



Structural and mechanical characteristics of film using modified corn starch by the same two chemical processes used in different sequences

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ABSTRACT

Structure of dual modified starches, cross-linked esterified corn starch (CES) and esterified cross-linked corn starch (ECS), and product films (CEF and ECF) were characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction and scanning electron microscopy (SEM). The peak 1730 cm^{-1} of IR spectra confirmed the formation of ester carbonyl groups in starch matrix. The sequence of modification procedure had an impact on the final modification degree, resulting in structural differences of modified starches and starch films. Compared to native starch film (NF), CEF and ECF showed improved transparency (77.59% and 74.39% respectively) with compact structure, lower crystallinity (6.5% and 7.4% respectively). Results of mechanical test indicated that structure of ECF was more flexible than CEF, whereas tensile strength was higher in CEF. Accordingly, complex modification could be an effective method to adequate properties of starch films for specific processing requirements.

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1. Introduction

Along with the growth of environmental concerns over chemically synthesized plastics, there has been an increasing interest in biodegradable films made from renewable and natural polymers. Starch is an attractive raw material for edible packaging because of its low cost, abundant resource, renewability, and biodegradability (Alves, Mali, Beleia, & Grossmann, 2007). Nevertheless, starch-based film exhibits several disadvantages such as brittleness and poor mechanical strength, which restrict its application for food packaging (Banker, 1966).

An alternative to mitigate these drawbacks is the application of modified starches in film-forming matrix. Starch modification is conducted by physical, chemical or enzymatic methods. Chemical modification could be a useful tool to modify the structure of native starches and consequently customize the overall properties of films (Bodîrlău, Teacă, Spiridon, & Tudorachi, 2012). Generally, chemical modification can be achieved by a variety of different chemical reactions such as acid hydrolysis, oxidation, etherification, esterification and cross-linking. Among these methods, cross-linking and esterification have been commonly used to modify native starches especially for producing low water sensitive materials. Esterification is one of the modifications, which can impart hydrophobicity to starch products by the substitution of free

available hydroxyl groups (Huijbrechts et al., 2008). Cross-linking treatment is intended to add intra- and inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule. Restrict water uptake could also be achieved by cross-linking method, due to the increased density of cross-links in the starch structure (Koo, Lee, & Lee, 2010).

Compared with independent modification, the combination of these two methods could be used to tailor starch to specific applications in food industry. Structural differences caused by modification process might affect the film forming capacity of modified starches (Lopez, Garcia, & Zartzy, 2008). Consequently, mechanical properties and water stability of product films could be improved expanding the application of starch films in food packaging.

Knowledge about chemical modification effects on starch granules structure is necessary to understand their functional properties and allow developing starch-based films with desired properties. However, few specific studies concerning starch films made from complexly modified starches have been reported. The objective of this study was to determine the influence of two different modification procedures on the microstructure of starch and physicochemical properties of starch-based films. In this study, films were prepared from two different dual modified starches, namely cross-linked esterified starch and esterified cross-linked starch. Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction and scanning electron microscopy (SEM) were used to study the product characteristics, with the aim to tailor film physicochemical properties based on starch structural characteristics.

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2. Materials and methods

2.1. Materials

Corn starch was obtained from National Starch Co. (America). Epichlorohydrin was purchased from Fuchen Chemical Reagent Co. (Tianjin, China). Succinic anhydride was purchased from Yonghua Fine Chemicals Co. (Jiangsu, China), glycerol was from Sinopharm Chemical Reagent Co. (Beijing, China). All chemicals were of analytical or better grade.

2.2. Preparation of multiply modified starches

2.2.1. Cross-linked starch samples

Cross-linked starches were prepared according to the method of [Jyothi, Moorthy, and Rajasekharan \(2006\)](#) with some modifications. Corn starch (40 g) was dissolved in 60 mL of distilled water containing a mixture of 50/50 (w/w) NaCl/Na₂SO₄ (2%, based on starch dry weight). The slurry was preheated at 40 °C for 10 min in a water bath with constant stirring. After the pH value was adjusted to 10 with 1 mol/L sodium hydroxide, the mixture was mixed with epichlorohydrin (0.6%, based on starch dry weight) and stirred for 2 h. The reaction solution was adjusted to pH 7 with 1 mol/L hydrochloric acid, then the residue was washed with distilled water for 4 times after filtering, and dried at 40 °C for 24 h in an oven to the constant weight. The dried samples were then grounded in a mortar and sieved (100 mesh).

2.2.2. Esterified starch samples

Esterified starches were prepared as described by [Song, He, Ruan, and Chen \(2006\)](#) with some modifications. Corn starch (40 g) was dissolved in 60 mL of distilled water. After the pH value was adjusted to 8.5 with Na₂CO₃ (3%, w/w), the solution was stirred at 30 °C for 30 min. Succinic anhydride (SA) (4%, based on starch dry weight) was slowly added into the solution for several times, the pH value of the solution was kept stable with Na₂CO₃ (3%, w/w). After reacted for 3 h, the mixture was acidified to pH 6.5 with hydrochloric acid (1%, w/w), and filter residue was washed with distilled water for 4 times after filtering, and dried at 40 °C for 24 h in an oven to the constant weight. The dried samples were then grounded in a mortar and sieved (100 mesh).

2.2.3. Preparation of complexly modified starches

Cross-linked esterified starches (CES) were made from the cross-linked starches prepared in Section 2.2.1 according to the esterification method described in Section 2.2.2.

Esterified cross-linked starches (ECS) were made from the esterified starches prepared in Section 2.2.2 according to the cross-linking method described in Section 2.2.1.

2.3. Films preparation

Modified starch films were prepared by casting method. Fillogenetic solutions (2%, w/w) were prepared by dispersing 2 g of starch sample in 98 mL of distilled water. After mixed with glycerol (25%, based on starch dry weight), the starch suspension was stirred at 90 °C for 30 min until the solution became transparent. The transparent solution was then filtered and the filtrate was degassed under vacuum (0.09–0.1 MPa), followed by casting onto glass plates. After drying at 40 °C and 50% of relative humidity (RH) for 24 h, the films were cooled to ambient temperature before peeled off from the plates and stored at 25 °C and 50% RH prior to test. Five replications were done.

2.4. Determination of the degree of cross-linking

In case of cross-linking, sedimentation volume (SV) is reduced because the hydrogen bonds between starch molecules was strengthened and then swelling was restrained during gelatinization. Therefore, the degree of cross-linking (DC) can be evaluated from SV as follows:

$$DC = SV(NS) - SV(\text{modified starch})$$

Considering that esterification has an opposite influence on SV, increasing caused by esterification must be removed. As for CES, DC was calculated as follows:

$$DC = SV(NS) - \{SV(CES) - [SV(NS) - SV(ES)]\}$$

As for ECS, DC was calculated as follows:

$$DC = SV(ES) - SV(ECS)$$

Cross-linked starches (2 g) were dissolved in 98 mL of distilled water, the suspension was then stirred at 85 °C for 2 min before cooled to room temperature. 10 mL of the starch paste were extracted into a measuring centrifuge tube and centrifuged at 4000 r/min for 2 min at room temperature before the volume of supernatant was measured. SV was calculated as follows:

$$SV = 10 - \text{Volume of supernatant (mL)}$$

2.5. Determination of the degree of esterification

The level of succinylation of the modified starches was determined using the titrimetric method of [Whistler and Paschall \(1967\)](#). Degree of esterification (SD) was determined according to [Jyothi, Rajasekharan, Moorthy, & Sreekumar, 2005](#). The SD is the average number of hydroxyl groups substituted per glucose unit. SD was calculated as follows:

$$SD = 162 \times \frac{\% \text{Succinylation}}{10,000 - (99 \times \% \text{Succinylation})}$$

where, 162 is the molecular weight of glucose unit; 10,000 = 100 × molecular weight of succinyl unit; 99 = molecular weight of succinyl group – 1.

2.6. X-ray diffraction and relative crystallinity

X-ray diffractograms of modified starches (CES, ECS) and starch films (CEF, ECF) were obtained by a D8 ADVANCE X-ray diffractometer (Rigaku-Denki Co., Tokyo, Japan) with a copper anode tube, a detector operated at 40 kV and 40 mA, scanning speed at 17.7 s/step, step interval of 0.02°, scanning range at 5–60° (2θ). The relative crystallinities (RC) were measured by ratio of the relative area of crystalline peak to total area of the diffractograms, expressed as percentage (%), and calculated by Jade 5.0 system.

2.7. Fourier transform infrared spectroscopy

Transmission FT-IR was measured (4000–500 cm⁻¹) with a Vector 33 FT-IR (Bruker, Germany). A small piece of modified-starch films or powder of modified starch was grinded together with KBr (Fluka) and then pressed at 10 mton to form a tablet.

2.8. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to investigate the surface photography of the modified starches, the fracture and surface of starch films by using S-3700N electron microscope (Hitachi, Japan). Starch samples were mounted on circular aluminum stubs with double sticky tape and then coated with 20 nm of gold and

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