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The properties of poly(lactic acid)/starch blends with a functionalized plant oil: Tung oil anhydride

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ABSTRACT

Bio-sourced polymers, polylactide (PLA) and starch, have been melt-blended by lab-scale co-extruder with tung oil anhydride (TOA) as the plasticizer. The ready reaction between the maleic anhydride on TOA and the hydroxyl on starch led TOA molecules to accumulate on starch and increased the compatibility of PLA/starch blends, which was confirmed by FT-IR analyses and SEM. The TOA could change the mechanical properties and physical behaviors of PLA/starch blends. DSC and DMA analysis show that the TOA layer on starch has an effect on the thermal behavior of PLA in the ternary blend. The enrichment of TOA on starch improves the toughness and impact strength of the PLA/starch blends. The adding amount of TOA in PLA/starch blends primarily determined the compatibility and mechanical properties of the resulted ternary blends. The tensile and impact fracture modes of the PLA/starch blend with or without TOA has also been investigated by SEM analysis.

1. Introduction

In recent years, in viewing of environmental concerns and shortage of petroleum resources have driven efforts on the development of biodegradable and renewable materials, which are known as "green materials" (Bledzki & Sperber, 1999). Poly(lactic acid) (PLA) is a biodegradable aliphatic polyester with excellent properties for various applications, which is an important candidate in the future markets of renewable resources. However, the disadvantages of brittleness and high cost of PLA limit PLA's wide spread applications (Anderson, Schreck, & Hillmyer, 2008; Auras, Harte, & Selke, 2004). In order to resolve these two problems, plasticizers and cheap fillers were frequently used (Huda, Drzal, & Misra, 2006; Jacobsen, Fritz, & degee, 2000). Starch, as a common and inexpensive biopolymer, is an attractive candidate as an organic filler for PLA. PLA/starch blends are well-explored biodegradable materials. Nevertheless, PLA and starch are thermodynamically incompatible (Wang, Sun, & Seib, 2001). Obviously, the incorporation of native starch into PLA could increase its rigidity but at the same time greatly reduce elongation at break and the impact strength (Jacobsen & Fritz, 1999).

Many factors are believed to cause the deterioration in mechanical properties of PLA/starch blends. Firstly, PLA is a material with inherent brittleness. Previous research has showed that the mechanical properties of PLA are similar to that of polystyrene (Anderson, Schreck, & Hillmyer, 2008; Bhardwaj & Mohanty, 2007), and like polystyrene, one of the deficiencies of the material is its brittleness, as evidenced by relatively low tensile strain at break, toughness, and impact strength. Secondly, native starch is of rigid granular structure and its particle diameter is ranging from 10 to 200 μm (Dhital, Shrestha, & Flanagan, 2010), which would further increase the intrinsic brittleness of PLA (Jiang, Yuan, An, & Jiang, 2002). Because the thermodynamic compatibility between PLA and starch is really poor, the starch particles dispersed in PLA matrixes will act as the defects and lead to serious stress concentration, which makes the material fractured more easily.

When attempting to improve the mechanical properties of PLA/starch system, research has mainly focused on two methods. One is the use of coupling agents. Interfacial adhesion plays a vital role in mechanical properties of polymeric composites. Reactive interfacial coupling agents are often used to improve interfacial properties and control morphologies of polymeric composites. Coupling agents containing reactive functional groups such as maleic anhydride (MA) (Zhang & Sun, 2004), acrylic acid (AA) (Wu, 2005) and methylene-diphenyldiisocyanate (MDI) (Wang, Sun, & Seib, 2001) are able to generate in situ formation of blocks or grafted copolymers at the interface by hot-melting blending. However, all above referred coupling agents used in PLA/starch blends are inefficient on the improvement of toughness.

Another method to improve the mechanical properties of PLA/starch blends is gelatinizing of starch. Thermoplastic starch (TPS) was prepared by inserting small molecular plasticizers into the polysaccharides to destroy the crystalline of starch. The commonly utilized plasticizers are water (Teixeira, Da Roz, Carvalho, & Curvelo, 2007), glycerol (Rodriguez-Gonzalez, Ramsay, & Favis,

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2004), urea (Ma, Yu, & Wan, 2006) and citric acid (Shi et al., 2007). In a melt blending process, although, the strong intermolecular hydrogen bond is broken and replaced by intra-molecular hydrogen bond between polysaccharide chains and low molecular weight plasticizer, the small molecule plasticizer may cause degradation of PLA during processing. What is more, TPS with small plasticizes is an unstable system. Because, these small plasticizes only react with starch particles through hydrogen bond and easily migrate from the matrix of TPS with the time lasting. In the result, the retrogradation of starch crystalline in TPS would be occurred, which could cause deterioration of the PLA/starch blends' mechanical properties.

To prevent the migration of the small plasticizers, chemical bond can be generated between the plasticizers and the starch. Wang, Zhai, & 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 additional PEG plasticizer in 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, which could have improved the compatibility between the starch and PLA and tuned PLA matrix from a brittle state to a ductile state. However, the grafting ratio of MA-PEG-MA onto starch was low due to the slow esterification reaction between MA and starch. Therefore, the above enhanced compatibility effect was also limited. It is also worth noting that, the used plasticizer PEG was derived from petrochemical resource.

Recently, bio-based plasticizers have attracted great attention due to their renewability. A series of studies have been done by Hillmyer's group on the utilization of triglyceride oils as toughening agents for PLA (Chang, Robertson, & Hillmyer, 2009; Gramlich, Robertson, & Hillmyer, 2010; Robertson, Chang, Gramlich, & Hillmyer, 2010; Robertson, Paxton, & Hillmyer, 2011). The oils cannot toughen the PLA matrix alone; rather, the PLA and oil form a phase separated mixture. Meanwhile, the plant oil is hydrophobic, and the starch is hydrophilic, which would cause the interaction between starch and plant oil weakly. Obviously, the PLA/starch blend would be more difficult to be plasticized by oil than neat PLA. However, the toughening problems of PLA/starch blends may be solved by a flexible interphase layer on starch particles (Wang, Zhai, & Zheng, 2012). Our motivation for using plant oils is to create a toughened PLA/starch composite which derived entirely from renewable resources. The method is analogous to the flexible interphase layer toughening techniques used to produce high-ductility PLA/starch blends.

This paper follows our previous papers on the utilization of plant oil such as epoxidized soybean oil (ESO), castor oil (CO) as the reactive toughening agents for PLA/starch blends (Xiong et al., 2013a, 2013b). But, the epoxidized soybean oil or castor oil cannot neither directly toughen the PLA/starch blends due to the low reactivity of ESO or CO with native starch particles. Then, the native starch particles need to be modified in organic solvent, which is not of environmental and economical benefits. Thereof, we focus on tung oil anhydride (TOA), a novel fully biodegradable monoglyceride derived from tung oil. Fig. 1 describes the solvent-free Diels–Alder addition of maleic anhydride to the highly reactive conjugated hexatriene system of tung oil to give the structure of tung oil anhydride (Biermann, Butte, Eren, Haase, & Metzger, 2007). Thus, in the melt-blended process, the TOA might directly toughen the PLA/starch blends due to the high reactivity of anhydride groups on TOA with hydroxyl groups on native starch particles, which is similar with our previous works (Xiong et al., 2013a, 2013b).

To evaluate the efficiency of tung oil anhydride as a renewable resource blending plasticizer for PLA/starch blend, we explored the morphology, thermal, mechanical and rheological properties of PLA/starch blends containing different amount of tung oil anhydride.

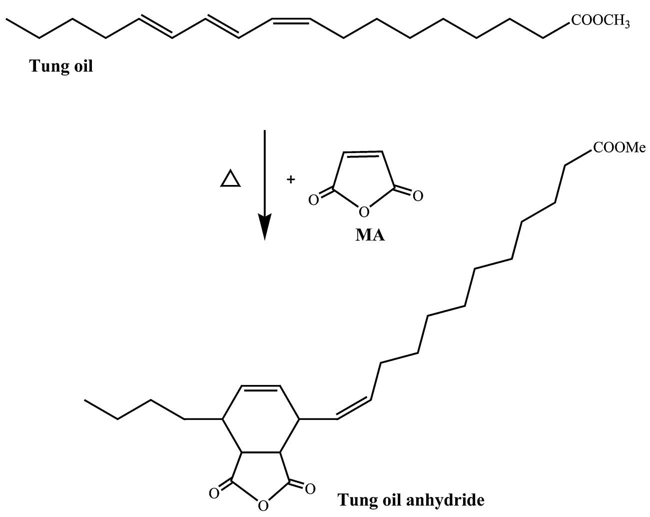

Fig. 1. The solvent free Diels–Alder addition of maleic anhydride with the tung oil.

2. Experiment

2.1. Materials

A semi-crystalline extrusion grade, PLA 4032D was supplied by NatureWorks (Minnesota, USA). It was vacuum dried at 80 °C for 8 h prior to use. The native food grade corn–starch is bought from Zhucheng Stimulation Trade and Corn Development Co., Ltd., Shangdong, China, which was dried in a vacuum dryer for 24 h at 100 °C before use. The industrial grade tung oil anhydride (TOA), 98% purity, is purchased from Jinan Licheng Chengyang Chemical Co., Ltd., Shangdong, China, and used directly without further purification. Analytical pure grade chloroform was purchased from the Aladdin Reagent (Shanghai, China) and was used directly as Soxhlet extraction solvent.

2.2. Preparation of the blends

Neat PLA or PLA/starch blends with and without TOA are firstly melt-blended in a SJSZ-10A miniature twin screw extruder (Ruiming Plastics Machinery, Wuhan city, China). The rotation rate, mixing temperature and time were set at 40 rpm, 175 °C and 5 min, respectively. Whereafter, the PLA blends were extruded into an SZ-15 micro-injection molding machine, which is made by Ruiming plastic Machinery. All the standard test bars for measurements were prepared under an injection pressure of 5 MPa for 30 s at 200 °C with mold temperature of 40 °C. In the PLA/starch/TOA blends, the content of starch was fixed at 30 wt.%, but the adding amount of TOA is varied from 5 to 12 wt. %. Lastly, the prepared samples were preserved in the dryer to avoid the moisture.

2.3. Morphological characterization

The morphology of the blends was recorded by a low expansion scanning electron microscope (SEM, Hitachi TM-1000). A field emission scanning electron microscope (SEM) instrument (S-4800, JEOL, Japan) was used to observe the tensile longitudinal fracture section and impact fracture section of neat PLA, PLA/TOA blend (95/5) PLA/starch blend (70/30), and PLA/starch/TOA blend (63/30/7) to investigate the fracture mode of the materials. The tensile longitudinal sections were fractured in liquid nitrogen. The resulting tensile and impact fractured surfaces were sputtered with gold prior to examination.

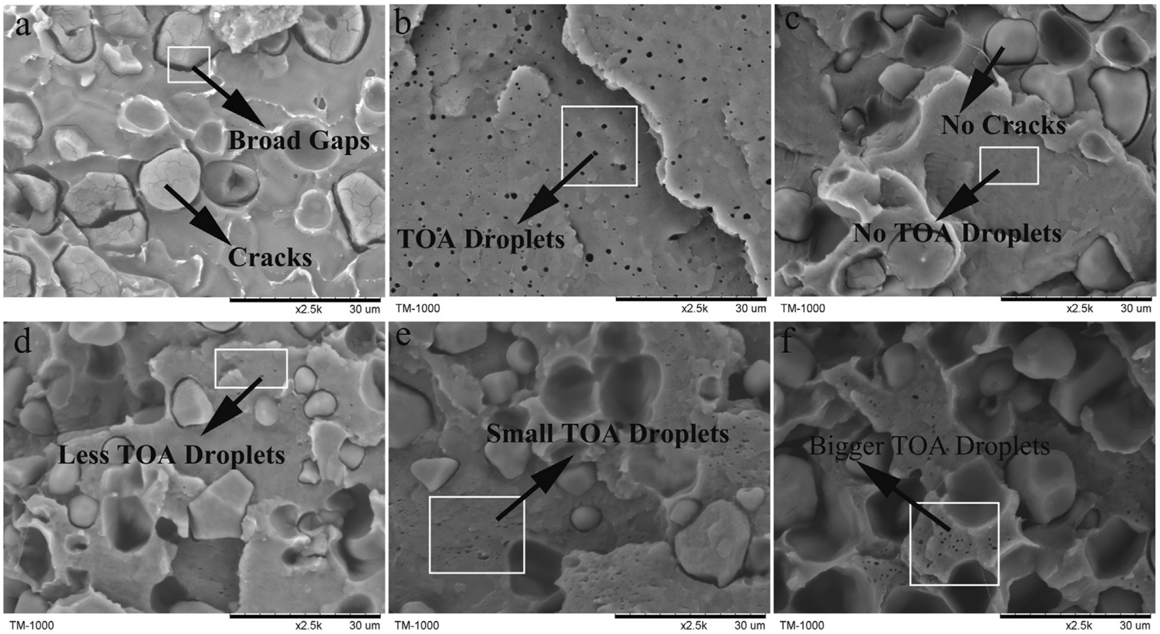

Fig. 2. The fracturated surfaces of PLA/starch blend (70/30) (a), PLA/TOA blend (95/5) (b), and PLA/starch/TOA blends (65/30/5, 63/30/7, 60/30/10, and 58/30/12) (c–f).

2.4. The FT-IR measurements

In order to prove the reaction between starch and TOA, the starch particles obtained by Soxhlet extraction and dried at 60 °C for 24 h in vacuum oven for the FT-IR analysis. The FT-IR (Nicolet FTIR 6700 infrared spectrophotometer, KBr powder) was used to characterize the separated starch particles powder over a range of 4000–400 cm^{-1}.

2.5. Thermal analysis

The thermal properties of the blends were characterized by a METTLER TOLEDO TGA/DSC1 analyzer (Mettler-Toledo, Switzerland). Firstly, the samples were kept at 30 °C for 1 min before they were heated to 200 °C at 10 °C/min, and then the samples were held at 200 °C for 2 min to erase thermal history prior to cooling down to 30 °C at 50 °C/min. Lastly, after 1 min at 30 °C, a second scan from 30 °C to 200 °C at 10 °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), melting temperature (T_m), and degree of crystallinity (χ_c) were determined from the second heating scan. T_m and T_c were taken as peak values, and T_g was taken as the midpoint of heat capacity changes. When multiple endothermic peaks were obtained, the peak temperature of the main endotherm was taken as T_m. The degree of χ_c is defined as the enthalpy difference between melting and crystallization peaks divided by the enthalpy of 100% crystalline PLA (93.6 J/g) according to Eq. (1) (Fisher, Sterzel, & Wegner, 1973)

$$\chi_c(\%) = \frac{(\Delta H_{m1} + \Delta H_{m2} - \Delta H_c) \times 100}{93.6 \times \delta_{PLA}} \qquad (1)$$

where ΔH_{m1}, ΔH_{m2} and ΔH_c are the enthalpies (J/g) of fusion at lower melt temperature, the enthalpies (J/g) of fusion at higher melt temperature and crystallization of the blend, respectively; 93.6 J/g is the enthalpy of fusion of a PLA crystal of infinite size; and δ_{PLA} is the PLA content. All samples were tested in triplicate.

2.6. Measurements of mechanical properties

An Instron 5567 (Wuhan, China) was used for the mechanical property measurements following the GB/T 1040.1-2006. System control and data analysis were performed using the instrument software. The standard bar-shaped samples were used in order to determine the tensile strength (TS), tensile modulus (E) and elongation at break (EB). Four samples for each composite were tested at a cross head speed of 20 mm/min. The impact test was performed according to ISO179-1: 98. A 5.5 J pendulum was used to determine the Charpy impact strength of the bar samples (80 × 10 × 4 mm). The impact testing was performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China). Four samples for each composite were tested.

2.7. Rheological characterization

The rheological behavior of the samples was studied by dynamic oscillation made using a dynamic analyzer Physica MCR-301 of Rheometric (Anton Paar, Austria) with parallel plate tools. The plate diameter and its gap were 25.0 mm and 1 mm, respectively. The dynamic frequency sweep was carried out from 1 to 100 rad/s at 180 °C with strain of 1%. The samples used for the rheological behavior characterization came from extruded samples.

3. Results and discussion

3.1. Morphology

The fractured surfaces of PLA/starch blend (70/30), PLA/TOA blend (95/5), and PLA/starch/TOA blends (65/30/5, 63/30/7, 60/30/10, and 58/30/12) were examined by SEM and are showed in Fig. 2. A clear broad gap between PLA matrix and starch granules was seen as well as many cracks on the surface of starch particles (Fig. 2a). The broad gaps imply that the compatibility between PLA and starch is poor. As for the cracks, they may be produced by the squeezing between PLA matrix and starch particles during the melt-blended process. The SEM image of PLA/TOA blends (95/5) is also shown in Fig. 2b, and from which ∼2 μm diameter TOA

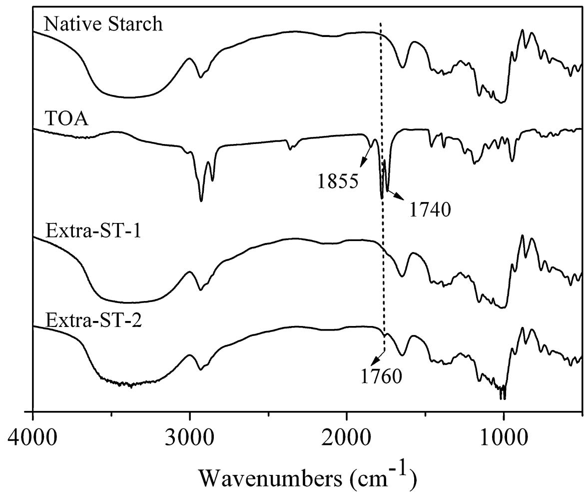

Fig. 3. The FT-IR spectra of native starch, TOA, and two different kinds of extracted starches from PLA/starch blends with or without TOA, namely Extra-St-1 and Extra-St-2, respectively.

micro-droplets were found in the PLA matrix, indicating that the compatibility of the two components was very weak.

When PLA, Starch and TOA were melt-blended at the ratio of 65/30/5, the amount of gaps between PLA and the starch seem to become less, indicating that the compatibility between the two components was improved (Fig. 2c). Meanwhile, the TOA droplets and cracks were disappeared from the PLA matrix and the surface of starch granules, respectively (Fig. 2c). These results may be caused by that, the maleic anhydride groups of TOA could react with the hydroxyl groups of starch particles, which could let the TOA molecules accumulate on starch granules from PLA matrix. Fig. 2d–f exhibit PLA/starch/TOA blends with the increasing amount of TOA (7 wt.%, 10 wt.%, and 12 wt.%). From the Figures, it is shown that the gaps between PLA and the starch become more and more narrowly until a blurring interface found in Fig. 2f, indicating the compatibility of the two components was gradually improved with the increasing TOA. But, the TOA droplets are again found in PLA matrix and both the number and the size of the TOA dispersed phase increased with the increasing amount of TOA in PLA/starch/TOA blend. Obviously, the assimilation of TOA on starch granules via the reaction seems to be saturated after a certain amount of TOA adding. Meanwhile, it is also concluded that, although a large amount of TOA into PLA/starch blends could improve the compatibility between starch particles and PLA matrix, an excess of TOA molecules would again form droplets in the PLA matrix, as observed in Fig. 2e and f.

3.2. The FT-IR analysis of starch with or without TOA

In order to further prove the reaction between the maleic anhydride groups on TOA and the hydroxyl groups on the starch particles in melt-blended process, the FT-IR spectra of native starch, TOA molecules, and two different kinds of extracted starches, namely Extra-St-1 and Extra-St-2, was shown in Fig. 3. The Extra-St-1 extracted from PLA/native starch (70/30) blend exhibited the similar FT-IR spectra with native starch. Obviously, it was inferred that the PLA matrix could not bond onto the surface of native starch and affect the structure of starch particles in the melt-blended process.

For TOA, the peaks at 1855 and 1740 cm^{-1} are belong to maleic anhydride group, and that the peak at 1760 cm^{-1} is assigned to carboxyl stretching frequency (Lu, Khot, & Wool, 2005). With the aim of proving the reaction between TOA and native starch particles in melt blending, the Extra-St-2 particles extracted from the PLA/starch/TOA (65/30/5) blend was analyzed by FT-IR. Interestingly, it is observed that the peak at 1760 cm^{-1} attributed to carboxyl (—C=O—) group appeared in the FT-IR spectra of Extra-St-2, but not in the FT-IR spectra of native starch. Meanwhile, the peaks at 1855 and 1740 cm^{-1} were not observed in the FT-IR spectra of Extra-St-2. These results may be explained by the reaction between hydroxyl groups of starch particles and maleic anhydride of TOA molecules, which resulted in the appearance of carboxyl peak in the FT-IR spectra of Extra-St-2. Thus, the TOA layer formed on the starch particle via the possible reaction between hydroxyl groups of starch and maleic anhydride groups of TOA during the melt-blending process could be schematized in Fig. 4.

3.3. Thermal properties

As shown in Table 1, the pure PLA shows a glass transition at 62 °C (T_g), an exothermic cold crystallization peak at 120 °C (T_c) and a endotherm peak at 164 °C with the temperature increasing from 25 to 200 °C, which is attributed to the melt temperature (T_m). In order to know the effect of starch, TOA, and TOA/Starch combinations on the thermal properties of PLA, the relevant experiments were carried out and the results were exhibited in Table 1. It was observed the starch particles could decrease T_c of PLA from 120 to 117 °C, made a higher T_m at 170 °C, and increased the χ_c from 3 to 6%, which might be due to the effect of starch on inducing crystallization of PLA matrix in PLA/starch blend. The similar conclusion was also proved by Ke (Ke & Sun, 2003).

Surprisingly, the thermal behavior of PLA was changed in different way by the addition of TOA/starch combinations in contrast with that of PLA/TOA or PLA/starch blend. With 5 wt.% TOA and 30 wt.% starch mixture in PLA, T_c decreased up to 111 °C, which is lower than that of PLA/starch blend (70/30). Meanwhile, it is observed that the χ_c were greater than that of PLA/starch (70/30) blend, the χ_c were increased up to 21%. It was inferred that the TOA molecules have a positive effect on the lamellar rearrangement of the PLA's poor crystalline regions in PLA/starch blend. But, for the PLA/TOA (95/5) blend, the T_c of PLA increased up to 125 °C and χ_c could not be calculated out due to the value of $|\Delta H_c|$ higher than that of ΔH_m. Obviously, TOA could not play a positive role on the crystalline of PLA in PLA/TOA (95/5) blend. Thus, the thermal behavior of PLA in PLA/starch blends is not only influenced by TOA, but also by starch particles.

In our above discussions, it was well known that, the TOA molecules could accumulate on the surface of starch particles in PLA/starch/TOA (65/30/5) blend via the reaction. Maybe, the crystallization behavior of PLA in PLA/starch blends are improved by the TOA accumulated starch particles. The result is very similar with Yan' research (Yan et al., 2007), in which, Yan used SiO_2 and L-lactic acid oligomer loaded SiO_2 as the filler for PLA, respectively. In results, he found that the L-lactic acid oligomer loaded SiO_2 could serve as an effectively nucleating agent for the crystallization of PLLA, but not for pure SiO_2 particles in the resulted composites. Thus, it could be also concluded that, if the starch granules covered by TOA molecules, the crystallization properties of the PLA might be improved by these modified starches in PLA/starch blends.

However, when the amount of TOA in PLA/starch blends increased from 5 to 12 wt.%, the T_c of PLA could be increased instead, and the value of χ_c were reduced up to 11% for PLA/starch/TOA (58/30/12) blend, which indicates that increasing amount of TOA molecules played an negative effect on the crystallization PLA. This result may be caused by the reformation of TOA droplets in PLA matrix when the amount of TOA over 5 wt.%, as observed in Fig. 2d–f. Thereof, with the TOA content increasing, it could be concluded that the PLA thermodynamic transitions were largely affected by TOA small molecules instead of TOA enriched starch

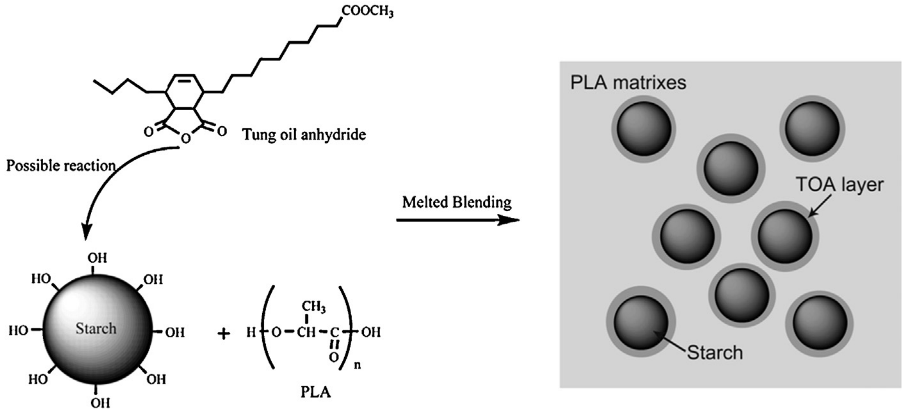

Fig. 4. The diagram of TOA layer formed on the starch particle via the possible reaction between hydroxyl groups of starch and maleic anhydride groups of TOA during the melt-blending process.

particles. As a result, the thermal behavior of PLA/starch/TOA blends with more TOA adding incline to that of PLA/TOA blend (95/5), especially for PLA/starch/TOA blend (58/30/12). But the deep reasons of TOA effected the crystalline of PLA/starch blends were not very clear and needed to be further investigated.

3.4. Mechanical properties

The morphology changes brought up the change of the mechanical properties of the PLA/starch blends. The changes of mechanical properties were exhibited in Fig. 5. A pure PLA is a fairly rigid material with a high tensile strength (∼66 MPa), but quite brittle, with the elongation at break (EB) and impact strength of ∼5% and ∼19 kJ/m^2, respectively. The addition of TOA to PLA matrixes caused a large reduce in tensile strength (∼55 MPa), but has less effect on the elongation at break (∼7%) and impact strength (∼21 kJ/m^2). It was also well known that PLA and starch are not chemically compatible and in addition, starch granules might make the PLA even more brittle. Thereof, a weak elongation at break (∼6%) and impact strength (∼11 kJ/m^2) for PLA/starch (70/30) blend could be seen.

However, with only 5 wt.% TOA in PLA/starch blend, all properties of PLA/starch blend has changed. The elongation at break and impact strength increased to ∼17% and ∼41 KJ/m^2, respectively, but the tensile strength decreased up to ∼ 30 MPa. Thus, the TOA works might be acted well as a plasticizer to tune the PLA/starch blend from rigid to ductile state. Similar with our previous researches (Xiong et al., 2013a, 2013b), with two other types of plant oil, epoxidized soybean oil (ESO) and castor oil (CO), adding to the functionalized Starch/PLA blends, the plant oil could accumulate on the surface of starch particles and form a flexible layer via the reaction between plant oil and functional starch, which caused the improvement of ductility of PLA/starch blend. Meanwhile, the flexible layer toughened the PLA/starch blend has also been investigated by Wang (Wang, Zhai, & Zheng, 2012), in their paper, a plasticizer PEG was grafted onto the surface of starch and then mixed with PLA/PEG blend. The results showed that the free PEG molecules would enrich onto the PEG grafted starch and formed a PEG flexible layer, which could greatly cause tensile energy diffusion and led to large-scaled plastic deformation of PLA matrix. Thus, the reason of our present study about the improvement of toughness of PLA/starch/TOA blend might be also attributed to the formed TOA layer on the surface of starch.

Moreover, with the amount of TOA increasing in Fig. 5, it could be observed that, for PLA/starch/TOA (63/30/7), the elongation at break and impact strength would increase to ∼32% and ∼43 KJ/m^2, respectively, but the tensile strength (∼28 MPa) was slightly declined in contrast with that of PLA/starch/TOA (65/30/5) blend. This result may be explained by that, in Fig. 2d, few TOA droplets existed in the PLA matrix, and most of TOA molecules might have been enriched on the starch granules. Thus, it could be inferred that the flexible TOA layer in PLA/starch/TOA (63/30/7) blend might be thicker than that of PLA/starch/TOA (65/30/5) blend, and could better consume the tensile energy resulted in the improved toughness in the tensile process.

However, when the content of TOA exceeds 7 wt.%, the TOA droplets on PLA matrix gradually appear again (Fig. 2e and f) and cause tensile properties of the ternary composites deteriorated, as showed in Fig. 5. But, the impact strength of PLA/starch/TOA blends has no much changed with the increasing amount of TOA. According to Hillmyer' studies (Chang et al., 2009; Gramlich et al., 2010; Robertson et al., 2010, 2011), the plant oil such as soybean oil and castor oil was immiscible with PLA matrix and did not improve ductility without the addition of a compatibilizer. Obviously, The TOA droplets existed in the PLA matrix would go

Table 1
Thermal and crystalline properties of PLA/starch blends with or without TOA.

Samples	T_g (°C)	T_c (°C)	ΔH_c (mJ)	T_{m1} (°C)	ΔH_{m1} (mJ)	T_{m2} (°C)	ΔH_{m2} (mJ)	χ_c (%)
Neat PLA	62	120	−133	164	136	–	–	3
PLA/TOA (95/5)	57	125	−131	164	129	–	–	–
PLA/starch (70/30)	62	117	−117	164	73	170	47	6
PLA/starch/TOA (65/30/5)	57	111	−99	162	36	168	76	21
PLA/starch/TOA (63/30/7)	57	114	−101	162	41	168	70	16
PLA/starch/TOA (60/30/10)	57	116	−103	162	48	168	63	13
PLA/starch/TOA (58/30/12)	57	118	−108	162	57	168	58	11

T_g, T_c, ΔH_c, T_{m1}, T_{m2}, ΔH_{m1}, ΔH_{m2}, and χ_c represented glass transition temperature, cold crystallization temperature, crystallization enthalpy, low melt temperature, high melt temperature, low melt peak fusion enthalpy, high melt peak fusion enthalpy, and degree of crystallinity, respectively. "–" represented uncalculated value from Eq. (1).

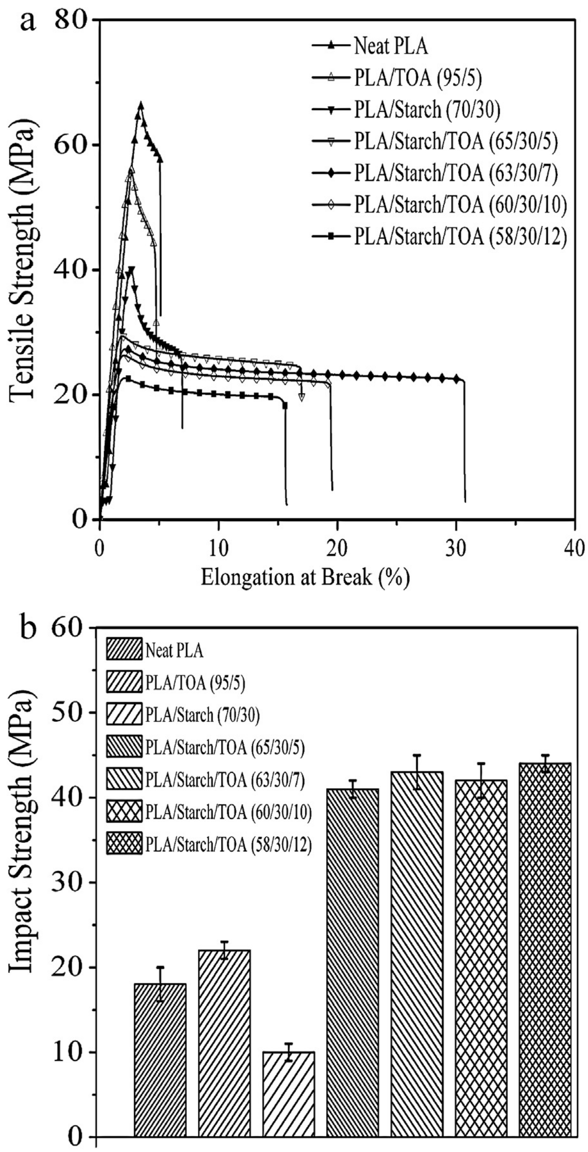

Fig. 5. The stress–strain curves (a) and impact strength (b) of PLA, PLA/TOA blend, and PLA/starch blends with or without TOA.

against the energy diffusion on tensile process, leading to the tensile properties decreasing.

3.5. *The morphology of tensile and impact fracture surface*

The SEM analysis has also been performed in order to investigate the tensile and impact fracture mode of the materials. For neat PLA sample, a lot of parallel fracture lines occurred on the tensile fracture surface along the tensile direction (Fig. 6a), but only one apparent fracture line was observed in the impact fracture section (Fig. 6e). According to Yan' work (Yan et al., 2007), this tensile and impact fracture behavior of the PLA materials could be attributed to the semi-brittle failure. For PLA/TOA blend (95/5) in Fig. 5b and f, a lot of similar parallel fracture lines in the tensile and impact fracture surfaces could be found. Maybe, the tensile and impact fracture behavior of PLA/TOA blend is also attributed to the brittle failure. Thus, it is inferred that the TOA droplets stayed in the PLA matrix could not play a very effective action for the tensile and impact energy diffusion, which have been proved by the results of mechanical properties in Fig. 5.

The tensile and impact fracture behavior of PLA/starch composites containing 30 wt.% starch particles in Fig. 6c and g showed that the starch inside acts as rigid particles. No deformation of PLA/starch composites is shown during the tensile process and all starch particles in PLA matrix have almost been fallen off after impact. Obviously, the starch particles could not act as an energy undertaker during tensile and impact progress. However, for PLA/starch/TOA blend (63/30/7), the tensile and impact fracture behavior of the ternary blend has been obviously changed by TOA. In Fig. 6d, it could be seen that the starch particles inside seemed to be squeezed by the moving PLA matrix and oriented after tensile, and in Fig. 6h, almost all starch granules are remained in PLA matrix after impact process. Obviously, the tensile deformation of PLA/starch blend and the interaction between PLA matrix and starch granules in impact process has been both enhanced by TOA. According to the above discussion in Figs. 2 and 3, it has drawn a conclusion that the TOA could be accumulated on starch and formed a layer via reaction, as schemed in Fig. 4. Meanwhile, it was known that the TOA had no much effect on the tensile and impact fracture behavior of PLA matrix in PLA/TOA blend (95/5). Thus, the changed tensile and impact fracture behavior of PLA/starch/TOA blend (63/30/7) may be caused by the TOA enriched starch, not only by TOA. Similar conclusion about the enrichment layer on starch toughening the PLA/starch blend has been reported by Wang's work (Wang, Zhai, & Zheng, 2012). But, in our research, the theory of plant oil accumulation on starch via reaction toughening the PLA/starch blends needs to be further investigated.

3.6. *Rheological characterization*

The rheological properties of polymers are very sensitive to the existence of plasticizers in the melted blend process, which attracts practical and fundamental interest in the current study. Fig. 7 depicts the shear viscosity as a function of frequency (s^{-1}) for neat PLA, PLA/TOA, and PLA/starch with or without TOA blends. The neat PLA shear viscosity data exhibits a shear shinning behavior in the investigated range. However, with 5 wt.% TOA or 30 wt.% starch in PLA, it can be observed that, although the PLA matrix also presents the shear thinning behavior in the investigated range, the viscosity of PLA matrix is apparently decreased by TOA or starch.

Interestingly, after the three components melt-blending, the resulted shear viscosity behavior of the ternary blends is very different from that of neat PLA, PLA/starch or PLA/TOA blends. For PLA/starch/TOA (65/30/5) ternary blend, the value of shear viscosity is much higher than that of PLA/starch or PLA/TOA blends in the low frequency range, but lower in the high frequency range, which exhibits a highly shear thinning curve in the investigated shear rate range. This is typical of branched or highly entangled polymer melts shear viscosity behavior with a shear thinning effect in polymer composites (Huneault & Li, 2007).

Meanwhile, according to the above discussion in Figs. 2 and 3, it was well known that the TOA molecules could be accumulated on the surface of starch particles and form a TOA layer at the particle-PLA boundaries via the reaction. Thus, it was reasonable to suppose that the TOA layer could enhance the interaction between PLA and starch granules, and generated some extent of entanglement among PLA, TOA and starch, which resulted in this shear thinning behavior in PLA/starch/TOA (65/30/5) ternary blend. However, with the TOA weight fraction in PLA/starch/TOA ternary blend increasing from 5 to 12 wt.%, the viscosity curve of PLA/native starch/TOA blends will be gradually declined in the investigated frequency range. This is because that, with TOA increasing from 5 to 12 wt.%, the redundant unreacted TOA will aggregate and exist in the PLA matrix with the formation of droplets again, as observed in

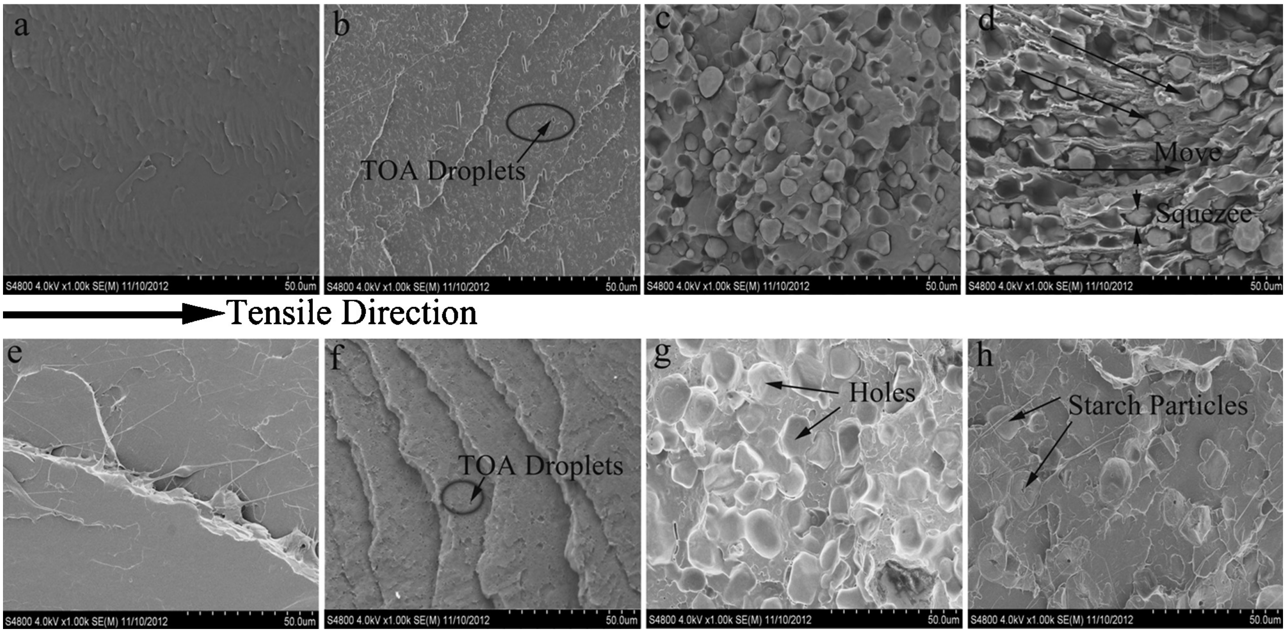

Fig. 6. The SEM of the tensile longitudinal fracture surfaces (a–d) and impact fracture sections (e–h) of neat PLA (a and e), PLA/TOA blend (95/5) (b and f), PLA/starch blend (70/30) (c and g), and PLA/starch TOA blend (63/30/7) (d and h).

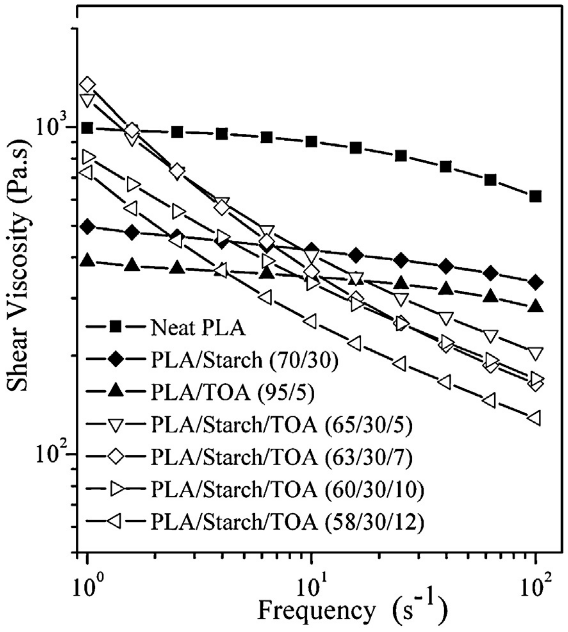

Fig. 7. Comparison of the shear viscosity curves of neat PLA, PLA/TOA, and PLA/starch with or without TOA blends.

Fig. 2d–f, which may play an negative effect on the shear viscosity of PLA/starch/TOA ternary blends.

4. Conclusions

Tung oil anhydride (TOA) could be used as a bio-based reactive plasticizer for PLA/starch blends via the ready reaction of maleic anhydride on TOA with the hydroxyl groups on starch, which could let these three components together and form a TOA layer on the surface of starch. The characterization of the obtained ternary blends with TOA by differential scanning calorimetry (DSC) demonstrated that the thermal properties of PLA were obviously influenced by the formation of TOA layer on starch granule. Tensile and impact properties of PLA/TOA/Starch (63/7/30) increased markedly compared to the PLA/starch (70/30) binary blend due to the produced TOA layer on starch. Meanwhile, the viscous behavior of PLA/native starch blends with TOA are very different from that of PLA/starch or PLA/TOA blends, which exhibit a typical branched or highly entangled polymer melts shear viscosity behavior in the investigated shear rate range, which resulted from the entanglement among PLA, TOA and starch generated by the TOA layer as well.

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