered, concentrated and then vacuum-dried. $CDCl_3$ was used as solvent for NMR characterization.

Tensile properties of blends were measured at room temperature using a tensile tester (Shimadzu, Autograph AGS-D) according to ASTM D638M. Specimens with the dimension of 130 mm length, 8 mm width and 1 mm height, respectively, were compression molded at 210 °C. Crosshead speed was 5 mm/min and average values of at least five tests were reported.

Results and Discussion

In order to determine which functional polymers are effective in compatibilizing PLA/LDPE blends the morphology of PLA/olefinic polymers binary blends was investigated, as shown in Figure 1. The blends were prepared by melt mixing at 210 °C using a mini-molder. The fraction of PLA was fixed at 80 wt% and acted as matrix. In the SEM micrograph of 80/20 PLA/LDPE blend, LDPE domains have well defined spherical shape, very broad size distribution, and also smooth fracture surface. This is a typical morphology of immiscible polymer blends. A similar morphology is also observed for the PLA/EAA blend, indicating that AA units in EAA do not affect the compatibility with PLA.

When PE-GMA8 is blended with PLA, its domain size significantly reduces compared to the PLA/LDPE or PLA/EAA blends. For PE-GMA25, as shown in Figure 1(D), the morphology changes much dramatically; even though some small craters corresponding to PE-GMA25 domains separated from PLA matrix during cryofracture are seen, the interface between PLA and PE-GMA25 is not well defined. It is typical morphology observed for compatibilized blend systems. According to Sundararaj and Macosko [7], when reactive polymers are melt-mixed, chemical reactions occur at the interface between them and create graft or block type copolymers. They contribute to reduce coalescence of dispersed

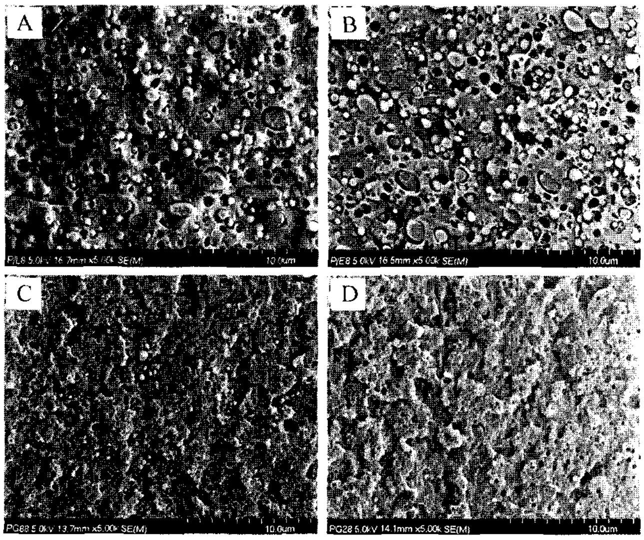
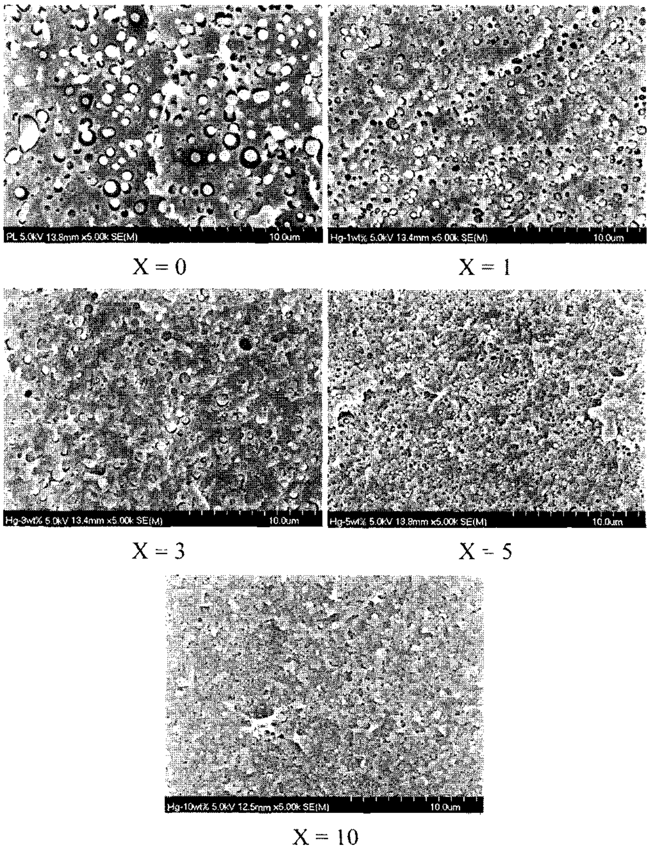


Figure 1. SEM micrographs of binary blends of PLA and (A) LDPE, (B) EAA, and (C) PE-GMA8, and (D) PE-GMA25, respectively. PLA was applied as matrix of 80 wt%.


X = 0 X = 1

X = 3 X = 5

X = 10

Figure 2. SEM micrographs of 80/20 PLA/LDPE blends compatibilized with PE-GMA8. X is the parts of PE-GMA8, by weight, in the blends.

phases and produce the morphology with very fine dispersion. The chemical reactions between PLA and PE-GMA can occur more readily at higher GMA content, leading to the formation of more copolymer chains and thus more effective suppression of coalescence. The reaction products formed between PLA and PE-GMA are going to be characterized using a ^{1}H-NMR spectroscopy, as shown in Figure 5. Based on the result of Figure 1, we use PE-GMA as a reactive compatibilizer for immiscible PLA/LDPE blends.

Figure 2 shows the SEM micrographs of 80/20 PLA/LDPE blends compatibilized with PE-GMA8. When PE-GMA8 is added, the morphology changes dramatically into a more uniform and finer dispersion. At 10 % loading level the dispersed phase of LDPE is not well distinguished with PLA matrix. This indicates that PE-GMA8 effectively acts as reactive compatibilizer at the interface between PLA and LDPE, as expected. Although the decrease is not significant, similar results are also obtained for LDPE matrix blends, as shown in Figure 3. When 10 parts PE-GMA8 are added, very tiny nodes, which are embedded in the LDPE matrix, are observed. The nodes are clearly seen in the magnified SEM micrograph of X = 10 case. This seems to be the PE-GMA8 phase, which is not dissolved in the LDPE matrix due to the immiscibility between LDPE and PE-GMA8. It is well known that the miscibility of polyolefin blends is strongly dependent on the type and content of comonomer, even with similar chemical structure. For example, when PP is melt-mixed with ethylene-propylene random copolymers (EPR), the two is immiscible in the melt (at 200 °C), even the case where EPR contains only 8% of ethylene [8]. Therefore, it is not surprising that the introduction of polar GMA units into PE increases the mismatch in the solubility parameters between LDPE and PE-GMA, $|\delta_{LDPE} - \delta_{PE\text{-}GMA8}|$, and leads to phase-separation.

Figure 4 shows the SEM micrographs of 80/20 PLA/LDPE blends compatibilized with PE-GMA25. Although the size of LDPE domains decreases from 0.9 to 0.5 μm only with one part of PE-GMA25, further increase of PE-GMA25 content does not make the domain size finer. This result is slightly different to that shown in Figure 2 and indicates that higher GMA content in PE-GMA is not always desirable for compatibilizing PLA/LDPE blends.

It is clear from Figures 2 to 4 that the GMA units in PE-GMA have opposite effect on the morphology of PLA/

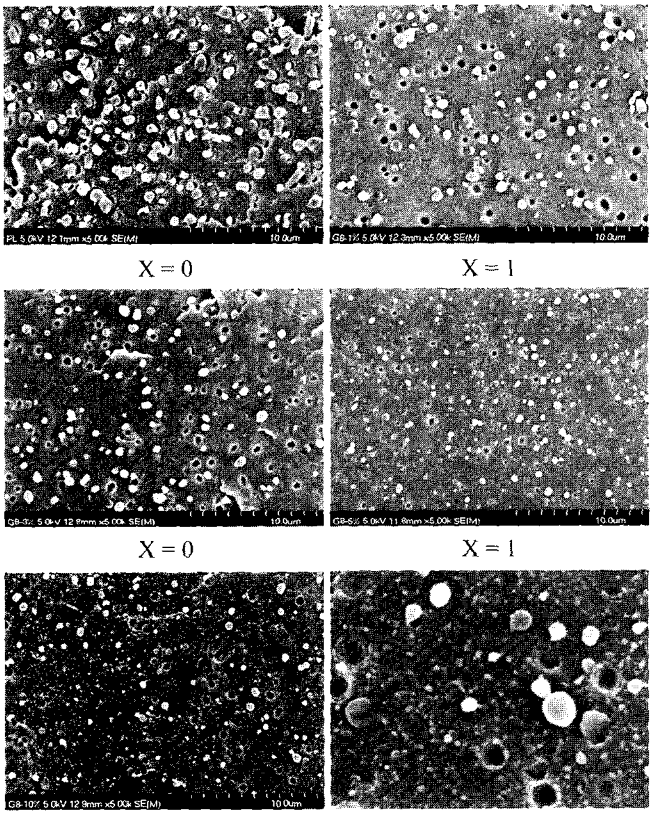

X = 0 X = 1

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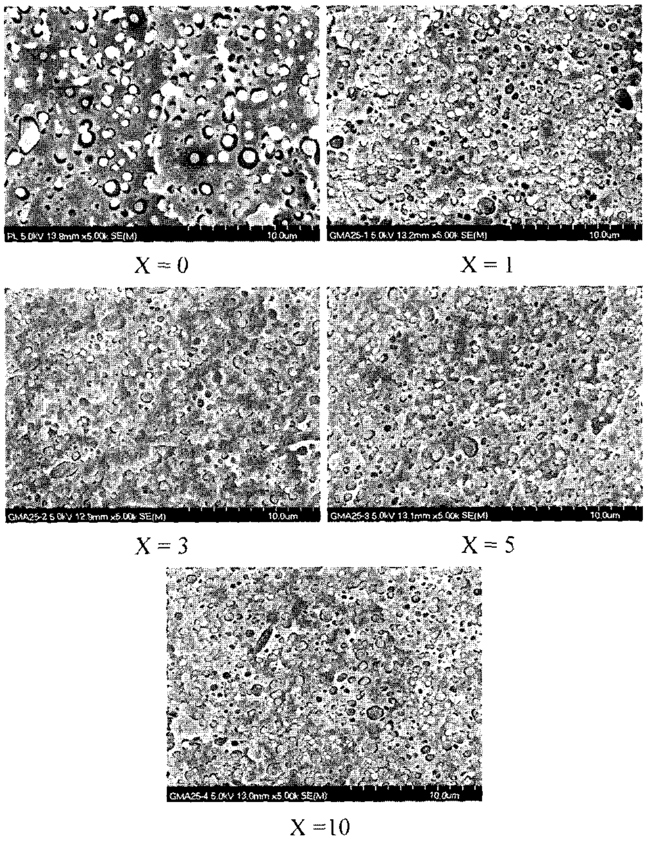
Figure 3. SEM micrographs of 20/80 PLA/LDPE blends compatibilized with PE-GMA8. X is the parts of PE-GMA8, by weight, in the blends.


X = 0 X = 1

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X =10

Figure 4. SEM micrographs of 80/20 PLA/LDPE blends compatibilized with PE-GMA25. X is the parts of PE-GMA25, by weight, in the blends.

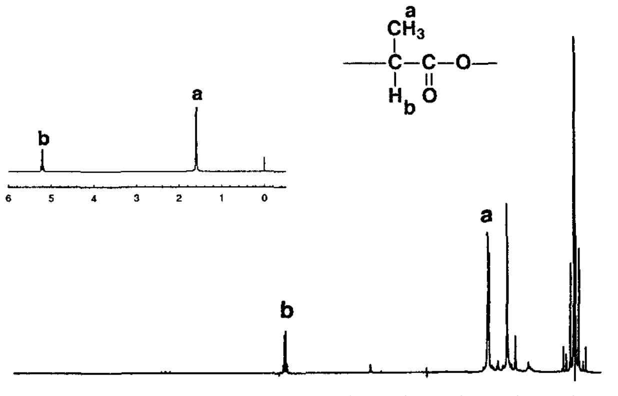
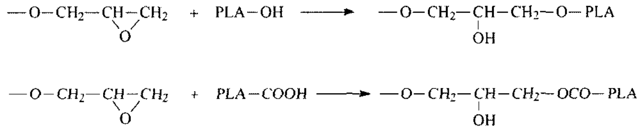


Figure 5. ^{1}H-NMR spectrum of $CHCl_3$-soluble fraction in the 80/20/5 PLA/LDPE/PE-GMA8 blends. The insert represents ^{1}H-NMR spectrum of neat PLA.

LDPE blends. The reaction between PLA and PE-GMA and thus the formation of copolymer chains increase with increasing the GMA content. This is favorable for reducing the size of dispersed phase. On the other hand, the miscibility between LDPE and PE-GMA becomes poorer at higher GMA content, causing the more significant phase separation between LDPE and PE-GMA. The PE-GMA chains separated from the LDPE phase is not effective as compatibilizer, because intermolecular interaction between PLA and PE-GMA does not take place at the interface between PLA and LDPE.

The formation of reaction products between PLA and PE-GMA during melt mixing was characterized using a ^{1}H-NMR spectroscopy. Figure 5 shows the ^{1}H-NMR spectrum of $CHCl_3$-soluble fraction extracted from 80/20/5 PLA/LDPE/PE-GMA8 blend. The spectrum of neat PLA is also shown for comparison. New peaks, not seen in neat PLA, are observed around 1.00 ppm for the ternary blend. Since the protons in -CH_2- in ethylene units have chemical shifts around 1.30 ppm [9], they are considered to come from PE-GMA8 chains. Considering that LDPE and PE-GMA8 are insoluble in $CHCl_3$, the peaks from PE-GMA8 results from a chemical reaction between PLA and GMA in PE-GMA and the formation of chemically linked copolymers during melt mixing.

Copolymers with epoxy groups have been widely used as reactive compatibilizers: for example, styrene-GMA copolymers in poly(ethylene terphthalate) (PET)/PS blends [10] and PE-GMA in PET/PE blends [11]. A major reason for the use of such copolymers is that epoxy can be easily grafted onto many polymers at normal melt processing conditions. Especially, polymers with hydroxy, carboxylic acid, or amine units can be effectively compatibilized using GMA-functionalized copolymers [12]. Since PLA used in this study has the -OH and -COOH groups at the chain ends, it can form interchain linkages with the GMA units in PE-GMA by the following reactions:



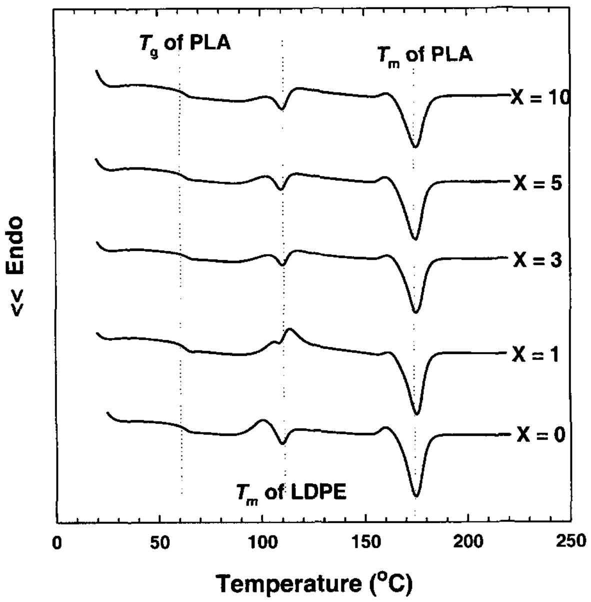


Figure 6. DSC thermograms of 80/20/X PLA/LDPE/PE-GMA8 blends. X is the parts of PE-GMA8, by weight, in the blends.

The resultant products will act as a reactive compatibilizer between PLA and LDPE.

Figure 6 show DSC thermograms of 80/20/X PLA/LDPE/PE-GMA8 ternary blends, where X is the parts of PE-GMA8. Two distinct endotherms around 110 and 170 °C, corresponding to melting temperatures of LDPE and PLA, respectively, are clearly seen. The position and relative size of the endotherms do not change even with 10 parts PE-GMA. Moreover, the T_g of PLA is independent of the addition of PE-GMA8. Broad exotherm around 110 °C is melt-crystallization peak of PLA. The other blend series with the matrix of LDPE show similar tendency (not shown here). The DSC thermograms shown in Figure 6 indicate that PE-GMA8 does not affect the thermal properties of PLA and LDPE. It may be due to that the interchain reactions between PLA and PE-GMA occur at the interface of PLA and PE-GMA. Similar thermal behavior to this blend system has been observed for the polypropylene (PP)/polyamide 6 (PA6) blends compatibilized with PP-g-maleic anhydride (PP-MAh) [13]. Even though PP-MAh is critical to control and stabilize the morphology of the PP/PA6 blends, it does not affect the melting behaviors of PP and PA6, similar to Figure 6.

Mechanical properties of immiscible polymer blends are strongly dependent on the size of dispersed domains and the

Table 2. Tensile properties of PLA/LDPE blends compatibilized with PE-GMA

Blends	Stress at maximum (kgf/mm^2)	Strain at break (%)
PLA/LDPE/PE-GMA8		
80/20/0	0.80	6.6
80/20/5	0.94	77.9
20/80/0	0.72	16.4
20/80/5	1.17	50.5
PLA/LDPE/PE-GMA25		
80/20/5	3.26	4.0
20/80/5	0.76	29.5

interfacial adhesion between matrix and dispersed phase [14, 15]. Good adhesion is essential for appropriate stress transfer without interfacial debonding, if the size of dispersed phase is less than a critical one. The tensile properties of PLA/LDPE/PE-GMA blends are summarized in Table 2. Average values from at least five specimens are given. Except for 80/20/5 blend compatibilized with PE-GMA25, the addition of PE-GMA is effective in enhancing the tensile properties of PLA/LDPE blends. Especially for the PLA matrix blends the contribution of PE-GMA is significant. Although the 80/20 PLA/LDPE blend without PE-GMA8 shows typical brittle fracture behavior, the fracture behavior changes from brittle to ductile fracture when PE-GMA8 is added. The enhancement in tensile properties is the result of reactive compatibilization by PE-GMA; the chemical reaction between PLA and PE-GMA contributes to strengthen the interface between PLA and LDPE. However, we believe that more elaborate work is required in order to completely understand the effect of PE-GMA on mechanical properties of PLA/LDPE/PE-GMA blends.

Conclusions

Immiscible blends of PLA and LDPE were compatibilized using PE-GMA with glycidyl methacrylate as a reactive compatibilizer. A copolymer of ethylene and acrylic acid was not effective. The PE-GMA reduces the domain size of dispersed phase and enhances the tensile properties of PLA/LDPE blends. From ^{1}H-NMR analysis of 80/20/5 PLA/LDPE/PE-GMA8 blend it was confirmed that a chemical reaction occurred between PLA and PE-GMA8 and chemical linked copolymers, which were considered to act as reactive compatibilizers, were formed.

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