



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 ^1H 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 $\sim 100^\circ$. 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.

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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 hydrophobic 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 ^1H 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 ^1H NMR. The infrared spectrum (FT-IR) was recorded with NICOLET 6700 FT-IR (NICOLET, America). ^1H 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 $\pm 0.1^\circ$. 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

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