



Preparation and characterization of thermoplastic starches and their blends with poly(lactic acid)



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ABSTRACT

Two different thermoplastic starches (TPS), namely maleic anhydride grafted starch (MA-g-starch) and epoxidized cardanol grafted starch (Epicard-g-starch), were successfully prepared by chemical modification without the addition of any plasticizer. The structure and properties were characterized by nuclear magnetic resonance (NMR), X-ray diffraction (XRD), hot press testing, scanning electron microscopy (SEM) and contact angle meter, respectively. Results from XRD showed that the highly crystalline structure of native starch was destroyed after modification. Continuous phase was obtained from both of the chemically modified starches after hot pressing at 130 °C, indicating that they have good thermoplasticity. Subsequently, they were melt-blended with PLA. It was found that the Epicard-g-starch had a much finer dispersed phase size than MA-g-starch in PLA matrix due to its better hydrophobicity. As a result, the mechanical properties of PLA/Epicard-g-starch blend were superior to those of PLA/MA-g-starch blend.

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1. Introduction

In recent years, driven by the ever-increasing concern on environmental pollution and the shortage of petroleum resources, biodegradable and renewable polymers have attracted significant attention [1,2]. Poly(lactic acid) (PLA), produced from the fermentation of annually renewable resources, has gained growing interests as an alternative to conventional synthetic polymers [3]. PLA possesses high modulus, high strength, excellent clarity, good biocompatibility and biodegradability, and all these merits make it become a promising polymer for a great variety of application, such as biomedical applications, industrial packaging and disposable tableware [4]. However, the wide applications of PLA have been hampered by its native defects, such as low heat distortion temperature, brittleness and poor impact resistance [5]. Its high price, in particular, significantly limits its uses for disposable items. Starch, an inexpensive and renewable biopolymers which can be easily available from many plants, is an ideal candidate as an organic filler for PLA to make fully biodegradable composites. Unfortunately, PLA and starch are thermodynamically immiscible, if the starch is directly blended with PLA, their interfacial adhesion is very poor

and a brittle composite is usually obtained, especially at high starch concentrations [6].

Many efforts have been made to improve the interfacial adhesion and mechanical properties of PLA/starch blend. The first one involves the use of coupling agents or reactive compatibilizers, which have difunctional groups to chemically link the starch particles to the PLA matrix, and improve the compatibility between them. Typical examples are methylene-diphenyldiisocyanate (MDI) [6,7] and maleic anhydride (MA) [8]. A second approach consists in chemically bonding the surface of starch particles with polymeric side chains that are miscible with the polymer matrix. For instance, PLA oligomers were grafted onto the surface of starch particles by in situ polymerization to improve their interfacial affinity with PLA [9–11].

Another potential route to increase the ductility of PLA/starch blends is the use of gelatinized starch rather than granule starch, namely thermoplastic starch (TPS). Because of the strong hydrogen bond interaction existing in starch molecules, the melting temperature of starch is very close to its decomposition temperature, so thermal degradation occurs before the starch crystalline melting point is reached [12–14]. Many methods have been explored to prepare TPS, the most familiar one is to use small molecular plasticizers. A great deal of literatures have focused on this field, and the commonly plasticizers are water [15,16], glycerol [17], urea [18], sorbitol [19,20] and citric acid [21]. During the process of preparing TPS, the strong intramolecular hydrogen bond is broken and

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replaced by intermolecular hydrogen bond between the polysaccharide chains and plasticizer under high temperature and shear, leading to a much finer dispersed phase size in PLA matrix [22].

Nevertheless, the use of small molecule plasticizer may cause the degradation of PLA during processing [23]. What's more, this kind of TPS contained plasticizers is an unstable system, as time goes on, the retrogradation of starch crystalline and the migration of small molecule plasticizer can cause accelerated aging of products and finally deteriorate its mechanical properties. In order to avoid the adverse effects, it is necessary to prepare a new type of TPS uncontained any plasticizer.

Chemical modification of starch usually refers to the reaction with the hydroxyl groups on the starch molecules and replaces them with other functional groups, thus it has the potential to reduce the intramolecular and intermolecular hydrogen bonds of starch and increase the thermoplasticity of starch without adding any small molecule plasticizer. Although previous studies [24–26] have been devoted to preparing various modified starches to increase its hydrophobicity by using this method, their interest was only focused on modifying the surface of starch granules, thus the starch still exists in the form of rigid granules after melt-blending with PLA. However, to the best of our knowledge, very little work has been done to prepare TPS by chemical modification without using any plasticizer, in particular, no literatures have considered the thermoplasticity of the chemically modified starch.

In this work, we devoted ourselves to preparing TPS without adding any plasticizer by chemical modification, that is, substituting hydroxyl groups on starch molecules with maleic anhydride (MA) and epoxidized cardanol (Epicard) in a homogenous solution system. The chemical structure, crystalline structure, thermoplasticity and morphologies of them were investigated in details. In addition, the change in the hydrophilic/hydrophobic character of starch after modification was also discussed. To the end, PLA/TPS blends were prepared by melt-blending, the morphologies and mechanical properties of PLA/TPS blends were studied in detail.

2. Material and methods

2.1. Materials

PLA 4032D (207 kDa, PDI 1.74) was obtained from Nature-Works LLC (USA), and it was dried under vacuum at 80 °C for 8 h prior to use. The native food grade corn starch was supplied by Zhucheng Stimulation Trade and Corn Development Limited Company (Shandong, China), and it was dried in vacuum at 100 °C for 24 h before use. Maleic anhydride (MA), dimethyl sulfoxide (DMSO), tetrabutylammonium bromide (TBAB) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and

used as received. Epicard was prepared following our previous report [27], and its epoxide number was 0.27.

2.2. Synthesis of TPS

First, 100 g dried starch, 10 g MA and 200 ml DMSO were added to a 500 ml three-neck flask, and then reacted at 110 °C for 1 h. The crude product, a colorless transparent viscous liquid, was precipitated with 1000 ml ethanol, and rinsed with 500 ml ethanol. The process of precipitation and rinse was repeated for several times, and the as-formed product (MA-g-starch) was dried at 110 °C under vacuum. The synthetic route was shown in Fig. 1.

50 g MA-g-starch, 50 ml DMSO, 1 g TBAB and 10 g Epicard were put into a 250 ml three-neck flask, and reacted at 110 °C for 5 h. The crude product was precipitated with 500 ml ethanol, and rinsed with 250 ml ethanol. The process of precipitation and rinse was also repeated for several times, and the as-formed product (Epicard-g-starch) was dried at 110 °C under vacuum. The synthetic process can be seen from Fig. 1.

2.3. Processing of TPS by hot press molding

The native starch, MA-g-starch and Epicard-g-starch were put into a 10 cm × 5 cm × 0.1 cm mold separately, which were subsequently kept in a hot press machine at 130 °C and 10 MPa for 20 min.

2.4. Preparation of PLA/TPS blends

PLA/MA-g-starch and PLA/Epicard-g-starch blend (weight ratio 70/30) were first melt-blended in a SJSZ-10A miniature twin screw extruder (Ruiming Plastics Machinery, Wuhan city, China) at 175 °C for 10 min with the rotation rate of 40 rpm. Whereafter, they were extruded into an SZ-15 micro-injection molding machine, which was also made by Ruiming plastic Machinery. All the standard testing samples for measurements were prepared at 200 °C under an injection pressure of 2 MPa for 30 s, and the mold temperature was held at 45 °C. Finally, the prepared samples were kept in a dryer to avoid moist.

2.5. Nuclear magnetic resonance

Native starch, MA-g-starch and Epicard-g-starch were analyzed by Bruker Avance III 400 Fourier transform nuclear magnetic resonance spectrometer (Bruker, Switzerland) operating at 400 MHz (¹H NMR), and DMSO-d₆ was used as a solvent.

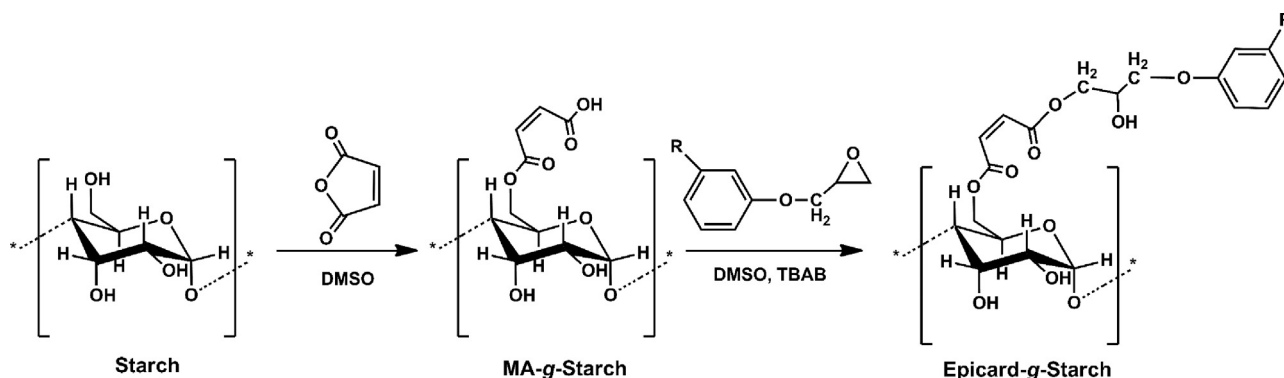


Fig. 1. Synthetic route of the two chemically modified starches ($R = C_{15}H_{31-2n}$, $n (n = 0, 1, 2, 3)$ denotes the number of double bonds in the side chain of cardanol).

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