Physicochemical properties of potato starches oxidised by different concentrations of sodium hypochlorite, and their application in yogurt

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Abstract

Potato starch was modified by oxidation with different concentrations of active chlorine (0.5, 1.0, 2.0, 3.0, and 4.0%); and the physicochemical properties of the oxidised potato starch samples and the use of these starches in set yogurt were investigated as a function of their degree of oxidation. The carboxyl content, carbonyl content, and solubility of the oxidised starches increased with increasing sodium hypochlorite concentrations, while the swelling power decreased. Scanning electron microscopy showed that oxidation caused cracks or pores on the surfaces of the starch granules, and these morphological changes were enhanced by increased oxidant concentrations. Analysis with a Rapid Visco Analyser showed that high degrees of oxidation could improve the starch thermodynamic stability and resistance to retrogradation. Set yogurts made with oxidised potato starches had higher water-holding capacities, higher apparent viscosities, and better sensory qualities than those prepared with native starch.

List of abbreviations

NPS, native potato starch; POS, potato oxidised starch; WHC, water-holding capacity.

Introduction

Oxidised starch is obtained by reacting starch with an oxidising agent. The carboxyl and carbonyl groups generated during oxidation reactions can greatly improve the water solubility of starch, and increase its reactivity in further applications (Wang and Wang, 2003). Although most oxidised starch samples are used as surface sizing agents and adhesives in the papermaking industry, oxidised starch is increasingly used in the food processing industry due to its low viscosity, high binding and film-forming capacities, high thermal stability, and good paste transparency (Kuakpetoon and Wang, 2001). Oxidised starch has been widely used in batters for coating diverse food products such as candy and pastry items; as an adhesive and filmogen; in bread to improve its quality (Mazur *et al.,* 1989); in milk products as a texturiser (Singh *et al.,* 2007); in cake fillings as a stabiliser; in ketchup manufacturing as a gelatinisation agent; and in creams, puddings, sauces, and jellies as a thickener (Lewicka *et al.,* 2015).

Different starch sources, oxidant concentrations, and reaction conditions (pH, temperature, and time) lead to differences in the content of carboxyl and carbonyl groups, oxidation location, degradation degree, and oxidation properties of the starch (Kuakpetoon and Wang, 2001). The pH of the reaction mainly influences the rate of oxidation and the formation of functional groups. The oxidation rates of many kinds of starch are higher near neutral pH than under acidic or basic conditions (Sangseethong *et al.,* 2009). However, acid/alkaline reaction conditions are beneficial for forming carbonyl and carboxyl groups (Schmorak and Lewin, 1963).

A host of recent studies have shown that the origin of starch has a substantial influence on the properties of oxidised starch. Starches from different sources have different proportions of amylose and amylopectin, granular sizes and shapes (Kuakpetoon

and Wang, 2001), crystallinities, crystalline patterns, chain-length distributions of amylopectin (Das *et al.,* 2010), and lipid and protein contents (Lewicka *et al.,* 2015). As compared to cereal starches, tuber starches such as potato starch, are more easily oxidised, which might be due to their B-type X-ray diffraction patterns, and because their crystalline arrangements are looser, and their crystallinities are lower than those of A-type starches (Kuakpetoon and Wang, 2001).

In addition to the pH of the reaction system and starch origin, another variable which has a significant impact on the properties and applicability of oxidised starch is the oxidant concentration. Starches oxidised with higher concentrations of active chlorine are more suitable for use than native starch, and oxidised starch prepared with less concentrated active chlorine is used in batters for coating different foods such as candies and pastries, as adhesives and filmogens, and in bread to improve its quality (Zhou *et al.,* 2016). Moreover, using a highly concentrated oxidant significantly improves the whiteness of oxidised starch, which helps it meet the requirements of the paper industry (Vanier *et al.,* 2012). Films prepared from starches oxidised by highly concentrated active chlorine have a lower solubility, whiteness, extension strength, and water vapour transmission than those prepared from starches made using dilute oxidants (Fonseca *et al.,* 2015).

Although many studies have examined the effect of the oxidant concentration on oxidation, the oxidant concentrations previously studied were within a narrow range (Fonseca *et al.,* 2015; Zhou *et al.,* 2016). The properties and functionality of oxidised starches are significantly different when oxidants of different concentrations are used. Furthermore, no studies have reported the qualities of set yogurt containing starches oxidised by sodium hypochlorite at different concentrations. Therefore, the purpose of the present work was to investigate the effects of different active chlorine concentrations (0.5, 1.0, 2.0, 3.0, and 4.0%) on the physicochemical properties of potato starches, and the application of these starches in set yogurt.

Materials and methods

Materials

Native potato starch was obtained from Xiya Reagent Company, China (product number: 1010191), with a dry matter content of 87.5% and an amylose:amylopectin ratio of approximately 23:77. The lipid, protein, and ash contents were approximately 0.3% (w/w), 0.31% (w/w), and 0.2% (w/w), respectively (data obtained from the supplier). The active chlorine in sodium hypochlorite is 8.0 g/100 g. All chemicals used in the present work were of analytical grade.

Modification of potato starch by oxidisation

Starch oxidation was performed following the method described by Vanier *et al.* (2012) with some changes. Potato starch (100 g d.b.) was weighed and dispersed in deionised water to prepare 35% (w/w) starch slurry. The starch slurry was then stirred at 35°C using a magnetic stirrer, and the pH was adjusted to 9.5 using 0.5 mol/L NaOH. Solutions containing different concentrations of sodium hypochlorite (0.5, 1.0, 2.0, 3.0, and 4.0 g active chlorine for 100 g of starch) were slowly dropped into the starch suspension over 30 min, and the pH was maintained at 9.5 using 1 mol/L HCl during NaClO addition. After the addition of NaClO, the pH was maintained at 9.5 using 1 mol/L NaOH for 60 min. Once the oxidation completed (as demonstrated by a negative reaction with 0.1 mol/L AgNO$_3$), the suspension was adjusted to pH 7 using 1 mol/L HCl, filtered through a Buchner funnel, washed with distilled water several times, and dried in a drying cabinet at 45°C overnight.

Carbonyl content

The method described by Sánchez-Rivera *et al.* (2005) was used with some modifications to determine the carbonyl contents of the starch samples. Briefly, 2 g of starch sample was placed in 500 mL flask, and 100 mL of distilled water was added. The mixture was stirred until it became homogeneous slurry, gelatinised in a boiling water bath for 20 min, and then cooled to 40°C. The pH of the solution was adjusted to 3.2 using 1 mol/L HCl, hydroxylamine hydrochloride (15 mL) was added, and the solution was mixed until it was uniform. The mixture was vibrated at 40°C for 4 h in a conical flask. Then, the pH of the slurry was rapidly titrated to 3.2 using 0.1 mol/L HCl to determine the amount of excess hydroxylamine. The same procedure using only hydroxylamine hydrochloride was used as the blank. The carbonyl content was calculated using Eq. 1:

CO/100 GU =

$$\frac{(\text{Blank} - \text{Sample})\text{mL} \times \text{molarity of HCl} \times 0.028 \times 100}{\text{Sample weight (dry basis)}} \quad \text{(Eq. 1)}$$

Carboxyl content

The carboxyl content of the oxidised starch was determined following the method of Lawal and Adebowale (2005) with some modifications. Starch (2.0 g) was accurately weighed into a beaker, and 25 mL of 0.1 mol/L hydrochloric acid solution was added. The mixture was agitated by intermittent magnetic stirring for 30 min, filtered through a Buchner funnel, and washed with distilled water until there were no chloride ions in the filtrate (as demonstrated by a negative reaction with 0.1 mol/L $AgNO_3$). The starch sediment was transferred into a beaker, 300 mL of distilled water was added, and the mixture was heated and stirred in a boiling water bath for 15 min to ensure sufficient starch gelatinisation. The hot starch sample was diluted to 450 mL with distilled water, and the pH was titrated to 8.3 using 0.01 mol/L NaOH. The same procedure using unmodified starch was used as the blank. The carboxyl content was calculated using Eq. 2:

COOH/100 GU =

$$\frac{(\text{Sample} - \text{Blank})\text{mL} \times \text{molarity of NaOH} \times 0.045 \times 100}{\text{Sample weight (dry basis)}} \quad \text{(Eq. 2)}$$

Amylose content

Starch sample (100 mg) was weighed into 100 mL conical flask, and 1 mL of ethanol solution was added to the sample. Next, 9 mL aliquot of 1.0 mol/L sodium hydroxide solution was transferred into the conical flask by pipetting, and the mixture was gently shaken. The mixture was heated in a boiling water bath for 10 min to disperse the starch, then cooled to room temperature, and transferred to a 100 mL volumetric flask. The solution was then diluted to volume with water and shaken vigorously to mix well. Next, 1.0 mL aliquot of the solution was mixed with 40 mL of water, 1.0 mL of acetic acid solution, 5.0 mL of I_2/KI solution (0.0079 M I_2 and 0.12 M KI), and then diluted with water to the appropriate volume. The solution was allowed to stand for 10 min, and the absorbance was measured at 720 nm.

Swelling power and solubility

The swelling power (SP) and solubility (SL) were determined following the method described by Zhang (2001) with a minor modification. Briefly, 0.5 g of starch sample (d.b.) was added to 24.5 mL of distilled water, and the solution was heated in an incubator shaker at 90°C for 30 min to prevent precipitation. The slurry was then cooled and centrifuged at 3,000 *g* for 30 min, and the supernatant was collected and dried at 110°C until the weight was constant. The SP and SL of the starch sample were calculated using Eqs. 3 and 4, respectively:

$$SL\,(\%) = \frac{Dry\ weight\ of\ supernatant \times 100}{Dry\ weight\ of\ starch} \quad \text{(Eq. 3)}$$

$$SP\,(g/g) = \frac{Sediments\ wet\ weight \times 100}{Dry\ weight\ of\ starch*(100 - \%SL)} \quad \text{(Eq. 4)}$$

Pasting characteristics

The pasting characteristics of the starch samples were measured by a Rapid Visco Analyser (RVA-4, Newport Scientific, Australia). Briefly, 3.0 g of starch sample (d.b.) was directly weighed into the RVA canister, 25 mL of distilled water was added, and the solution was mixed until it was uniform. After incubating for 1 min at 50°C, the sample was heated to 95°C for 3.5 min, maintained at 95°C for 2.5 min, cooled to 50°C for 3.75 min, and maintained at 50°C for 2 min. The sample was stirred at 960 rpm for 10 s, and at 160 rpm for the remainder of the procedure. The parameters were obtained from the RVA viscogram. The viscosity of the starch suspension was expressed in rapid visco units (mPa·s).

Morphology of starch granules

The structures of the starch granules were observed by scanning electron microscopy (SEM) (Su8010, HITACHI Corporation, Japan). Starch samples were suspended in acetone to obtain 1% (w/v) slurry, and then ultrasonically treated for 15 min. The samples were dried at 32°C for 1 h, sprinkled lightly onto carbon double-sided adhesive tape on a metal specimen stub, coated with a thin film of gold, and then examined by SEM at an acceleration voltage of 15 kV, and micrographs were recorded at 3,000× magnification.

Set yogurt preparation

Whole milk powder (12%; YiLi, China) (21.1% fat, 19.5% protein), 6.0% sucrose, and 1.0% native starch or oxidised starch prepared using different concentrations of active chlorine were dissolved in water at 50°C, and the mixture was stored in a refrigerator at 4°C for 24 h. After refrigeration, the solution was preheated to 60°C, homogenised at 20 MPa, sterilised at 95°C for 10 min,

cooled to 43°C, and added to yogurt strains. The mixtures were stirred until they were uniform. The incubation period lasted approximately 6 h, and was stopped by cooling the mixtures to 4°C. Finally, the yogurt samples were stored in a refrigerator at 4°C for 24 h.

Evaluation of the properties of the yogurt

Properties such as comprehensive taste, structure, and smoothness made up the overall sensory assessment of yogurt, and were representative of overall liking. The criteria for scoring are provided in Table 1. Sensory evaluation was performed at the tasting room of Lushan College,

Guangxi University of Science and Technology, People's Republic of China. Freshly prepared yogurt samples were placed into 50 mL beakers, and the colour and texture were observed under natural light. A total of 30 panellists assessed the smell of the sample, rinsed their palate with warm boiled water, and then assessed the taste of the sample. The yogurt samples were assigned by random numbered labels, and panellists scored the different yogurt samples from one (dislike extremely) to ten (like extremely) based on personal preference (Wongsagonsup *et al.,* 2014). Most of the panellists had backgrounds in food technology, and they were trained using an explanation of the sensory evaluation technique.

Table 1. Sensory scoring standard of yogurt.

Index evaluation score	Poor quality (1 - 5)	Medium quality (6 - 8)	Excellent quality (9 - 10)
Comprehensive taste (30%)	Abnormal flavour	Without abnormal flavour	Without abnormal favour, strong fermented milk flavour
Structure (40%)	Unstable curd and more whey separation	Homogenous but less fine, a small amount of whey is separated	Homogenous and fine, curd firm, only a small amount of whey is separated
Smoothness (30%)	Rough surface, lacks consistency	Flat, smooth surface, good consistency but too sticky	Flat, smooth surface, good consistency, and smooth taste

Apparent viscosity was determined by a rotational viscometer (NDJ-79, Shangyi Corporation, China). The rotor and measuring cups were cooled to 4°C, and then refrigerated yogurt samples were added. The rotor was rotated at 60 rpm, and the viscosity was read after 10 s.

The water-holding capacity (WHC) was tested following the method of Celik and Bakirci (2003) with some modifications. Briefly, 20 g yogurt sample was transferred to a centrifuge tube, and centrifuged at 4°C and 4,000 rpm for 20 min. After centrifugation, the supernatant was discarded. The WHC (%) was expressed as the weight of separated sediment per 100 g of yogurt.

Statistical analysis

All tests were performed in triplicate, and the effects of different concentrations of active chlorine on the physicochemical properties of potato starch and set yogurt were analysed by ANOVA using SPSS statistical software. Differences were significant at $p < 0.05$, as determined by Duncan's test.

Results and discussion

Contents of carbonyl and carboxyl groups

The breaking of intermolecular bonds and depolymerisation of polysaccharide main chains during oxidation allow hydroxyl groups to be oxidised into carboxyl and carbonyl groups (Kuakpetoon and Wang, 2001; Lewicka *et al.,* 2015). As shown in Table 2, neither the carboxyl nor carbonyl contents changed when starch was oxidised with the least-concentrated sodium hypochlorite solution (0.5%), but subsequently, the carbonyl and carboxyl contents of the modified starches increased with increasing concentrations of sodium hypochlorite, thus indicating that the sodium hypochlorite concentration directly affected the degree of oxidation (Sánchez-Rivera *et al.,* 2005). The highest carbonyl (0.586%) and carboxyl (0.1964%) contents were obtained when the sodium hypochlorite concentration was 4.0%. Similar results were also reported by other authors such as Vanier *et al.* (2012), Zhou *et al.* (2016), and Dias *et al.* (2011), who indicated that the active chlorine content could significantly increase the contents of carbonyl and carboxyl groups. According to Zhou *et al.* (2016), when starch was modified with low concentrations of

active chlorine (0.1 and 0.2%), the number of carbonyl groups produced in the oxidation reaction was higher than the number of carboxyl groups, and the results were reversed when starch was oxidised with more concentrated active chlorine solutions (1.0, 2.0, 3.0, and 4.0%). However, in the present work, the carbonyl content was higher than the carboxyl content in every sample, regardless of the active chlorine concentration used. This difference might have been due to the concentration of the starch slurry. If the concentration is appropriately high (35% in the present work), the number of hydroxyl groups present in the starch molecules available for oxidation is much higher than the number of carbonyl groups; thus, the probability of a carbonyl group being oxidised into a carboxyl group is lower. This discrepancy led to the carbonyl contents being higher than the carboxyl contents in the oxidised starches. In addition, when the concentration of the starch slurry is low (such as 10%), the higher concentrations of sodium hypochlorite are in excess of that necessary to oxidise the hydroxyl groups; thus, higher concentrations of sodium hypochlorite facilitate the oxidation of the carbonyl groups to carboxyl groups (Yi *et al.*, 2014).

Table 2. Contents of carbonyl and carboxyl groups in native and oxidised potato starches.

Starch	Carbonyl content (CO/100 GU)	Carboxyl content (COO/100 GU)	Amylose content (g/100 g)
NPS	0.0440 ± 0.003^e	0	28.41 ± 0.75^b
POS-0.5%	0.0733 ± 0.007^e	0.0171 ± 0.002^e	32.63 ± 0.11^a
POS-1.0%	0.1466 ± 0.012^d	0.0882 ± 0.006^d	28.95 ± 0.74^b
POS-2.0%	0.2932 ± 0.020^c	0.1099 ± 0.010^c	27.26 ± 0.74^c
POS-3.0%	0.4397 ± 0.031^b	0.1382 ± 0.013^b	26.75 ± 0.72^d
POS-4.0%	0.5863 ± 0.039^a	0.1964 ± 0.018^a	25.31 ± 0.83^e

Different lowercase superscripts in a column indicate significant difference ($p < 0.05$).

Swelling power (SP) and solubility (SL)

The SP and SL of the starch samples are listed in Table 3, and the SP decreased with increasing active chlorine concentrations. The results implied that the oxidisation reaction had a negative influence on the hydratability of the starch. This negative influence might have been due to the depolymerisation of starch during oxidisation. Similar results were reported by Fonseca *et al*. (2015) and Zhou *et al*. (2016) who also attributed the decrease in SP to damage to the starch structure during oxidation. However, the SP results reported by Vanier *et al*. (2012) were slightly different. They found that although the SP of starch oxidised by more-concentrated active chlorine (1.5%) was lower than that of unmodified starch, it was higher than that of starch modified with a lower concentration of active chlorine (0.5 and 1.0%). These results were likely due to amylopectin, which is more susceptible to depolymerisation at higher concentrations of active chlorine, and the depolymerisation of amylopectin could improve the SP of starch.

The solubility increased with increasing degrees of oxidation. The increased solubility upon oxidisation might be attributable to depolymerisation of the starch chain during oxidation, and the extent of depolymerisation increased with the degree of oxidation. These results were similar to the results of previous studies (Wang and Wang, 2003; Sánchez-Rivera *et al.*, 2005; Vanier *et al.*, 2012).

Table 3. Swelling power and solubility of native and oxidised potato starches.

Starch	Swelling power (g/g)	Solubility (%)
NPS	19.56 ± 0.73^a	1.65 ± 0.15^f
POS-0.5%	19.11 ± 0.65^{ab}	2.25 ± 0.21^e
POS-1.0%	18.40 ± 0.58^b	2.87 ± 0.28^d
POS-2.0%	17.43 ± 0.52^c	4.43 ± 0.43^c
POS-3.0%	16.67 ± 0.49^c	5.80 ± 0.54^b
POS-4.0%	15.39 ± 0.35^d	6.53 ± 0.62^a

Different lowercase superscripts in a column indicate significant difference ($p < 0.05$).

Pasting properties

The RVA test results are presented in Table 4. The pasting characteristics of the oxidised potato starches were significantly different from those of native starch, especially when the degree of oxidisation was higher.

Zhang, J. Y., et al./IFRJ 29(3) : 582 - 592

Table 4. Pasting characteristics of native and oxidised starch samples.

Starch	Peak viscosity (mPa·s)	Breakdown (mPa·s)	Final viscosity (mPa·s)	Setback (mPa·s)	Pasting temperature (°C)
NPS	5.932 ± 92[a]	4.098 ± 89[a]	3.082 ± 73[d]	1.248 ± 42[a]	68.8 ± 1.2[b]
POS-0.5%	5.432 ± 88[b]	2.172 ± 65[b]	4.269 ± 85[a]	1.009 ± 38[b]	70.4 ± 0.8[a]
POS-1.0%	5.278 ± 75[c]	2.035 ± 58[c]	3.676 ± 76[b]	433 ± 15[c]	68.8 ± 1.0[b]
POS-2.0%	4.810 ± 56[d]	1.580 ± 24[d]	3.659 ± 43[c]	429 ± 21[c]	68.8 ± 1.0[b]
POS-3.0%	3.751 ± 35[e]	1.235 ± 18[e]	2.643 ± 26[e]	126 ± 14[d]	67.9 ± 0.9[b]
POS-4.0%	2.963 ± 12[f]	1.027 ± 10[f]	1.954 ± 11[f]	18 ± 3[e]	68.6 ± 1.1[b]

Different lowercase superscripts in a column indicate significant difference ($p < 0.05$).

The pasting temperature of starch oxidised with a less-concentrated oxidant (0.5 g/100 g) was significantly higher than that of unmodified starch and the other oxidised starches, and there was no significant difference between the pasting temperatures of starch samples oxidised with other oxidant concentrations (1.0, 2.0, 3.0, and 4.0 g/100 g) and native potato starch. This behaviour is contrary to the findings reported by Zhou *et al*. (2016). They found that the pasting temperature of starch increased only when the degree of oxidisation was high (as seen in starches prepared using 2.0, 3.0, and 4.0 g/100 g active chlorine), while low degrees of oxidation (as seen in starches prepared using ≤ 1.0 g/100 g active chlorine) had no significant effect on the pasting temperature of starch relative to unmodified starch. The reason why starch treated with 0.5% active chlorine had a higher pasting temperature than that of unmodified starch might have been the low degree of oxidation, thus resulting in the presence of aldehyde groups, which could form hemiacetal cross-links that could decrease the mobility of amorphous regions, and enhance the stability of the swollen starch, leading to a small increase in the pasting temperature (Wang and Wang, 2003; Singh *et al.*, 2007). However, when the degree of oxidation increased, the effect of starch depolymerisation was far greater than the effect of hemiacetal cross-linking; thus, the pasting temperatures of starches treated with more-concentrated oxidants (1.0, 2.0, 3.0, and 4.0%) were lower.

The peak viscosity of every oxidised starch in the present work (5332 - 2963 mPa·s) was significantly lower than that of unmodified starch (5932 mPa·s). The peak viscosities of oxidised starches decreased with increasing oxidant concentrations. This decrease was probably because of the partial rupture of glycosidic bonds during oxidation, which led to the depolymerisation of

amylose and amylopectin, and decreased the molecular weight of the starch molecules (Kuakpetoon and Wang, 2001; Sangseethong *et al.,* 2009; Dias *et al.,* 2011), thus causing the peak viscosity to decrease. The final viscosity tended to decrease with increasing oxidant concentrations; however, the final viscosities of starch oxidised with less-concentrated active chlorine (0.5 and 1.0%) were higher than those of unmodified starch. This result was likely due to the lower degree of depolymerisation when less-concentrated oxidants were used, which stabilised the swelling of the starch particles. Similar results were reported by Fonseca *et al*. (2015).

Breakdown, which is the difference between the peak and trough viscosities, reflects the stability of starch paste, including its ability to resist shear and heat treatments (Hazarika and Sit, 2016). A high breakdown value indicates that the physical structures of the starch particles are weaker, thus rendering the starch molecules more likely to collapse under thermal or shear processing (Pinto *et al.,* 2015). Consequently, lower breakdown values mean that starch pastes are more stable during shearing or heating.

As seen in Table 4, the breakdown values of the oxidised starch samples (2172 - 217 mPa·s) were significantly lower than those of unmodified starch (4098 mPa·s). The results indicated that oxidation could increase the stability of starch under heating and mechanical stirring. This stability might have been due to the hemiacetal cross-links generated during oxidation, as these cross-links could maintain the integrity of the swollen particles and decrease the reduction in the degree of viscosity.

Setback, which is the difference between the final and trough viscosities, represents the retrogradation tendency of starch paste, and this value decreased as the concentration of sodium

hypochlorite increased, which was likely due to reduced reassociation of starch molecules due to the excessive degradation of amylose during oxidation (Kuakpetoon and Wang, 2006; Sukhija *et al.,* 2016). Additionally, the spaces between the amylose chains were larger following oxidation (Vanier *et al.,* 2012), and the reassociation of starch molecules was prevented. Both of these phenomena led to decreased setback values. Lower setback values indicate that starch pastes are less prone to retrogradation, which suggests that starch pastes oxidised with high concentrations of active chlorine are better able to resist starch retrogradation. In yogurt, a certain degree of starch retrogradation can increase the overall gel hardness, but dense structures formed by the long-term retrogradation of starch will separate water from the curd, thus resulting in severe whey precipitation and a decline in the yogurt quality. Therefore, excessive retrogradation of starch should be avoided when starch is used as a thickener or stabiliser in sour dairy products. Many studies have reported similar conclusions. For example, rice with a low amylose content effectively reduced the negative effect of starch aging on the quality of yogurt (Kumari *et al.,* 2015).

Morphologies of the starch granules

SEM images of the oxidised and native starch granules are presented in Figure 1.
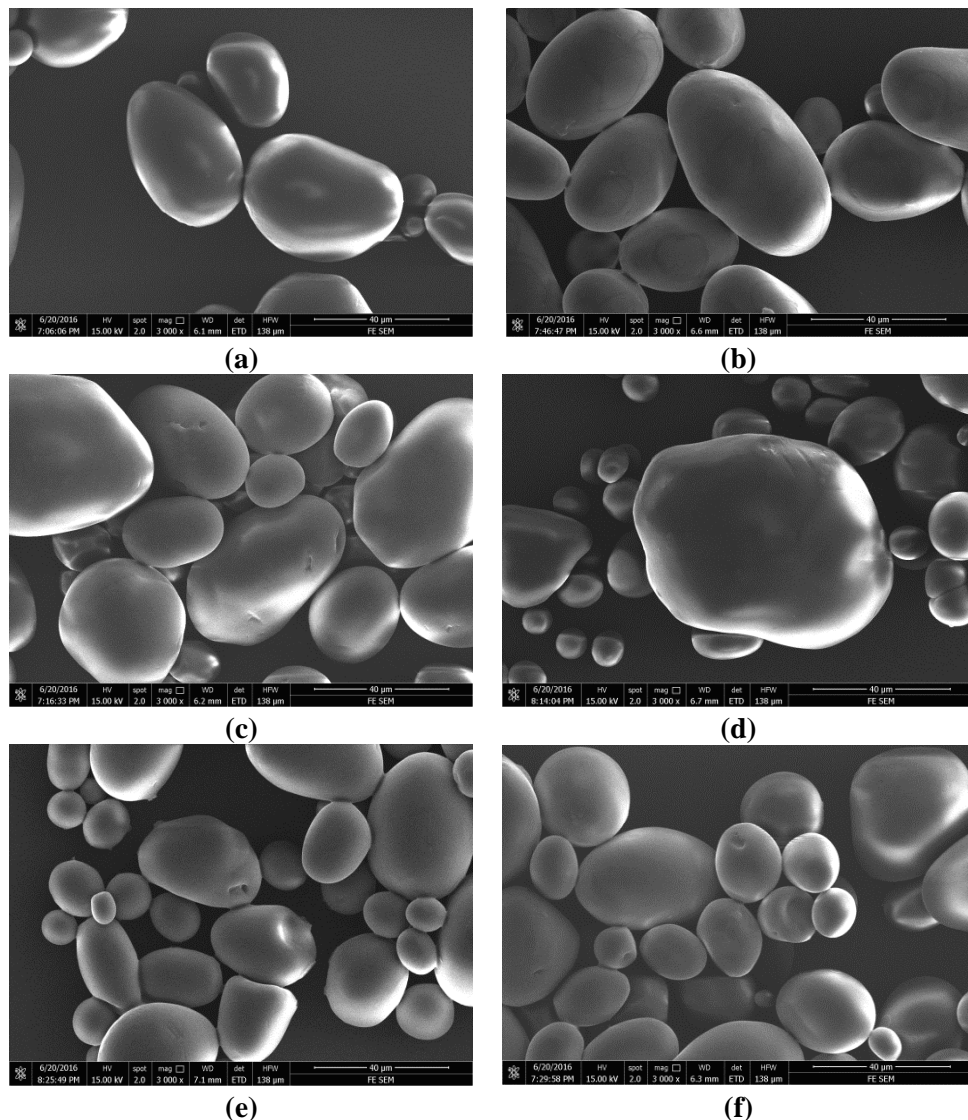

Figure 1. SEM images of native and oxidised potato starches. **(a)** NPS. **(b)** POS-0.5%. **(c)** POS-1%. **(d)** POS-2%. **(e)** POS-3%. and **(f)** POS-4% at 3.000× magnification.

At 3,000× magnification, the native starch granules were oval-shaped, and their surfaces were smooth (Figure 1a). The surfaces of the starch oxidised with 0.5% active chlorine (Figure 1b) were

not significantly different from those of the unmodified starch granules. However, fissures and pores began to appear in starch oxidised with 1.0% active chlorine (Figure 1c), and starches oxidised with 2.0, 3.0, and 4.0% active chlorine (Figures 1d, 1e, 1f) exhibited even more fissures and pores. Zhou *et al*. (2016) and Vanier *et al*. (2012) found similar results. They found obvious cracks and pores occurred in potato starches oxidised with higher concentrations of sodium hypochlorite. In contrast, Kuakpetoon and Wang (2001) and Martínez-Bustos *et al*. (2007) found no obvious differences in the morphologies of native and oxidised starch samples.

Yogurt properties

The results of the WHC, viscosity, and overall liking of yogurts made with native and oxidised potato starches are shown in Table 5. The water that remained in the yogurt after centrifugation was mostly bound firmly within the macromolecular gel, while most of the free water bound only by capillary action within the three-dimensional network of the gel was removed by centrifugation. Higher WHC indicate that the content of bound water is higher and that the possibility of whey separation is lower. As shown in Table 5, the WHC of the yogurts increased when prepared with starches oxidised with increasing concentrations of active chlorine. The highest value was obtained when the concentration of the oxidant was 2.0%, but at higher oxidant concentrations, the WHC was slightly decreased. This trend might have been because lower active chlorine concentrations (0.5, 1.0, and 2.0%) led to more amylose depolymerisation (Table 2), which enhanced the WHC of the starch. More concentrated oxidants are more likely to lead to amylopectin depolymerisation, which prevents starch from retaining water (Sánchez-Rivera *et al.,* 2005; Vanier *et al.,* 2012).

The apparent viscosities of the oxidised starches are shown in Table 5. The viscosity of native potato starch was 15,447 mPa·s, and the viscosities of oxidised starches were higher than that of unmodified starch. The highest viscosity was obtained when the concentration of the oxidant was 2.0% (21,111 mPa·s). This effect was due to the degradation of amylose, which is better able to form gels at intermediate molecular weights. The apparent viscosity decreased at higher concentrations of active chlorine (3.0 and 4.0%), which might have been due to depolymerisation or the weakening of the hydrogen

bonds between molecular chains (Fonseca *et al.,* 2015; Zhou *et al.,* 2016).

The results of sensory analysis of the yogurt containing native and oxidised potato starch are shown in Table 5. As shown by the scores presented in Table 5, the sensory results of yogurt containing native potato starch were outside the acceptable range (< 6). Yogurts containing oxidised potato starches had significantly higher overall liking scores than yogurt containing native potato starch. Yogurt containing starch oxidised with 2.0 or 3.0% sodium hypochlorite showed the highest sensory scores for overall liking among all yogurts made with oxidised starches. This result showed that the degree of oxidisation influenced the quality of yogurt. Among the native and oxidised starch samples prepared in the present work, oxidised starch made with 2.0% sodium hypochlorite showed a better potential for improving the WHC, apparent viscosity, and sensory score of set yogurt, and starch made using 3.0% sodium hypochlorite showed the next-best potential. This phenomenon might have been due to the fact that the presence of oxidised starch could increase the strength and molecular tightness of the gel network in set yogurt, and to a certain extent, the intensity of this effect increases as the degree of oxidation in the starch increases (Cui *et al.,* 2014). However, the WHC of yogurt prepared with 4.0% oxidised starch was lower than those of yogurt prepared with 2.0 and 3.0% oxidised starch. This trend might have been due to the decrease in WHC caused by the lower swelling power of 4.0% oxidised starch (Table 3) having a greater impact than the increased WHC caused by the increased degree of oxidation.

Conclusion

The present work demonstrated the effects of changes in the degree of oxidation from low to high on the properties of oxidised starch. The oxidation reaction destroyed the morphology of starch granules, and degraded starch molecules, thereby increasing the swelling degree and solubility of starch, and the degree of this change increased with an increase in the degree of oxidation. Different degrees of oxidation had no effect on starch paste, but oxidation at the 0.5% level slightly increased the gelatinisation temperature of starch, and the thermal stability and anti-aging properties of starch paste after oxidation were improved. Thus, different degrees of oxidation

Table 5. Effect of the starches oxidised with different concentrations of active chlorine on water-holding capacity, apparent viscosity, and overall liking of yogurt.

Starch	WHC (%)			Apparent viscosity (mPa·s)			Overall liking		
	0.5%	1.0%	1.5%	0.5%	1.0%	1.5%	0.5%	1.0%	1.5%
NPS	42.29 ± 2.3^f	48.44 ± 2.8^e	50.37 ± 3.3^e	12.606 ± 42^f	15.240 ± 59^e	18.350 ± 64^e	5.04 ± 0.4^f	5.82 ± 0.4^f	5.15 ± 0.5^e
POS-0.5%	51.45 ± 3.1^{cd}	58.31 ± 3.8^c	61.67 ± 4.2^c	14.648 ± 48^e	16.427 ± 70^d	19.164 ± 73^d	6.11 ± 0.6^e	6.85 ± 0.6^e	6.22 ± 0.5^d
POS-1.0%	55.55 ± 3.1^c	58.43 ± 3.7^c	62.10 ± 4.0^c	15.061 ± 68^d	16.435 ± 68^c	20.165 ± 80^c	6.83 ± 0.4^c	7.24 ± 0.5^c	6.94 ± 0.7^b
POS-2.0%	72.55 ± 5.4^a	79.13 ± 5.1^a	82.46 ± 5.8^a	18.767 ± 70^a	21.148 ± 65^a	22.753 ± 78^a	7.76 ± 0.5^a	8.11 ± 0.8^a	7.81 ± 0.6^a
POS-3.0%	60.73 ± 4.1^b	63.44 ± 4.9^b	70.83 ± 5.2^b	18.233 ± 69^b	20.228 ± 71^b	21.653 ± 74^b	7.14 ± 0.6^b	7.95 ± 0.7^b	7.67 ± 0.7^a
POS-4.0%	50.65 ± 5.1^e	56.72 ± 4.3^d	60.43 ± 4.8^d	17.413 ± 52^c	18.328 ± 68^c	20.317 ± 79^c	6.26 ± 0.7^d	7.13 ± 0.6^d	6.46 ± 0.6^c

Different lowercase superscripts in a column indicate significant difference ($p < 0.05$).

reactions gave native starch new processing characteristics. Upon using oxidised starch as a thickener and stabiliser in yogurt, the water-holding capacity, viscosity, and taste of yogurt improved, and the best application effect was obtained with oxidised potato starch at 2.0% oxidation degree and 1.0% addition amount.

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Reference

Celik, S. and Bakirci, I. 2003. Some properties of yoghurt produced by adding mulberry pekmez (concentrated juice). International Journal of Dairy Technology 56(1): 26-29.

Cui, B., Lu, Y. M., Tan, C. P., Wang, G. Q. and Li, G. H. 2014. Effect of cross-linked acetylated starch content on the structure and stability of set yoghurt. Food Hydrocolloids 35: 576-582.

Das, A. B., Singh, G., Singh, S. and Riar, C. S. 2010. Effect of acetylation and dual modification on physico-chemical, rheological and morphological characteristics of sweet potato (Ipomoea batatas) starch. Carbohydrate Polymers 80(3): 725-732.

Dias, A. R. G., Zavareze, E. R., Elias, M. C., Helbig, E., da Silva, D. O. and Ciacco, C. F. 2011. Pasting, expansion and textural properties of fermented cassava starch oxidised with sodium hypochlorite. Carbohydrate Polymers 84(1): 268-275.

Fonseca, L. M., Gonçalves, J. R., El Halal, S. L. M., Pinto, V. Z., Dias, A. R. G., Jacques, A. C. and Zavareze, E. R. 2015. Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films. LWT - Food Science and Technology 60(2): 714-720.

Hazarika, B. J. and Sit, N. 2016. Effect of dual modification with hydroxypropylation and cross-linking on physicochemical properties of taro starch. Carbohydrate Polymers 140: 269-278.

Kuakpetoon, D. and Wang, Y. J. 2001. Characterization of different starches oxidized by hypochlorite. Starch 53(5): 211-218.

Kuakpetoon, D. and Wang, Y. J. 2006. Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content. Carbohydrate Research 341(11): 1896-1915.

Kumari, A., Ranadheera, C. S., Prasanna, P., Senevirathne, N. D. and Vidanarachchi, J. K. 2015. Development of a rice incorporated synbiotic yogurt with low retrogradation properties. International Food Research Journal 22(5): 2032-2040.

Lawal, O. S. and Adebowale, K. O. 2005. Physicochemical characteristics and thermal properties of chemically modified jack bean (Canavalia ensiformis) starch. Carbohydrate Polymers 60(3): 331-341.

Lewicka, K., Siemion, P. and Kurcok, P. 2015. Chemical modifications of starch: microwave effect. International Journal of Polymer Science 2015: article ID 867697.

Martínez-Bustos, F., Amaya-Llano, S. L., Carbajal-Arteaga, J. A., Chang, Y. K. and Zazueta-Morales, J. J. 2007. Physicochemical properties of cassava, potato and jicama starches oxidised with organic acids. Journal of the Science of Food and Agriculture 87(7): 1207-1214.

Mazur, P., Stoljarowa, L. and Djatlow, W. 1989. Modified starches as dough conditioners for bread. Nutrition 13(3): 155-156.

Pinto, V. Z., Vanier, N. L., Deon, V. G., Moomand, K., El Halal, S. L., da Rosa Zavareze, E., … and Dias, A. R. 2015. Effects of single and dual physical modifications on pinhão starch. Food Chemistry 187: 98-105.

Sánchez-Rivera, M. M., García-Suárez, F. J. L., Velázquez del Valle, M., Gutierrez-Meraz, F. and Bello-Pérez, L. A. 2005. Partial characterization of banana starches oxidized by different levels of sodium hypochlorite. Carbohydrate Polymers 62(1): 50-56.

Sangseethong, K., Lertphanich, S. and Sriroth, K. 2009. Physicochemical properties of oxidized cassava starch prepared under various alkalinity levels. Starch 61(2): 92-100.

Schmorak, J. and Lewin, M. 1963. The chemical and physicochemical properties of wheat starch mildly oxidized with alkaline sodium hypochlorite. Journal of Polymer Science Part A - General Papers 1(8): 2601-2620.

Singh, J., Kaur, L. and McCarthy, O. J. 2007. Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications—a review. Food Hydrocolloids 21(1): 1-22.

Sukhija, S., Singh, S. and Riar, C. S. 2016. Effect of oxidation, cross-linking and dual modification on physicochemical, crystallinity, morphological, pasting and thermal characteristics of elephant foot yam (*Amorphophallus paeoniifolius*) starch. Food Hydrocolloids 55: 56-64.

Vanier, N. L., da Rosa Zavareze, E., Pinto, V. Z., Klein, B., Botelho, F. T., Dias, A. R. G. and Elias, M. C. 2012. Physicochemical, crystallinity, pasting and morphological properties of bean starch oxidised by different concentrations of sodium hypochlorite. Food Chemistry 131(4): 1255-1262.

Wang, Y. J. and Wang, L. 2003. Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. Carbohydrate Polymers 52(3): 207-217.

Wongsagonsup, R., Pujchakarn, T., Jitrakbumrung, S., Chaiwat, W., Fuongfuchat, A., Varavinit, S. and Suphantharika, M. 2014. Effect of cross-linking on physicochemical properties of tapioca starch and its application in soup product. Carbohydrate Polymers 101: 656-665.

Yi, X., Zhang, S. and Ju, B. 2014. Preparation of water-soluble oxidized starch with high carbonyl content by sodium hypochlorite. Starch 66: 115-123.

Zhang, Y. P. 2001. Manufacturing and application of modified starch. Beijing: Chemical Industry Press.

Zhou, F., Liu, Q., Zhang, H., Chen, Q. and Kong, B. 2016. Potato starch oxidation induced by sodium hypochlorite and its effect on functional properties and digestibility. International Journal of Biological Macromolecules 84: 410-417.