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Physicochemical properties of chemically modified starches from different botanical origin

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Starches from various botanical origins (rice, maize and potato starches) were cross-linked in the presence of epichlorohydrin (EPI), respectively. Then, the cross-linked starches were further oxidized with sodium hypochlorite (NaOCl, 2.5% w/w) to obtain oxidized cross-linked starches (OCS). The chemically modified methods on the physicochemical properties of different starches were investigated. It was found that cross-linking treatment increased peak, setback and final viscosities of rice and maize starches but decreased those of potato starch. The paste clarities of cross-linked rice and maize starches significantly reduced, whereas those of cross-linked potato starch increased. Oxidation treatment significantly decreased peak, final and setback viscosity values of all starches and significantly increased paste clarities. Dual-modified starches had higher peak, final viscosities and the ability to resistant to shear compared with oxidized starches, meantime it had lower tendency of retrogradation and higher paste clarities compared with cross-linked starches. Under those conditions of dual-modification, undesirable starch properties were counteracted.

Key words: Rice, maize, potato, starch, cross-linking, oxidation, oxidized cross-linking.

INTRODUCTION

Potato and maize starches are widely used in food and non-food industry in the world. Meantime, rice starch has paid much attention to research and development in recent years due to its distinctive structure and physicochemical characteristics. Starch origin and granule size have a significant influence on the physicochemical properties of native starch and modified starch (Morikawa and Nishinari, 2000). The numerous industrial and food applications of native starches are limited because of their tendency to retrograde. Starch derivatives like etherification, esterification, cross-linking and oxidation have been used to improve the gelatinisation and cooking characteristics and to prevent retrogradation (Morikawa and Nishinari, 2000). Chemical cross-linking imparts structural integrity of starch. These

chemically cross-linked starches are usually resistant to shear, low pH, and high temperature during food processing conditions. Cross-linked starches are prepared by reacting starch with several polyfunctional reagents such as sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), epichlorohydrin (EPI) and phosphoryl chloride (POCl$_3$). Singh et al. (2007) observed decrease in retrogradation rate and increase in gelatinization temperature with cross-linked starch, and these phenomena are related to the reduced mobility of amorphous chains in the starch granule as a result of intermolecular bridges. However, Jyothi et al. (2006) showed that cross-linked starch has more pronounced synaeresis than native starch because of ordered structure in the starch paste, thus resulting in a higher degree of retrogradation.

In recent times, oxidized starches have attracted much attention and are widely used in food and industrial applications to provide surface sizing and coating properties (Lawal et al., 2005).

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The food products where oxidized starch is used are neutral tasting and low-viscosity such as a lemon curd, salad cream and mayonnaise (Lawal, 2004). Oxidized starch is commonly prepared by reacting starch with a specified amount of oxidant under controlled temperature and pH. Periodate, chromic acid, permanganate, nitrogen dioxide and sodium hypochlorite have been commonly used to oxidize starches. The commercial production of oxidized starch generally employs sodium hypochlorite as the oxidizing agent. The factors affecting hypochlorite oxidation include pH, temperature, hypochlorite concentration, starch molecular structure, and starch origin (Wang and Wang, 2003; Kantouch and Dokki, 1998). Kuakpetoon and Wang (2001) studied the structure and physicochemical properties of oxidized corn starches with varied amylose contents (Kuakpetoon and Wang, 2006). The bulky carboxyl group on the starch molecules results in low retrogradation of oxidized starch paste whereas carbonyls play a minor role in the prevention of retrogradation of starches. Modified starch meets the functional properties required in food products such as thickening and stabilization. However, modified starch does not still overcome some undesirable properties. Cross-linking also reduces paste clarity and stability under cold storage. Oxidation significantly decreases the viscosity of starch paste and the ability to resistant to shear (Atichokudomchai and Varavinit, 2003; Brouch, 1985). Therefore, dual-modification was used to improve the undesirable characteristics of starch. Thus, starch is chemically modified by, for example, cross-linking, esterification and/or etherification are done depending on the application in the end-used products (Atichokudomchai and Varavinit, 2003; Wattanachant et al., 2003). However, data on the comparison in the physicochemical properties of modified and dual-modified starches from different botanical origin are still scarce.

The objective of this study was to investigate the physicochemical properties of oxidized cross-linked starches, and compared oxidized starches and cross-linked starches from various botanical origins. The effects of starch origin and modified method on swelling power, paste clarity, gel stability, pasting and thermal properties were systemically investigated.

MATERIALS AND METHODS

Native unmodified rice starch (NRS), maize starch (NMS) and potato starch (NPS) were purchased from Pure Biological Technology Company Limited (Yunnan province, China). Sodium hypochlorite containing 5% active chlorine and epichlorohydrin (0.3%, w/w, on a dry starch basis) were purchased from NongHe Company Limited (Hunan province, China). All chemicals and reagents used in this study were of analytical grade.

Preparation of cross-linked starches

Cross-linking reaction of starch was performed according to the method of Reddy and Seib (2000) with a slight modification. Starch

(100 g, dry basis) was suspended in distilled water (150 ml) with adding 3 g of NaCl and was continuously stirred at 25°C. After adjusting to pH 10.0 with 1 mol/L NaOH, epichlorohydrin (0.3%, w/w, on a dry starch basis) was added directly to the slurry with stirring at 25°C for 3 h, then adjusted to pH 6.0 to 6.5 with 0.2 mol/L HCl and the cross-linked starch (CS) was isolated by centrifugation (3,000 × g, 15 min). After washing with distilled water, the sediment was dried at 45°C for 48 h in a vacuum oven.

Degree of cross-linking analysis

The degree of cross-linking of the cross-linked starches was determined from the viscosity values, according to the method of Chatakanonda et al. (2000). The peak viscosities of the starch samples were recorded using a Rapid Visco Analyser (RVA super 4, Newport Scientific, Australia). The starch slurry (10% by weight) was heated from 50 to 95°C at 12°C/min at 160 rpm, and then held at 95°C for 2 min. Afterwards the paste was cooled to 50°C at 12°C /min and finally kept at 50°C for 2 min. The degree of cross-linking was calculated as follows:

$$\text{Degree of cross-linking} = \frac{A - B}{B} \times 100$$

Where, A is the peak viscosity in RV units of the native starch and B is that of the cross-linked starch.

Preparation of oxidized and oxidized cross-linked starches

The oxidized starch (OS) was prepared by following the method of Wang and Wang (2003) with a slight modification. Starch (100 g, dry basis, db) was suspended in distilled water (150 ml), and maintained at 30°C in a heating mantle and the pH was adjusted to 8.5 with 2 mol/L NaOH. 50 g (2.5 g Cl/100 g starch, 2.5% w/w) Sodium hypochlorite (NaOCl) was slowly added into the starch slurry over 30 min while maintaining the pH 8.5 with 1 mol/L H_2SO_4. After the addition of NaOCl, the pH of the slurry was maintained at 8.5 with 1 mol/L NaOH for an additional 30 min. The slurry was then adjusted to pH 6.5 to 7.0 with 1 mol/L H_2SO_4, the oxidized starch was isolated by centrifugation (3,000 × g, 15 min), washed with water and dried in a vacuum oven at 45°C for 48 h. Oxidized cross-linked starch (OCS) was also prepared by first cross-linking with EPI (0.3%, w/w, on a dry starch basis) as described above. After cross-linking, the pH of the slurry was adjusted to 8.5 with 1 mol/L H_2SO_4 and then NaOCl (2.5% active chlorine concentration) was added as previously described. The OCS was also recovered using the same procedure as for the CS.

Determination of carboxyl content (%)

The carboxyl group content of oxidized starch was determined according to the modified procedure of Chattopadhyay et al. (1997). Oxidized starch sample (about 2 g) was mixed with 25 m of 0.1 mol/L HCl with constant stirring for 30 min with a magnetic stirrer.

The slurry was then carried out vacuum filtration and washed with 400 ml of distilled water. The starch cake was then carefully transferred to a 500 mL beaker with 300 ml distilled water. The starch slurry was heated in a boiling water bath with continuous stirring for 15 min to ensure complete gelatinization. The hot starch dispersion was then adjusted to 450 m with distilled water and titrated to pH 8.3 with standardized 0.01 mol/L NaOH. A blank test was performed with unmodified starch. Carboxyl group content was calculated as follows:

$$\text{Carboxyl content}\ (\%) = \left(\frac{V_1}{m_1} - \frac{V_2}{m_2} \right) \times C \times 0.045 \times 100\%$$

Where V_1 is consumed volume with standardized NaOH titrating for oxidized starch sample (ml); m_1 is oxidized starch sample weigh (g, dry basis); V_2 is consumed volume with standardized NaOH titrating for unmodified starch (ml); m_2 is unmodified starch sample weigh (g, dry basis); C is the concentration of standardized NaOH (mol/L).

Measurement of carbonyl content (%)

The carbonyl content was determined by following the titrimetric method of Smith (1967). 4 g of starch was suspended in 100 mL of distilled water in a 500 mL flask for 20 min, cooled to 40°C, adjusted to pH 3.2 with 0.1mol/L HCl, and added to 15 mL of hydroxylamine reagent. The flask was stoppered and placed in a 40°C water bath for 4 h with slow stirring. The excess hydroxylamine was determined by rapidly titration the reaction mixture to pH 3.2 with standardized 0.1 mol/L HCl. A blank determination with only hydroxylamine reagent was prepared by first dissolving 25 g hydroxylamine hydrochloride in 100 mL of 0.5 mol/L NaOH before adjusting the final volume to 500mL with distilled water. Carbonyl content was calculated as follows:

$$\text{Carbonyl content}\ (\%) = \frac{(V_2 - V_1) \times 0.1 \times 0.028}{m} \times 100\%$$

Where V_1 is consumed volume with standardized HCl titrating for oxidized starch sample (mL); V_2 is consumed volume with standardized HCl titrating for unmodified starch (mL); m is sample weight (g, dry basis).

Determination of swelling power (SP), paste clarity

The SP of native and modified starches was measured according to the method of Sasaki and Matsuki (1998) with a slight modification. The starch (0.16 g, db) was suspended in 5 ml of distilled water in glass tubes coated by screw caps. Then the slurry was heated at 90°C in a shaking water bath for 30 min. After cooling quickly to room temperature in a cold water bath, the samples were centrifuged at 3,000 × g for 15 min. The supernatant was removed carefully and the SP was determined as weight of the sediment according to:

$$\text{Swelling power}\ (g/g) = \frac{W_2 - W_1}{W}$$

Where W_2 is weight of tube after supernatant was removed (g); W_1 is weight of dry tube (g) and W is weight of db starch (g). The paste clarity of native and modified starch was determined based on the method of the Perera and Hoover (1999). For the determination, 1% aqueous suspension of each sample was heated in a water bath at 95°C for 30 min with constant stirring. The paste was cooled to room temperature. The paste was stored for 24 h in a refrigerator at 4°C and transmittance was measured at 650 nm against a water blank using a UV–Visible spectrophotometer Model UV 1601 Version 2.40 (Shimadzu, Japan).

Pasting properties

The pasting properties of rice starch were determined with the (RVA

super 4, Newport Scientific, Australia). Viscosities of starches were recorded with starch suspensions (Moisture Content 12.0%, sample 3.00 g, water 25.00 ml). Underwent a controlled heating and cooling cycle under constant shear where the sample was held at 50°C for 1 min, heated from 50 to 95°C at 5°C /min and held at 95°C for 2.7 min, cooled from 95 to 50°C at 5°C /min and held at 50°C for 2 min. The initial speed of blender in 10 s is for 960 rpm, after that maintain 160 rpm. Pasting parameters such as pasting temperature, peak viscosity, breakdown (peak viscosity-hot paste viscosity), final viscosity, setback (final viscosity-hot paste viscosity) were recorded.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry analysis was performed according to the method described by Morikawa and Nishinari (2000) with a modification using a differential scanning calorimeter (STA 449C, NET2SCH, Germany). Starch samples were weighed into aluminum DSC pans, and deionized water was added by micropipette to achieve a water-sample ratio of 2:1. The sample pans were sealed and allowed to stabilize at room temperature for 24 h before heating. Thermal scans were carried out from 25 to 100°C at a heating rate of 10°C/min using an empty pan as reference. The onset temperature (T_o) and peak temperature (T_p) were determined from the run heating DSC curves. Enthalpy of gelatinization (ΔH_{gel}) was evaluated based on the area of the main endothermic peak.

Measurement of flow behavior

8% starch paste was put into the testing platform of dynamic rheometer (ARES, TA, Limited, America). Viscometry was performed using a controlled strain rheometer using parallel plate mould (40 mm diameter and 1 mm gap). After trimming off the over-loaded portion of samples around plates, the open side of samples was covered with a thin layer of silicon oil to prevent moisture loss. Shear stress with increasing shear rate (0 to 500 s^{-1}) was obtained at 20°C to characterize flow behavior.

Statistical analyses

The data reported in the tables were average of triplicate observations. Data obtained were analyzed by single factor analyses of variance (ANOVA) using spass for windows version 13.0 following the procedure described by Miller and Miller (1993). Confidence interval of sample means was reported at the 95% confidence probability. Comparisons of means were made using least significant difference (LSD) and shortest significant ranges (SSR) at 5% significance level ($P<0.05$).

RESULTS

Degree of cross-linking and contents of carboxyl and carbonyl groups

The carboxyl and carbonyl groups contents of oxidized starches from rice, maize and potato are listed in Table 1. There was no significant difference in carbonyl content for different starches at the same reaction conditions ($P > 0.05$). In contrast, carboxyl contents varied significantly according to starch types, oxidized potato starch had the highest carboxyl content (0.95%), and whereas oxidized rice starch had the lowest (0.48%). For dual-modified

Table 1. Degree of cross-linking and contents of carboxyl and carbonyl groups of oxidized and oxidized cross-linked starches from different botanical origins.

Sample	Carboxyl content (%)	Carbonyl content (%)	Degree of cross-linking
CRS∗	—	—	ND
ORS	0.48±0.02[d]	0.08±0.003[a]	—
OCRS	0.24±0.01[e]	0.05±0.002[b]	ND
CMS	—	—	ND
OMS	0.73±0.03[b]	0.09±0.003[a]	—
OCMS	0.54±0.02[c]	0.05±0.002[b]	ND
CPS	—	—	60.1±2.2[a]
OPS	0.95±0.04[a]	0.09±0.003[a]	—
OCPS	0.79±0.03[b]	0.06±0.002[b]	20.0±1.5[b]

∗ CRS, cross-linked rice starch; ORS, oxidized rice starch; OCRS, oxidized cross-linked rice starch; CMS, cross-linked maize starch; OMS, oxidized maize starch; OCMS, oxidized cross-linked maize starch; CPS, cross-linked potato starch; OPS, oxidized potato starch; OCPS, oxidized cross-linked potato starch; The values are average ± standard deviation, n=3; ND: not detectable.

starches, carboxyl content of oxidized cross-linked potato starches was also highest, oxidized cross-linked rice starch had the lowest carboxyl content. It can be observed that the carboxyl content of all oxidized starches was higher than that of oxidized cross-linked starches. It indicated that the starch was difficult to oxidation due to the strengthened structure of starch after cross-linking. The degree of cross-linking of the modified starches was determined from the RVA viscosity values are also presented in Table 1. It was observed that at lower level of EPI (0.3%), the degree of cross-linking of rice and maize starch was not detectable by the viscosity method, the degree of cross-linking of theses starches was not great enough to restrict the swelling of the granules and these exhibited higher peak viscosity values than that of the native starch (Jyothi et al., 2006). However the degree of cross-linking of cross-linked and oxidized cross-linked potato starch was detectable (60.1 and 20.0, respectively), higher level of cross-link of potato starch retarded the swelling of granules, resulting in a lower peak viscosity.

Swelling powers and paste clarity of starches

The swelling powers and paste clarity of native and modified starches are presented in Table 2. The swelling powers of native rice, maize and potato starches were 10.1, 9.9 and 18.8 g/g, respectively. It is well known that potato starch has high swelling power and disperses volume fraction compared with starches from other tropical root and tuber crops. A significant reduction in SP after oxidation was observed. Among oxidized starches, the highest SP for potato starch (1.3 g/g) and the lowest for rice starch (0.6 g/g) were observed. It is also suggested that the SP of rice and maize starches had a significant increase after cross-linking. However, the SP

of cross-linked potato starch decreased. Higher level of cross-linking caused reduced swelling and viscosity (Tables 2 and 3). The SP of dual-modified starches oxidized cross-linked rice starch (OCRS), oxidized cross-linked maize starch (OCMS) and oxidized cross-linked potato starch (OCPS) was significantly higher than that of their native and oxidized starches, but lower than cross-linked starch. When native and cross-linked starches were oxidized, the cross-linked starch was more different to be oxidized than native starch. In addition, oxidation and cross-linking reagents had opposite influence on SP of starch granules.

The clarity of starch reflected a light through the paste. Compared with the native starches, the paste clarity of cross-linked starches significantly decreased except potato cross-linked starch, and the paste clarity of dual-modified starches significantly increased, whereas the paste clarity of oxidized starches increased greatly (Table 2), the result was similar to rice, maize and potato starch. Effect of different varieties of starch on the SP and clarity are also shown in Table 2, it was found that the SP and transmittance of native and modified starches of potato were the highest compared those of native and modified starches of rice and maize, it may be due to the larger average granule size of potato starch. It was observed that SP and transmittance of dual-modified starches from rice, maize and potato were significantly higher than those of native and oxidized starches.

Pasting properties

The pasting characteristics of the native and modified starches analyzed with a RVA are presented in Table 3. Native and cross-linked starch exhibited high pasting temperature. After being oxidized, the pasting temperatures of starches significantly decreased. The

Table 2. Swelling power and paste clarity of native, cross-linked, oxidized and oxidized cross-linked starches from different botanical origins.

Sample	Swelling power (g/g)	Transmittance (%T$_{650}$)
NRS*	10.1 ± 0.3^g	3.8 ± 0.1^j
CRS	13.9 ± 0.4^d	1.8 ± 0.06^l
ORS	0.6 ± 0.02^j	86.4 ± 3.1^b
OCRS	11.6 ± 0.4^f	4.9 ± 0.2^i
NMS	9.9 ± 0.3^g	5.4 ± 0.2^h
CMS	12.8 ± 0.4^e	3.2 ± 0.1^k
OMS	0.9 ± 0.03^i	81.2 ± 2.9^c
OCMS	11.4 ± 0.4^f	7.6 ± 0.3^g
NPS	18.8 ± 0.6^c	23.3 ± 0.9^f
CPS	24.4 ± 0.9^a	29.2 ± 1.1^e
OPS	1.3 ± 0.04^h	96.4 ± 3.4^a
OCPS	20.2 ± 0.7^b	31.3 ± 1.2^d

*NRS, native rice starch; CRS, cross-linked rice starch; ORS, oxidized rice starch; OCRS, oxidized cross-linked rice starch; NMS, native maize starch; CMS, cross-linked maize starch; OMS, oxidized maize starch; OCMS, oxidized cross-linked maize starch; NPS, native potato starch; CPS, cross-linked potato starch; OPS, oxidized potato starch; OCPS, oxidized cross-linked potato starch; The values are average ± standard deviation, n=3.

Table 3. Pasting properties of native, cross-linked, oxidized and oxidized cross-linked starches from different botanical origins.

Sample	Pasting temperature (°C)	Paste viscosity (cP)				
		Peak	Trough	Final	Breakdown	Setback
NRS*	79.2 ± 0.6^a	3096 ± 38^c	1622 ± 18^c	3327 ± 40^b	1474 ± 16^c	1705 ± 19^b
CRS	79.2 ± 0.5^a	3346 ± 41^a	1582 ± 17^d	3526 ± 42^a	1764 ± 21^a	1944 ± 21^a
ORS	72.6 ± 0.3^e	498 ± 6^i	59 ± 1^h	121 ± 2^i	439 ± 5^g	62 ± 1^i
OCRS	77.5 ± 0.4^b	3198 ± 39^b	1558 ± 16^d	2152 ± 25^e	1640 ± 17^b	594 ± 6^e
NMS	75.9 ± 0.4^c	2868 ± 35^e	1718 ± 18^a	2690 ± 32^d	1150 ± 12^e	972 ± 9^d
CMS	75.9 ± 0.3^c	3332 ± 41^a	1707 ± 18^a	2953 ± 37^c	1625 ± 17^b	1246 ± 13^c
OMS	67.8 ± 0.2^f	1085 ± 12^h	95 ± 2^g	159 ± 3^h	990 ± 10^f	64 ± 1^i
OCMS	75.2 ± 0.3^d	2933 ± 36^d	1698 ± 18^b	2084 ± 25^f	1235 ± 13^d	386 ± 4^h
NPS	66.9 ± 0.2^g	2701 ± 33^f	1671 ± 18^b	2183 ± 26^e	1030 ± 11^f	512 ± 6^f
CPS	79.1 ± 0.5^a	1078 ± 13^h	748 ± 9^f	1204 ± 14^g	330 ± 4^h	456 ± 5^g
OPS	59.1 ± 0.1^i	352 ± 4^j	12 ± 0.4^i	17 ± 0.5^j	340 ± 4^h	5 ± 0.1^g
OCPS	66 ± 0.2^h	2160 ± 26^g	1180 ± 12^e	1245 ± 14^g	980 ± 10^f	65 ± 1^i

*RS, native rice starch; CRS, cross-linked rice starch; ORS, oxidized rice starch; OCRS, oxidized cross-linked rice starch; NMS, native maize starch; CMS, cross-linked maize starch; OMS, oxidized maize starch; OCMS, oxidized cross-linked maize starch; NPS, native potato starch; CPS, cross-linked potato starch; OPS, oxidized potato starch; OCPS, oxidized cross-linked potato starch; The values are average ± standard deviation, n=3.

phenomenon suggested that oxidized starch granules were easier to swell. The peak and final viscosities of 2.5% NaOCl oxidized starches were significantly lower than those of the non-oxidized starches. Kuakpetoon and Wang (1999) also observed a similar phenomenon for rice, corn and potato starches at 2% NaOCl-oxidized concentration. The oxidized potato starch had significantly low peak and final viscosity, indicating that potato starch was easier to be oxidized than other two starches as supported by its higher carboxyl contents. In pasting properties parameter, setback is more likely related to the retrogradation tendency of amylose (Abd et al., 2000). The setback values of all oxidized starches significantly decreased; whereas potato oxidized starch had a great decrease in setback, indicating its lowest tendency to retrograde. The pasting temperature of

Table 4. Thermal properties (DSC) of native, cross-linked, oxidized and oxidized cross-linked starches from different botanical origins.

Sample	T_o (°C)	T_p (°C)	ΔH_{gel} (J/g)
NRS*	59.3±0.9[d]	87.6±1.3[d]	9.8±0.1[f]
CRS	83.7±1.2[a]	99.6±1.5[a]	11.5±0.3[b]
ORS	57.5±0.8[f]	84.1±1.2[h]	8.9±0.1[i]
OCRS	58.4±0.8[e]	86.1±1.3[e]	11.0±0.2[d]
NMS	59.3±0.9[d]	86.8±1.3[f]	10.2±0.2[e]
CMS	67.2±1.1[b]	90.4±1.4[c]	11.8±0.3[a]
OMS	54.7±0.7[h]	78.3±1.1[j]	9.1±0.1[h]
OCMS	56.3±0.7[g]	81.8±1.1[i]	11.2±0.2[c]
NPS	58.4±0.8[e]	85.4±1.2[g]	8.2±0.1[j]
CPS	65.3±1.0[c]	98.1±1.5[b]	11.2±0.2[c]
OPS	52.8±0.6[i]	72.1±1.0[k]	7.6±0.1[k]
OCPS	58.5±0.8[e]	73.9±1.0[k]	9.3±0.1[g]

∗ NRS, native rice starch; CRS, cross-linked rice starch; ORS, oxidized rice starch; OCRS, oxidized cross-linked rice starch; NMS, native maize starch; CMS, cross-linked maize starch; OMS, oxidized maize starch; OCMS, oxidized cross-linked maize starch; NPS, native potato starch; CPS, cross-linked potato starch; OPS, oxidized potato starch; OCPS, oxidized cross-linked potato starch; The values are average ± standard deviation, n=3.

cross-linked rice and maize starches had no difference from that of their native counterpart starches ($P > 0.05$), whereas the pasting temperature of cross-linked potato starch increased compared with its native starch. The increased peak and final viscosities of cross-linked rice and maize starches were observed, in contrast, potato cross-linked starch showed a decrease in the peak and final viscosities, which gave a further proving that the degree of cross-linking of potato starch was higher than that of rice and maize starches at the same cross-linking condition of 0.3% EPI.

Strengthening the bonding between starch chains through cross-links might have increased the resistance of the granules to swelling, leading to the higher pasting temperature and lower peak viscosity. Introducing low degrees of cross-linking in starch has been reported to increase the peak and cold paste viscosities of starch (Kartha and Srivastava, 1985). In this study, cross-linked rice and maize starch showed an increase in the peak and final viscosities. At lower levels of cross-linking in rice and maize starch, the setback viscosity was found to be higher. This could be attributed to the observed high peak viscosity values. In addition, cross-linking resulted in ordered structure in the starch pastes, thus resulting in a higher degree of retrogradation. However, with an increase in the degree of cross-linking for potato starch, the setback viscosity was also decreased. The breakdown viscosities of cross-linked and oxidized cross-linked potato starches were significantly lower than those of native starch. Whereas those of cross-linked and oxidized cross-linked starches of rice and maize were significantly higher than those of their native counterpart

starches and this was probably due to less cross-linking occurring in rice and maize starch. This confirms that potato starch was prone to cross-linking. Cross-linked starches had higher peak viscosity but exhibited higher retrogradation trend. In contrast, oxidized starches had lower degree of retrogradation, however showed lower peak viscosity value. When cross-linked starch was subjected to oxidation, its ordered structure in the starch pastes was disrupted. The retrogradation trend of oxidized cross-linked starch significantly decreased, and oxidized cross-linked starch had higher peak viscosity value due to cross-linking in starch molecules.

Thermal properties

The thermal transitions of the native, cross-linked, oxidized and oxidized cross-linked starches from rice, maize and potato measured by DSC are presented in Table 4. The T_o, T_p and enthalpy of gelatinization (ΔH_{gel}) of oxidized starches from rice, maize and potato were lower than those of their native counterpart starches at the same oxidized conditions of 2.5% NaOCl. The enthalpy of gelatinization represents the needed thermal energy to destroy the structure of crystallites in the gelatinization process. The decrease in T_o, T_p and ΔH_{gel} resulted from the degradation of crystalline lamella. The T_o, T_p and ΔH_{gel} of potato oxidized starch was the lowest compared with oxidized rice and maize starches, oxidation greatly weaken the structure of potato starch granules, implied that potato starch was easier to be oxidized. Compared with oxidation, cross-linking
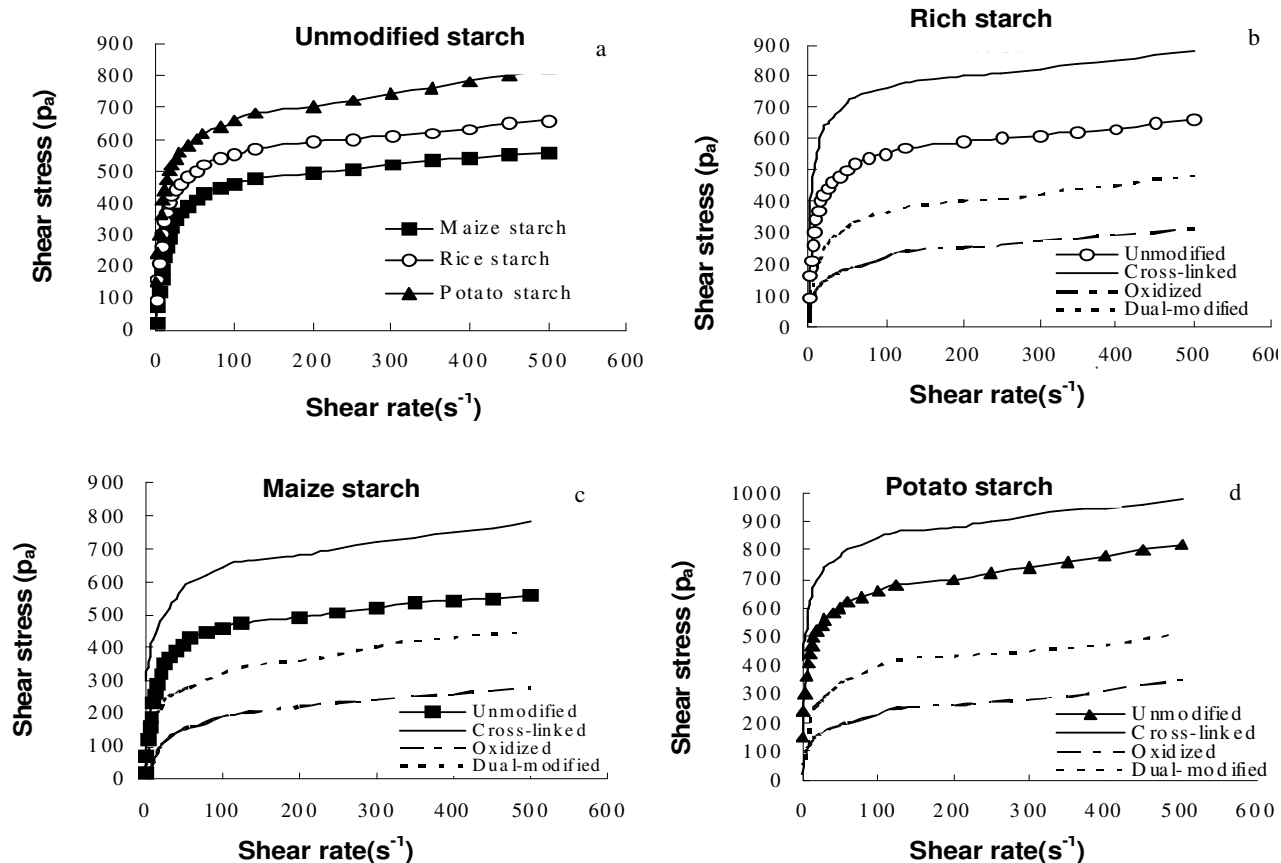
Figure 1. Shear stress as a function of shear rate for native, cross-linked, oxidized and oxidized cross-linked (dual-modified) starches from different starches; **a**, unmodified starch; **b**, rice starch; **c**, maize starch; **d**, potato starch.

reinforces the structure of starch granules; more heat will be required for gelatinization. Yeh and Yeh (1993) also reported that cross-linking increased the heat of gelatinization for rice starch. However, according to Yook et al. (1993), the cross-linked rice starch exhibited a lower value of heat of gelatinization than native rice starch because cross-linking reduced the portion of starch granules that could be gelatinized. In this study, the T_o, T_p and ΔH_{gel} of cross-linked starches from rice, maize and potato were higher than those of their native counterpart starches at the same reaction conditions of 0.3% EPI. T_o, T_p and ΔH_{gel} values of oxidized cross-linked starches were in between oxidized starches and cross-linked starches for rice, maize and potato, and significantly higher than those of native counterpart starches.

Flowing characteristics

As was shown by the flow curves in Figure 1, shear stress of all native and modified starches increased with the shear rate increasing. For native rice, maize and potato starches, potato starch had the highest shear

stress, whereas maize starch had the lowest shear stress at the same shear rate. Compared with native rice starch, cross-linked rice starch had the highest shear stress, oxidized rice starch had the lowest shear stress, and the shear stress of dual-modified rice starch was between cross-linked and oxidized starch. The similar phenomenon was observed in maize and potato starch. Gibinski et al. (2006) indicated that high values of shear stress pointed to a high stability of the structure of the starch. According to Gibinski et al. (2006) cross-linked starch had the most stable structure and the strong ability to resistant to shear, the structure of oxidized starch was weaken and loss the ability to resistant to shear, and the ability to resistant to shear of oxidized starch was improved through dual-modification.

DISCUSSION

The comparison in the physicochemical properties of modified and dual-modified starches from different botanical origin was studied. The present results suggested that carboxyl contents varied significantly

according to starch types, oxidized potato starch had the highest carboxyl content, and whereas oxidized rice starch had the lowest, which differed from those by Kuakpetoon and Wang (2001), but agreed with those by Hebeish et al. (1999). Kuakpetoon and Wang indicated that potato starch had the highest carboxyl content, whereas corn starch had the lowest. The high carboxyl content observed in oxidized potato starch suggests that this starch was more susceptible to oxidation due to the larger granule size and the more linear nature of the amylose (Wang and Wang, 2003). A significant reduction in SP after oxidation has been reported previously for normal and waxy corn starches (Sandhu et al., 2008). A similar decrease in the SP after oxidation was observed in the present work. Leach et al. (1950) proposed that bonding forces within the granules of starch affected its swelling power. The reduction in the SP after oxidation may be attributed to structural disintegration within the granules of the starch during the process of modification (Lawal, 2004). The SP of rice and maize starches had a significant increase after cross-linking. However, the SP of cross-linked potato starch decreased. The bonding forces within the granules of starch were strengthened by cross-linked reaction, which result in an increase in SP. A study indicated that the granule size of potato and maize starch was bigger than that of rice starch, the average granule size of potato, maize and rice starch was 38.3, 17.8 and 6.4 μm, respectively (Li and Yeh, 2004).

The SP of potato starch reduced after cross-linking, it was probably that great granule size resulted in more cross-linking occurring under the same reaction conditions. Paste clarity was the result of rupture of swollen starch granules, and cross-linking improved the integrity of swollen granules, reducing paste clarity (Zheng et al., 1999). In this study, the result that paste clarity of oxidized starches increased greatly supported the study of Brouch (Brouch, 1985), which indicated that oxidation resulted in an increase transmittance of corn starch suspension due to electrostatic repulsion between starch molecules caused by negative charges of carboxyl groups introduced in the molecules. Many studies have reported the influence of oxidation on the gelatinization properties of starch but the results are somewhat inconclusive and seem to depend on starch origin as well as the modification conditions. Forssell et al. (1995) observed an increase in T_o of oxidized barley starch, while the T_o of oxidized potato starch remained unchanged. Wang and Wang (2003) reported an increase in T_o of oxidized waxy and common corn starches, when a low concentration of hypochlorite (≤1.25% active chlorine) was used in the modification process. However, Kuakpetoon and Wang (2006) indicated that T_o of oxidized starches decreased when the oxidant concentration was increased up to 5% active chlorine. In this study, The T_o, T_p and enthalpy of gelatinization (ΔH_{gel}) of oxidized starches from rice, maize and potato were lower than those of their native counterpart starches at

the same oxidized conditions of 2.5% NaOCl, and oxidation greatly weaken the structure of potato starch granules.

Conclusions

In conclusion, the differences in physicochemical properties among native and chemically modified potato, maize and rice starches are attributed to their differences in granular size and molecular structure. At the same condition, potato starch was easier to oxidize and cross-link than rice and maize starches. Cross-linked starches had higher ability to resistant to shear and higher peak and final viscosity, but had higher retrogradation trend and lower clarity. Oxidation significantly decreased the peak viscosities of rice, maize and potato starch pastes and the abilities to resistant to shear. An oxidized starch was difficult to retrogradation. Paste clarity of starch was significantly increased after oxidation. Oxidized cross-linked starches provided higher peak viscosity and stronger ability to resistant to shear as compared to oxidized starches. Oxidized cross-linked starches exhibited higher paste clarity and lower retrogradation trend compared with cross-linked starches. The study indicated that the undesirable properties in native, cross-linked and oxidized starches from rice, maize and potato could be overcome by dual-modification.

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Abbreviations: NRS, Native rice starch; **CRS,** cross-linked rice starch; **ORS,** oxidized rice starch; **OCRS,** oxidized cross-linked rice starch; **NMS,** native maize starch; **CMS,** cross-linked maize starch; **OMS,** oxidized maize starch; **OCMS,** oxidized cross-linked maize starch; **NPS,** native potato starch; **CPS,** cross-linked potato starch; **OPS,** oxidized potato starch; **OCPS,** oxidized cross-linked potato starch; **SP,** swelling power; **EPI,** epichlorohydrin; **OCS,** oxidized cross-linked starches; **STMP,** sodium tripolyphosphate; **STPP,** sodium tripolyphosphate; **POCl₃,** phosphoryl chloride; **CS,** oxidized starch; **RVA,** rapid visco analyser; **DSC,** differential scanning calorimetry; **STA,** scanning calorimeter; **LSD,** significant difference; **SSR,** shortest significant ranges.

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