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Preparation and characterization of poly(lactic acid)/starch composites toughened with epoxidized soybean oil

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ABSTRACT

Blends of entirely bio-sourced polymers, namely polylactide (PLA) and starch, have been melt-compounded by lab-scale co-extruder with epoxidized soybean oil (ESO) as a reactive compatibilizer. The starch granules were grafted with the maleic anhydride (MA) to enhance its reactivity with ESO. The ready reactions between the epoxy groups on ESO, the MA groups on MA-grafted starch (MGST) and the end carboxylic acid groups of PLA brought blending components together and formed a compatible compound. An elongation at break (EB) of 140% was obtained in the blend of PLA/MGST/ESO (80/10/10), increased from 5% of a pure PLA. The grafting content of the MA on the starch granules primarily determined the compatibility and properties of the ternary blends, which was also affected by the relative amount of MGST and ESO.

1. Introduction

With the environmental concerns and the scarce supply of the crude oil, a revival in the development of bio-based and compostable materials is coming. They are in general being called the "green" materials (Mohanty, Misra, & Drzal, 2002; Mohanty, Misra, & Hinrinchsen, 2000), among which, poly(lactic acid) (PLA) got the most extensive attention due to its good combined properties, including the renewable feedstock, the compostability, and its good mechanical properties, especially the Young's modulus and the stiffness.

Currently, PLA has found numerous applications in, for example, the bi-axially oriented films, the thermoformed food/beverage serving utensils, and the injection stretch blow molding (ISBM) bottles (Tweed, Stephens, & Riegert, 2006). Thus, among all the synthetic biopolymers, PLA is considered having the highest potential to replace some regular petroleum based plastics. However, PLA has its own shortcomings, i.e., its brittleness, low heat distortion temperature (HDT) (Tang et al., 2012), and relatively high cost, which limit its broad acceptance (Anderson, Schreck, & Hillmyer, 2008; Auras, Harte, & Selke, 2004). Plasticizers were used to improve PLA's impact strength and low cost fillers to bring down its total cost (Jacobsen et al., 2000; Huda et al., 2005).

As a low cost nature renewable material, starch is a good filler candidate for the PLA. However, they are not chemically compatible (Wang, Sun, & Seib, 2001), and in addition, starch granules might make the PLA even more brittle. To solve these issues, two general measures were taken: (a) using compatibilizers between PLA and the starch granules; and (b) plasticizing the starch granules to make them easier dispersed into PLA matrix.

Some examples of the measure (a) including maleic anhydride (MA) (Zhang & Sun, 2004), acrylic acid (AA) (Wu, 2005) and methylene-diphenyldiisocyanate (MDI) (Wang et al., 2001),etc. were used as the reactive compatibilizers. However, all above referred coupling agents used in PLA/starch blends are inefficient on the improvement of toughness.

As a general way of the measure (b), starch plasticizers, such as water (Teixeira et al., 2007), glycerol (Rodriguez-Gonzalez, Ramsay, & Favis, 2004), sorbitol (Li & Huneault, 2011), urea (Ma, Yu, & Wan, 2006) and citric acid (Shi et al., 2007), were used to break the crystallinity and the strong hydrogen bond within the starch granules. Under the melt blending process, these small molecular plasticizers destroy the starch granules and make the plasticized starch, in essence, a thermoplastic starch (TPS), more compatible with PLA matrix. A problem of the above small molecular plasticizers is that they are hydrophilic chemicals and could accelerate the hydrolysis degradation of PLA in the melt-blended process. Moreover, these small molecules may migrate out of the blends and deteriorate the blending system as well as cause the retrogradation of the starch.

To prevent the migration of the small plasticizers, chemical bond can be generated between the plasticizers and the starch. Wang, Zhai, and Zheng (2012) caped polyethylene glycol (PEG), a plasticizer, with MA and then grafted this MA-PEG-MA onto the native starch. This modified starch was then blended with PLA and more

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Table 1
Degrees of substitution with different level of MA contents.

	Starch (g)	MA (g)	DMAc (mL)	Toluene (mL)	Time (h)	DS
MGST1	60	2.6	100	50	1	0.04
MGST2	60	5.4	100	50	1	0.067
MGST3	60	8.0	100	50	1	0.12

DS reported here were degrees of substitution.

PEG plasticizer from an extruder. The resultant compound showed good compatibility between MA-PEG-MA modified starch and the PLA. Free PEG was trapped within the interface of MA-PEG-MA modified starch and PLA, well plasticizing the starch and improving the compatibility between the starch and PLA, turning PLA matrix from a brittle state into a ductile state. However, the grafting content of MA-PEG-MA onto starch was low due to the slow esterification reaction between MA and the starch, therefore the above enhanced compatibility effect was also limited. Meanwhile, the blending plasticizer PEG used was derived from petroleum.

Recently, bio-based plasticizers have attracted the general attention due to their renewability. Epoxidized soybean oil (ESO) is one of such plasticizers. It is manufactured through the process of epoxidation of the carbon–carbon double bonds on the aliphatic long chain moiety of the soybean oil molecules. ESO is mainly used as a plasticizer for PVC and chlorinated rubber (Ishiaku et al., 1997). Ali et al. (2009) used ESO as an effective plasticizer for PLA, which depressed PLA's glass transition temperature and improved its cold crystallization capability. Broström, Boss, and Chronakis (2004) studied the effects of ESO on the morphology and the mechanical properties of PLLA-co-PCL/triethyl citrate blends. It was shown that the compatibility between triethyl citrate and the PLLA-co-PCL copolymer was improved in the presence of ESO with the EB of the blend increased significantly to 272%. It was proposed that the reactions between epoxy groups on ESO and hydroxyl and/or carboxyl groups on PLLA-co-PCL, as well as the hydroxyl group on triethyl citrate (as a plasticizer) generated the chemical interaction within the system and also improved the toughness of the compound.

Considering that there were abundant hydroxyl groups provided by the starch molecules and ester carboxyl groups existed on PLA. Thus, ESO might also be used as a reactive plasticizer in PLA/starch system. Very few studies have been made in this area.

2. Experimental

2.1. Materials

The PLA 4032D, a semi-crystalline extrusion grade, was supplied by NatureWorks LLC (Minnesota, USA). It was vacuum dried at 80 °C for at least 8 h before use. The food grade native corn-starch was obtained from the Zhucheng Stimulation Trade and Corn Development Limited Company, Shangdong, China, which was dried in vacuum for 24 h at 100 °C before use. The chemical pure grade ESO was purchased from the Aladdin Reagent (Shanghai, Chain) and used directly without further purification. The analytical pure grade MA, dim-ethylacetamide (DMAc) and toluene were purchased from Aladdin Reagent and used directly without further purification.

2.2. Synthesis of MA-grafted starch

The MA-grafted starches were prepared in a three-neck flask equipped with a Dean-Stark distilling receiver, a condenser and a mechanical agitator. Starch (60 g) and MA (2.6–8.0 g) were first charged into the flask, followed by the addition of DMAc (100 mL) and toluene (50 mL) as the solvent. The reaction temperature was then brought up to 130 °C with the agitation. The reaction was kept at this temperature for 1 h and then cooled to room temperature. The reaction mixture was washed with acetone six times to remove the reaction solvents and the residual anhydride by filtration. The final product was dried in vacuo at 80 °C for 24 h and then kept in a desiccator. The resultant grafted starches from different amount of MA were listed in Table 1. The MA grafting ratio was characterized by the degree of substitution (DS), determined according to the method described in (Huang et al., 2004).

2.3. Blends

The PLA/starch, PLA/ESO, PLA/ESO/starch, and PLA/ESO/MA-graft-starch (MGST) blends were melt-blended in a SJSZ-10A miniature twin-screw extruder (Ruiming Plastics Machinery, Wuhan, China) with 40 rpm at 175 °C for 10 min. The extrudants were then injection molded into the standard testing bars with the barrel temperature of 200 °C, mold temperature of 45 °C, an injection pressure of 5 MPa and a cycle time of 30 s. In the PLA/starch blends, the content of starch was 10 wt.% and 30 wt.%, respectively. In the PLA/ESO blend, the addition of ESO was 10 wt.%. In MGST/ESO/PLA blends (10/10/80), the DS was from 0 to 0.12. In MGST3/10 wt.% ESO/PLA ternary blends, the content of MGST3 was ranges from 0 to 30% based on all weight. Meanwhile, the content of ESO in 30 wt.% MGST3/ESO/PLA ternary blends was from 0 to 15 wt.%.

2.4. The FTIR measurements

The chemical structures of different MGST were characterized by FTIR (Nicolet FTIR 6700 infrared spectrophotometer, KBr powder) over a range of 4000–400 cm^{-1}.

2.5. Thermal analysis

The thermal properties of the blends were characterized by differential scanning calorimetry (DSC) on a Pyris Diamond DSC instrument. The samples were stabilized at 30 °C for 1 min and then heated to 200 °C at a rate of 10 °C/min, followed by the cooling back down to 30 °C at 25 °C/min. After 1 min at 30 °C, the second scan from 30 °C to 200 °Cat10 °C/min was performed. Throughout the whole process, the sample cell was kept under a nitrogen flow of 20 mL/min. The glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) were determined from the second scan.

2.6. Morphological characterization

The morphology of the blends was studied by a scanning electron microscope (SEM, Hitachi TM-1000). The surfaces fractured under liquid nitrogen were examined after a gold sputter coating.

2.7. Measurements of mechanical properties

An Instron 5567 was used for the mechanical property measurements following the GB/T 1040.1-2006, the Chinese standard equivalent to ISO 527-4. The impact testing was performed according to ISO179-1:98. A 5.5 J pendulum was used.

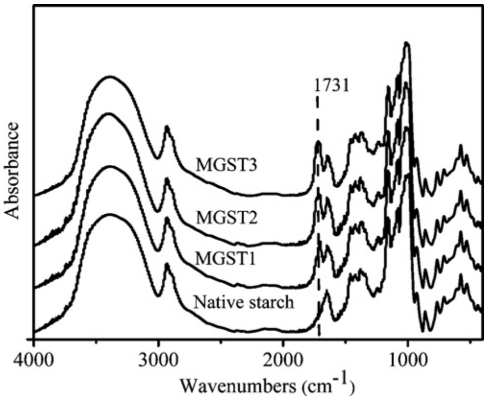

Fig. 1. The FTIR spectra of MGST with various DS.

3. Results and discussion

3.1. The FTIR analysis of MGST with various DS

Fig. 1 shows the FTIR spectra of MGST with various DS. The peak at 1731 cm^{-1} represents the C═O stretching vibration peak from MA grafted starch, which does not show for the native starch. The intensity of this peak increases with the increase of DS, which reflects the amount of the MA groups grafted.

3.2. Thermal properties

The pure PLA shows a glass transition at 61 °C (T_g), an exothermic cold crystallization peak at 117 °C (T_c) and a sharp endotherm peak at 164 °C with a shoulder peak to its right. (Fig. 2a). This phenomenon of PLA was reported to be a result of lamellar rearrangement during crystallization of the polymer as well as the reorganization of poor crystalline regions with different crystalline structures within PLA (Cartier et al., 2000; Martin & Averous, 2001; Nijenhuis et al., 1996). Similar thermal properties were observed for PLA/native starch (90/10) blend. When ESO was added to PLA and PLA/native starch blend (Fig. 2a), T_g and T_c both decreased due to ESO's plasticizing effect toward PLA. Meanwhile, the lower T_m peak declined, indicating that ESO facilitated the formation of the crystalline corresponding to the higher T_m peak in PLA or PLA/native starch system.

MA grafted starch did not significantly change the thermal behavior of PLA/starch/ESO (Fig. 2b). The minor changes were that with the increase of DS, T_c increased slightly and the lower T_m peak showed higher, both of which are in consistent with a less or harder molecular chain movement of PLA, indicating a less plasticizing effect of ESO on PLA. This may be due to that the functional groups on the MA grafted starch reacted with ESO, trapped ESO and prevent it from dispersing into PLA phase to plasticize it, also grafted MA reacted with ESO and PLA, forming more crosslink nodes which restricted the movement of PLA chain.

The crosslink effect above can also be illustrated in Fig. 2c, which shows a series of PLA/MGST/ESO blends with fixed MGST3 content, 30 wt.%, but varying ESO contents, from 0 wt.% to 15 wt.%. By adding 5 wt.% of ESO to the PLA/MGST3 system, T_g and T_c of PLA both moved to a much lower temperature from those of those of PLA/MGST3 blend (70/30) as well as the higher T_m peak increased, all of which showed the plasticizing effect of ESO. However, further increasing ESO content did not further increase the plasticizing effect of ESO on the PLA matrixes but decreased it, reflecting by the increase of T_g, T_c and the lower T_m peak. This phenomenon again indicates the

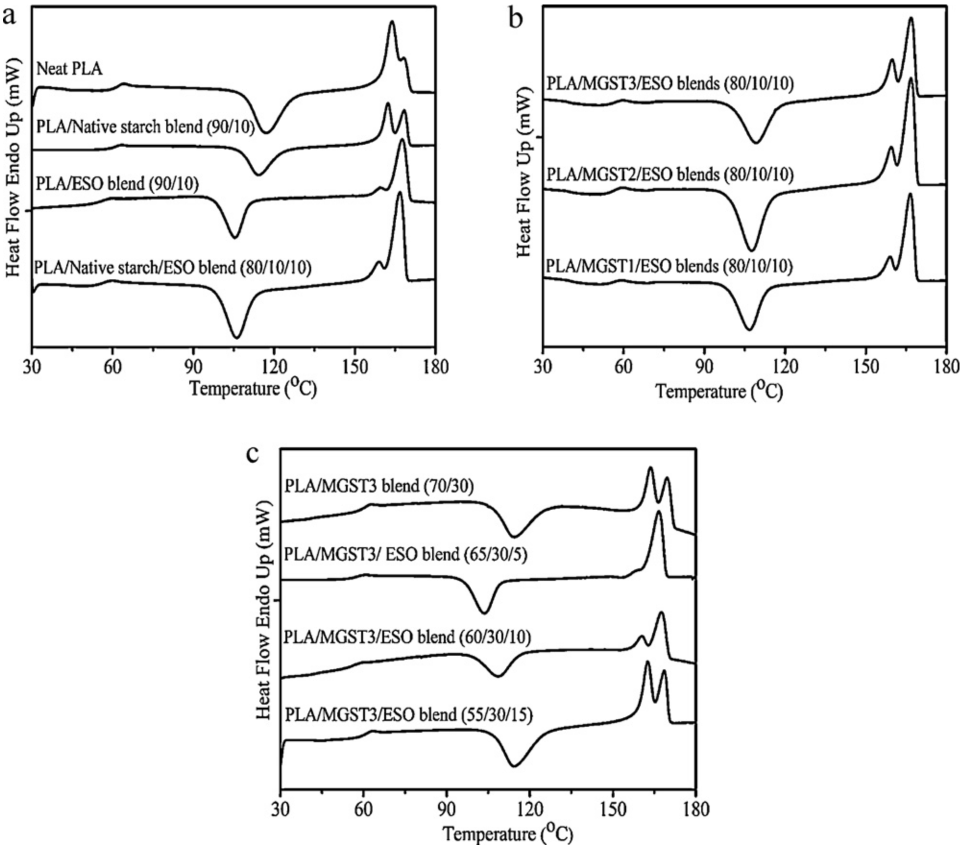

Fig. 2. DSC thermograms of plasticized neat PLA and PLA/native starch blends with 10 wt.% ESO, respectively (a) and PLA/MGST/ESO blends (80/10/10) with different DS in MGST (b) and PLA/30 wt.% MGST3 blends with different ESO content (d).

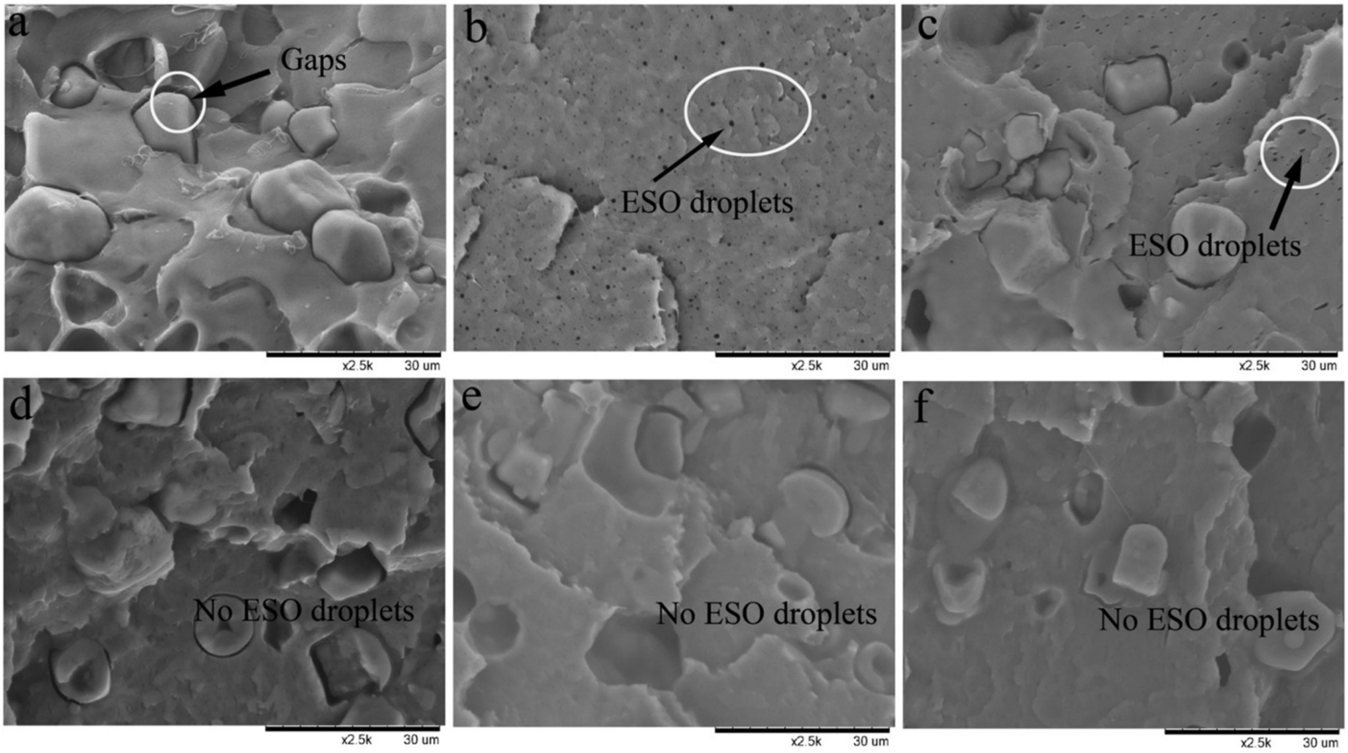

Fig. 3. SEM images of (a) PLA/native starch blend (90/10), (b) PLA/ESO blend (90/10), (c) PLA/native starch/ESO blend (80/10/10) and (d)–(f) PLA/MGST/ESO blend (80/10/10) with different DS in MGST.

cross-linking effect of ESO on PLA and MGST, which reduced the movement of PLA chains.

3.3. Morphology

The fractured surfaces of PLA/native starch blend (90/10), PLA/ESO blend (90/10), PLA/native starch/ESO composite (80/10/10) and PLA/ESO/MGST blends (80/10/10) with different DS in MGSTs were examined by SEM and shown in Fig. 3. A clear gap between PLA matrix and the native starch granules is seen, showing no compatibility between PLA and the native starch (Fig. 3a). The SEM image of PLA/ESO blends (without starch) is shown in Fig. 3b and ESO is seen as scattered micro-droplets within the PLA matrix, was also observed by (Ali et al., 2009). When PLA, native starch and ESO in 80/10/10 ratio were melt blended together, ESO improved the compatibility between PLA and the native starch to an extent that some interface between the two phases became blurring. However, clear cut interface still existed, indicating that the compatibility was still weak. Meanwhile, micro-droplets of ESO can still be seen in the PLA matrixes (Fig. 3c).

When the starch granules were grafted with MA and then blended with PLA and ESO, the morphology changed. Fig. 3d–f show PLA/MGST/ESO blends with different grafting levels of MGSTs. The MA grafted native starch granule made starch more compatible with the PLA matrix, and the higher extent of MA grafted on the starch particles (indicated by higher DS), the better compatibility between PLA and the starch was obtained, which gradually caused a more blurring interface. Meanwhile, the ESO micro-droplets disappeared. Thus, the results could be explained that the introduction of MA group onto the starch surface improved its reactivity with epoxy groups on ESO and the multiple epoxy groups there may react with end carboxylic acid groups on PLA, forming a compatible region of PLA, MGST and ESO around the grafted starch granule, schematized in Fig. 4. The extra ESO micro-droplets would migrate and accumulate in this region.

The relationship between the PLA/starch compatibility and the relative amount of MGST and ESO was further studied. While the content of ESO in blends was fixed at 10 wt.%, Fig. 5 shows the compatibility versus the amount of MGST in the blend. It was observed that the dispersed dense of MGST in PLA matrix increased and the gaps between starch granules and PLA matrix gradually occurred. This phenomenon may be explained by that, with the increase of the MGST amount, the ESO was “used up” and the compatibility gradually lost. To determine if the compatibility between MGST and PLA matrix could be improved by the ESO, the SEM pictures with the ESO content increasing were exhibited in Fig. 6. A general trend was summarized as follow: the higher amount of ESO was used, the better compatibility between PLA and the starch was obtained, especially for the content of ESO was 15 wt.% in PLA/MGST3 blends, the MGST3 granules seemed to embed in PLA matrixes. Thus, it can be concluded that the compatibility of MGST with PLA matrix could be improved by ESO.

3.4. Mechanical properties

The morphology changes brought up the change of the mechanical properties of the PLA/starch blends. Table 2 shows these changes. A pure PLA is a fairly rigid material with a high modulus (∼3018 MPa) and tensile strength (∼69 MPa), but quite brittle, with the elongation at break and impact strength of 5% and 18 kJ/m^2, respectively. The addition of ESO to PLA matrixes caused a decrease in Young’s modulus (∼2727 MPa) and tensile strength (∼62 MPa), but no effect on the elongation at break (∼6%) and impact strength (∼19 kJ/m^2). Meanwhile, it was well known that PLA and starch are not chemically compatible and in addition, starch granules might make the PLA even more brittle. It was observed that the elongation at break and impact strength were 6% and 14 kJ/m^2 for PLA/starch (90/10) blend, respectively, in Table 2. If ESO was added into the PLA/native starch blend, the elongation at break and impact strength both increased, to 64% and ∼30 kJ/m^2, respectively, which

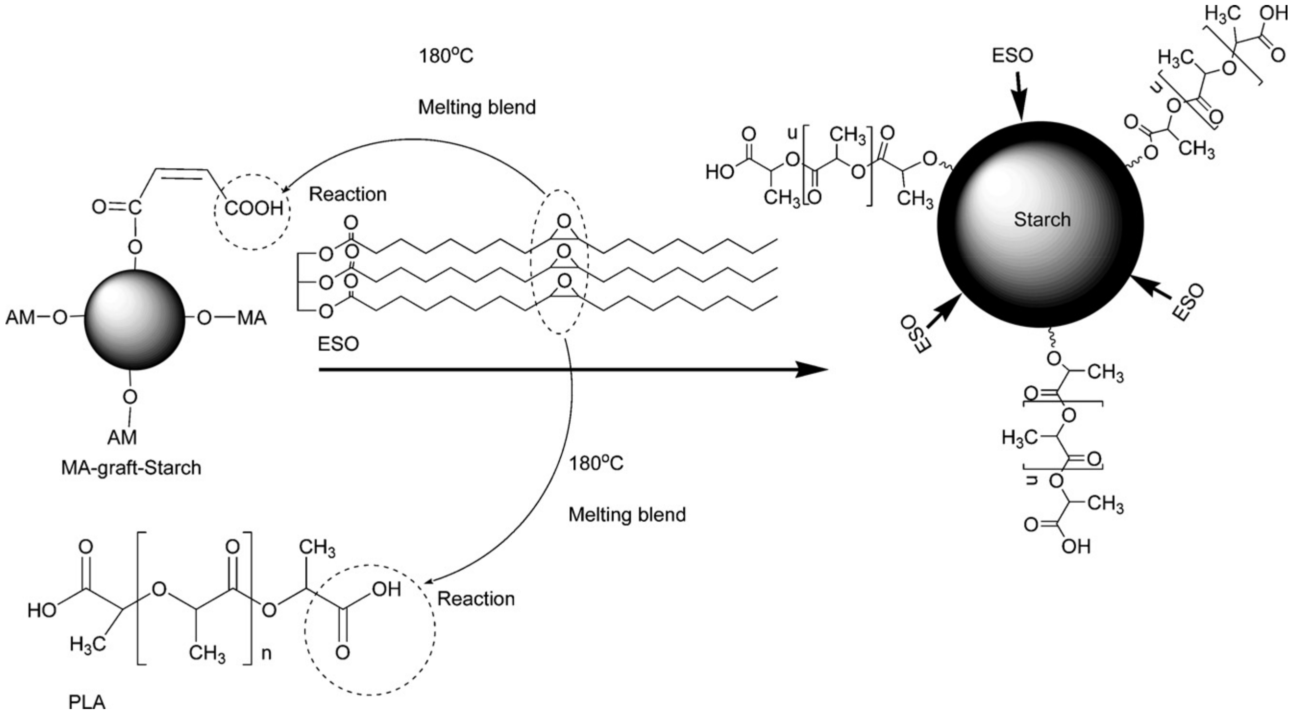

Fig. 4. The possible chemical reaction diagram in PLA/MGST blends compatibilized by ESO during melting blend process.

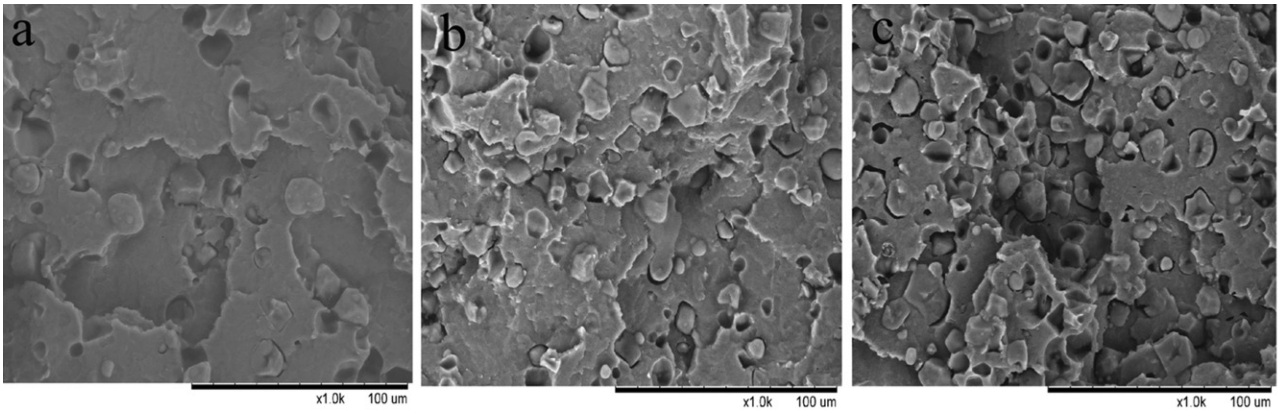

Fig. 5. SEM images of PLA/10 wt.% ESO blends with the different content of MGST3: (a) 10 wt.%, (b) 20 wt.%, and (c) 30 wt.%.

Table 2
Mechanical properties of neat PLA and PLA blends with different DS in MGST, various content of MGST3, and different content of ESO.[a]

Composition	Impact strength (kJ/m^2)	Tensile strength (MPa)	Elongation at bleak (%)	Tensile modulus (MPa)
Neat PLA	18(±1.0)	69(±1)	5 (±1)	3018(±50)
PLA/ESO (90/10)	19(±0.5)	62(±2)	6 (±2)	2727(±15)
PLA/starch (90/10)	14(±1.0)	57(±2)	6 (±1)	2855(±20)
PLA/native starch/ESO (80/10/10)	30(±1.0)	38(±2)	64(±5)	2406(±10)
PLA/MGST1/ESO (80/10/10)	34(±0.5)	36(±1)	78(±5)	2264(±13)
PLA/MGST2/ESO (80/10/10)	38(±0.7)	41(±1)	112(±10)	2412(±30)
PLA/MGST3/ESO (80/10/10)	42(±1.0)	43(±2)	140(±10)	2510(±20)
PLA/MGST3/ESO (70/20/10)	36(±1.2)	35(±1)	96(±6)	2318(±18)
PLA/MGST3/ESO (60/30/10)	31(±1.0)	25(±2)	63(±5)	1769 (±20)
PLA/MGST3/ESO (65/30/5)	28(±1.0)	32(±1)	56(±5)	2063(±15)
PLA/MGST3/ESO (58/30/12)	36(±0.8)	19(±1)	68(±3)	1366(±10)
PLA/MGST3/ESO (55/30/15)	23(±1.0)	16(±2)	32(±5)	1057(±25)

[a] Values reported here are averages of four tensile bar tests according to the test standard. IS, TS, EB and TM represented the impact strength, tensile strength, elongation at break and tensile modulus, respectively.

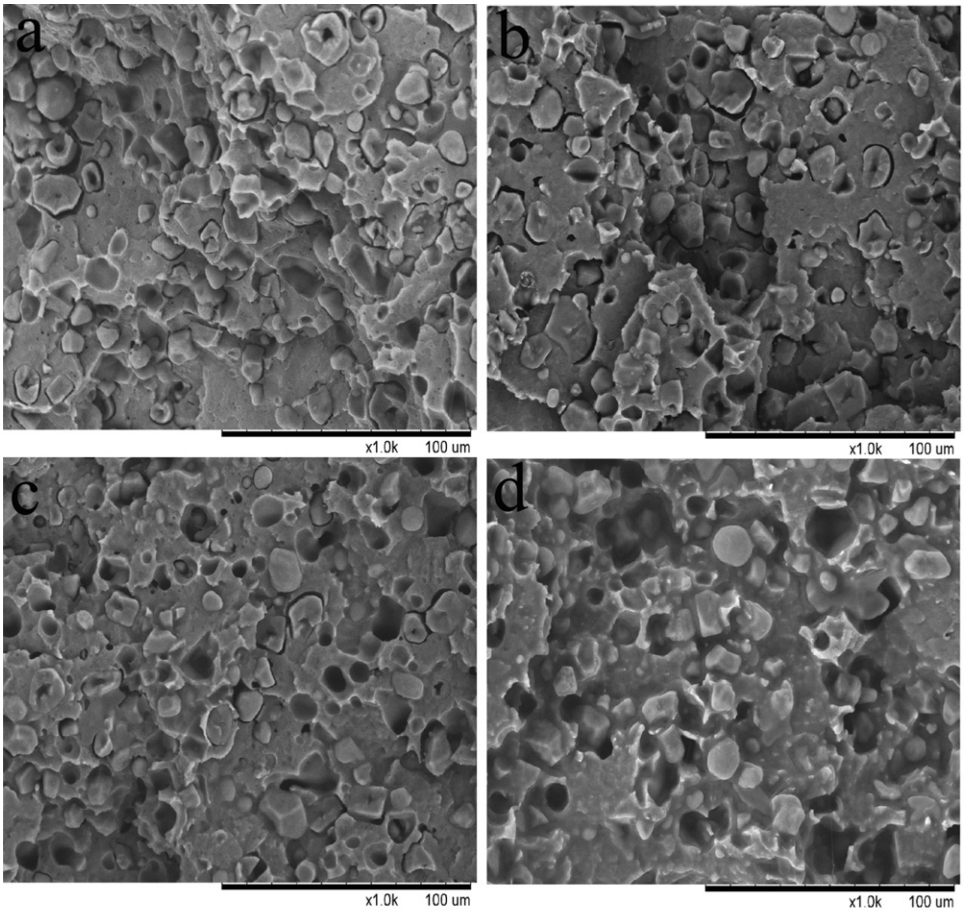

Fig. 6. SEM images of PLA/30 wt.% MGST3 blends with various content of ESO: (a) 5 wt.%, (b) 10 wt.%, (c) 12 wt.%, and (d) 15 wt.%.

is in consistent with the improved compatibility (Fig. 4c) and the plasticized effect of ESO. The observation is similar to Wang's work (Wang et al., 2012).

With the MA grafted starch, the compatibility between PLA and the starch improved even better, therefore, EB, impact strength increased to as high as 140%, and 42 kJ/m^2, respectively, in the blend of PLA/MGST3/ESO (80/10/10). The higher the DS of MGST, the higher are the elongation at break and impact strength.

The relationship between the mechanical properties and the relative amount of MGST and ESO was also studied. It was observed that the tensile and impact properties all decreased as the content of MGST increased in the PLA/MGST3/10 wt.% ESO blends, which is consistent with the compatibility observation in the morphology part: the more amount of MGST granules decreased the compatibility and brought in more brittleness; ESO's effect on the mechanical properties are two folds – it acted as a plasticizer to soften the PLA and also as a compatibilizer to improve the interaction of PLA and MGST. With the increase of ESO content, PLA got better plasticized and therefore the blend turned softer, causing a lower tensile strength and higher EB and impact strength, which was reflected well in the changes of ESO amount from 5 wt.% to 12 wt.%.

Meanwhile, an increase of ESO also formed a better interfacial bonding between PLA and MGST phases, which may cause more brittleness to the blend, showed by the elongation at break and impact strength changes from 12 wt.% to 15 wt.%. Similar observations were reported by Hillmyer (Chang et al., 2009; Gramlich et al., 2010; Robertson et al., 2010; Robertson, Paxton, & Hillmyer, 2011). In their study, if the concentration of vegetable oil in PLLA matrixes increased up to a certain value, it was observed that the phase-inverted occurred and caused a significant deterioration of mechanical property. But, the concrete reason is still not very clear in our tropic, and to the best of our knowledge, no previous study has proposed plant oil such as ESO that compatibilized and plasticized PLA/starch blend material.

4. Conclusions

Epoxidized soy-bean oil (ESO) could be used as a bio-based reactive plasticizer for PLA and the starch compounds. This effect could be enhanced by chemically grafting the starch granules with the maleic anhydride (MA). The characterization of the obtained blends by differential scanning calorimetry (DSC) demonstrated that the cold crystallization temperature (T_c) of PLA was obviously declined by the addition of ESO, whereas the content of 5 wt.% ESO in PLA/MGST blends was the key point. The ready reactions between the epoxy groups on ESO, the MA groups on MA-grafted starch (MGST) and the end carboxylic acid groups of PLA brought the components of this blend together and formed a more compatible compound. The elongation at break and impact strength of PLA/ESO/starch increased markedly compared to the virgin composites of PLA/starch blends. The PLA/MGST3/ESO composites at a constant weight ratio of 80/10/10 exhibited the highest elongation at break of 140% and impact strength of 42 kJ/m^2.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.09.007.

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