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Surface hydrophobic modification of starch with bio-based epoxy resins to fabricate high-performance polylactide composite materials

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ABSTRACT

The surface hydrophobic modification of starch was firstly made by use of two bio-based epoxy resins to fabricate the fully bio-based polylactide (PLA)/starch composites with superior mechanical and thermal properties. As demonstrated by FT-IR and ^{1}H NMR, the surface of starch was successfully modified with the epoxidized itaconic acid (EIA) or epoxidized cardanol (Epicard) to produce hydrophobicity with the contact angle increasing from 44° to ~100°. After modification, the interfacial adhesion between starch and PLA was obviously improved, which can be clearly observed by SEM. As a result, an obvious increase of tensile strength from about 35 MPa to over 50 MPa was obtained. Moreover, with the strong interaction formed at the interface between modified starch and PLA, the crystallization ability of PLA was also enhanced as confirmed by DSC and DMA. This study suggested us a simple but effective surface modification technique by utilizing the bio-based epoxidized modifiers to improve interfacial adhesion in fabricating fully bio-based PLA/starch composites with superior properties.

1. Instruction

In recent years, environmental concerns and shortage of petroleum resources have driven the efforts on the development and production of biodegradable and recyclable materials, which are known as “green materials” to solve disposal problem [1–3]. Among biodegradable polymers, polylactide (PLA) is one of promising polymers with high biodegradability, recyclability and good mechanical properties for industrial plastic applications [4–6]. However, the disadvantages of high cost of PLA limit its usage for disposal items. Starch, as a common, inexpensive and environmentally friendly biopolymer, is an attractive candidate as an organic stiffness filler for PLA. Development of advanced materials technology to introduce starch into PLA as the formation of fully bio-based composite with superior properties is becoming an important research topic and attracts great attention in the past few years [7,8].

Understanding the difference between hydrophilicity of starch and hydrophobicity of PLA [9], weak interfacial adhesion between the two components is essentially realized as the primary issue to fabricate PLA/starch composite with high mechanical properties. Reported by recent researches, strong interfacial adhesion between starch and PLA could be achieved by producing hydrophobicity on the surface of starch with chemically grafting of hydrophobic polymer. A first potential route is to use some hydropholic vinyl polymers such as polystyrene [10], methacrylonitrile [11], polyvinyl alcohol [12], and acrylonitrile [13] for surface modification. Although, these grafted vinyl polymer branches on starch could enhance the interfacial adhesion between starch and PLA, the biodegradation of starch was decreased by the presence of the non-degradable part of vinyl polymer on starch.

A second approach was related to chemically bond starch with biodegradable polymers such as PCL and PLA via the ring open polymerization (ROP) technique or esterification reaction [14–19]. The graft-copolymers of starch-g-PCL and starch-g-PLA with the complete biodegradability by bacteria or under natural conditions had the excellent compatibility with the PLA matrix [17–19]. Through this method, the compatibility was improved due to the hydrophilic starch encapsulated with hydrophobic PLLA or PCL chains. The tensile strength of the PLA/starch composites was obviously increased. However, because almost all catalysts for CL or LA copolymerization or esterification reaction are sensitive to moisture, the only problem during graft polymerization of PCL or PLA is associated with water absorption. As a result, the surface hydrophobic modification of the starch by PCL or PLA was hard to operate.

Based on the literatures reviewed, an effective potential method by utilization of the bio-based hydrophobic modifiers is considered. It is exhibited in our previous researches [20–22] that hydrophobic plant oil containing the structures of isocyanate, epoxy and maleic anhydride was used to react with starch then provide hydrophobicity on starch surface. So that, the interfacial adhesion between starch and PLA was improved. Though the improvement of hydrophobicity on starch surface was experimentally confirmed,

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the low content of active groups on these plant oils can only provide low reactivity with starch. As a result, the interfacial adhesion between starch and PLA was not high enough, which needs to be further improved to fabricate the superior mechanical properties of PLA/starch composites.

In order to formulate and develop PLA/starch biodegradable blends with good interfacial adhesion and thus excellent properties, we considered to explore kinds of low-molecular weight bio-based hydrophobic compounds with high reactivity as the surface modifier for starch. It was well known that the epoxidized compounds had the high reactivity with the hydroxyl groups of starch under tetrabutylammonium bromide (TABA) as a catalyst [23]. Thereof, in this paper, we used two types of hydrophobic bio-based epoxy compounds (namely Epicard and EIA) with high epoxy value to modify starch. The change of molecular structure and hydrophobic characteristic of starch is analyzed by ^{1}H NMR, FTIR, and contact angle measurements in detail. Subsequently, the modified starch was directly blended with PLA via a co-extruder to investigate the importance of the surface hydrophobic modification of starch on the improvement of interfacial adhesion with PLA matrix in SEM. Furthermore, tensile testing, DSC and DMA analysis were used to show the effect of surface modification of starch on mechanical and thermal properties.

2. Experiment section

2.1. Materials

A semi-crystalline extrusion grade, PLA 4032D was supplied by NatureWorks (Nebraska, USA). It was vacuum dried at 80 °C for 8 h prior to use. The native food grade corn-starch with the particle diameters about 5–20 μm 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. Toluene and acetone as the solvents were obtained from Aladdin Reagent, China. Tetrabutyl ammonium bromide (TBAB) was supplied by Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were used as received.

The low molecular weight epoxy compounds used were a novel bio-based ester epoxidized itaconic acid (EIA) with a high epoxy value of 0.625, and a bio-based ether epoxidized cardanol (Epicard) with a high epoxy value of 0.3 and a purity of 90%. The bio-based ester EIA was synthesized by our own group [24], whereas, the bio-based ether Epicard was purchased from Cardolite Company, America. The two bio-based epoxy compounds were hydrophobic. The structure of the two types of bio-based epoxidized compounds were exhibited in Fig. 1.

2.2. Surface modification of starch granules by EIA and Epicard

Two samples of grafting EIA and Epicard onto the starch surface (or epoxidized starch) were synthesized by a heterogeneous method and marked as EIA-g-starch, and Epicard-g-starch, respectively. In brief, a three-necked flask equipped with a 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 dried starch, EIA or Epicard (20 wt% with relation to the starch) and 150 mL of toluene was introduced into the flask, and the reaction went on for 24 h at 130 °C with continuous stirring. After the reaction, the epoxidized starch products were then obtained by six successive filtrations with acetone to remove the toluene solvents and unreacted epoxy compounds. The resulting product was dried in a vacuum oven at 80 °C for 12 h for further use. The synthetic scheme was shown in Fig. 1.

2.3. Preparation of the blends

PLA/starch and PLA/modified starch blends are firstly melt-blended in a Brabender twin screw extruder (Brabender, Germany). The rotation rate and the mixing temperature were set at 40 rpm and 170 °C/175 °C/180 °C/175 °C/175 °C, respectively. Where-after, the melting blends were water-cooled and sent to a LQ-25 granulator (Hengxi Machinery manufacturing Co., Ltd., Taizhou, China) to make pellets. At last, the pellets of PLA blends were dried at 85 °C in a vacuum drying oven for 24 h before injection molding.

2.4. Characterizations

The structures of native starch, EIA-g-starch and Epicard-g-starch were analyzed by the infrared spectrum (FT-IR) and ^{1}H NMR. The infrared spectrum (FT-IR) was recorded with NICOLET 6700 FT-IR (NICOLET, America). ^{1}H NMR was performed on a 400 MHz AVANCE III Bruker NMR spectrometer (Bruker, Switzerland) with DMSO-d_6 as a solvent. The SEM images were obtained with a low expansion scanning electron microscope TM-1000 from Hitachi after the sputter coating of gold on the specimen surface.

The morphologies of the native starch and modified starch as well as their respective surface morphology for contact angle testing were recorded by this SEM. The microstructure of the fracture surfaces of PLA/starch and PLA/modified starch samples with the dimension of 80 × 10 × 4 mm were also recorded by this TM-1000 SEM.

The static contact angles with water at equilibrium were measured on an apparatus named Data physics instrument (OCA20, Germany), which is equipped with camera with a precision of ±0.1°. Six points at least of each sample were recorded and averaged to determine the contact angles.

The thermal properties of the blends were characterized by a METTLER TOLEDO TGA/DSC1 analyzer. For the non-isothermal crystallization, the samples were heated to 200 °C and kept in the molten state for 3 min to erase the prior thermal history. The samples were then cooled at 5 °C/min to 25 °C in order to evaluate their ability to crystallize upon cooling. Subsequently, the samples were heated to 200 °C with the rate of 5 °C/min to assess crystallization behavior upon heating.

According to GB/T 1040.1-2006 (China), the samples were injection molded into 1 A type dumbbell-shaped samples with a thickness of 4.0 mm in a HTF90W injection molding machine (Haitian Plastics Machinery, Ningbo, China). The tensile testing was carried out at a rate of 20 mm/min based on GB/T 1040.1-2006 (China). Four samples for each composite were tested. These samples were conditioned at room temperature for a week prior to test.

Based on the America standard of ISO179-1:98 (USA), the samples were injection molded into a type of rectangular solid with a dimension of 80 × 10 × 4 mm for impacting test in a HTF90W injection molding machine (Haitian Plastics Machinery, Ningbo, China). In order to conduct the impact test, the samples were then notched on a WAY-240 universal sampling machine (Chengde Kecheng Testing Machine Co., Ltd., China), the depth of notch on these samples were arranged from 1.9 to 2.1 mm. The notch impact test was performed on a mechanical impact tester (XJ-50Z, Chengde Dahua Testing Machine Co. Ltd., Chengde, China). In the process of notch impact test, a 2.75 J pendulum was used to determine the notch impact strength. These samples were conditioned at room temperature for a period of one week prior to testing, and five samples for each composite were tested.

Dynamic mechanical analysis (DMA) was carried out on Mettler Toledo DMA/SDTA861 using a three points bending fixture. All the samples with the dimension of 80 mm × 10 mm × 3 mm were

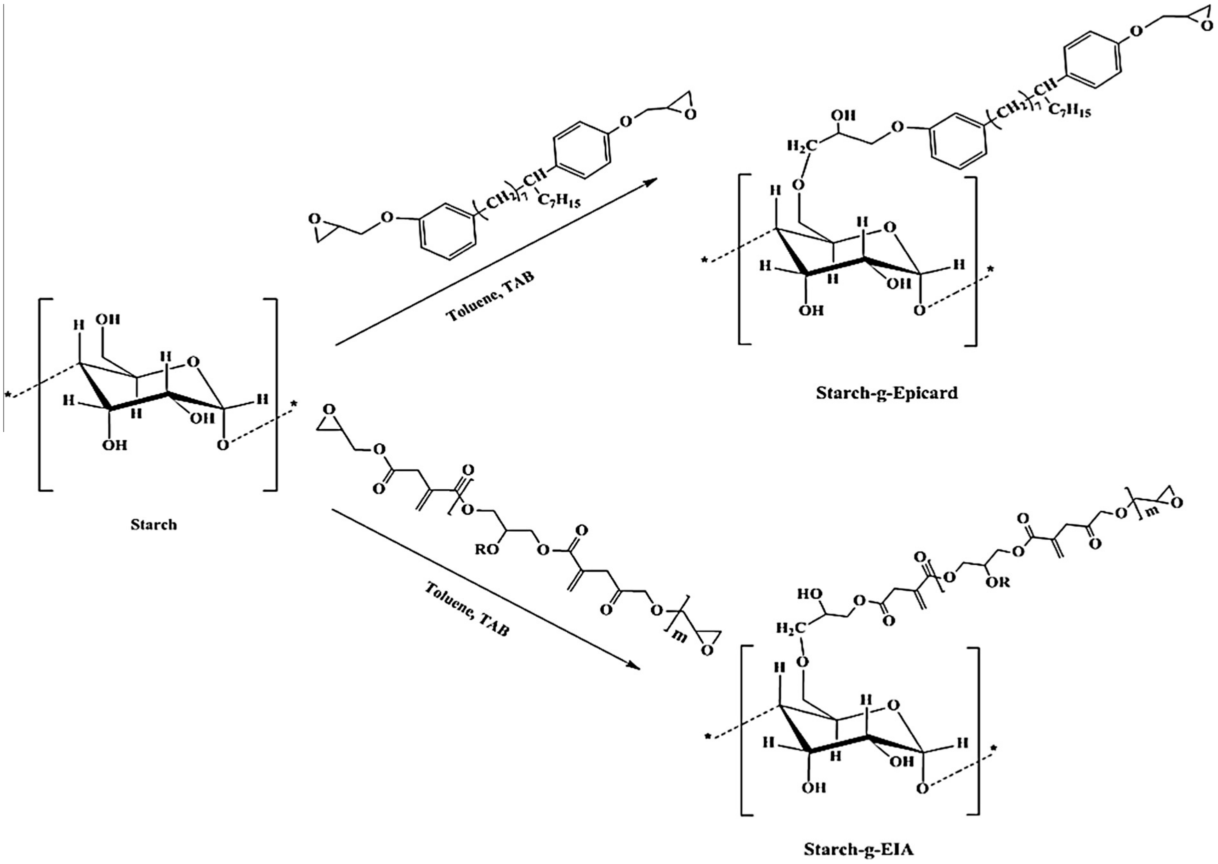

Fig. 1. The surface modification of starch with the two kinds of bio-based epoxy resins.

tested from $-50{\sim}150$ °C at a heating rate of 2 °C/min^{-1} and a frequency of 1 Hz. The storage modulus (E), and tan δ were recorded as a function of temperature.

3. Results and discussion

3.1. Surface modification of starch

The FT-IR spectra of native starch, the Epicard grafted starch, and the EIA grafted starch were shown in Fig. 2. In Comparison with the spectrum of native starch with the surface modified starches, the new strong absorptions emerged at 1742 cm^{-1} can be assigned to carbonyl (—C=O) in the ester epoxidized itaconic acid (EIA) in the spectra of EIA-g-starch. It indicated that a small amount of EIA was successfully grafted on the surface of starch. However, the FT-IR spectra of Epicard grafted starch did not show too much change in comparison with that of native starch.

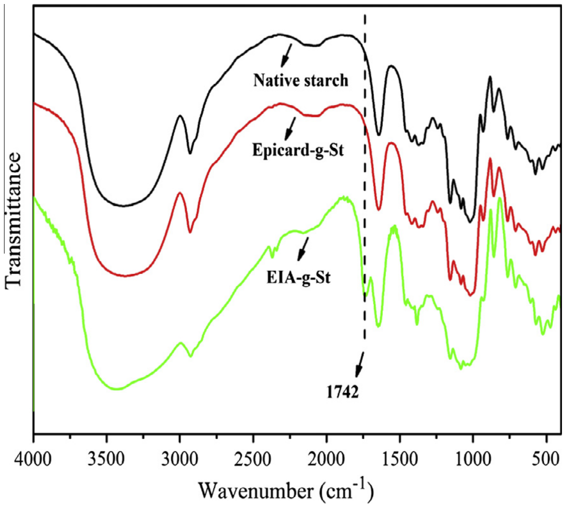

Fig. 2. The FT-IR analysis of the starch before and after modification.

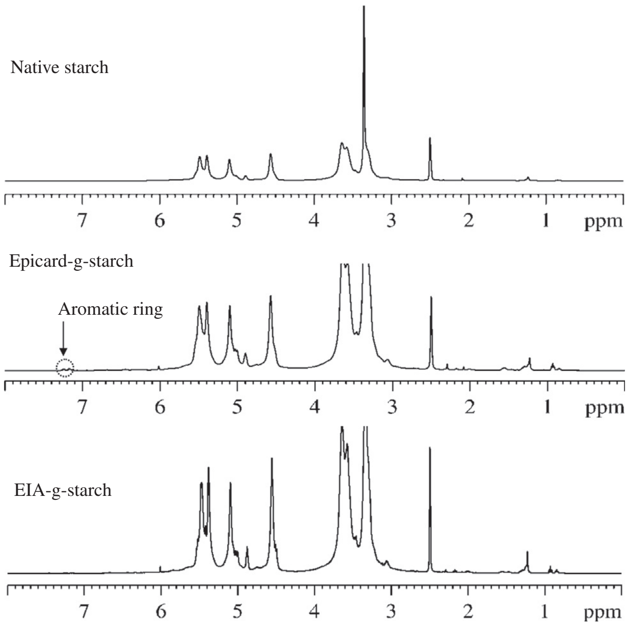

Fig. 3. The ^{1}H NMR spectrums of the starch before and after modification.

In order to reveal the chemical reaction between Epicard and starch, starch was characterized by ^{1}H NMR. In Fig. 3a and c, no peaks can be found around 6.9–7.2 ppm from the ^{1}H NMR curves of native starch and EIA-g-starch. However, in Fig. 3b, some peaks appeared at 7.22 ppm and 6.95 ppm concerning with the para-disubstituted benzene ring of Epicard-g-starch [25]. That is to say, a small amount of Epicard was successfully bonded to the surface of starch particles via the chemical reaction.

3.2. Hydrophobicity of the modified starch and its interfacial adhesion with PLA

Contact angle (CA) measurements were used to estimate the change in hydrophobicity of the grafted substrates compared to unmodified starch. Although, the SEM morphology and size distribution of modified starches had no much change with the un-modified starch in Fig. 4a_1–c_1, a distinct difference in hydrophobicity was observed in Fig. 4a_2–c_2. Moreover, while a droplet was placed on the surface of the un-grafted starch substrate, it was rapidly adsorbed with a low CA (37°), whereas the droplet on the grafted starches remained on the surface with a large CA of 110° and 95° for EIA-g-starch and Epicard-g-starch, respectively. It indicated the hydrophilic starch changed into hydrophobic one with the Epicard or EIA grafting on its surface. A distinct change of the hydrophilic starch or cellulose into the hydrophobic ones via the surface modification with some hydrophobic polymers grafting was also observed in other literatures via the contact angle (CA) measurements [16,26].

Microstructure of PLA/starch composite was analyzed to show the change of interfacial adhesion at the interface between PLA and starch with the modification of starch by hydrophobic epoxy resins. In Fig. 4a_3–c_3), many holes with sharp edge were observed at the fracture surface under SEM. Because of the typical characteristics of the difference between hydrophilicity of starch and hydrophobicity of PLA, the compatibility and interfacial adhesion between PLA and starch was poor. Starch particles can be easily removed from PLA matrix to form the holes with sharp edges [27]. However, with the hydrophobic modification on the starch surface, starch particles were well embedded in the PLA matrix and almost no holes appeared in the PLA matrix (see Fig. 4b_3 and c_3). Considering hydrophobic Epicard and EIA on the surface of starch granules as well as the hydrophobic characteristic of PLA, the interfacial adhesion between PLA and starch was possibly increased by the good inter-diffusion of molecular layer between PLA and hydrophobic epoxy resins on the starches, as schemed in Fig. 5. The similar method of modifying the surface of starch granules with the hydrophobic polylactide to improve the interfacial adhesion between starch granules and PLA matrix in starch/PLA blends was also obtained by Yang and the co-workers [19].

3.3. Mechanical properties of PLA/Starch composites

The change in morphology initiated the change in the mechanical properties of the PLA/starch composites. In Fig. 6, the addition of starch fillers into PLA matrix significantly reduced the mechanical properties due to the poor filler/matrix interfacial adhesion. When epoxy resins modified starches were used, the mechanical properties of PLA/modified starch composites including modulus, tensile strength and elongation at break were all improved greatly (see Fig. 6). The major reason for the increased mechanical properties of PLA/modified starch composites was the reinforcement of interfacial adhesion between PLA matrix and modified starch, which illustrated in Fig. 5. The similar result was also discussed in Sun' research paper [28], in which, it reported that if a strong

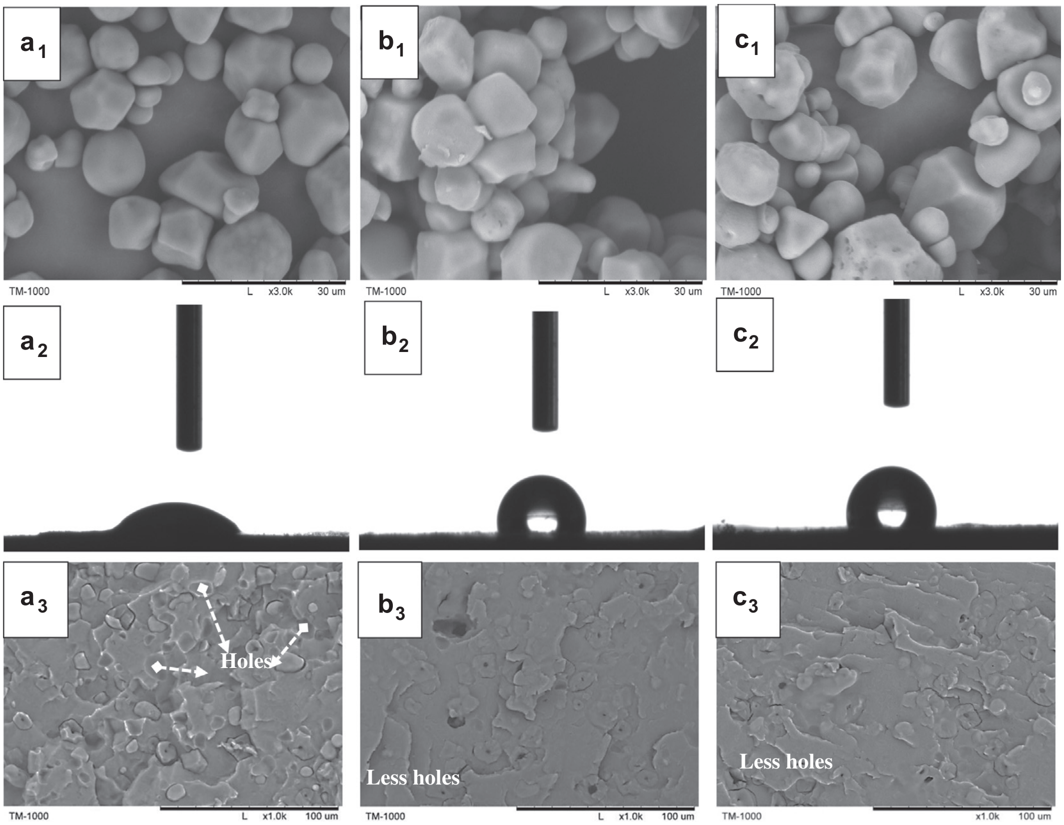

Fig. 4. The morphology and water contact angle of the native starch (a_1 and a_2), EIA-g-starch (b_1 and b_2) and Epicard-g-starch (c_1 and c_2) as well as the starch granules in PLA/native starch composite (a_3), PLA/EIA-g-starch composite (b_3) and PLA/Epicard-g-starch composite (c_3).

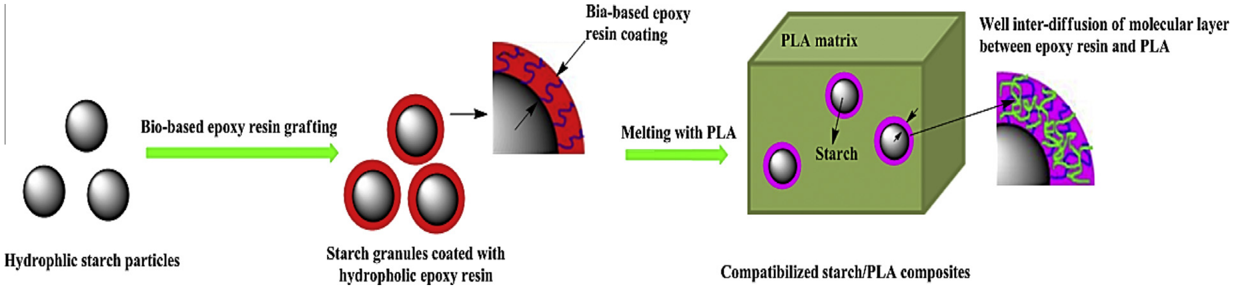

Fig. 5. Schematic illustration of the process for the formation of bio-based epoxy resin grafted starch/PLA composites with improved compatibility between starch and PLA.

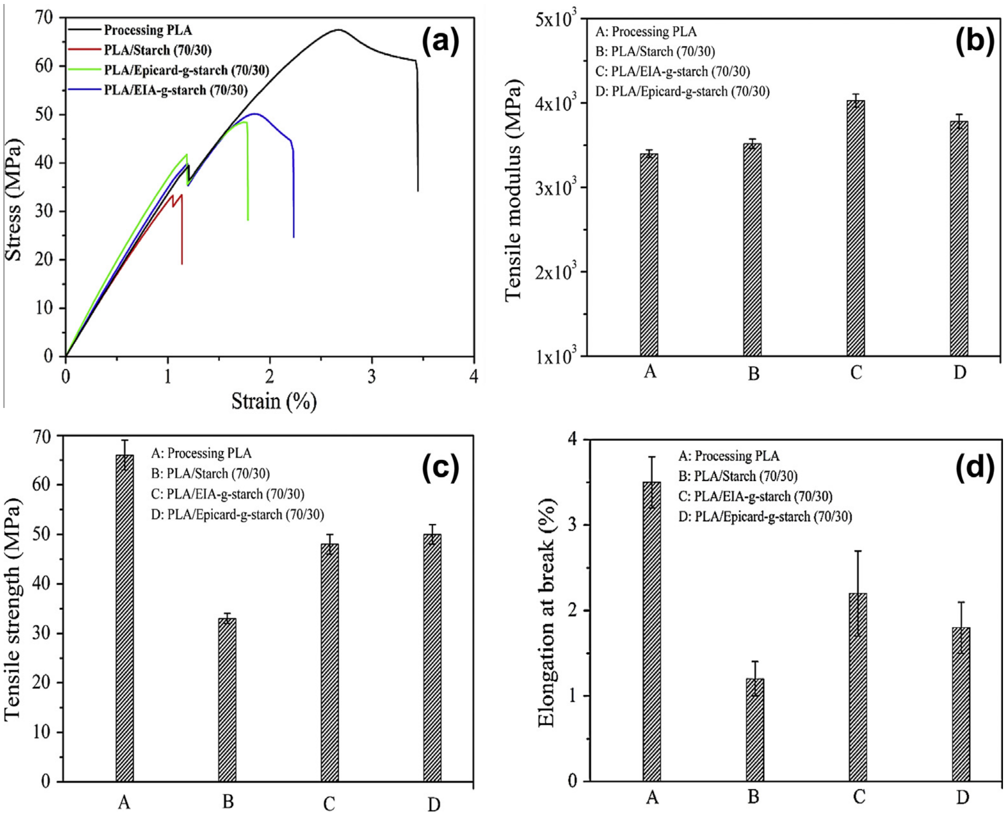

Fig. 6. Mechanical properties of PLA and PLA blends with native starch and modified starches: (a) stress–strain curves, (b) tensile modulus, (c) ultimate tensile strengths, and (d) elongation at break.

interfacial adhesion between PLA and starch was formed, an enhanced modulus, tensile strength and elongation at break would be obtained for PLA/starch composite.

Although the mechanical properties of PLA/modified starch composites cannot reach the level of PLA, this simple technique of hydrophobic epoxy resin modification of starch obviously improved the mechanical properties and provide the composites fit for industrial use.

3.4. Thermal properties of PLA/starch composites

The effect of starch before and after epoxy resins modification on the non-isothermal crystallization kinetics of PLA was investigated in Fig. 7. The DSC thermograms of PLA and PLA/native starch composites obtained for the cooling at a rate of 5 °C/min were shown in Fig. 7a. The neat PLA exhibited no crystallization peak upon cooling, but during reheating in Fig. 7b, a crystallization peak appeared at around 104 °C showing that the ability of PLA chains began to crystallize. It reduced the crystallization induction period of PLA due to the production of crystalline nuclei during cooling process, although no crystallization peak upon cooling was found. Thus, upon reheating, the PLA crystalline structure was easier to be formed than when the PLA polymer was being cooled from the melt, which indicated the weak crystallization ability of PLA [29–31].

As to the starch modified by EIA and Epicard, a very sharp crystallization peak upon cooling was found and this peak was shifted up to 110 °C for the PLA/EIA-g-starch and PLA/Epicard-g-starch composite, respectively. On subsequent heating, no crystallization peak was observed for the two PLA/modified starch composites since the PLA was already crystallized to its maximum in the cooling cycle. Based on these results, the crystallization ability of PLA in the upper temperature window was greatly promoted by the two

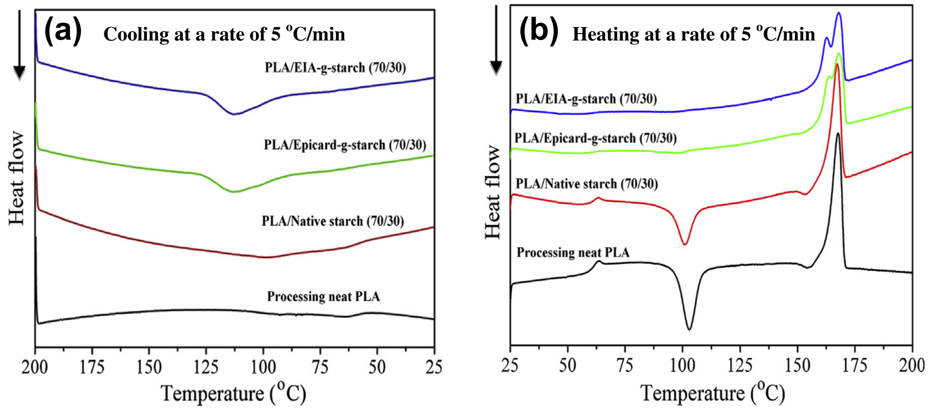

Fig. 7. DSC thermograms for PLA and PLA blends with native starch and modified starches cooled at 5 °C/min (a) and subsequently heated at 5 °C/min (b).

types of modified starches. Thus, it was inferred that the increase in the hydrophobicity of the modified starch provided the starch particles the ability to act as a nucleating agent for PLA as exhibited in Fig. 4.

3.5. Thermomechanical properties of PLA/starch composites

The efficiency of modified starch as the filler for PLA was investigated in detail in DMTA. The DMTA curve of pure PLA (Fig. 8a and b) showed a remarkable drop in E', a sharp tan δ peak at around 74.9 °C relating to the glass transition (T_g), and an increase in E' above 90.8 °C due to the crystallization of amorphous PLA. Obviously, the chain mobility of the amorphous areas was increased above T_g, which favors the crystallization process [32]. Due to the high stiffness of starch particles [33], the storage modulus occurring over the temperature range of 25–50 °C for the PLA/starch composite was increased. Moreover, at a slow heating rate for PLA/starch, an increase in E' attributed to the initial crystallization temperature in Fig. 8a was shifted to the lower temperature than that of pure PLA, indicating some extent of induced crystallization ability of starch for PLA, as reported by Cai and the co-workers [34].

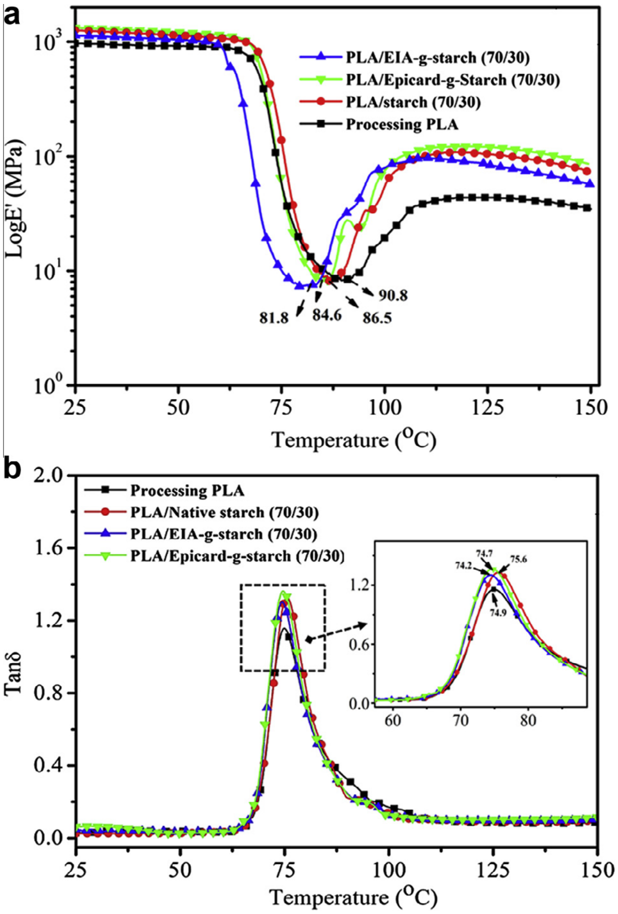

Fig. 8. Storage modulus (a) and tan δ (b) (DMTA) curves of pure PLA, PLA/native starch composite and PLA/modified starch composites.

In Fig. 8a, the starch modified by the two bio-based epoxy resins had a better effect in inducing crystallization of PLA than native starch, as shown by the fact that the increases in E' for the two PLA/modified starches composites were both shifted to the lower temperatures. Furthermore, as exhibited in Fig. 8b, the tan δ peaks of PLA/modified starch composites corresponding to the T_g were both shifted to lower temperatures than in pure PLA, but not for PLA/native starch, indicating that the epoxy resin-grafted starches were sufficiently miscible with PLA molecules in the composites. Therefore, attractive interactions were likely present between modified starch and PLA molecules, which were mediated by the surface-grafted epoxy resin chains, as schemed in Fig. 5. The similar phenomenon of the improved crystallization ability of PLA was also achieved in the PLA/cellulose composites via the flexible compounds modifying the surface of cellulose by Fujisawa and the co-workers [35].

4. Conclusions

In this work, in order to improve the interfacial adhesion between PLA and starch, two types of the hydrophobic surface modifying starches (Epicard-g-starch and EIA-g-starch) were successfully prepared by utilization of the bio-based epoxy resins (Epicard and EIA) to serve as the surface modifiers. The results revealed that a small amount of bio-based epoxy resins bonded onto the surface of starch via chemical reaction could provide hydrophobicity and then improve the interfacial adhesion between starch and PLA. The increase of interfacial adhesion did not only promote the overall mechanical properties of PLA/starch composites, but also enhanced the efficient crystallization ability of PLA. By this simple process, a fully bio-based PLA/starch composite with superior mechanical and thermal properties was obtained by the modification of starch with bio-based epoxy resins.

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