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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 transparence (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.

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, & Zaritzky, 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 physiochemical properties of starch-based films. In this study, films were prepared from two different dual modified starches, namely cross-linked esterificated starch and esterificated 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 physiochemical 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/Na_2SO_4 (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 Na_2CO_3 (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 Na_2CO_3 (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. Filmogenic 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 to 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 diffractorgrams, 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

Table 1
Degree of modification of dual modified starches.

Sample	Sedimentation volume caused by cross-linking (DC, mL)	Degree of esterification (SD, %)
CES	0.77 ± 0.04	2.56 ± 0.06
ECS	0.40 ± 0.03	2.33 ± 0.09

examined and photographed. Film samples were cut into strips, frozen in liquid nitrogen and then fractured. The fracture surface was sputtered with a layer of gold.

2.9. Mechanical properties

The thickness of films were measured by a micrometer at six random positions at each film and averaged.

Mechanical properties of tensile strength (TS) and percent elongation (E) at break were measured with a TA-XT2i texture analyzer (Stable Micro Systems, London, U.K.). Samples were preconditioned at 25 °C and 50 ± 3% RH in a desiccator for at least 2 d prior to analysis. The tests were carried out with 15 replicates for each kind of films, then the averages were taken as the data.

2.10. Transparence of starch films

Film samples were cut into rectangles and placed on the internal side of a spectrophotometer cell. The transmittance of each film samples was measured by T6 spectrophotometer (Purkinje General Instrument Co., Beijing, China) at 500 nm. Average value of five tests of each sample was recorded.

2.11. Statistical analysis

Jade 5.0, Microsoft Excel 2003 and SPSS 17.0 were used for the statistical analyses. Data were subjected to analysis of variance (ANOVA), and comparison of means was carried out by Duncan's multiple-range test. Differences were considered to be significant at $p < 0.05$. Jade 5.0 was used to analyze the crystallinity in X-ray diffraction.

3. Results and discussion

3.1. Characterization of modified starches

3.1.1. Fourier transform infrared spectroscopy

The FT-IR spectra of native and modified starches are presented in Fig. 1a and b. In the spectrum of native starch, there are several discernible absorbencies at 1159, 1082, and 1014 cm^{-1}, which are attributed to C—O bond stretching (Goheen and Wool, 1991). Additional characteristic absorption bands at 992, 929, 861, 765, and 575 cm^{-1} are due to the entire anhydroglucose ring stretching vibrations. The extremely broad band between 3000 and 3600 cm^{-1} and the peak at 2950 cm^{-1} correspond to OH and CH stretchings respectively, while the peaks at 1647 cm^{-1} corresponds to δ (OH) bending (Mano, Koniarova, & Reis, 2003). Compared with NS, the spectrums of CES and ECS showed two new peaks at 1730 and 1570 cm^{-1}, which indicated that ester carbonyl groups replaced hydroxyl groups in the starch molecules (Fang, Fowler, Sayers, & Williams, 2004). Compared to ES, the small peak at 1730 cm^{-1} in ECS indicated some ester groups disappeared while the relatively strong peak at 1730 cm^{-1} in CES was shown, which was consistent with the degree of esterification in Table 1. This was due to the hydrolysis of esterified starch produced by alkali during the process of cross-linking. As seen in Fig. 1b, the sequence of modification procedure showed significant influence on the structure of modified starches.

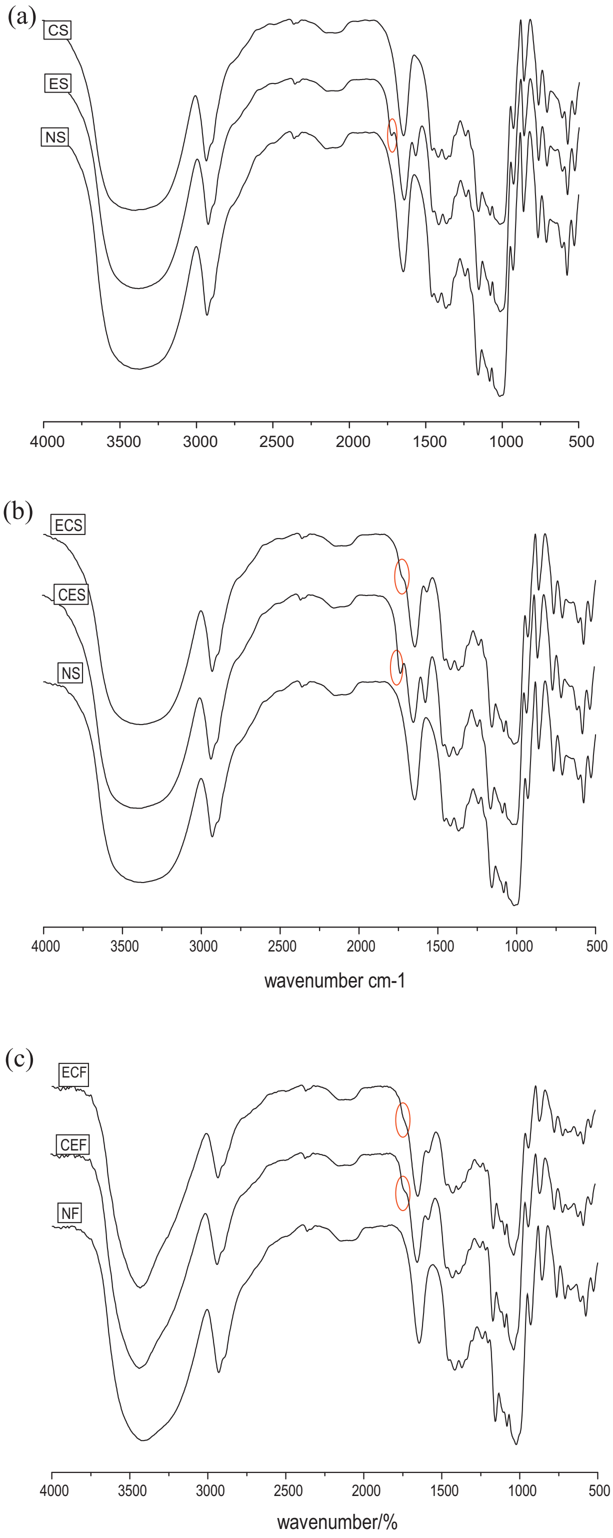


Fig. 1. FT-IR spectra recorded for (a) native starch (NS), cross-linked starch (CS), esterified starch (ES); (b) native starch (NS), cross-linked esterified starch (CES), esterified cross-linked starch (ECS); (c) films of NS (NF), CES (CEF), ECS (ECF).

3.1.2. X-ray diffraction

XRD measurements were performed to check if chemical dual modification altered the crystallinity of starch. The XRD patterns of native and modified starches are shown in Fig. 2a. Both native and modified starches exhibited typical A-type diffraction patterns (Zobel, 1988) with strong peaks at 15, 17, 18, and 23° (2θ),

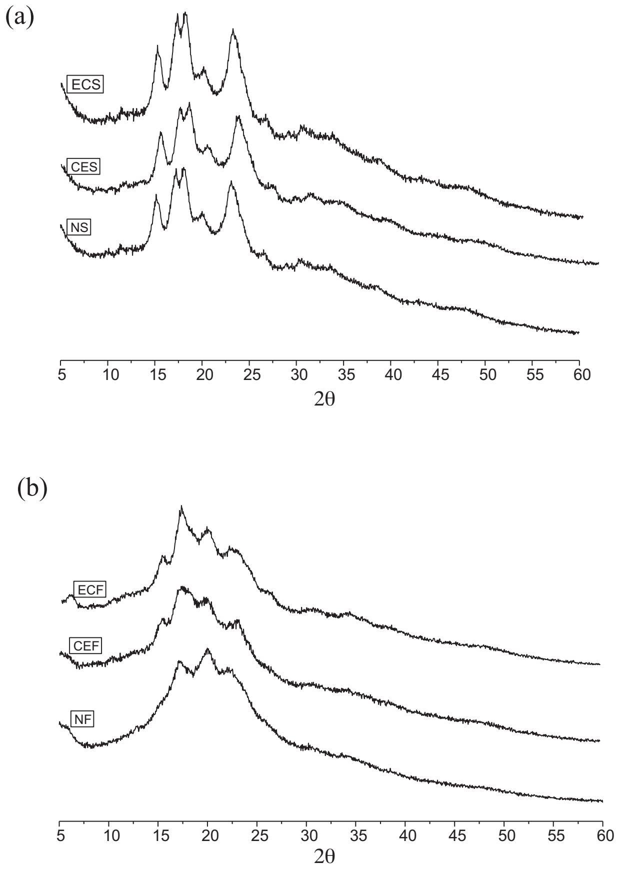


Fig. 2. XRD diffractograms recorded for (a) native starch (NS), cross-linked esterified starch (CES), esterified cross-linked starch (ECS); (b) films of NS (NF), CES (CEF), ECS (ECF).

suggesting that multiple modifications did not change the crystalline pattern of corn starch. The reason was that esterification and cross-linking occurred mainly in the amorphous regions of starch granules (Hoover & Sosulski, 1986; Xu et al., 2012). The RC of ECS (20.6%) increased significantly compared to NS (17.6%), while that of CES (17.7%) did not change. Liu, Ramsden, and Corke (1999) suggested that relative ratio of crystalline region increased with the reaction proceeding when the slight modification only occurred in amorphous region of starch granule.

3.1.3. SEM

The SEM micrographs of native and modified starch are presented in Fig. 3. The results showed that chemical modifications did not cause dramatic changes in the shape and appearance of starch granule, since the incorporation of esterifying agent or cross-linking agent into amorphous area of starch granule was cooperated by the permeation of water molecules (Garg & Jana, 2007). As can be seen, native corn starch granules had round or polygonal shapes with various sizes, and the surfaces of the granules were smooth and had no fissures. In comparison with the unmodified starch, both ECS and CES granules exhibited relatively wrinkled and rough surfaces due to modification.

3.2. Characterization of modified starch-based films

3.2.1. Fourier transform infrared spectroscopy

Compared with the infrared spectra of starch, characteristic peaks of starch film did not change significantly, indicating that chemical groups in starch-based films were almost the same as that in starch granules. While the intensity of peak at 1730 cm^{-1} decreased in CEF compared to that of CES, mainly due to the disappearances of some carbonyl groups during film-forming process, such as gelatinization and drying. The increase of intensity at 3300–3500 cm^{-1} was attributed to the increase of hydroxyl groups (Xu et al., 2012). In comparison with NF, the remaining of carbonyl and carboxyl groups in CEF and ECF could play an important role in modifying the structure and property of product films, as these groups might produce hydrogen bridges with hydroxyl groups, and these linkages would impart stronger interaction to the matrix and more compact structure to the film (Zamudio-Flores, Vargas-Torres, Pére-Gonzálea, Bosquez-Molina, & Bello-Pérez, 2006).

3.2.2. X-ray diffraction

In Fig. 2, crystalline patterns of NF, CEF and ECF were differed from those of corresponded starch. A layered organization with alternating amorphous and semi-crystalline radial growth rings was present in starch granules. The amorphous rings consist of amylose and amylopectin in a disordered conformation, whereas the semi-crystalline rings are formed by a lamellar structure of alternating crystalline and amorphous regions. It has been known a complex could be formed between glycerol and amylopectin (Kim, Na, & Park, 2003), which might account for the changes in crystalline pattern. The complex may alter the association between amylose and amylopectin, and the formation of hydrogen-bonding between glycerol and amylose or amylopectin may occur in the amorphous phase, which generates starch with a more amorphous structure. What is more, disruption of native crystalline structure during gelatinization and re-crystallization during cooling stage (Hu, Chen, & Gao, 2009) might be responsible for the changes in crystalline patterns.

Crystallinity decreased in modified starch films as shown in Fig. 2b. During gelatinization, the crystalline regions of starch granules were partly destroyed by heating and mechanical stir, and the permeation of esterifying and cross-linking agents could strengthen this destruction (Hu et al., 2009). However, the degree of destruction differed in varying the sequence of dual modification, thus resulting in different crystallinity. The crystallinity of NF (8.9%) was higher than that of ECF (6.5%) and CEF (7.4%), indicating relatively poor mechanical properties in NF while the improvement in modified starch films. Generally, the re-crystallization would be induced by the remained crystalline particles which acted as nucleus during cooling stage, and the relative crystallinity might be re-growth again (Cyras, Tolosa Zenklusen, & Vazquez, 2006). Whereas ether or ester groups formed by chemical modification could block rearrangement of starch segments resulting in lower growth of crystal in modified starch films by forming strong chemical bond with hydroxyl groups on starch chains and inter- or intramolecular hydrogen bonds (Lopez, Zaritzky, & Garcia, 2010). Since esterification mainly occurred in amylose, which was the main cause of crystallizing, the relative crystallinity of modified starch films decreased with increased SD.

3.2.3. SEM

Fig. 4 shows the SEM micrographs of native and modified starch films. CEF showed the smoothest and the most homogeneous surface with no pores or cracks, followed by ECF, while NF had rough surface and fracture with pores. Reaction of epichlorohydrin with the starch chains could lead to cross-linking of the starch, limiting starch chain mobility and thus ensuring ether groups remain as reinforcing agent in the corn starch matrix (Rivard, Moens, Roberts, Brigham, & Kelley, 1995). As higher crystallinity observed from Fig. 2b, surface of NF was more wrinkled than modified starch films (Fig. 4a), resulting from the prohibition of re-crystallization of starch chains by structural modification on starch molecules via multiply chemical modifications. It also showed that the method of cross-linked esterification could effectively enhance and improve

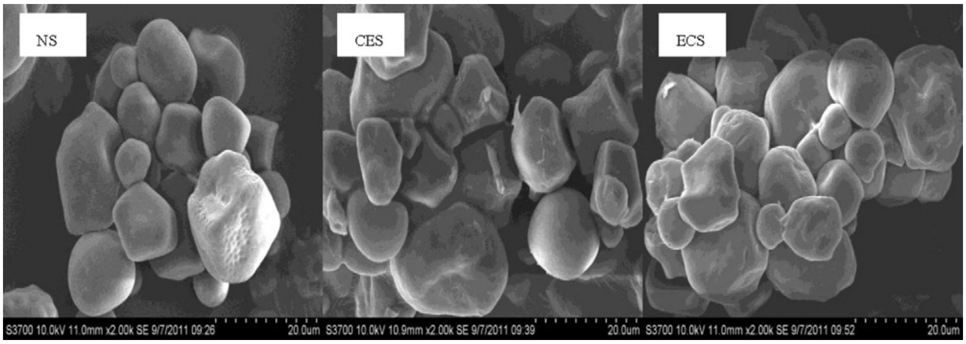


Fig. 3. SEM micrograph from surface analysis of native starch (NS), cross-linked esterified starch (CES), esterified cross-linked starch (ECS).

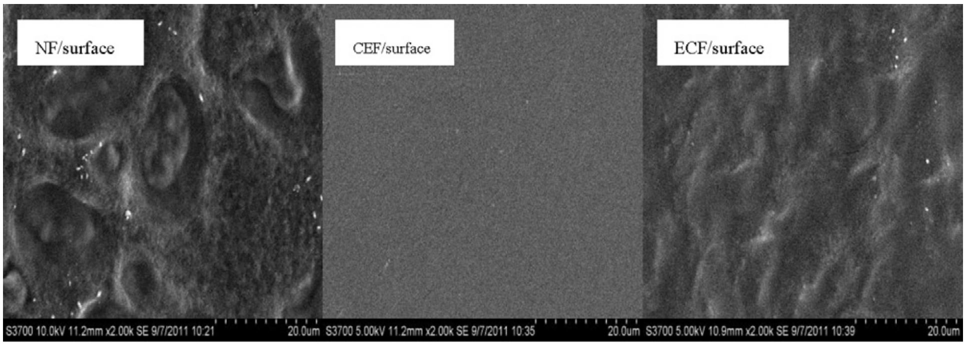
the structure of final films, which improved mechanical properties. While the multilaminar fractures in ECF and CEF might be caused by the repulsion of similar charge of starch granules, which were introduced by esterification.

3.2.4. Films characterization

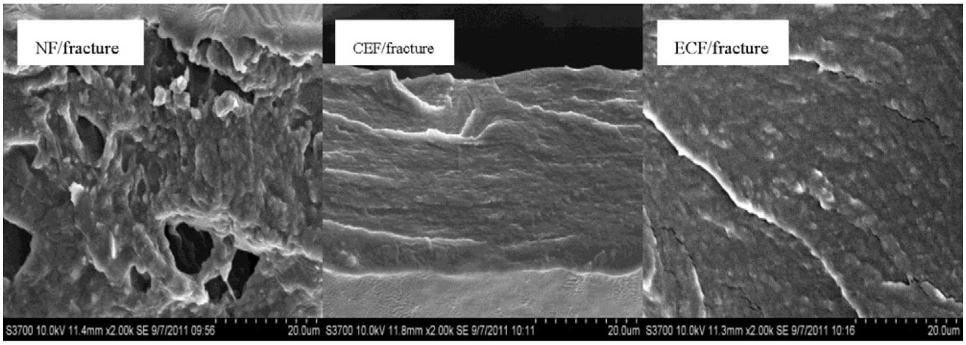
3.2.4.1. Mechanical properties. Mechanical property is one of the most important parameters to evaluate polymer films, especially for those used as packaging materials, since only strong enough films can undergo high external forces and protect inner articles perfectly. Table 2 showed tensile strength (TS) and percent elongation at break (%*E*) of NF, CEF and ECF.

In general, TS of the cross-linked starch films was higher than that of the native starch films (Kim & Lee, 2002), and TS of the esterified starch films was lower than the native starch films attributed to the internal plasticization provided by the ester groups (Thiebaud et al., 1997). The similar effect on TS by cross-linking and plasticization was also made by Garg and Jana (2007). Compared to native starch film, higher TS was present in ECF and the highest TS in CEF (Table 2). As TS increased with increased DC while reduced with increased SD, the final TS in ECF and CEF was depended on the balance between these divergent effects. And the results indicated that cross-linking gave predominant influence on TS (Tables 1 and 2).

The %*E* value of polymeric materials depended on the flexibility of molecular chains. During the processing of starch films, the granular and crystalline structure of starch were mostly destroyed by high temperature and shear force, and became mainly amorphous phase (Mali, Karam, Ramos, & Grossmann, 2004). In modified starches, the permeated epichlorohydrin and succinic anhydride molecules could further affected the interactions (intra- and intermolecular) among the starch macromolecules, because of the formation of chemical groups between hydroxyl groups of starch macromolecules and small modification agents. As seen in SEM micrographs (Fig. 4a and b), mobility of molecular chains in CEF decreased with integrated and compact film structure, resulting in the decrease of flexibility of final films. Compared to CEF, the structure of ECF was relatively more favorable for the movement and rearrangement of the macromolecule chains of starch, which caused the increase of flexibility of starch films and slight increase in *E* value of ECF. In case of cross-linking, the hydroxyl groups in starch molecules reacted with epichlorohydrin forming



(a)



(b)

Fig. 4. SEM micrograph from (a) surface; (b) fracture of films of NS (NF), CES (CEF), ECS (ECF).

Table 2
Characterization of starch films.

Sample	Thickness (mm)	TS (MPa)	*E* (%)	Transparence (%)
NF	0.0860 ± 0.0019	9.23 ± 0.70	12.17 ± 0.54	58.98 ± 1.89
CEF	0.0862 ± 0.0013	17.70 ± 1.20	7.2 ± 0.30	77.59 ± 2.49
ECF	0.0870 ± 0.0014	11.38 ± 0.76	18.41 ± 1.02	74.39 ± 3.11

mono/di-glycerol ether starch (Jyothi et al., 2006). The cross-linked starch has more branch chains than native starch by cross-linking, which resulted in more inter- and intramolecular hydrogen bonds. The restricted mobility of cross-linking starch chains caused by inter- and intramolecular hydrogen bonds could contributed to a reduction of *E* value (Cyras et al., 2006). Along with higher level of cross-linking degree, CEF showed a significant decrease in *E* value in comparison with NF and ECF. Introduction of carbonyl groups by esterification would increase the hydrophobicity of final films. Due to the steric effect and charge effect of succinic anhydride, molecular association was reduced in the polymeric matrix, and motion of molecular starch chains would be facilitated in film matrix. Since ECF was based on esterified starch, further cross-linking in the matrix was prohibited and resulted in a less compact structure with higher *E* value than CEF.

3.2.4.2. Transparence of films. Transparence is a vital property in surface food coating, and the high light transmittance of films means low opacity. Films transparence may be affected by different factors, including film thickness and the molecular regularity (Spiridon, Teaca, & Bodirlau, 2011). The modified starch films formed by casting method were transparent and homogeneous. CEF and ECF had comparatively higher transmittance (*T*), about 77.59% and 74.39% respectively, than that of 58.98% in NF. The increase in ordered zones leads to reduced absorbance and increases film transparency (Bodîrlău et al., 2012). The presence of carboxyl groups formed by esterification and ether bonds produced by cross-linking induced modified starch molecular chains to form ordered zones in the film matrix, finally resulting in prominent increases in film transparence.

4. Conclusion

In this study, the modified starch was modified by the same two processes in different sequences, esterified cross-linked starch (ECS) and cross-linked (CES) were prepared, and starch-based films were obtained by the casting process. The relationship between microstructural and physicochemical characteristic was analyzed.

For dual modifications in this study, the morphology of starch granules and the crystallinity pattern were not affected, while ECS was characterized by a higher crystallinity degree.

All of modified starches were able to form transparent films. The sequence of esterification and cross-linking procedure had an impact on the degree of final modification, as CES and ECS differed in values of DC and SD, and then resulted in differences of modified starches and starch films in structure and property.

CEF and ECF exhibited smooth, uniform and compact surface and fracture, while NF had the rough surface and friable fracture. Films (CEF) made from CES with lower crystallinity than NF, had lower *E* value but higher TS and transparence. The strong interaction formed by cross-linking has a prioritized improving effect on strengthening structure of film and also weakening mobility of starch molecular chains in film-forming matrix which would account more for lower *E* value in CEF but higher TS and transparence. And the ester produced by esterification would contribute more for lower crystallinity in CEF and ECF, higher *E* value in ECF. However, higher transparence should attribute to cross-linking and esterification.

Given all results in our study, chemical modification is a powerful tool to get adequate starch functional properties enhancing their uses in food packaging with specific processing requirements.

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