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Effects of hydrothermal pretreatment on subsequent octenylsuccinic anhydride (OSA) modification of cornstarch

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ABSTRACT

Cornstarch granules were hydrothermally pretreated and then esterified with octenylsuccinic anhydride (OSA). The physicochemical properties of cornstarch and hydrothermally pretreated OS-starch (H-OS-starch) were investigated. Results showed that hydrothermal pretreatments significantly increased the degree of substitution (DS) and reaction efficiency (RE) of H-OS-starch compared with the control. The higher the pretreatment temperature was, the more the OSA could go deep into the internal starch granules. The optimal pretreatment temperature for the OSA modification was 60 °C. In addition, the OS groups appeared to be distributed throughout the OS-starch granules, especially on the surface, as shown by confocal laser scanning microscopy (CLSM). H-OS-starch had a slightly higher peak viscosity (Pv) and break down (BD) values, but lower pasting temperature (Tp) compared with the control OS-starch.

1. Introduction

Octenylsuccinate (OS) starch is an effective emulsifier in food, pharmaceutical, and cosmetic industry due to the addition of hydrophobic groups to hydrophilic starch chain. OS-starch has been permitted by US FDA to be used in foods, and usually been prepared in a two-phase system by reacting octenylsuccinic anhydride (OSA) in slurry with the solid starch (Wetzel, Shi, & Schmidt, 2010). The degree of substitution (DS) and reaction efficiency (RE) of the synthesis was about 0.016–0.019 and 69–82%, respectively, under following reaction conditions: pH 8–9, reaction temperature 25–35 °C, starch concentration 35%, 3% OSA (based on the weight of starch) and 3–6 h reaction time (Hui, Chen, Fu, Xu, & He, 2009; Song, He, Ruan, & Chen, 2006; Zhang et al., 2011). Normally, the reaction between OSA and starch is retarded because of poor penetration of the big oily droplets of OSA into starch granules in an aqueous suspension. The distribution of OS groups in starch granules has been reported by previous studies (Huang et al., 2010; Shogren, Viswanathan, Felker, & Gross, 2000; Zhang et al., 2011), and it has been noted that: (a) the OS groups were probably distributed in the interior, amorphous domains of amylopectin molecules as well as on the outside of the granule (Shogren et al., 2000); (b) the concentration of OS groups on the periphery of the OS-starch granules was about 2–4 times that of the bulk (Shogren et al., 2000).

Heat-moisture treatment (HMT) and annealing (ANN) are two types of hydrothermal treatment that modify the physicochemical properties of starch without destroying its granular structure (Maache-Rezzoug, Zarguili, Loisel, Queveau, & Buléon, 2008; Zavareze & Dias, 2011). Hydrothermal treatment have been used to produce the swelled starch and for structural analysis and modification of starch granules. HMT causes structural alterations within the amorphous and crystalline regions to different extents, which in turn influence granular swelling, solubility, pasting properties, granule morphology, gelatinization characteristics and susceptibility to enzymatic or acidic hydrolysis (Zavareze & Dias, 2011). ANN specifically changes the physicochemical properties of starch by improving its crystalline perfection and facilitating interactions between the starch chains. The main changes in annealed starches are as follows: (1) a reduction in granular swelling and a change in the potential for and extent of amylose leaching (Lan et al., 2008; Waduge, Hoover, Vasanthan, Gao, & Li, 2006); (2) a change in pasting profile (Adebowale, Henle, Schwarzenbolz, & Doert, 2009); (3) the formation of double helices (Chung, Liu, & Hoover, 2009); (4) a reorganization of the granular structure (Waduge et al., 2006); (5) an increase in crystallinity (Lan et al., 2008; Waduge et al., 2006); (6) an elevation in the starch gelatinization temperature and a sharpening of the gelatinization range (Lan et al., 2008; Waduge

Abbreviations: ANN, annealing; BD, breakdown; BU, Brabender units; CLSM, confocal laser scanning microscopy; Cv, cold paste viscosity; DS, degree of substitution; DSC, differential scanning calorimetry; HMT, heat-moisture treatment; H-OS-starch, hydrothermal pretreated OS-starch; LSD, least significant difference; MB^+, Methylene Blue; NMS, normal maize starch; OSA, octenylsuccinic anhydride; PMT, photomultiplier; Pv, peak viscosity; RE, reaction efficiency; SB, setback; SP, swelling power; Tp, pasting temperature; XRD, X-ray diffraction.

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et al., 2006); (7) an increase in granular stability; (8) an increase in the interactions between starch chains in the amorphous and crystalline regions of the granules. These changes in starch properties are influenced by the interplay between crystallite disruption, starch chain associations, and disruption of double helices in amorphous regions (Vieira & Sarmento, 2008).

Although the synthesis and physicochemical characteristics of OS-starch have been studied extensively (Bao, Xing, Phillips, & Corke, 2003; Bhosale & Singhal, 2007; Huang et al., 2010; Song et al., 2006), little work has been reported on the structure and properties of starch modification with OSA after hydrothermal pretreatment. We hypothesize that the swelled starch after the hydrothermal treatment may increase the accessibility of the starch granules and make it easier for the OSA droplets to penetrate into the starch granule. In this study, OS-starch was prepared by a novel method with hydrothermal pretreatment. The effects of pretreatment temperature on the OSA modification and physicochemical properties of the products were investigated.

2. Materials and methods

2.1. Materials

Commercially available cornstarch (13.5% moisture, amylose content 27.5%) was obtained from Dacheng Company (Changchun, China). High purity 2-octen-1-ylsuccinic anhydride (OSA) was purchased from Sigma–Aldrich Chemical Company (St. Louis, MO, USA). Other chemicals used in the study were all analytical grade.

2.2. Hydrothermal pretreatment and preparation of OS-starch

Cornstarch was suspended in distilled water (35%, w/w) with agitation at different temperatures (48.0, 52.0, 57.0, 60.0, and 62.0 °C) for 3 h. The H-OS-starch was prepared by treating starch with octenylsuccinic anhydride (OSA) according to previous studies (Ruan, Chen, Fu, Xu, & He, 2009; Zhang et al., 2011). Cornstarch and hydrothermally pretreated cornstarch were suspended in distilled water (35%, w/w) with agitation. The pH of the suspension was adjusted to 8.5 with a pH meter by adding 3% NaOH solution. OSA (3.0%, dry starch basis, dsb) was added slowly within 2 h while maintaining the pH at 8.0–8.5. The reaction was allowed to proceed for a total of 3 h at 35 °C. After the reaction, the pH was adjusted to 6.5 with diluted HCl solution. The mixture was centrifuged and washed two times with distilled water and two times with ethanol. The starch samples were oven-dried at 40 °C for 24 h, and then passed through a 100 mesh nylon sieve.

2.3. Polarized light microscopy

Birefringence of native and hydrothermal pretreated starches was observed under an Olympus BX-51 light microscope (Tokyo, Japan) with polarized light. By using 35% aqueous suspension of cornstarch treated at different temperatures (48.0, 52.0, 57.0, 60.0, and 62.0 °C) for 3 h, and then one drop of starch suspension was placed on the microscope slide before covering with a coverslip, and the images were recorded at 400× magnification.

2.4. Swelling power

Swelling power was determined by using 35% aqueous suspension of cornstarch treated at different temperatures (25.0, 48.0, 52.0, 57.0, 60.0 and 62.0 °C) for 3 h. Measurement of swelling power was according to a previous report (Chang, He, & Huang, 2013; Singh, Singh, Isono, Noda, & Singh, 2009). The suspension was stirred and centrifuged at 2200 rpm. Supernatants were siphoned off, the starch residue weighed and the swelling power calculated as the weight of starch residue per gram of starch (dsb) according to the following equation:

$$\mathrm{SP} = \frac{Mr}{Ms} \times 100\%$$

where *Mr* is the mass of starch residue after supernatants were centrifuged (g), and the *Ms* is the mass of the dry weight (g) of the hydrothermal treated starch.

2.5. Determination of the degree of substitution (DS)

The DS is the average number of hydroxyl groups substituted per glucose unit. The OS-starch sample (5 g, dsb) was accurately weighed and suspended by stirring for 30 min in 25 mL of HCl-isopropyl alcohol solution (2.5 M). Then 100 mL of aqueous isopropyl alcohol solution (90%, v/v) was added and stirred for an additional 10 min. The suspension was filtered through a glass filter, and the residue was washed with 90% isopropyl alcohol solution until Cl^- could no longer be detected (using 0.1 M $AgNO_3$ solution). The starch was re-dispersed in distilled water (300 mL) and heated in a boiling water-bath for 20 min with stirring. The starch dispersion was titrated with standard NaOH solution (0.1 M), using phenolphthalein as an end-point indicator. A blank was simultaneously titrated with native starch as a control (Ruan et al., 2009; Zhang et al., 2011). The DS was calculated using the following equation:

$$\mathrm{DS} = \frac{0.162 \times (A \times M)/W}{1 - [0.209 \times (A \times M)/W]}$$

where *A* is the titration volume of NaOH solution (mL), *M* is the molarity of NaOH solution, and *W* is the dry weight (g) of the OS-starch.

The RE was calculated as follows:

$$\mathrm{RE} = \frac{\text{Actual DS}}{\text{Theoretical DS}} \times 100\%$$

The theoretical DS was calculated by assuming that all the added OSA reacted with starch to form the ester derivative.

2.6. Pasting properties

Starch slurry (35%, w/w, dry starch base, dsb) was treated at different temperatures (48.0, 52.0, 57.0, 60.0, and 62.0 °C) for 3 h, and then diluted to 6% (w/w, dsb) with distilled water. The pasting properties were analyzed on a Brabender Viscograph E (Brabender OHG, Germany). The pasting properties of H-OS-starch were also analyzed with the same equipment. Starch sample (28.0 g, dsb) was suspended in 432.0 g distilled water (6.0%). A 700 cm/g cartridge was fitted with the rotation speed set at 75 rpm, The suspension was heated at 1.5 °C/min to 95 °C from 30 °C, then held for 30 min at 95 °C, cooled to 50 °C at 1.5 °C/min, and held for 30 min for pasting properties. The pasting temperature (Tp), peak viscosity (Pv), hot paste viscosity (Hv), cold paste viscosity (Cv), break down (BD) and setback (SB) values were recorded.

2.7. Confocal laser scanning microscopy

Native starch and H-OS-starch samples were dye-stained for CLSM as follows. Specimens (0.5 g) were suspended in 30 mL water. The pH of the suspensions was adjusted to 8.0, and 1% Methylene Blue (MB^+) solution was added into each sample. The mixture was incubated in a shaking water bath at room temperature for 3 h and the granules were washed with methanol to remove the excess dye.

A TCS SP5 CLSM equipped with an Argon ion laser (Leica, Wetzlar, Germany) was used for the detection of the fluorescence signal

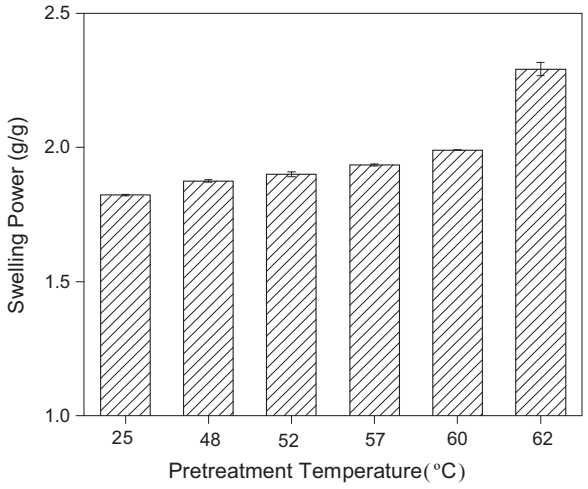

Fig. 1. The swelling power of cornstarch after pretreatment at different temperatures.

from the dye-stained starch granules. The details of the Leica objective lens used were 40×/1.25 oil. The excitation wavelength was 514 nm with 56 capacity (Jayaraj, Umadevi, & Ramakrishnan, 2001). During the image acquisition, each line was scanned four times and averaged to reduce noise.

2.8. Statistical analysis

The mean values and differences among mean values were analyzed using Duncan' s multiple-range test. Treatment means were tested separately for least significant difference (LSD) with SPSS 20.0 statistical software for Windows (SPSS, Inc., Chicago, IL, USA). The significance level was set at $P < 0.05$.

3. Results and discussion

3.1. Effects of hydrothermal treatment on starch properties

3.1.1. Swelling power

The swelling power (SP) of cornstarch with different pretreated temperature is shown in Fig. 1. There was a strong positive correlation between the pretreated temperature and the expansion of the starch granule. It is obvious that the higher the pretreatment temperature was, the greater the SP of starch granules became, as shown in Fig. 1. The SP significantly was improved from 60 °C to 62 °C and ultimately achieved the maximum (2.29). Previous studies showed that SP was affected by amylopectin and amylose content and amylose could inhibit starch granule swelling (Singh et al., 2009). Chang et al. (2013) studied the swelling power (SP) of native cornstarches with different amylose content and reported that normal maize starch (NMS) showed a sharp increase of SP when the incubation temperature increased from 60 °C to75 °C. Similar reports found that swelling power varied with different temperature for the native starch and it increased considerably between the temperature range 60–90 °C (Bhandari & Singhal, 2002; Perez, Bahnassey, & Breene, 1993). Swelling is known to begin in the relatively mobile amorphous fractions and in more restrained amorphous regions immediately adjacent to the crystal line regions (Hoover & Manuel, 1996). Therefore, the increase in swelling power may be due to water moving from amorphous area into the crystallization area and attributed to the internal rearrangement of starch components in amorphous regions of the granule.

Table 1
Pasting characteristics of cornstarch after pretreatment at different temperatures.[a]

Sample	Tp (°C)	Pv (BU)	Hv (BU)	Cv (BU)	BD (BU)	SB (BU)
NMS	80.5	250	160	354	90	194
48-Starch	80.1	266	194	435	72	241
52-Starch	81.4	270	197	454	73	257
57-Starch	81.8	268	195	452	73	257
60-Starch	83.0	224	176	403	48	227
62-Starch	82.8	243	189	426	54	237

[a] Tp, pasting temperature; Pv, peak viscosity; Hv, hot paste viscosity; Cv, cold paste viscosity; BD, breakdown; SB, setback; BU, Brabender units.

Hydrothermal treatment induces changes in the physicochemical properties of starch without destroying the granule structure. The physical force or friction between these highly-swollen granules and interactions with large solubilized polymers causes the paste to thicken. Therefore degree of swelling of starch is important in thickener of food application, which depends on the starch species and extent of modification.

3.1.2. Polarized light microscopy

The morphology of native and hydrothermal treated starch was analyzed by optical microscopy (Fig. 2). Polarized light micrographs of native starch showed a characteristic birefringence pattern with a Maltese cross centered at the hilum. After the heat pretreatment, the Maltese cross in the center of particles became larger and fuzzier. The absence of a Maltese cross pattern when the pretreated temperature increased was attributed to the swelling of a large amount. The onset temperature (T_o) of cornstarch was 66.2 °C, as determined by differential scanning calorimetry (DSC). In the review on effect of annealing on the molecular structure and physicochemical properties of starches from different botanical origins (Hoover, 2008), it has been shown that the effect of annealing on starch structure is more pronounced if the annealing temperature is set (close) to but below T_o. However, if the annealing temperature is set very close to T_o, then it would cause starch gelatinization. The Maltese cross patterns of some granules began to disappear at 62 °C, which indicated that partial disruption of double helix crystalline structure may occurred (Primo-Martín, Nieuwenhuijzen, Hamer, & van Vliet, 2007).

3.1.3. Pasting properties

Brabender viscosity curve of cornstarches treated at different temperatures are shown in Fig. 3a and Table 1. The Brabender viscograms of swelled starch showed the same pasting tendency of cornstarch with different pretreatment temperatures. Compared with native starch, hydrothermal pretreated starches showed higher Tp, lower BD and higher SB. ANN is the hydrothermal treatment of starch in the presence of excess water for an extended period of time, which is performed at a temperature above the glass transition temperature (between the glassy and rubbery states) but below the gelatinization temperature of starch (Gomes, Silva, & Ricardo, 2005; Jayakody & Hoover, 2008). Generally, annealing has been shown to increase the pasting temperature, thermal stability and decrease peak viscosity and the viscosity at the end of the cooling cycle (Jacobs, Eerlingen, Clauwaert, & Delcour, 1995; Jacobs, Eerlingen, & Delcour, 1996; Stute, 1992). The increase in pasting temperature after hydrothermal treatments supports the fact that the modification process tends to increase the region of crystallinity and make double helix structure more compact as a result of the reorientation of the starch granules. While the peak viscosity of starch increased when the pretreatment temperature was below 60 °C, and then reduced with the increase of the heating temperature. This may have been the result of ANN phenomena occurring when the pretreated temperature reached 62 °C.

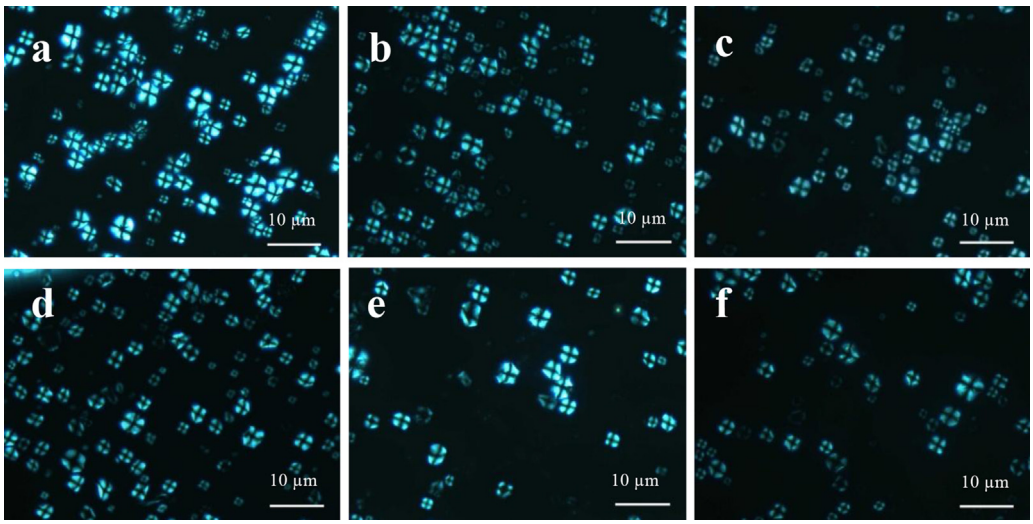

Fig. 2. The changes of Maltese cross of cornstarch after pretreatment at different temperatures: (a) NC; (b) 48-starch; (c) 52-starch; (d) 57-starch; (e) 60-starch; (f) 62-starch.

3.2. Effects of pretreatment temperature on esterification

3.2.1. DS and RE

Table 2 shows the effect of pretreatment temperature on the DS and RE of OS-starch while holding the starch concentration at 35%, pH at 8.0–8.5, and reaction time of 3 h. With the increase of pretreatment temperature, the DS of OS-starch increased from 0.0164 to 0.0190, and then reduced to 0.0179. Reaction efficiency (RE) was raised from 72.20% (control) to the highest of 81.76%, and then decreased to 77.37% at 62 °C, which showed the optimal pretreatment temperature for the OSA modification was 60 °C. Low temperature hindered the expansion of the starch granules and resulted in insufficient mixing between the water-insoluble OSA and starch granules (Ruan et al., 2009). It is obvious that the higher the pretreatment temperature was, the greater the swelling power (SP) of starch granules became (Fig. 1). This may be the explanation of the increasing DS and RE. In addition, when the pretreated temperature reached 62 °C, ANN phenomena might occur more easily (Hoover, 2008). There were more interplay between the extent of crystalline perfection and the amylose–amylose and/or amylose–amylopectin interactions of ANN. Therefore the ANN was not favorable to the combination of OSA and starch. This could be the reason for the change of DS between 60 °C and 62 °C.

Table 2
Degree of substitution (DS) and reaction efficiency (RE) of OSA modified starch after pretreatment at different temperatures.[a]

Sample	DS	RE (%)
OS-Starch (control)	0.0164 ± 0.00004[b]	72.20 ± 0.20[b]
48-OS-Starch	0.0168 ± 0.00004[b]	72.47 ± 0.15[b]
52-OS-Starch	0.0176 ± 0.00005[bc]	76.03 ± 0.15[bc]
57-OS-Starch	0.0178 ± 0.00006[bc]	76.68 ± 0.18[bc]
60-OS-Starch	0.0190 ± 0.00007[c]	81.76 ± 0.05[c]
62-OS-Starch	0.0179 ± 0.00005[d]	77.37 ± 0.15[d]

[a] All data are averages of two measurements with standard deviation. Means in a column with different superscript letters are significantly different ($p < 0.05$) by least significant difference (LSD) test.

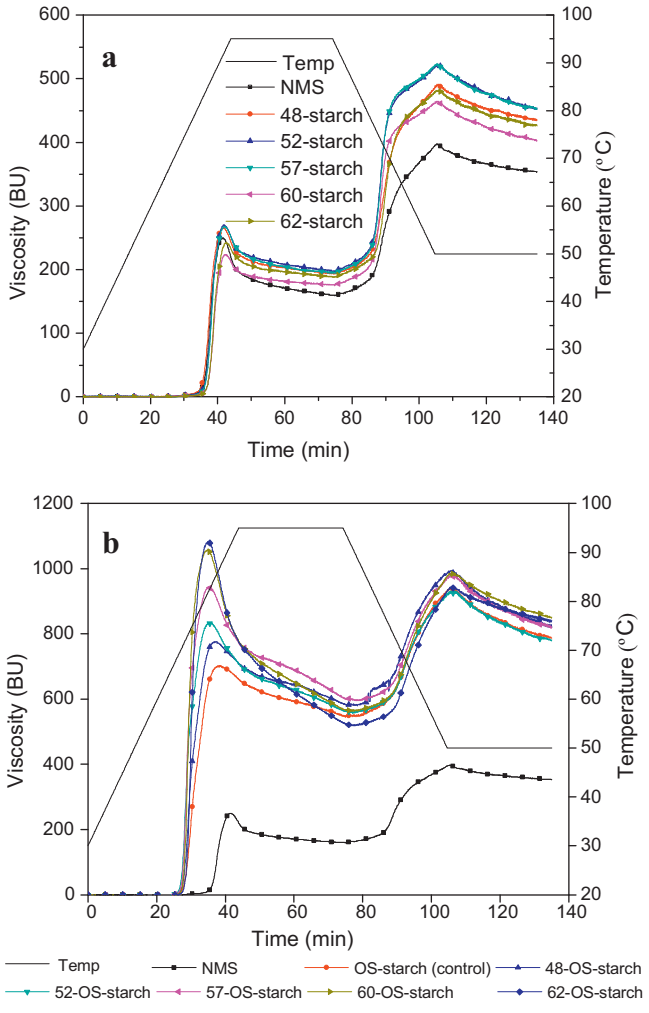

Fig. 3. Pasting characteristics of cornstarch at different temperatures (a) and OSA modified starch (b).

3.2.2. Paste properties of OS-starch

Pasting properties of native starch and OS-starch are shown in Fig. 3b and Table 3. All OS-starch exhibited lower Tp, higher Pv, BD and SB compared with native cornstarch, which was consistent with previous studies (Bao et al., 2003; Song et al., 2006). These results indicated that the substitution by the OS groups facilitated the disruption of the starch granule, allowing for a greater degree of swelling at lower temperature. It has been reported that the peak viscosity is mainly related to the swelling of starch granules (Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). Shogren et al. (2000) suggested that the OS group facilitated an increase in water percolation within the granules as a result of steric hindrance and

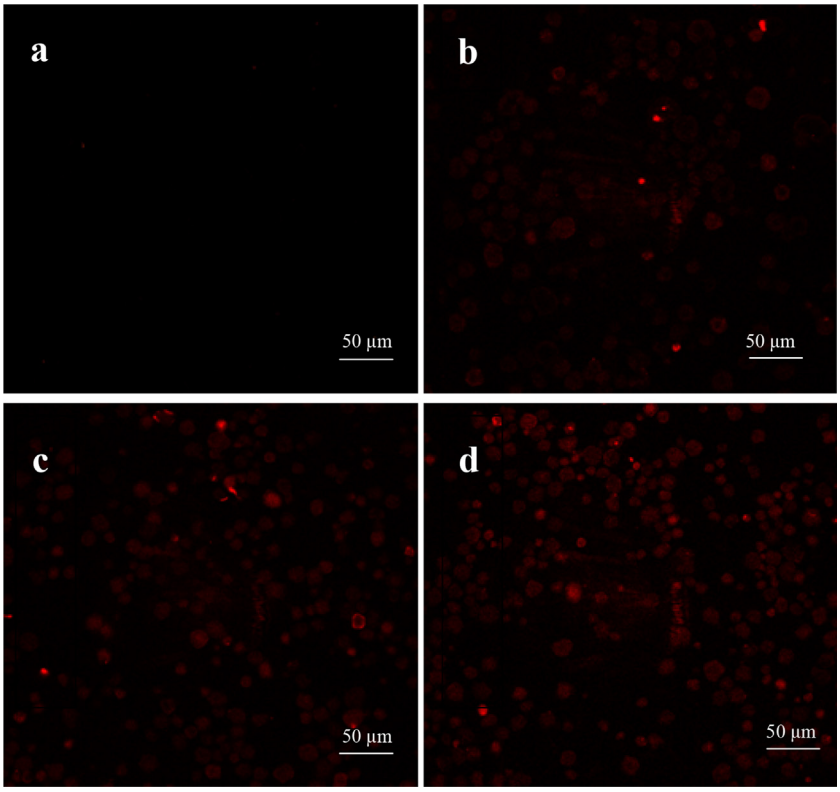

Fig. 4. The CLSM optical sections of native and OS-starches: (a) NC; (b) OS-starch (control); (c) 48-OS-starch; (d) 62-OS-starch.

repulsion, allowing an increase in swelling volume. The results suggested that the OSA modification significantly changed the viscosity properties of the cornstarch. The incorporation of a bulky OS group enhances the overall pasting capacity of the starch and destroys their ordered structure. Our result was consistent with previous reports (Huang et al., 2010; Zhang et al., 2011).

In addition, compared with the control OS-starch, a slightly higher Pv, BD and lower Tp were also observed in the H-OS-starch. The pretreated temperature showed a pronounced effect on the viscosity profile of OS-starch. With the pretreated temperature increasing, the Tp, Pv and BD of the H-OS-starch would increase. The breakdown viscosity is the difference between the peak viscosity and the viscosity after holding for 30 min at 95 °C (Huang, Li, & Fu, 2007). The higher breakdown viscosity indicates granule disruption or the lower tendency of starch to resist shear force during heating.

Hydrothermal treatment for OSA substitution substantially changed the pasting profile of the starch. It was noteworthy that the greater increase of peak viscosity in H-OS-starch was positively related to the DS value (Table 2) and the viscosity of native counterpart (Fig. 3a). Theoretically, during the reaction between the cornstarch and OSA, the crystalline regions of the starch granule are less permeable to reactive solution. Therefore, the results further confirmed that hydrothermal treatment is favor of the combination of OSA and starch granules. Compared with control OS-starch, the high viscosity of H-OS-starch may have potential application in thickening agent such as in the instant noodles and salad oil in food.

Table 3
Pasting characteristics of OSA modified starch after pretreatment at different temperatures.[a]

Sample	Tp (°C)	Pv (BU)	Hv (BU)	Cv (BU)	BD (BU)	SB (BU)
NMS	80.5	250	160	354	90	194
OS-starch	69.3	703	549	787	154	238
48-OS-starch	68.7	776	585	820	191	235
52-OS-starch	68.0	834	563	782	271	219
57-OS-starch	68.4	945	603	822	342	219
60-OS-starch	68.8	1058	569	852	489	283
62-OS-starch	69.7	1083	526	841	557	315

[a] Tp, pasting temperature; Pv, peak viscosity; Hv, hot paste viscosity; Cv, cold paste viscosity; BD, breakdown; SB, setback; BU, Brabender units.

3.2.3. Distribution of OS groups revealed by CLSM

CLSM was used to study the internal structure of starch granules without the use of complicated or invasive sample preparation methods, such as sectioning and chemical etch (Chen et al., 2009; Zhang et al., 2011). Previous researchers have used CLSM to visualize the internal structures of starch granules, such as channels, growth rings, equatorial grooves, distribution of amylose, protein and phosphate (Chen et al., 2009; Glaring, Koch, & Blennow, 2006; Jiang et al., 2010).

In this study, the distribution of OS groups in the starch granules was investigated using CLSM after being stained with MB^+ dye. MB^+ is one of the fluorescence dyes that highlight anionic substances. It has previously been used for specific labeling of anionic head groups of sodium dodecyl sulphate (Jayaraj et al., 2001). In addition, the CLSM images were taken at middle of the cornstarch granules. Fig. 4 shows the CLSM optical sections of OS-starch granules of different pretreatment temperature obtained at the same photomultiplier (PMT) after being stained with MB^+. The native starch granules (Fig. 4a) did not show fluorescence, whereas the OS-starch granules (Fig. 4 b–d) had fairly uniform bright fluorescence. In addition, OS groups appeared to be distributed throughout the OS-starch granules, especially on the surface. This showed that MB^+ specifically stained the $-COO^-$ of OS groups, and the distribution of OS groups in starch granules could be clearly revealed.

It would seem likely that the granular surface has higher fluorescence than the interior because the granular surface can react with OSA droplets as well as with dissolved OSA. The results revealed

that the higher pretreatment temperature of OS-starch granules showed stronger fluorescence intensity, indicating that there were more negatively charged groups available to stain with MB^+. In addition, OS groups appeared to be distributed throughout the OS-starch granules, especially on the surface. The higher the pretreated temperature was, the more the OS groups could penetrate into the internal starch granules. This was consistent with the result concerning about degree of substitution (DS) characteristics of results from Table 2.

Huber and BeMiller (2000) have reported on the architecture and permeability of cornstarch granules. They have shown that pores on the surface of starch granules, internal cavities at the granule hilum, and channels connecting the two could significantly influence the granule reactions to chemicals. Therefore cornstarch has some pinholes on the surface and serpentine-like channels inside of the granules. The starch granules are porous particularly after the hydrothermal treatment. OSA has low solubility in water and as a result, a mixture of dissolved reagent and small drops of reagent in dispersion exists during the reaction. OSA droplets could react with the granular surface or, depending on drop size, penetrate into granule (Segura-Campos, Chel-Guerrero, & Betancur-Ancona, 2008; Shogren et al., 2000). Only dissolved or extremely dispersed OSA could penetrate the entire granule. The swelled starches after hydrothermal treatment increased its accessibility, which made it easier for the OSA droplets to migrate inside of starch granules.

4. Conclusions

Hydrothermal treatment preferentially occurred in the amorphous parts of starch granules, which kept the DS of H-OS-starch at high levels compared with the control OS-starch. Octenylsuccinic groups were distributed mostly on the surface and amorphous region of the OS-starch, while the substituted groups were found more in the inner parts of the H-OS-starch granule. Hydrothermal pretreated OS-starch had a slightly higher peak viscosity (Pv) and break down (BD) values, but lower pasting temperature (Tp) compared with the control OS-starch. Hydrothermal treatment could be used in the heterogeneous system to improve the reaction efficiency.

Acknowledgments

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