



# How does epoxidized soybean oil improve the toughness of microcrystalline cellulose filled polylactide acid composites?



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## ABSTRACT

Chemical effect is mainly utilized to induce the accumulation of epoxide soybean oil (ESO) on the surface of microcrystalline cellulose (MCC) particles as the formation of flexible layer to produce superior toughness of polylactide acid (PLA) composites. MCC is firstly maleated to produce appropriate chemical reactivity with ESO and thus ESO is induced to form a flexible layer around MCC particles by chemical reaction happened in melt-blending, which is proved by the results from XPS and contact angle measurements. This flexible layer increases the interfacial adhesion and provides an easy deformation region. As a result, high toughness is provided. The elongation and impact strength of PLA/ESO/MCC ternary composites can be respectively improved to 38.5% and 31.7 KJ/m<sup>2</sup>. This particular structure also helps to increase plasticization effect leading to a slightly decrease in  $T_g$ . The whole process elaborates a simple but an effective methodology to improve the toughness of PLA/cellulose composite in virtue of chemical effect. Toughness of PLA/ESO/MCC composites can be also controlled by the degree of chemical reaction (adjusted by the substitution degree of MA on MCC). Fully biodegradable PLA/ESO/MCC composite with high toughness is finally fabricated.

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## 1. Introduction

Bio-resourced and bio-degradable polyesters have been extensively researched as responses to concerns about sustainable energy and environmental protection. Polylactide acid (PLA) as one of the commercially available biopolyesters exhibits many attractive merits [1] such as environment-friendly behavior, excellent processibility and good mechanical strength. These advantage properties generally enable PLA to compete with petroleum-based plastics in many application areas [2]. Nevertheless, the drawbacks of elevated price, inherent brittleness, and slow crystallization rate restrict the industrial applicability of PLA [3–5]. A preferred solution referring to blending PLA with low-cost renewable fillers and bio-based toughening agents is mainly considered in producing environment-friendly composite materials with superior properties.

Cellulose as an important renewable filler of PLA attracts great attention because of its low price and easy availability. It can be treated by acid to remove the amorphous regions in producing a kind of filler with high specific surface and strength, which is called microcrystalline cellulose (MCC) [6]. As similar as other polymer composites, the critical issue concerning cellulose or MCC as the

reinforcement filler to promote the overall properties of PLA composites is essentially related to the improvement of interfacial compatibility between components. Conventionally, the interfacial compatibility between PLA and cellulosic fillers was enhanced by surface modification of cellulose [7] or addition of compatibilizers [8–10]. Although tensile strengths and moduli were increased, toughnesses of the composites decreased undesirably. In order to prepare toughening PLA composites, plasticizers including of triacetin, poly(ethylene glycol) and poly(propyleneglycol) were attempted to be applied in PLA/cellulose composites [11–13]. However, without sufficient chemical or physical interactions, various plasticizers could not provide PLA/cellulose composites the capability of effective brittle-toughness transition. With understanding of the process of compatibilization and plasticization in PLA/cellulose composites, reactive plasticizers are selected to modify the overall property of the composites.

Epoxidized soybean oil (ESO) is manufactured through the process of epoxidation of the C=C on the long aliphatic chain moiety of the soybean oil molecules. With the nature of chain flexibility and reactivity between epoxy functional group and the groups of –OH and –COOH on other polymers [14,15], ESO can be recognized as one of potential reactive plasticizers. Our previous work demonstrated the reaction of ESO with starch fillers in extrusion and then successfully changed the brittle nature of PLA/starch composites [16]. With our best knowledge, no direct reference has suggested an effective methodology for toughness

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improvement of PLA/cellulose composite via simple melt-blending. In this manuscript, ESO as the reactive plasticizer is extended to the composite including of PLA and MCC. MCC is firstly modified with maleic anhydride (MA) to produce carboxyl for the reactivity with epoxy functional group of ESO. And then ESO, MA-modified MCC and PLA are blended simultaneously by means of a miniature two-screw extruder to form toughening PLA/ESO/MCC composite. The distribution state of ESO in the ternary composites is systematically evaluated by SEM, XPS and contact angle measurements. Thermal and mechanical properties are characterized by DSC, tensile test, and impact characterization in order to discuss the effects of chemical reaction between ESO and MCC on properties of the composites.

## 2. Experimental section

### 2.1. Materials

Semi-crystalline PLA (4032D) was obtained from NatureWorks LLC (Minnesota, USA). Food grade MCC fillers were supplied by Yuzhong Biotechnology Company (Henan, China), and the average length and diameter of the fillers were about 80 and 20  $\mu\text{m}$ , respectively. The chemical pure grade ESO from Aladdin Reagents (Shanghai, China) was used without further purification. The analytical pure MA and toluene (purchased from Aladdin Reagent) were used as received without further purification as well.

### 2.2. Preparation of maleated MCC

Three samples of grafting MA onto MCC (or maleated MCC) surface were synthesized by heterogeneous method and marked as MAMCC1, MAMCC2 and MAMCC3 respectively. In brief, a three-necked flask equipped with Dean–Stark trap, a condenser and a mechanical agitator, was immersed in an oil bath to be heated to 130 °C. Subsequently, a mixture of MCC after dried at 75 °C for 4 h, MA (10 wt%, 20 wt%, and 67 wt% with relation to the MCC) and 150 mL toluene was introduced into the flask, and the reaction went on for 1 h at 130 °C with continuous stirring. After the reaction, the maleated MCC products were then obtained by several successive filtrations with acetone to remove the toluene solvents and residual anhydride. The resulting product was dried in a vacuum oven at 80 °C for 12 h for further use. The degree of substitution (DS) of MCC was measured by the method of chemical titration, which was described in Ref. [17].

### 2.3. Fabrication of PLA/MCC blends

PLA and MCC were firstly vacuum-dried at 80 °C for 12 h. And then pure PLA, PLA/MCC (weight ratio of 75/25, 80/20 and 90/10), PLA/ESO (95/5, 90/10, 85/15), and PLA/Maleated MCC/ESO (70/20/10) were melt-blended by a lab-scale conical twin screw extruder (Ruiming Plastics Machinery, Wuhan, China) with rotational speed 40 rpm at 175 °C for 5 min. All of the materials were sequentially injected into standard test bars via a miniature injection machine (SZ-15, Wuhan, China). The injection pressure, injection temperature and time were 3 MPa, 200 °C and 30 s, respectively, and the mold temperature was controlled at 40 °C.

### 2.4. MCC fillers extracted from ternary blends

Cellulosic fillers from ternary composites were obtained by Soxhlet extraction with methylene chloride for at least 3 days to remove unbonded monomers. The resulting extractants were denoted separately as extracted MCC, extracted MAMCC1, extracted MAMCC2, and extracted MAMCC3 according to the corresponding

composites. Thereafter, the extracted fillers were then vacuum-dried for 5 h at 50 °C before characterization.

## 2.5. Characterizations

Fourier transform infrared (FT-IR) spectra of MCC or MA-g-MCC samples prepared with KBr were recorded by one spectrophotometer (Nicolet FTIR6700 infrared spectrophotometer) over wave numbers range of 4000–400  $\text{cm}^{-1}$ . The distribution state of components in ternary blends was studied by a scanning electron microscope (SEM, Hitachi TM-1000). The samples was prepared by cryogenically fracture under liquid nitrogen and then analyzed by SEM after sputter coated by gold. The elemental composition analysis of the surface layers of MCC fillers was performed on Kratos AXIS Ultra DLD photoelectron spectrometer (Shimadzu, Japan) with a hemispherical sector energy analyzer. Al  $K\alpha$  X-ray was used as the excitation resource. All spectra were calibrated with graphitic carbon at a binding energy of 284.8 eV. The static contact angles with water and diiodomethane at equilibrium were measured on an apparatus named Data physics instrument (OCA20, Germany), which was equipped with camera with a precision of  $\pm 0.1^\circ$ . Six points at least of each sample were recorded and averaged to determine the contact angles. The surface energy parameters of water and diiodomethane contact test liquids to calculate the surface energy were obtained in Ref. [18]. DSC measurement, charactering the thermal behaviors, was conducted on a Pyris Diamond DSC instrument. The glass transition temperature ( $T_g$ ) as well as melting temperature ( $T_m$ ) were obtained by the first heating scan, in which the samples were scanned at a rate of 10 °C/min from 25 °C to 200 °C under a nitrogen flow of 20 mL/min. The tensile properties were characterized by an Instron5567 according to GB/T 1040.1-2006 (equivalent to ISO527-4) at the speed of 20 mm/min. And, the unnotched impact testing was performed according to ISO179-1.98 and 5.5 J pendulum was employed.

## 3. Results and discussion

### 3.1. Surface modification of MCC

In the experiment, MCC is chemically modified with MA in an inert solvent to improve the surface reactivity with ESO. Results of FT-IR spectroscopic analysis are shown in Fig. 1(a). The absorption band at 3100–3600  $\text{cm}^{-1}$  on the spectrum of MCC is attributed to the hydroxyl stretching vibrations. Some peaks in relation to the deformation of glucopyranose ring at 1110  $\text{cm}^{-1}$ ,  $\beta$ -(1,4) glycosidic linkages at 897  $\text{cm}^{-1}$ , and C–O stretching of skelton at 1058  $\text{cm}^{-1}$  and 1027  $\text{cm}^{-1}$  are also exhibited. It agrees well with the pure cellulose (see Refs. [19,20]). After the surface modification, the absorption band associated with carboxyl functions (see Ref. [20]) appears at 1727  $\text{cm}^{-1}$ . From Fig. 1(a), no absorption band associated to anhydride functions [21] is detected at 1786  $\text{cm}^{-1}$ . It indicates that the unbonded MA is completely removed after successive filtration. These results clearly show that MA is successfully bonded on MCC surface via chemical reaction. The substitution (DS) of maleated MCC is controlled at 0.2–0.5, which is confirmed by chemical titration. Absorption band intensity is gradually enhanced with the increase in DS.

Morphologies of transverse sections of the ternary composites including of PLA, ESO and cellulosic fillers are presented in Fig. 2. Many gaps and clear interfaces are observed between MCC and PLA in PLA/MCC/ESO composite (see Fig. 2(a)). It reflects the poor interfacial adhesion. After using MA modified MCC in ternary composites, the rupture interface gradually becomes obscure (see Fig. 2(b)–(d)). This result exhibits that the interfacial adhesion can be improved by the surface modification of MCC.

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