

Functional Properties and Enzymatic Digestibility of Cationic and Cross-Linked Cationic *ae*, *wx*, and Normal Maize Starch

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The functional properties and enzymatic digestibility of cationic and cross-linked cationic *ae*, *wx*, and normal maize starches were studied. Cationization reduced the endothermic transition temperatures (T_0 , T_p , and T_c), however, it increased peak viscosity, swelling power, solubility, clarity, and digestibility of all the starches compared to the corresponding native starch. After cationization, the enthalpy of waxy and normal starches was little changed but *ae* starch showed a decrease. For gel texture, cationization increased the hardness, adhesiveness, and springiness of all the starches, except for the hardness and adhesiveness of normal starch which showed a decrease, and the springiness of waxy starch did not show much change compared to the corresponding control starch. Cross-linking of cationic starch increased the endothermic transition temperatures, as well as peak viscosity. However, it reduced the swelling power and solubility, clarity, and enzymatic digestibility of all the cationic starches.

Keywords: *Cationic starch; cross-linked cationic starch; maize starch; viscoamylography; texture analysis; starch digestibility*

INTRODUCTION

Cationic starch is widely used as a wet end additive in paper making to improve the strength of paper and to decrease biological oxygen demand (BOD) of paper mill effluent; increase filler, pigment, or dye retention without losing sheet strength; increase size retention; and speed paper production, as well as improve the running of the paper machine, especially with recycled fiber (Jensen and Winters, 1986; Wurzburg, 1986). Cationic starches are produced by the chemical reaction of starch with cationic reagents containing amino, imino, ammonium, sulfonium, or phosphonium groups. These reagents contribute a positive charge which has a strong affinity for negatively charged substrates (Mentzer, 1984; Solarek, 1986). Cationic starches are produced commercially from corn, waxy corn, wheat, and potato with varying DS and by a variety of cationizing agents and methods (Mentzer, 1984; Solarek, 1986).

Cationic corn starches exhibit high peak viscosity at low pasting temperatures on the amylograph, but the viscosity decreases markedly during cooking with only intermediate set back on cooling (Yook and Bhirud, 1994; Kweon et al., 1997; Quan et al., 1997). The lower final (cold) viscosity relative to high peak viscosity is undesirable in many starch applications. Cross-linking the starch granule with epichlorohydrin (Kantha and Srivastava, 1985) and phosphorus oxychloride (Hoover and Sosulski, 1986; Quan et al., 1997) decreased peak viscosity but increased the degree of positive set back. At low levels of cross-linking, the viscosity of these cross-linked starch pastes were more uniformly high during the heating and cooling cycle (Quan et al., 1997). Rayford and Wing (1979) prepared cross-linked cationic

and anionic starches for use as chelating agents to bind heavy metals in wastewater treatment.

No systematic studies have been conducted, across a wide range of amylose levels, on the potential for cross-linking to improve the viscosity properties of cationic starches and their functionality in paper manufacture. Cationic normal corn, pea, and barley starches and waxy corn and barley starches have been prepared (Kweon et al., 1997; Vasanthan et al., 1997), and their functional properties were studied. The results showed that cationization increased swelling power and peak viscosity and decreased onset of endothermic transition of all starches. Quan et al. (1997) reported the effect of cross-linking on functional properties of cationic normal corn starch.

High amylose (*ae*) corn starch has limited uses in food or industrial applications because of its difficulty to gelatinize and resistance to hydrolytic enzymes (Liu et al., 1997). Acetylation of *ae* corn starch (Liu et al., 1997) improved certain functional properties such as decreasing gelatinization temperatures and increasing amylograph viscosity. Very little has been reported on the cationization of *ae* corn starch.

The objective of the present study was to prepare cationic and cross-linked cationic *ae*, *wx*, and normal maize starches and determine their functional properties and digestibility. Functional properties included thermal and pasting properties, swelling power and solubility, gel texture, and clarity.

MATERIALS AND METHODS

Starch Samples. All native starch samples were supplied by Starch Australasia Limited (Lane Cove, Australia), and amylose contents were confirmed with an amylose/amylopectin assay kit (Megazyme Pty Ltd., Bray, Ireland). Samples were two high-amylose maize starches, i.e., Hi-Maize (H) with 66% amylose and GELOSE 50 (G) with 47% amylose, one waxy,

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i.e., MAZACA 3401X (W) with 3.3% amylose and one normal, i.e., MAIZE CORNFLOUR 3401C (N) with 22.4% amylose.

Preparation of Cationic and Cross-Linked Cationic Starches. The method of Kweon et al., (1997) was used to prepare cationic starches. The aqueous ethanolic-alkaline solution was prepared by dissolving 1.7 g of NaOH in sufficient distilled water to give a starch-to-water ratio of 1:1 (w/w) and adding 93 mL of 100% ethanol to make a 65% alcohol solution. The solution was added to preweighed starch (50 g, dry basis) in a centrifuge bottle, mixed thoroughly, and incubated for 10 min at 50 °C. Then 60% CHPTAC (3-chloro-2-hydroxypropyl-trimethylammonium chloride) solution (2.1 or 4.2 mL) was added to the starch slurry for 1 min, and the reaction mixture was incubated for 6 h in a shaker bath at 50 °C. After reaction, the slurry was adjusted with 3 M HCl in 100% ethanol to pH 6, using a Sentron 2001 pH meter suitable for use on pastes (Integrated Sensor Technology, Roden, The Netherlands), and centrifuged at 2500 rpm for 3 min, and the derivatized starch was washed 3 times with 95% ethanol and then oven-dried at 40 °C.

Nitrogen levels in cationic starches were determined by the micro-Kjeldahl method (AACC, 1995). The DS of a starch derivatized with the *N*-trimethyl-2-hydroxypropyl group as the substituent group was calculated on the basis of the increase in the nitrogen concentration compared to the control native starch (Kweon et al., 1997)

$$DS = (162 \times \% \text{Nitrogen}) / (1400 - (117 \times \% \text{Nitrogen}))$$

Cross-linking cationic starch was done following the method of Kasemsuwan et al., (1994), slightly modified. Cationic starch (50 g, prepared using 4.2 mL of CHPTAC) was suspended in distilled water with 2% Na₂SO₄ to a 35% slurry and adjusted to pH 11 with 3% NaOH, and 0.05% POCl₃ (w/w, dry starch) was added. The pH was continuously maintained at 25 °C for 1 h by manual adjustment as needed, then the slurry mixture was adjusted to pH 6.0 with 0.5 M HCl to stop the reaction and centrifuged at 2500 rpm for 3 min, and the slurry was washed twice with distilled water and once with 95% ethanol and then oven-dried at 40 °C.

Viscoamylography. A Rapid Visco-Analyzer (RVA) (Newport Scientific Pty. Ltd., Warriewood, Australia) was employed to determine the pasting properties of starch samples. Starch sample (3 g, dry basis) and a weighed amount of distilled water were combined and stirred in the aluminum RVA sample canister to make a 10.7% starch suspension (w/w). A programmed heating and cooling cycle was used, where the sample was held at 50 °C for 1 min, heated to 95 °C in 7.5 min, held at 95 °C for 5 min, cooled to 50 °C in 8.5 min, and then held at 50 °C for 3 min. Triplicate tests were used in each case. Because the viscosity of cationic N (4.2 mL of CHPTAC) and cross-linked cationic W, N, and G were so high, the concentration of the starches used were decreased to 9.4%, 4.6%, 6.7%, and 9.4%, respectively. Recorded values were peak viscosity (PV), holding or hot paste viscosity (HPV), i.e., minimum viscosity during stirring at 95 °C, final or cool paste viscosity (CPV), i.e., viscosity at the end of the cycle at 50 °C, breakdown (BD), i.e., PV - HPV, and setback (SB), i.e., CPV - HPV.

Differential Scanning Calorimetry. Thermal analysis was performed with a Mettler DSC 20 instrument (Mettler, Naenikon-Uster, Switzerland) equipped with a Mettler TC 11 data analysis station. Starch (2.5 mg, dry basis) was weighed directly into a 40 μL pan, and then 7.5 mg of deionized water was directly added into the pan by a microsyringe. After sealing, the pan was left for 1 h to allow the sample to mix and equilibrate. Then the sample was heated from 30 to 120 °C at a heating rate of 10 °C/min. An empty pan was used as a reference. Standard parameters of onset (*T*_o), peak (*T*_p), and completion (*T*_c) temperatures and energy of enthalpy (ΔH) were noted. Two replicates of each sample were run.

Swelling Power and Solubility. The swelling power of starches was determined as described by Subramanian et al., (1994) with minor modifications. The 0.5% suspension (w/w) of starch and distilled water was heated to the desired

temperature for 30 min. Lump formation was prevented by stirring. The mixture was centrifuged at 3000 rpm for 15 min. The supernatant was carefully removed, and the swollen starch sediment was weighed the swelling power was the ratio in weight of the wet sediment to the initial weight of dry starch. An aliquot of supernatant was evaporated overnight at 130 °C and weighed. The solubility was calculated as the ratio in weight of dried supernatant to the initial weight of the dry starch.

Clarity. The clarity of starches was determined as described by Wu and Seib (1990). A 1% starch paste was heated in a boiling water bath for 30 min and cooled to 25 °C. The clarity was evaluated using percent transmittance (*T*) at 650 nm against a water blank in a spectrophotometer.

Enzymatic Digestibility Using α -Amylase. The method of Zhang et al. (1995) was slightly modified as follows. A 30 mL sample of phosphate buffer (0.2 M, pH 6.9) was mixed with 1.0 g (dry basis) of starch in a 50 mL test tube. After heating in a waterbath at 95 °C for 30 min and cooling to 25 °C, 320 units of bacterial α -amylase (item A-6380, Sigma Chemical Co., St. Louis, MO) was added. After incubation at 30 °C in a shaking water bath for 14 h, the reaction was stopped by addition of 5 mL of 1.0% (w/v) sulfuric acid. Samples were centrifuged, and the resulting pellet of undigested flour residue was washed with 80% ethanol, recentrifuged, and dried to constant weight. For each sample, a blank of starch without enzymatic hydrolysis was included to correct for the initial concentration of soluble sugar. Starch digestibility was expressed as percent weight loss after α -amylase digestion.

Texture Analysis. After RVA testing, the starch paste (10.7%, w/w) was covered and kept at 25 °C for 4 h to cool. The gel texture was determined in triplicate using a TA-XT2 Texture Analyzer (Stable Micro Systems, Godalming, England). The gel was compressed in a two-cycle program at a speed of 1.0 mm/s to a distance of 10 mm using a 5 g force trigger point, with a cylindrical flat-ended probe (diameter = 5 mm). The height of the peak on the output curve at 10 mm compression was termed hardness (g), the negative area of the curve during retraction of the probe was termed adhesiveness (g/s), and the ratio of the distance of compression in the second cycle to that in the first cycle was termed springiness (dimensionless). Because waxy maize was so soft, native and modified waxy maize were also tested with a larger probe (diameter = 20 mm).

RESULTS AND DISCUSSION

Pasting Properties and Thermal Analysis. The pasting curves of native cationic and cross-linked cationic starches are shown in Figure 1 and the results summarized in Table 1; the DSC thermograms are shown in Figure 2 and the gelatinization temperatures and enthalpies given in Table 2. After cationization, all the maize starches had a higher PV than the corresponding native starch and an increase in the DS resulted in a further increase in PV. Similarly, after cationization, all the starches had reduced gelatinization temperatures (*T*_o, *T*_p, *T*_c). Increasing the DS of the starches also resulted in a further decrease in the transition temperatures.

The introduction of cationic groups into the starch results in a weakening of the starch granule structure due to repulsion between neighboring groups inhibiting interchain associations. This structural loosening permits greater uptake of water with a consequent increase in the swelling of the granule which leads to a higher PV. As the uptake can take place more rapidly, the gelatinization can occur more easily and at a lower temperature. After the granules are swollen, the looser structure also permits the more rapid loss of granule integrity, and this was observed in the higher values for breakdown with the cationized starches. The effect

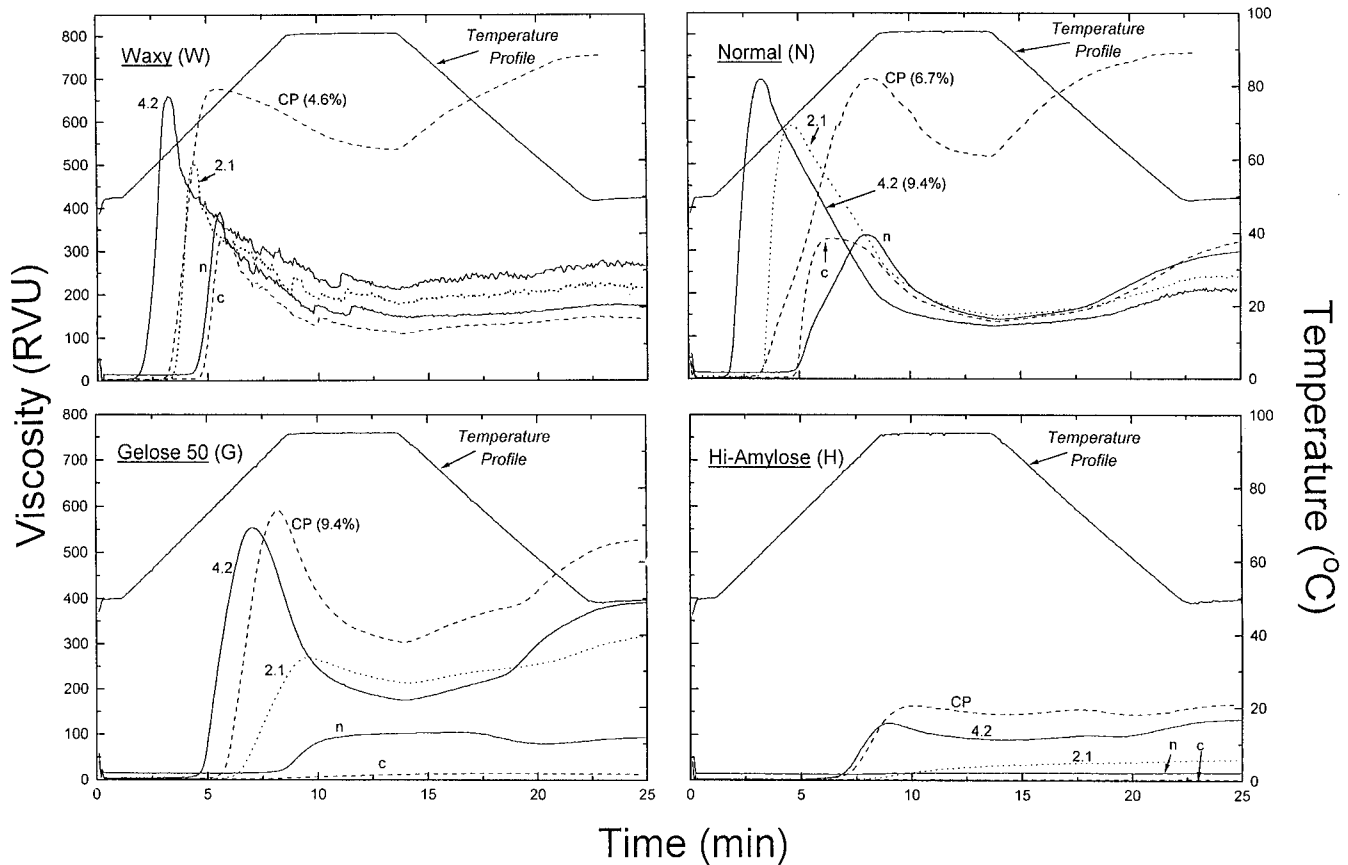


Figure 1. RVA pasting curves of cationic and cross-linked cationic maize starches. Native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

Table 1. Pasting Properties of Cationic and Cross-Linked Cationic Maize Starches

starch ^a	degree of substitution	PV (RVU)	HPV (RVU)	CPV (RVU)	BD (RVU)	SB (RVU)
W n	native	391	148	172	243	24
W c	0	335	110	144	225	34
W 2.1	0.022	501	177	217	324	40
W 4.2	0.043	661	213	258	448	45
W CP (4.6%) ^b		677	536	735	141	199
N n	native	337	142	270	195	128
N c	0	329	135	268	194	133
N 2.1	0.020	589	149	223	440	74
N 4.2 (9.4%) ^b	0.038	695	126	196	569	70
N CP (6.7%) ^b		698	520	745	178	225
G n	native		103	86		-17
G c	0		13	14		1
G 2.1	0.024	270	215	285	55	70
G 4.2	0.046	554	177	364	377	187
G CP (9.4%) ^b		592	307	493	285	186
H n	native		17	18		1
H c	0		4	3		-1
H 2.1	0.021		33	44		11
H 4.2	0.043	125	90	121	35	31
H CP		164	146	156	18	10

^a Samples are waxy (W), normal (N), Gelose 50 (G), and Hi-Maize (H) starches, which are native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP). ^b Indicates starch concentration used in pasting if not 10.7%.

of cationization was particularly strong with the high-amylose starches, where the native starch fails to exhibit a gelatinization peak, but after the higher level of cationization a PV of 125 RVU was recorded. These starches also showed a very large increase in CPV which may be attributed to the effective release of amylose from the swollen granules which can now participate

Table 2. Thermal Properties, Clarity, and Digestibility of Cationic and Cross-Linked Cationic Maize Starches

starch ^a	degree of substitution	T ₀ (°C)	T _p (°C)	T _c (°C)	ΔH (J/g)	clarity (T%)	digestibility (%)
W n	native	62.9	72.8	84.3	13.6	45.2	98.9
W c	0	63.8	72.8	82.7	12.1	44.5	99.1
W 2.1	0.022	59.8	67.3	75.4	9.9	86.6	99.4
W 4.2	0.043	55.2	62.3	72.3	7.2	91.4	99.4
W CP		57.3	64.8	75.8	7.4	16.4	98.3
N n	native	65.3	71.3	80.9	11.0	16.6	90.3
N c	0	64.3	71.8	80.3	10.7	16.1	91.8
N 2.1	0.020	58.7	64.3	73.9	7.9	78.5	95.1
N 4.2	0.038	51.7	55.8	68.4	4.0	82.6	96.8
N CP		53.3	58.3	69.8	4.1	8.0	95.5
G n	native	66.7	77.3	104.0	14.7	2.7	55.7
G c	0	66.1	79.9	105.3	10.5	2.8	55.0
G 2.1	0.024	63.9	73.4	87.2	6.5	17.2	75.2
G 4.2	0.046	60.9	66.8	77.7	3.1	64.8	82.3
G CP		62.1	67.4	78.6	2.5	16.0	80.3
H n	native	69.9	92.3	104.5	13.7	1.6	40.1
H c	0	70.2	97.4	107.3	6.3	1.5	41.7
H 2.1	0.021	62.6	74.4	87.1	2.8	5.1	50.6
H 4.2	0.043	62.3	70.9	80.0	1.1	33.9	62.1
H CP						9.9	59.4

^a Samples are waxy (W), normal (N), Gelose 50 (G), and Hi-Maize (H) starches which are native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

in widespread interchain associations to produce a strongly linked viscous paste. For the waxy and normal starches, as the additional release of amylose from greater swelling is more limited, the effect on the CPV is consequently smaller.

Cross-linking of the cationic starch caused increases in the gelatinization temperatures accompanied by a slower rate of gelatinization and increases in PV. As

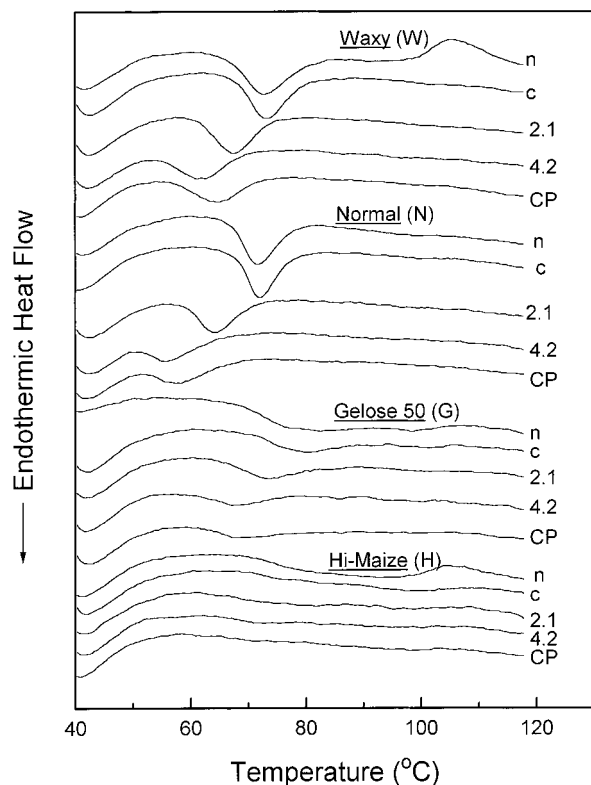


Figure 2. Differential scanning calorimetry thermograms of cationic and cross-linked cationic maize starches. Native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

cross-linking will reinforce granule structure, it is anticipated that the granule will be more resistant to breakdown and consequently be able to swell longer and

achieve a higher PV before some breakdown ultimately occurs. In conformance with this model, all the cross-linked starches showed reduced breakdown. The presence of covalent cross-links could also overcome the repulsion of cationic groups in the cool paste, and high values for CPV were recorded in all the cross-linked samples. The level of cross-linking present will, however, be critical to the pasting properties observed. Quan et al. (1997) found that high levels of cross-linking of cationic starches could cause loss of PV and CPV as strongly cross-linked granules were resistant to swelling and would also fail to break down to form paste.

Solubility and Swelling Power. The swelling power and solubility of native, cationic, and cross-linked cationic maize starches is shown in Figures 3 and 4. The solubility of all the native starches was rather similar; however, after cationization, the high-amylose starches showed a much greater increase in solubility than was the case for the normal and waxy starch. In all cases, cross-linking reduced an increase in solubility due to cationization. Native *ae* starch was very restricted in swelling power, and the swelling power of waxy starch was higher than both the native normal and *ae* starch. Overall, the swelling power increased as the amylose content of the starch decreased. Cationization increased the swelling power of all the starches compared to their corresponding control starch, and increasing the DS of cationic starches led to an increase in swelling power.

An increase in the charge density of starch through cationization will serve to increase the hydrophilicity of the starch and thus increase its ability to attract water. Repulsion between neighboring cationic groups may also serve to loosen the structure of the starch granule and further facilitate water permeation. It has been suggested that cationic substitution takes place

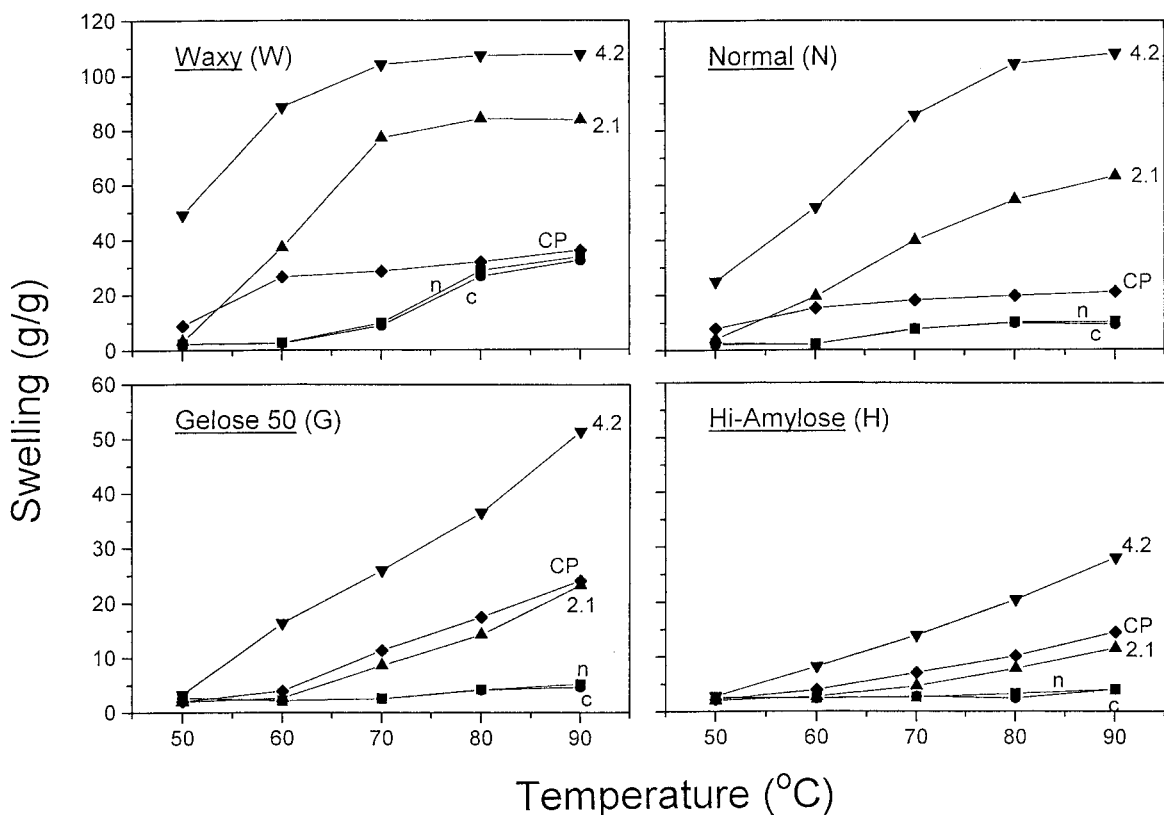


Figure 3. Swelling power of cationic and cross-linked maize starches. Native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

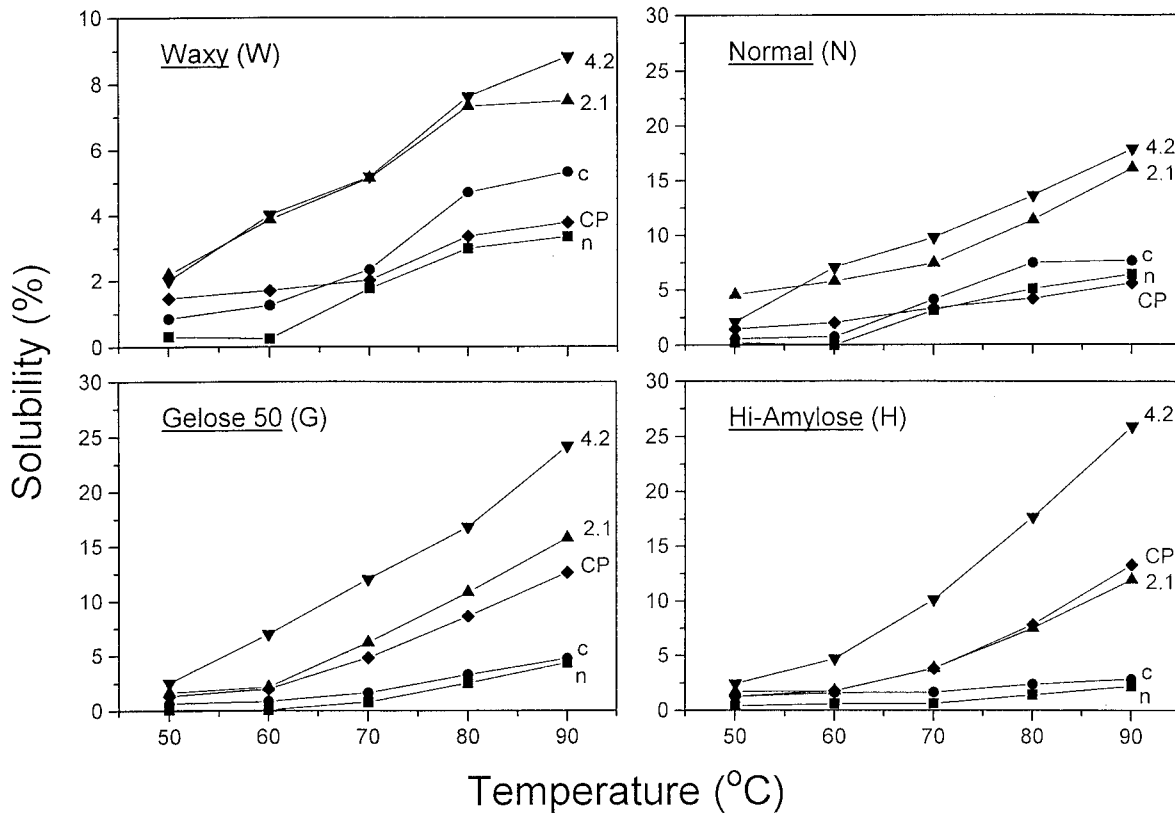


Figure 4. Solubility of cationic and cross-linked maize starches. Native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

predominantly in the amylose regions (Yook et al., 1994), and this would agree with the observed greater increase in solubility of the high-amylose starches after cationization. This interpretation is far from conclusive, and we are investigating this point further using more direct methods. The smallest increase in swelling power was observed with the waxy starch which already benefited from a structure capable of good swelling due to the high amylopectin content. With both swelling and solubility, the increases observed attributable to cationization were reversed by cross-linking. The formation of covalent cross-links within the starch will serve to reinforce the interchain associations and prevent the loosening of the structure that allows easy uptake of water.

Clarity. The clarity of native, cationic, and cross-linked cationic starches is shown in Table 2. Cationization increased the clarity greatly for all the starches compared to the corresponding native starch, and increasing DS of cationic maize starches also resulted in increased clarity. The cationization served to make the gelatinization easier by loosening intermolecular associations and thus increasing the clarity. Increased amylose content resulted in more difficult gelatinization and more crystalline regions, so the clarity of cationic and native starches showed negative correlation with amylose content.

After cross-linking, the clarity of all the cationic starches dramatically decreased. There were two reasons for this: (1) cross-linking increased the bond strength of starch molecules, which made gelatinization difficult; (2) loss of clarity in starch is associated with increasing crystallinity during retrogradation which is largely due to amylose association (Liu et al., 1997). Cross-linking increased the trend of starch chain association, thus decreasing the clarity of cationic starches.

Enzymatic Digestibility. The enzymatic digestibility of native, cationic, and cross-linked cationic starches is shown in Table 2. Except for waxy starch, cationization increased the digestibility of all the starches, especially for *ae* starches. This is attributed to the higher swelling power of cationic starch granules which increases accessibility of the starch to enzymic attack. Although there was little change in the digestibility of waxy starch after cationization, cationic waxy starch still showed the highest level of digestibility in all the starches because of the highest swelling power. Cross-linking decreased the enzymatic digestibility of all the cationic starch, since the cross-linking reinforced the starch granule structure, making it less susceptible to enzymic attack.

Texture. Some textural parameters for native, cationic, and cross-linked cationic maize starches are shown in Table 3. Cationization had little effect on the texture of waxy starch gels (which were in any case very weak) and caused a decrease in gel hardness and adhesiveness in normal starch. The cationization of high-amylose starches markedly increased the hardness and the springiness of the gel. The action of cationization in loosening the starch granule structure will on gelatinization permit extensive loss of amylose, which on cooling will be able to associate to form an extensive gel network that gives high-viscosity cool pastes and hard cold gels. Where the degree of substitution is very high, however, it would be expected that repulsion between cationic groups would also inhibit amylose association in the gel leading to a loss of hardness. This is precisely what we see with the normal and G starch at high DS. That we do not observe this effect with H starch is a consequence of the very high amylose content of this starch and the number of cationic groups per amylose chain is not yet sufficiently high for repulsion

Table 3. Gel Texture of Cationic and Cross-Linked Cationic Starches

probe	starch ^a	hardness (g)	adhesiveness (gs)	springiness
5 mm	N n	66	66	0.94
	N c	73	61	0.95
	N 2.1	67	4	0.96
	N 4.2	33	0	1.00
	N CP	23	123	0.94
	G n	45	45	0.86
	G c	36	34	0.76
	G 2.1	152	124	0.96
	G 4.2	98	161	1.00
	G CP	122	130	0.95
	H n	15	19	0.52
	H c	13	22	0.47
	H 2.1	63	117	0.97
	H 4.2	106	151	0.97
H CP	116	214	0.96	
20 mm	W n	23	5	1.00
	W c	15	1	0.97
	W 2.1	14	3	0.96
	W 4.2	15	12	0.95
	W CP	194	667	0.96

^a Samples are waxy (W), normal (N), Gelose 50 (G), and Hi-Maize (H) starches, which are native (n), control (c), cationized with 2.1 mL of CHPTAC (2.1), cationized with 4.2 mL of CHPTAC (4.2), or cross-linked cationic (CP).

to occur in the cold paste. In the case of the waxy starch, the low level of amylose present is rapidly saturated by cationic groups, which by mutual repulsion prevent any further amylose association increasing the strength of the gel.

Cross-linking by increasing associations within the cold gel can, therefore, increase gel hardness. However, since cross-linking may restrict release of amylose from the starch granule, this can reduce the amount of amylose available to form associations in the cold gel and thus lead to a loss in hardness. This latter effect would appear to predominate in the normal starch, whereas in the high-amylose starches with abundant amylose available, this limitation does not cause a loss of gel hardness. The slight observed increase in hardness of the cross-linked cationic waxy starch may be attributed to the cross-linking of amylopectin.

CONCLUSIONS

We have seen that the effects of cationization on different starches depend largely on modifications of interchain associations which can affect starch granule swelling and the propensity for association to occur in the cool paste or gel. For any starch with a given amylose content it will be possible to determine an optimal level of cationization to maximize or optimize CPV or gel hardness. At the optimal level, high swelling will give good release of amylose from the granule but the DS will not be high enough to prevent interchain association in the gel.

Cross-linking of the cationic starch is a useful means of achieving high PV and CPV. Further optimization of the level of cross-linking matched to the degree of cationization used will permit the use of high-amylose starches throughout and beyond the performance range currently available from normal maize starches. In general, there was a complex interaction of amylose level and effect of chemical modification on maize starches. In optimizing the results of a chemical modification, careful selection and uniformity of the amylose content of the incoming raw material is essential. The future efforts of biotechnologists may increasingly be

successful in providing biological variation in starch properties that will respond in precisely targeted and predictable ways to the chemical modifications imposed.

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LITERATURE CITED

- American Association of Cereal Chemists *Approved Methods*; The Association: St. Paul, MN, 1995.
- Biliaderis, C. G.; Maurice, T. J.; Vose, J. R. Starch gelatinization phenomena studied by differential scanning calorimetry. *J. Food Sci.* **1980**, *45*, 1669–1674.
- Biliaderis, C. G. Physical characteristics, enzymatic digestibility and structure of chemically modified smooth pea (*Pisum sativum* cultivar Trapper) and waxy maize starches. *J. Agric. Food Chem.* **1982**, *30*, 925–930.
- Hoover, R.; Sosulski, F. Effect of cross-linking on functional properties of legume starches. *Starch/Stärke* **1986**, *38*, 149–155.
- Jensen, B. M.; Winters, J. C. Cationic potato starches proven effective as wet-end additives. *Pulp Pap.* **1986**, *60*, 83.
- Kasemsuwan, T.; Jane, J. Location of amylose in normal starch granules. II. locations of phosphodiester cross-linking revealed by phosphorus-31 nuclear magnetic resonance. *Cereal Chem.* **1994**, *71*, 282–287.
- Kartha, K. P. R.; Srivastava, H. C. Reaction of epichlorhydrin with carbohydrate polymers. *Starch/Stärke* **1985**, *37*, 297–306.
- Kweon, M. R.; Sosulski, F. W.; Han, H. S. Effect of aqueous ethanol cationization on functional properties of normal and waxy starches. *Starch/Stärke* **1997**, *49*, 202–207.
- Liu, H.; Ramsden, L.; Corke, H. Physical properties and enzymatic digestibility of acetylated *ae*, *wx*, and normal maize starch. *Carbohydr. Polym.* **1997**, *34*, 283–289.
- Mentzer, M. J. Starch in the paper industry. *Starch: Chemistry and Technology*, 2nd ed.; Whistler, R. L., BeMiller, J. N., Paschall, E. F., Eds.; Academic Press: Orlando, FL, 1984; pp 543–574.
- Quan, Y.; Kweon, M. R.; Sosulski, F. W. Effect of cross linking on functional properties of cationic corn starch. *Starch/Stärke* **1997**, *49*, 458–464.
- Rayford, W. E.; Wing, R. E. Crosslinked cationic and anionic starches: preparation and use in heavy metal removal. *Starch/Stärke* **1979**, *31*, 361–365.
- Solarek, D. B. Cationic starches. In *Modified Starches: Properties and Uses*; Würzburg, O. B., Ed.; CRC Press: Boca Raton, FL, 1986.
- Subramanian, V.; Hosney, R. C.; Bramel-Cox, P. Shear thinning properties of sorghum and corn starches. *Cereal Chem.* **1994**, *71*, 272–275.
- Vasanthan, T.; Bhatta, R. S.; Tyler, R. T.; Chang, P. Isolation and cationization of barley starches at laboratory and pilot scale. *Cereal Chem.* **1997**, *74*, 25–28.
- Wu, Y.; Seib, P. A. Acetylated and hydroxypropylated distarch phosphates from waxy barley: paste properties and freeze-thaw stability. *Cereal Chem.* **1990**, *67*, 202–208.
- Würzburg, O. B. 40 years of industrial starch research. *Cereal Foods World* **1986**, *31*, 897–903.
- Yook, C.; Sosulski, F.; Bhirud, P. R. Effects of cationization on functional properties of pea and corn starches. *Starch/Stärke* **1994**, *46*, 393–399.
- Zhang, D.; Collins, W. W.; Andrade, M. Estimation of genetic variance of starch digestibility in sweetpotato. *Hortic. Sci.* **1995**, *30*, 348–349.

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