

Functional Properties of Hydroxypropylated, Cross-Linked, and Hydroxypropylated Cross-Linked Tuber and Root Starches

Anil Gunaratne¹ and Harold Corke^{1,2}

ABSTRACT

Cereal Chem. 84(1):30–37

Functional properties of some underexploited tuber and root starches (true yam, gourd yam, taro, lotus, and sweet potato) were investigated before and after hydroxypropylation, cross-linking, and hydroxypropylation and cross-linking using potato starch as the reference. Low swelling ability, poor viscosity development but high shear stability, gel hardness, and resistance to enzyme hydrolysis was observed in starches from true yam and gourd yam. The extent of retrogradation was also highest in these two starches. Most of the functional properties of lotus starch were similar to those of potato starch. Hydroxypropylation to a molar substitution level of ≈ 0.1 increased the swelling factor and susceptibility to

α -amylase hydrolysis but decreased acid tolerance of paste viscosity, retrogradation, gelatinization parameters, gel hardness, and shear stability. Cross-linking decreased the swelling factor and amylose leaching, and increased shear stability and resistance to enzyme and acid tolerance. Cross-linking had very little influence on gelatinization and retrogradation properties but a larger effect on pasting properties. Increased or decreased peak viscosities and gel hardness values were noted for different cross-linked starches. Cross-linking of hydroxypropylated starches increased commonly desirable functional properties providing a wider range of potential applications.

Starch is the major reserve polysaccharide in higher plants and can be found in stems, tubers, roots, fruits, and grains, etc. Tropical tuber and root starches are the main staple food for many people in the world's hot and humid region. These crops are highly adapted to the tropical agro-climatic environment and can grow in great abundance with little or no artificial input. Although the agronomic and phenotypic properties are well documented, little effort has been made to exploit the functional properties of these starches and introduce them at a commercial level. A detailed knowledge of starch characteristics of underexploited starches may help to select suitable genotypes that behave like potato and cereal starches. Functionality is the key to applications, and for those starches that do not have desirable functional properties, modification techniques can be used to improve the functionalities.

Hydroxypropylation and cross-linking are two widely used methods for making modified starch. Hydroxypropylation increases freeze-thaw stability, decreases gelatinization and pasting temperatures, and increases paste clarity (Hoover et al 1988; Kim and Eliasson 1993; Perera et al 1997; Liu et al 1999; Pal et al 2002), while cross-linking provides more stable pastes at high temperature and at low pH (Wurzberg and Szymanski 1970; Woo and Seib 1997; Liu et al 1999). It can be expected therefore that cross-linking of hydroxypropylated starch may provide a wide range of functional properties permitting numerous applications. To date, most studies on, and production of, chemically modified starches have been limited to widely available starches such as wheat, maize, and potato. Studying the chemical modification of starches from other botanical sources may provide a deeper insight into the structure and physicochemical properties of starches. The objective here was to investigate the functional properties of some underexploited tuber and root starches and determine how the properties of these starches could be improved by means of hydroxypropylation, cross-linking, and hydroxypropylation with cross-linking.

MATERIALS AND METHODS

Materials

Potato starch, fungal α -amylase (EC 3.2.1.1, A-0273), phosphoryl chloride, and propylene oxide were from Sigma Chemical (St. Louis, MO). True yam (*Dioscorea alata*), gourd yam (*Cucurbita foetidissima*), taro (*Alocassia esculenta*), lotus (*Nelumbo nucifera*), and sweet potato (*Ipomea batatas*) were purchased in a local market.

Starch Isolation

Starches were isolated as described by Hoover and Hadziyev (1981) with some slight modifications. The tubers and roots were peeled, washed, diced, placed in ice-cold water containing 100 ppm of NaHSO_3 , and homogenized at low speed in a Waring blender. The slurry was filtered through a filtering cloth, the residue washed with a small amount of water, and the filtrate was centrifuged at $3,000 \times g$ for 10 min. The supernatant and the brown layer of material on the surface of the sediment were removed, and further purification was achieved by repeated suspension in water and centrifugation. The purified starch was dried at 35°C . Nitrogen content was estimated by the micro-Kjeldahl method to determine the purity of extracted starch.

Amylose Content

An amylose/amylopectin assay kit from Megazyme International (Ireland) was used to estimate the total amylose content of all the starches. This assay is based on the principle of formation of an amylopectin-lectin complex with Concanavalin-A (Con A) after a pretreatment to remove lipids.

Swelling Factor

Swelling factor, the ratio of the volume of swollen starch granules to the volume of dry starch, was determined by the method of Tester and Morrison (1990a), where starch (50 mg, db) was heated at 85°C for 30 min in 5 mL of water.

Amylose Leaching

Distilled water (10 mL) was added to starch (20 mg, db) in a screw-cap tube. Tubes were then heated at 85°C for 30 min with occasional stirring. After cooling to ambient temperature, samples were centrifuged at $2,000 \times g$ for 10 min. The amylose content in the supernatant (0.1 mL) was estimated as described by Chrastil (1987) and the percent of leached amylose was calculated based on starch weight.

¹ Cereal Science Laboratory, Department of Botany, University of Hong Kong, Pokfulam Road, Hong Kong.

² Corresponding author. Phone: 00852-2857-8522. Fax: 00852-2857-8521. E-mail: hcorke@yahoo.com

Differential Scanning Calorimetry

Gelatinization and dissociation parameters were measured using differential scanning calorimetry (TA 2920, a modulated thermal analyzer DSC) with a thermal analysis data station (TA Instruments, Newcastle, DE). Starch (3 mg, db) was directly weighed by a microbalance into the aluminum DSC pan and distilled water (9 μ L) was added with a microsyringe. Pans were sealed and allowed to stand for 1 hr at room temperature for even distribution of water. The scanning temperature and the heating rates were 30–120°C and 10°C/min, respectively. An empty pan was used as reference for all measurements.

Pasting Properties

Pasting properties of starches were determined using a Rapid Visco Analyser (RVA) model 3D (Newport Scientific, Warriewood, Australia). Distilled water or hydrochloric acid solution (pH 3) (25.5 g) was added to starch (2.3 g, db) in the RVA canister to obtain a total constant sample weight of 27.8 g (8.2% starch concentration). The slurry was then manually homogenized using the plastic paddle to avoid lump formation before the RVA run. A programmed heating and cooling cycle was set for 22 min, where it was first held at 50°C for 1.0 min, heated to 95°C in 7.5 min, further held at 95°C for 5 min, cooled to 50°C within 7.5 min, and held at 50°C for 1 min.

Gel Textural Analysis

Gel hardness was determined on the starch gel made in the RVA testing using a TA-XT2 texture analyzer (Stable Micro Systems, Godalming, England). After RVA testing, the paddle was removed and the starch paste in the canister was covered by Parafilm wrap and stored at 4°C for 7 hr. The gel was allowed to warm to room temperature, then compressed at a speed of 0.5 mm/sec to a distance of 10 mm with a 6-mm cylindrical probe. The maximum force peak in the TPA profile represents the gel hardness.

Enzymatic Hydrolysis

Enzymatic hydrolysis was measured using a RVA method as described by Li et al (2000). Development of peak viscosity was measured before and after adding 100 units of fungal α -amylase and then percent decrease of peak viscosity was calculated to estimate the extent of enzyme hydrolysis. In this analysis, the same heating-cooling program and the same starch concentration were used as in the measurement of pasting properties.

Retrogradation

After determining gelatinization properties, the DSC pans and their contents were stored at 4°C for 24 hr to initiate nucleation. Then the pans were kept at 40°C for 10 days to propagate crystal growth before rescanning by DSC. The temperature range and heating rate were 30–120°C and 10°C/min, respectively.

Hydroxypropylation

Hydroxypropylation of tuber and root starches was performed according to the method of Choi and Kerr (2004) with some slight modifications. Starch (50 g, db) was suspended in distilled water (110 mL) containing Na_2SO_4 (10 g) in a centrifuge bottle. After adjusting to pH 11.3 with 1M NaOH, 5.0 mL of propylene oxide was added and the bottle was immediately capped and shaken vigorously. The sample was then placed at 35°C in a shaking water bath with continuous shaking for 24 hr. The reaction was terminated by adding 1M HCl to pH 5.3. The slurry was then centrifuged at $3,000 \times g$ for 10 min and the recovered starch cake was washed three times with distilled water and dried at 35°C. The hydroxypropyl content was estimated by the spectrophotometric method of Johnson (1969) and expressed in terms of molar substitution (MS).

Cross-Linking

Cross-linking of starch with POCl_3 was done as described by Woo and Seib (1997) with some slight modifications. To make a starch slurry, starch (50 g, db) was mixed with water (70 mL) containing sodium sulfate (1 g) and stirred mechanically at 25°C for 1 hr. The slurry was adjusted to pH 11 by slowly adding 1M sodium hydroxide while maintaining the temperature at 25°C. Phosphoryl chloride (0.01% based on starch dry weight) was injected with a microsyringe into the starch slurry. After 1 hr, the slurry was adjusted to pH 5.5 with 1M HCl and the modified starch was recovered by centrifugation ($3,000 \times g$ for 10 min). The sediment starch cake was washed three times with distilled water and dried at 35°C.

Cross-Linking of Hydroxypropylated Starch

Hydroxypropylation was accomplished as stated above and the reaction mixture was cooled to room temperature (25°C). After adjusting to pH 11.0, phosphoryl chloride (0.01% based on starch dry weight) was injected with a microsyringe into the starch slurry. After 1 hr, the slurry was adjusted to pH 5.5 with 1M HCl and the modified starch was recovered and purified as previously described.

RESULTS AND DISCUSSION

Swelling Factor and Amylose Leaching

A wide variation in swelling ability in excess water was observed for native tuber and root starches at 85°C (Table I). These differences could be attributed to the variation in granule size, the level and structural characteristics of amylose and amylopectin, crystallinity, and to the phosphate content in the starch granules. Amylose content was 18.2–25.8% and nitrogen content was 0.02–0.08%. The low nitrogen content indicates the high purity of the extracted starches.

The ability to swell in hot water reflects the magnitude of starch chain interactions within the gelatinized granules (Hoover 2001). Potato had the highest swelling starch, followed by lotus, followed by the lowest value in true yam. It is believed that the high level of phosphate groups in potato starch imparts its great swelling ability because of the repulsion between the negatively charged phosphate groups in neighboring amylopectin chains, which weakens the hydrogen bonding between chains and leads to rapid hydration and swelling (Galliard and Bowler 1987).

Hydroxypropylation increased the swelling factor of all the starches compared with their corresponding native starches, whereas cross-linking decreased the swelling factor. Hydroxypropyl groups in the neighboring starch chains prevent interchain association and they facilitate water molecules to penetrate into the granules and thereby increase swelling. But cross-linking reinforces the structure of starch granules and limits water absorption, thereby restricting the mobility of starch chains in the amorphous region. As expected, cross-linking of hydroxypropylated starches also decreased their swelling. The molar substitution of hydroxypropyl groups was 0.095–0.114 and 0.093–0.112 for the hydroxypropylated and hydroxypropylated cross-linked starches, respectively. It appears that the low level of cross-links does not interfere in the Johnson method determining hydroxypropyl groups in hydroxypropylated cross-linked starch.

The amylose assay used in the leaching experiments assumes that hydroxypropyl groups with $\text{MS} \approx 0.1$ do not interfere with iodine binding and blue color formation. Except for potato and lotus starch, increased amylose leaching was observed after hydroxypropylation. Amylose is derivatized to a somewhat greater extent than amylopectin in hydroxypropylation (Kavitha and BeMiller 1998; Shi and BeMiller 2000), which facilitates amylose leaching from the starch granules. However, the preference for leaching of derivatized amylose decreases as the degree of modification of the whole starch granule increases (Shi and BeMiller

2002). As expected, cross-linking decreased amylose leaching substantially, even when a starch was hydroxypropylated (Table I).

Gelatinization

DSC curves recorded for the gelatinization of native and modified tuber and root starches are presented in Fig. 1, and gelatinization enthalpies are presented in Table II. The highest ΔH value was observed for true yam, followed by gourd yam, followed by the lowest in lotus starch. Both potato and lotus starch gelatinized nearly at the same temperature ($T_p \approx 65^\circ\text{C}$), whereas other starches gelatinized at higher temperature. After hydroxypropylation, the decreased gelatinization temperatures and decreased enthalpies in all the starches were anticipated because extensively hydrated granules require less driving force and energy to achieve gelatinization. Seow and Thevamar (1993) reported that hydroxypropylation facilitates water penetration and absorption into the starch granules and increases the initial rate of plasticization of the amorphous region, promoting gelatinization. Perera et al (1997) suggested that a possible disruption of double helices due to the rotation of the flexible hydroxypropyl groups within the amorphous region would leave fewer helices to melt during gelatinization. Theoretically, reduction of swelling resulting from cross-linking should delay gelatinization, however cross-linking had very little effect on the gelatinization parameters, in contrast to its marked effect on pasting properties. Introduction of cross-links in hydroxypropylated potato starch increased gelatinization temperature but other starches were unaffected.

Pasting Properties

Pasting curves of potato, lotus, and sweet potato starch showed pasting characteristics typical of tuber and root starches with high peak viscosity development and rapid shear thinning at high temperature, whereas the other starches showed greater resistance to shear thinning (Fig. 2, Table III). True yam starch behaved like a cross-linked starch. Strong internal bonding forces in a native starch with such behavior is evidenced by low swelling, delayed pasting onset, high pasting temperature, and high ΔH value in gelatinization. These parameters are consistent with a resistance to breakdown of starch granules in stirred paste at high temperature,

in other words, a shear-resistant starch paste. The highest peak viscosity was observed for lotus starch followed by potato starch and the lowest in taro starch. The greater peak viscosity development by lotus and potato starches is in agreement with the observed higher swelling factors for those starches. Generally, potato and lotus starches showed similar pasting characteristics such as an early onset of pasting, high peak viscosity, low pasting temperature, and rapid loss of viscosity at high temperature. They also showed high paste clarity (data not shown).

TABLE II
Gelatinization Enthalpies (ΔH_G) of Native, Hydroxypropylated (HP), Cross-Linked (CL), and Hydroxypropylated Cross-Linked (HP-CL) Tuber and Root Starches^a

Starch	Treatment	ΔH_G (J/g)
Potato	Native	15.1 ± 0.1
	HP	13.6 ± 0.2
	CL	15.3 ± 0.2
	HP-CL	13.7 ± 0.1
True yam	Native	17.5 ± 0.3
	HP	14.1 ± 0.1
	CL	16.8 ± 0.1
	HP-CL	14.4 ± 0.1
Gourd yam	Native	16.1 ± 0.2
	HP	13.8 ± 0.1
	CL	16.4 ± 0.3
	HP-CL	13.6 ± 0.2
Taro	Native	15.7 ± 0.3
	HP	14.0 ± 0.2
	CL	16.0 ± 0.1
	HP-CL	13.8 ± 0.1
Lotus	Native	14.2 ± 0.2
	HP	12.8 ± 0.1
	CL	14.0 ± 0.1
	HP-CL	12.7 ± 0.2
Sweet potato	Native	15.1 ± 0.3
	HP	12.3 ± 0.1
	CL	14.9 ± 0.2
	HP-CL	12.2 ± 0.1

^a Values are mean of triplicate determinations ± standard deviation.

TABLE I
Nitrogen and Amylose Contents, Molar Substitution of Hydroxypropyl Groups, and Swelling Factor and Amylose Leaching at 85°C of Tuber and Root Starches^{a,b}

Starch	Treatment	Swelling Factor	Amylose Leaching (%)	Amylose Content (%)	Nitrogen Content (%)	Molar Substitution
Potato	Native	50.2 ± 0.3	16.4 ± 0.2	24.7 ± 0.3	0.08 ± 0.01	0.108
	HP	60.1 ± 0.2	15.1 ± 0.2			
	CL	20.2 ± 0.1	4.0 ± 0.2			
	HP-CL	24.5 ± 0.2	5.0 ± 0.2			
True yam	Native	18.1 ± 0.4	17.2 ± 0.2	25.8 ± 0.5	0.04 ± 0.01	0.112
	HP	40.1 ± 0.1	19.2 ± 0.5			
	CL	16.7 ± 0.2	9.1 ± 0.1			
	HP-CL	26.4 ± 0.1	9.7 ± 0.1			
Gourd yam	Native	20.2 ± 0.4	12.1 ± 0.3	18.2 ± 0.2	0.03 ± 0.01	0.095
	HP	23.2 ± 0.1	14.1 ± 0.2			
	CL	15.0 ± 0.1	6.8 ± 0.3			
	HP-CL	15.4 ± 0.0	9.4 ± 0.4			
Taro	Native	35.0 ± 0.2	13.4 ± 0.2	20.7 ± 0.3	0.06 ± 0.02	0.103
	HP	40.1 ± 0.1	14.3 ± 0.5			
	CL	19.0 ± 0.4	6.4 ± 0.4			
	HP-CL	23.0 ± 0.1	6.3 ± 0.2			
Lotus	Native	45.0 ± 0.5	12.5 ± 0.3	19.5 ± 0.1	0.02 ± 0.001	0.093
	HP	47.1 ± 0.6	9.6 ± 0.1			
	CL	12.7 ± 0.2	1.0 ± 0.1			
	HP-CL	15.4 ± 0.1	1.0 ± 0.1			
Sweet potato	Native	39.0 ± 0.4	12.3 ± 0.4	19.2 ± 0.6	0.07 ± 0.02	0.114
	HP	43.2 ± 0.1	13.1 ± 0.3			
	CL	18.8 ± 0.3	4.1 ± 0.2			
	HP-CL	21.0 ± 0.1	5.3 ± 0.1			

^a HP, hydroxypropylated; CL, cross-linked; HP-CL, hydroxypropylated cross-linked.

^b Values are means of triplicate determinations ± standard deviation.

It has been reported that the phosphate groups located mainly on the amylopectin chains of potato starch are largely responsible for its high swelling and peak viscosity, rapid shear thinning, paste clarity, and low retrogradation rate (Jane et al 1996). Thus it can be speculated that the similar functional properties in lotus starch are related to a high level of phosphate groups on its amylopectin. Lim et al (1994) used ^{13}P -nuclear magnetic resonance studies to show that tuber and root starches contain a high level of organic phosphorus as phosphate monoesters in contrast to a low content in cereal starches where most phosphorus is found in the form of phospholipids.

Hydroxypropylation caused an increase in peak viscosity of the tuber and root starches studied, except for taro and gourd yam. A loosening of starch structure after hydroxypropylation could permit granules to swell to a greater extent, creating a high peak viscosity. In taro and gourd yam starches, it seems hydroxypropylation resulted in weaker granules compared with unmodified granules,

again by disrupting hydrogen bonds between starch chains. Structurally weak granules can undergo increased breakdown, causing rapid loss of peak viscosity, resulting in increased shear thinning. The slightly higher hot paste viscosity in potato and true yam starches after hydroxypropylation could be due to physical interaction between swollen granules.

Cross-linking slightly increased the peak viscosity of true yam starch but decreased the peak viscosity of other starches, especially gourd yam, lotus, and sweet potato (Fig. 2C, E, and F). The pasting properties of cross-linked starch vary widely depending on the level of cross-linking. Mild cross-linking has increased peak viscosity, but strong cross-linking decreases peak viscosity due to restricted granular swelling (Wurzburg and Szymanski 1970; Howling 1980). This implies that true yam was cross-linked to a lesser extent than the other starches under the given conditions. All starch pastes had greater stability of paste consistency after cross-linking.

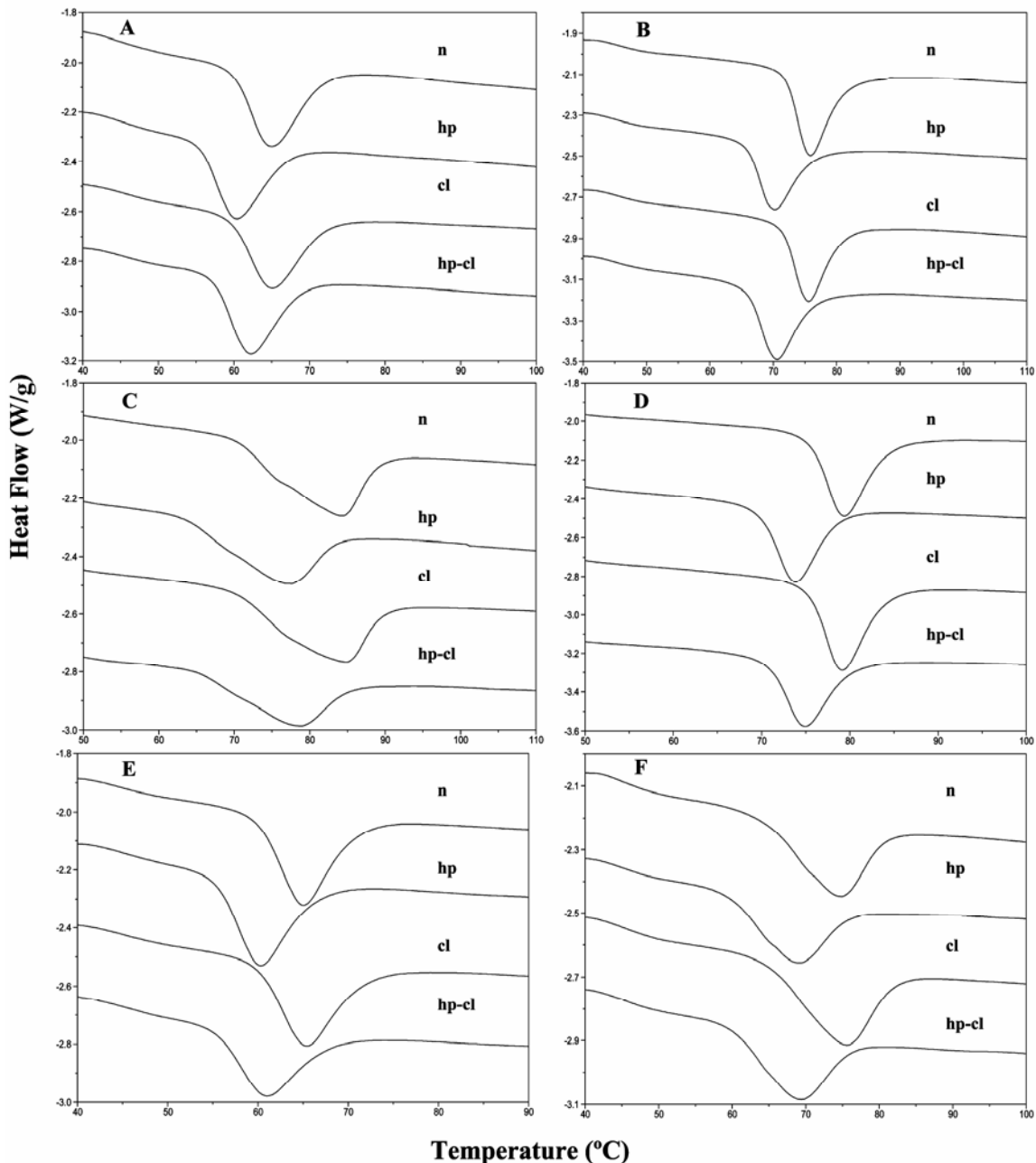


Fig. 1. Differential scanning calorimetry (DSC) curves of native, hydroxypropylated, cross-linked, and hydroxypropylated cross-linked potato (A), true yam (B), gourd yam (C), taro (D), lotus (E), and sweet potato (F) starches at $\approx 75\%$ moisture content. Abbreviations: n = native, hp = hydroxypropylated, cl = cross-linked, hp-cl = hydroxypropylated cross-linked.

The strengthened starch-granule structure after cross-linking resists rupture at higher temperature in a paste. Cross-linking of the hydroxypropylated potato and taro starches increased peak viscosity above that of the hydroxypropylated starches, in contrast to the other hydroxypropylated starches. Apparently cross-linking was especially effective in inhibiting granular breakdown in the cross-linked hydroxypropylated potato and taro starches. However, in all cases, introduction of cross-links to the hydroxypropylated starches resulted in a generally more thermally and mechanically stable starch paste. Cross-linking renders starch granules more resistant to low pH and thereby reduces shear thinning when a paste is heated under acid conditions (Table III). With the

exception of taro and lotus, a decreased peak viscosity was observed at low pH. Although there was a peak viscosity increase for taro and lotus starches at low pH, the pasting stability was decreased (Table III). Acidity could break hydrogen bonds to bring more rapid swelling, thereby creating higher peak viscosity but the weak granules, due to the disruption of hydrogen bonds, would gradually disintegrate at high temperature and prolonged stirring. Increased accessibility of starch granules to acid in hydroxypropylated starches decreased peak viscosity and shear resistance of all the starches. Introduction of cross-linking to hydroxypropylated starches increased peak viscosity and paste thermal stability at low pH over the corresponding hydroxypropylated starches.

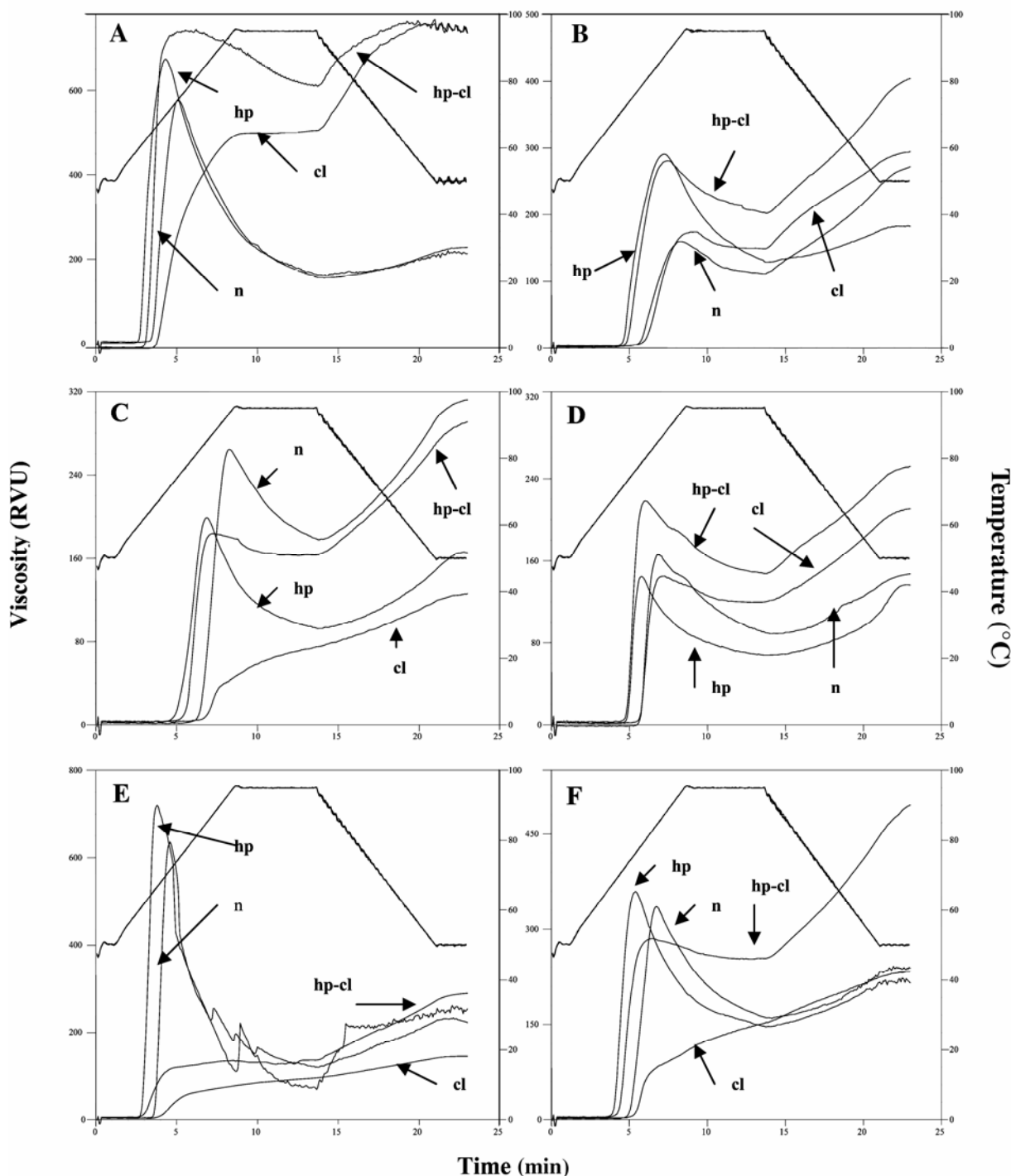


Fig. 2. Rapid viscoamylography (RVA) curves of native, hydroxypropylated, cross-linked, and hydroxypropylated cross-linked potato (A), true yam (B), gourd yam (C), taro (D), lotus (E), and sweet potato (F) starches at a concentration of 8.2% in water. Abbreviations: n = native, hp = hydroxypropylated, hp-cl = hydroxypropylated cross-linked.

Gel Hardness

Gel hardness of native starches (Table IV) followed the order of true yam > gourd yam > sweet potato > potato > taro > lotus. Strong gels for true yam and gourd yam are consistent with increased cold paste viscosities in the pasting curves. Initial gel firmness of starch is attributed to the short-term rapid reassociation of amylose chains within the cold starch paste. The textural and mechanical properties of a starch gel, where swollen gelatinized amylopectin-rich granules are embedded in the continuous amylose gel matrix, would depend on the amylose concentration and rheological characteristics of the amylose gel matrix; rigidity (deformability) of the swollen starch particles; volume fraction of the swollen granules; and interaction between swollen particles and the amylose matrix (Eliasson 1986; Doublier et al 1987; Morris 1990). Hydroxypropylation decreased the gel hardness of all the starches, but to a greater extent in potato and taro starches where gel hardness was too low to be measurable under the conditions used. The action of hydroxypropylation in loosening the starch granule structure would permit more granules to break down, leaving weaker cohesive swollen starch particles in the gel matrix, leading to a weaker starch gel. Hydroxypropyl groups on amylose chains may prevent amylose aggregation and interrupt the formation of junction zones.

Cross-linking increased the gel hardness of potato starch and decreased it in other starches. Cross-linking that strengthens the starch granules will allow stronger rigid granules to remain in the gel matrix. Also, the possible creation of more junction zones by the covalent cross-linked bonding could increase gel hardness. However, significant reduction of amylose leaching (Table I) upon cross-linking would decrease amylose concentration in the continuous network. This latter effect seems more influential in determining gel hardness of the other cross-linked starches, which resulted in a weaker gel structure after cross-linking.

Cross-linking of hydroxypropylated potato, true yam, and taro starches increased gel hardness but decreased it in hydroxypropylated gourd yam, lotus, and sweet potato starches. Although cross-linking would decrease the amylose leaching from hydroxypropylated potato, true yam and taro starches, it would also reduce the

deformability of gelatinized swollen granules in the gel matrix and introduce more junction zones. For the cross-linked hydroxypropylated gourd yam, lotus, and sweet potato starches, the reduced

TABLE IV
Gel Hardness of Native, Hydroxypropylated (HP), Cross-Linked (CL), and Hydroxypropylated Cross-Linked (HP-CL) Tuber and Root Starches^a

Starch	Treatment	Gel Hardness (g)
Potato	Native	27 ± 0.2
	HP	–
	CL	44 ± 0.3
	HP-CL	13 ± 0.2
True yam	Native	140 ± 0.2
	HP	12 ± 0.5
	CL	71 ± 0.6
	HP-CL	66 ± 0.2
Gourd yam	Native	66 ± 0.1
	HP	16 ± 0.3
	CL	31 ± 0.2
	HP-CL	9 ± 0.4
Taro	Native	12 ± 0.2
	HP	–
	CL	16 ± 0.3
	HP-CL	8 ± 0.4
Lotus	Native	12 ± 0.5
	HP	10 ± 0.6
	CL	7 ± 0.4
	HP-CL	7 ± 0.4
Sweet potato	Native	28 ± 0.5
	HP	13 ± 0.5
	CL	9 ± 0.6
	HP-CL	7 ± 0.4

^a Values are mean of triplicate determinations ± standard deviation. Gels were made in RVA canisters by cooling a paste at 4°C for 7 hr, then warming to room temperature.

TABLE III
Pasting Properties of Hydroxypropylated (HP), Cross-Linked (CL), and Hydroxypropylated Cross-Linked (HP-CL) Tuber and Root Starches in Distilled Water and Hydrochloric Acid Solution (pH 3)

Starch	Treatment	Distilled Water			Acid Solution (pH 3)		
		PV	HPV	CPV	PV	HPV	CPV
Potato	Native	575 ± 1.0	156 ± 1.6	228 ± 1.4	488 ± 1.2	149 ± 0.8	218 ± 0.6
	HP	678 ± 0.7	163 ± 0.6	212 ± 0.6	507 ± 0.9	129 ± 1.7	162 ± 1.4
	CL	503 ± 1.2	503 ± 1.2	736 ± 0.9	467 ± 0.7	456 ± 2.6	756 ± 1.2
	HP-CL	732 ± 1.3	668 ± 1.7	726 ± 1.7	662 ± 1.3	502 ± 1.2	747 ± 1.2
True yam	Native	159 ± 1.9	112 ± 0.9	272 ± 1.1	153 ± 1.7	106 ± 0.7	255 ± 2.2
	HP	290 ± 0.7	128 ± 0.6	182 ± 1.8	219 ± 2.7	113 ± 1.1	154 ± 0.9
	CL	173 ± 1.4	148 ± 1.1	294 ± 0.7	163 ± 1.4	142 ± 0.8	252 ± 0.7
	HP-CL	280 ± 1.0	202 ± 1.2	404 ± 1.8	274 ± 1.0	190 ± 1.2	374 ± 1.8
Gourd yam	Native	264 ± 0.9	177 ± 0.8	312 ± 1.5	248 ± 0.9	147 ± 0.8	241 ± 1.3
	HP	198 ± 1.9	92 ± 2.2	165 ± 1.2	176 ± 1.9	67 ± 2.2	115 ± 1.2
	CL	72 ± 0.7	72 ± 0.7	120 ± 1.0	140 ± 0.7	141 ± 0.7	208 ± 1.0
	HP-CL	183 ± 1.5	163 ± 1.1	290 ± 1.4	232 ± 1.5	212 ± 1.1	352 ± 0.4
Taro	Native	165 ± 1.2	88 ± 0.7	147 ± 1.9	193 ± 1.2	82 ± 1.2	138 ± 1.9
	HP	132 ± 0.8	63 ± 1.3	121 ± 0.5	132 ± 0.8	54 ± 2.3	88 ± 0.5
	CL	144 ± 1.4	119 ± 0.9	210 ± 0.4	203 ± 1.4	177 ± 1.9	285 ± 1.4
	HP-CL	218 ± 1.1	147 ± 1.8	252 ± 0.9	240 ± 0.8	175 ± 1.8	291 ± 0.9
Lotus	Native	636 ± 0.9	120 ± 1.4	222 ± 1.7	657 ± 1.6	88 ± 1.4	149 ± 1.7
	HP	720 ± 1.1	69 ± 0.8	253 ± 0.8	420 ± 1.1	50 ± 0.8	120 ± 0.8
	CL	94 ± 1.6	94 ± 1.6	145 ± 0.4	187 ± 1.6	187 ± 1.6	334 ± 0.4
	HP-CL	136 ± 0.7	135 ± 0.9	289 ± 1.2	250 ± 0.9	250 ± 0.9	563 ± 1.2
Sweet potato	Native	335 ± 0.6	159 ± 1.7	238 ± 1.1	322 ± 1.6	139 ± 0.7	212 ± 1.2
	HP	360 ± 1.5	146 ± 0.5	215 ± 0.7	345 ± 1.5	136 ± 0.9	204 ± 0.9
	CL	78 ± 1.1	78 ± 1.1	127 ± 1.3	147 ± 0.9	147 ± 2.1	233 ± 1.3
	HP-CL	284 ± 0.8	253 ± 1.9	495 ± 1.6	346 ± 0.6	309 ± 1.9	563 ± 1.6

^a PV, peak viscosity; HPV, hot paste viscosity; CPV, cold paste viscosity.

^b Values are means of triplicate determinations ± standard deviation.

TABLE V
% Decrease of Peak Viscosity (PV) of Native, Hydroxypropylated (HP), Cross-Linked (CL), and Hydroxypropylated Cross-Linked (HP-CL) Tuber and Root Starches After α -Amylase Treatment^a

Starch	Treatment	% Decrease of PV
Potato	Native	87 ± 0.8
	HP	89 ± 0.3
	CL	40 ± 0.4
	HP-CL	54 ± 0.9
True yam	Native	10 ± 0.7
	HP	68 ± 0.2
	CL	7 ± 0.6
	HP-CL	42 ± 0.3
Gourd yam	Native	24 ± 1.1
	HP	95 ± 0.7
	CL	11 ± 0.8
	HP-CL	83 ± 0.4
Taro	Native	53 ± 1.3
	HP	89 ± 0.6
	CL	14 ± 0.5
	HP-CL	51 ± 0.4
Lotus	Native	91 ± 0.8
	HP	93 ± 1.2
	CL	13 ± 0.7
	HP-CL	16 ± 0.4
Sweet potato	Native	90 ± 0.5
	HP	91 ± 0.3
	CL	19 ± 1.2
	HP-CL	65 ± 0.5

^a Values are mean of duplicate determinations ± standard deviation.

leaching appears more significant and explains the decrease in gel hardness values upon cross-linking.

Enzymatic Hydrolysis

The percent decrease of peak viscosity was used to estimate the extent of α -amylase hydrolysis (Table V). For native starches, the extent of enzymatic hydrolysis followed the order of lotus \approx sweet potato \approx potato $>$ taro $>$ gourd yam $>$ true yam. Hydroxypropylation increased the digestibility of all the starches by facilitating enzyme accessibility as the hydroxypropyl groups loosen the starch structure. The results showed that there is a strong positive association between swelling ability and enzymatic digestibility. A reduction of enzymatic hydrolysis for cross-linked starches was expected because strongly cross-bonded starch granules will resist the enzyme attack. This was verified by the reduction of enzymatic hydrolysis after introduction of cross-linking to hydroxypropylated starches.

Retrogradation

Reordering of branched amylopectin chains in a starch paste or gel is a slow process that occurs over a few days or several weeks. The extent of the retrogradation of native starches followed the order of true yam $>$ gourd yam $>$ potato $>$ sweet potato $>$ lotus $>$ taro (Table VI). The highest ΔH value recorded for true yam was more than twice that of potato starch. Taro starch retrograded to a much lesser extent. This diversity in the retrogradation behavior should relate to the structural properties of amylopectin that determine the quality and the quantity of the retrograded starch crystals. After hydroxypropylation, retrogradation decreased in all the starches, whereas cross-linking had no effect on retrogradation. No retrogradation was found for the hydroxypropylated tuber and root starches except in true yam starch (Table VI). By inhibiting formation of hydrogen bonding, the bulky hydroxypropyl groups

TABLE VI
Retrogradation Enthalpy (ΔH_R) of Native, Hydroxypropylated (HP), Cross-Linked (CL), and Hydroxypropylated Cross-Linked (HP-CL) Tuber and Root Starches^a

Starch	Treatment	ΔH_R (J/g)
Potato	Native	3.7 ± 0.3
	HP	0.0
	CL	3.6 ± 0.2
	HP-CL	0.0
True Yam	Native	9.2 ± 0.1
	HP	2.4 ± 0.4
	CL	8.9 ± 0.2
	HP-CL	2.5 ± 0.2
Gourd Yam	Native	6.3 ± 0.1
	HP	0.0
	CL	5.9 ± 0.1
	HP-CL	0.0
Taro	Native	0.4 ± 0.1
	HP	0.0
	CL	0.3 ± 0.1
	HP-CL	0.0
Lotus	Native	1.3 ± 0.1
	HP	0.0
	CL	0.9 ± 0.1
	HP-CL	0.0
Sweet potato	Native	2.8 ± 0.2
	HP	0.0
	CL	2.9 ± 0.1
	HP-CL	0.0

^a Values are mean of triplicate determinations ± standard deviation. Starch gel with $\approx 75\%$ moisture content were cooled 24 hr at 4°C then stored 10 days at 40°C.

attached to the amylopectin chains prevent the reordering of amylopectin chains. On the other hand, it seems the covalent bonds established by cross-linking, which can be thought of as adding to the hydrogen bonds in unmodified starch, did not increase the association of amylopectin. Also, cross-linking had no influence on the retrogradation of hydroxypropylated cross-linked starches. The great reduction of amylopectin retrogradation observed after hydroxypropylation suggests that although amylose has been shown to be substituted to a somewhat greater extent than amylopectin (Kavitha and BeMiller 1998; Shi and BeMiller 2000), the derivatization that takes place in the amylopectin severely retards retrogradation.

CONCLUSIONS

This investigation of the properties of some underexploited tuber and root starches has shown some useful functionalities such as increased shear stability at high temperature and at low pH and increased resistance to enzymatic hydrolysis in some starches. Properties that are generally undesirable in starch thickeners, such as retrogradation, low swelling, low viscosity development, and low shear resistance, can be improved by hydroxylpropylation and cross-linking. In this context, cross-linking of hydroxypropylated starches provides more desirable functional properties for tuber and root starches, permitting a wide range of applications.

LITERATURE CITED

- Choi, S. G., and Kerr, W. L. 2004. Swelling characteristics of native and chemically modified wheat starches as a function of heating temperature and time. *Starch* 56:181-189.
- Chrastil, J. 1987. Improved colorimetric determination of amylose in starches or flours. *Carbohydr. Res.* 159:154-158.

- Doublier, J. L., Llamas, G., and Le Meur, M. 1987. A rheological investigation of cereal starch pastes and gels. Effects of pasting procedures. *Carbohydr. Polym.* 7:251-275.
- Eliasson, A. C. 1986. Viscoelastic behavior during the gelatinization of starch. I. Comparison of wheat, maize, potato, and waxy-barley starches. *J. Texture Stud.* 17:253-265.
- Galliard, T., and Bowler, P. 1987. Morphology and composition of starch. Pages 55-79 in: *Starch: Properties and Potential*. T. Galliard, ed. Wiley: Chichester, England.
- Hoover, R. 2001. Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydr. Polym.* 45:253-267.
- Hoover, R., and Hadziyev, D. 1981. Characterization of potato starch and its monoglyceride complexes. *Starch/Stärke* 33:290-300.
- Hoover, R., Hannouz, D., and Sosulski, F. W. 1988. Effect of hydroxypropylation on thermal properties, starch digestibility and freeze-thaw stability of field pea (*Pisum sativum* cv. Trapper) starch. *Starch/Stärke* 40:383-387.
- Howling, D. 1980. The influence of the structure of starch on its rheological properties. *Food Chem.* 6:51-61.
- Jane, J., Kasemsuwan, T., and Chen, J. F. 1996. Phosphorus in rice and other starches. *Cereal Foods World* 41:827-832.
- Johnson, D. P. 1969. Spectrophotometric determination of the hydroxypropyl groups in the starch ethers. *Anal. Chem.* 41:859-860.
- Kavitha, R., and BeMiller, J. N. 1998. Characterization of hydroxypropylated potato starch. *Carbohydr. Polym.* 37:115-121.
- Kim, H. R., and Eliasson, A. C. 1993. The influence of molar substitution on thermal transition properties of hydroxypropyl potato starches. *Carbohydr. Polym.* 22:331-335.
- Li, W. D., Huang, J. C., and Corke, H. 2000. Effect of β -cyclodextrin on pasting properties of wheat starch. *Nahrung Food* 44:164-167.
- Lim, S. T., Kasemsuwan, T., and Jane, J. 1994. Characterization of phosphorus in starches using ^{31}P -NMR spectroscopy. *Cereal Chem.* 71:488-493.
- Liu, H. J., Ramsden, L., and Corke, H. 1999. Physical properties and enzymatic digestibility of hydroxypropylated *ae*, *wx*, and normal maize starches. *Carbohydr. Polym.* 40:175-182.
- Liu, H. J., Ramsden, L., and Corke, H. 1999. Physical properties of cross-linked and acetylated normal and waxy rice starch. *Starch/Stärke* 51:249-252.
- Miyazaki, K. I., Kumamoto, T. K., Kagoshima, K. K., and Komamoto, O. Y. 2000. Retrogradation of sweet potato starch. *Starch/Stärke* 52:13-17.
- Morris, M. J. 1990. Starch gelation and retrogradation. *Trends Food Sci. Technol.* 1:2-6.
- Pal, J., Singhal, P. S., and Kulkarni, P. R., 2002. Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. *Carbohydr. Polym.* 48:49-53.
- Perera, C., Hoover, R., and Martin, A. M. 1997. The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat-moisture treated potato starches. *Food Res. Int.* 30:235-247.
- Seow, C. G., and Thevamaralar, K. 1993. Internal plasticization of granular rice starch by hydroxypropylation: Effect on phase transition associated with gelatinization. *Starch/Stärke* 45:85-88.
- Shi, X., and BeMiller, J. N. 2000. Effect of sulfate and citrate salts on derivatization of amylose and amylopectin during hydroxypropylation of corn starch. *Carbohydr. Polym.* 43:333-336.
- Shi, X., and BeMiller, J. N. 2002. Aqueous leaching of derivatized amylose from hydroxypropylated common corn starch granules. *Starch/Stärke* 54:16-19.
- Tester, R. F., and Morrison, W. R. 1990a. Swelling and gelatinization of cereal starches. 1. Effects of amylopectin, amylose, and lipids. *Cereal Chem.* 67:551-557.
- Woo, K., and Seib, P. A. 1997. Cross-linking of wheat starch and hydroxypropylated wheat starch in alkaline slurry with sodium trimetaphosphate. *Carbohydr. Polym.* 33:263-271.
- Wurzburg, O. B., and Szymanski, C. D. 1970. Modified starches for the food industry. *J. Agric. Food Chem.* 18:997-1001.

[Received December 9, 2005. Accepted August 21, 2006.]