

Effect of Dry Heating with Ionic Gums at Controlled pH on Starch Paste Viscosity

H. S. Lim,¹ J. N. BeMiller,^{1,2} and S.-T. Lim³

ABSTRACT

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Waxy maize and potato starches were dispersed in pH 6.0 and 8.0 aqueous solutions (1%) of an ionic gum (sodium alginate, sodium carboxymethylcellulose, and xanthan). The mixture was dried at 45°C overnight and then heat-treated 2 hr at 130°C. Effects on the paste viscosity of the products in a pH 7.0 buffer were examined. Heating with sodium alginate or sodium carboxymethylcellulose (CMC) increased the paste viscosity of waxy maize starch but reduced that of potato starch. In both starches, xanthan effected greater viscogram changes than did sodium alginate or CMC. Use of xanthan in the treatment produced

products with restricted granular swelling and increased shear stability of the pastes. The pH of the starch-gum mixtures affected the thermally induced viscosity changes. Mild acidity (pH 6.0) effected a viscosity decrease for the heat-treated starch product, whereas alkalinity (pH 8.0) raised the viscosity regardless of the presence of gum. But pH 6 before heat treatment was favored for viscosity increase by sodium alginate, whereas pH 8 gave a greater increase in viscosity when xanthan was used. By using gum mixtures such as xanthan-alginate and xanthan-CMC, both viscosity increase and good shear-stability were achieved.

Dry starch granules are heat resistant up to a point. Excessive heating will effect thermal degradation (Greenwood 1967), but mild heating can change the physical characteristics of starch (Goto 1972; Seguchi 1984; Seguchi and Yamada 1988; Chiu et al 1998, 1999; Lim et al 2002). Heating dry starch or flour at >100°C, preferably for several hours, provides functionality equivalent to chemical cross-linking (Chiu et al 1998, 1999). Dehydration (<1% moisture) before heating and alkalinity (pH 8–9.5) facilitates the effect of heating.

Addition of reactive compounds can result in chemical reactions during dry heat treatment. A small amount of levoglucosan added to wheat starch before heating, and that produced by the dry heat treatment itself, introduced new enzyme-resistant glycosidic linkages (Theander and Westerlund 1987; Siljestrom et al 1989). Citric and itaconic acids have also been used as reactants in dry heating of starch (Klaushofer and Berghofer 1978; Klaushofer et al 1978; Wing 1996). It was assumed that citrate was first converted to its anhydride that reacted with starch hydroxyl groups (Wing 1996). Citrate incorporation increased as the pH of the citrate-starch mixture was lowered.

Gums are often used together with starch to improve the physical properties of final products (Christianson et al 1981; Alloncle et al 1989; Sudhakar et al 1992; Ferrero et al 1993a,b, 1994; Rayment et al 1995; Sekine 1996; Liu and Eskin 1999; Shi and BeMiller 2002), but to date, only physical mixtures of gums and starch have been made and cooked. Recently, we found that anionic food gums reacted with starch during dry heat treatment, producing significant changes in pasting properties of the starch, with the pasting properties of the heated products depending on the specific combination of gum and starch (Lim et al 2002). The properties of waxy maize starch were more affected by heating with an anionic gum than were those of potato starch, and xanthan produced greater changes in paste viscosity than did sodium alginate or sodium carboxymethylcellulose (Lim et al 2002).

In the present study, waxy maize and potato starches were impregnated with solutions of anionic gums (sodium alginate, sodium carboxymethylcellulose, and xanthan) adjusted to different pH values (6.0 and 8.0) before dry heat treatment, and effects of solution pH and gums on the paste viscosity of the products were examined.

MATERIALS AND METHODS

Starches and Gums

Waxy maize and potato starches were gifts from A.E. Staley Manufacturing (Decatur, IL) and Penford Food Ingredients (Englewood, CO), respectively. Food-grade xanthan gum (Keltrol F), and sodium alginate (Keltone LV) (alginate) were provided by Nutra-Sweet (Chicago, IL). Sodium carboxymethylcellulose (CMC) was a DS 0.7, low-viscosity type (7LF) provided by Hercules (Wilmington, DE).

Impregnation of Starch with Gum Solutions at Different pH Values

Sodium alginate, CMC, xanthan, and their mixtures (0.4 g, db) were slowly added to distilled water (70 mL) with vigorous stirring. After the gum was completely dissolved, granular starch (39.6 g, db) was dispersed into the gum solution. The percentage of total solids in the solution was ≈36%; the gum concentration was 1% (based on total solids). The dispersion was adjusted to pH 6.0 or 8.0 by adding aqueous HCl (0.2M) or Na₂CO₃ (0.1M) solution; then the dispersion was stirred for 30 min at room temperature. The dispersion was transferred to a glass dish and dried at 45°C in a convection oven until the moisture content reached <10%. The dried starch-gum mixture was ground to a powder and passed through a 100-mesh sieve.

Heat Treatment

The dried starch-gum mixture was heated in an electric drying oven at 130°C for 2 hr. Two kinds of controls were used. In one, a starch dispersion without added gum was adjusted to pH 6.0 or 8.0, dried, and heat-treated as described above (NoGum, Tables I–III). In the other, a starch dispersion with added gum was adjusted to pH 6.0 or 8.0 and the dispersion was dried as described above. But the heating at 130°C was omitted (NH, Tables I–III).

Paste Viscosity

Paste viscosities of the starch samples (7.0%, w/w, dsb) were determined in a neutral buffer solution (0.1M sodium phosphate, pH 7.0) using a Rapid Visco Analyser (RVA) (Newport Scientific, Australia). The standard procedure (No. 1) starting and ending at 50°C, 3-min holding at 95°C, 15-min total analysis time was used for the analysis.

RESULTS

Heat Treatment Without Gum

There were slight differences in the paste viscosity of corn and potato starches heated without gum (dispersions adjusted to pH

¹ Whistler Center for Carbohydrate Research, Food Science Building, Purdue University, West Lafayette, IN 47907-2009.

² Corresponding author. E-mail: bemiller@purdue.edu.

³ Graduate School of Biotechnology, Korea University, 5-1 Anam-dong, Sungbuk-ku, Seoul 136-701, Korea.

6.0 and pH 8.0 before heat treatment) as compared with the same starches treated with gum but not heated (NoGum and NH, Tables I and II, respectively). [Authors Note: Products of heat treatment of starch granules impregnated with a pH 6.0 solution (with or without gum) are referred to as products from pH 6 starch or as products from heating at pH 6, although it is understood that the usual concept of pH does not hold inside dry granules.] The same is true for products impregnated with pH 8.0 solution. The starches dispersed in solutions at pH 8 showed slightly higher values for peak and final viscosities. The paste viscosity was highly affected by the heat treatment, depending on the dispersion pH in both waxy maize and potato starches (H, Tables I and II).

Waxy maize starch. For waxy maize starch (Table I), heat treatment at pH 6 resulted in a substantial decrease in viscosity during both pasting and cooling; however, heat treatment at pH 8 increased the viscosity. We have already reported that slightly acidic waxy maize starch undergoes dextrinization under the heating conditions used in this research, resulting in a thinned product (Lim et al 2002).

Potato starch. Potato starch showed effects of dry heating and pH on paste viscosity (Table II) that were somewhat different from those found with waxy maize starch. The buffer solution used for pasting displayed the typical salt effect of inhibiting potato starch granule swelling (Lim and Seib 1993; Shi and BeMiller 2002), as shown by the peak viscosity values of the not-heated samples (2,770 and 2,380 cP at pH 6 and 8, respectively, as compared with values of $\approx 8,500$ cP in distilled water) (data not shown). Subsequent heat treatment reduced the paste viscosity; the viscosity decrease was greater with the pH 6 treatment than with the pH 8 treatment.

A noticeable reduction in peak viscosity of potato starch by dry heat treatment has been reported (Goto 1972; Chiu et al 1998, 1999), native potato starch being inherently more sensitive to dry heat treatment than is waxy maize starch (Goto 1972; Sekine et al 2000). But in this work, the viscosity reduction measured in buffer solution was less than that measured in water (viscogram not shown) due to the salt effect of the buffer solution.

One feature commonly observed with the heat-treated corn and potato starches was an apparent slight decrease in pasting temperature. This might result from a minor disintegration of granular structure by the heat treatment. The viscosity decrease from heating at pH 6 probably indicates some acid-catalyzed hydrolysis or transglycosylation. The increased viscosity by alkaline heating (pH 8) for waxy maize starch might be due to increased granule swelling resulting from chain dissociation because of hydrogen bond cleavage.

Heat Treatment in the Presence of Sodium Alginate

Waxy maize or potato starch was dispersed in aqueous, solutions at pH 6 or 8 of sodium alginate (1.0% based on total solids), recovered, dried, and heat-treated at 130°C for 2 hr. Treating the granular starch with the water-soluble gum in this way was necessary to provide heat-induced viscosity changes, although the proportion of the gum that actually impregnated the starch granules is unknown (Lim et al 2002), an aspect currently under investigation.

Waxy maize starch. Table I shows the effects of the presence of alginate (Algin) during heat treatment at different pH values on the viscogram of waxy maize starch, all viscosity measurements were made in the pH 7.0 buffer. The heated starch-alginate mixture at pH 8 (Algin-pH 8 and H, Table I) produced a viscogram with significantly higher peak and final viscosities than did the pH 6 mixture. Acid-thinning might have occurred in the heated pH 6 starch-alginate mixture as it did in the heated starch alone.

Therefore, to examine the real effect of the gum, comparison was done before and after the heat treatment (NH and H, Table I). When the pH 6 heated samples were compared, the presence of alginate raised the final viscosity by 200 cP (from 1,730 to 1,530), whereas the NoGum sample had a viscosity decrease of 340 cP

(from 1,590 to 1,250) (Table I). The pH 8 heated mixture displayed a viscosity increase of 620 cP, but the pH 8 heated starch alone also showed a viscosity increase (280 cP). Therefore, the effect of alginate in increasing viscosity was slightly greater at pH 6 than at pH 8. The effect of alkalinity on the heated waxy maize starch without gum was significant, but the viscosity of the pH 8 heated starch-alginate mixture was still greater.

Heating drives off moisture, which should facilitate reaction between the carboxyl groups in alginate and the hydroxyl groups in starch. Esterification should also be more pronounced when more carboxyl groups are in the acid form. The greater net viscosity increase under the more acidic condition supports the hypothesis that esterification occurs during dry heat treatment with a gum containing carboxyl groups.

Potato starch. Potato starch behaved differently than did waxy maize starch (Table II). The addition of alginate somewhat decreased the viscosity of potato starch, even without heating (Algin and NH). For example, pH 6 unheated potato starch produced peak and final viscosities in the pH 7.0 buffer solution of $\approx 2,800$ cP and 4,000 cP, respectively, but those were reduced by the addition of sodium alginate to $\approx 2,000$ and 3,500 cP, respectively, without any heating. Addition of alginate also shifted the peak temperature into the 95°C hold region. These changes were undoubtedly due to a salt effect, to which potato starch is particularly susceptible (Lim and Seib 1993; Shi and BeMiller 2002).

Dry heat treatment effected an even greater viscosity decrease in both NoGum and Algin samples, depending on the pH for heating (Table II). Dry heat treatment of potato starch at pH 6 without alginate resulted in substantial viscosity decreases (870 and 1,260 cP of peak and final viscosities, respectively). The viscosity decrease was less when alginate was present during the heat treatment (380 and 1,050 cP, respectively). At pH 8, alginate was even more effective in lessening the viscosity decrease (280 cP for final viscosity for Algin-pH 8). Assuming that the effect of alkali was the same in both No-gum and Algin samples, there was significantly less viscosity reduction in the alginate-treated samples (by $\approx 1,000$ cP). The effect of pH on heating potato starch with alginate was opposite to that on waxy maize starch. Although the assumed esterification should have been more pronounced when more of the carboxyl groups of the gum were in the acid form (pH 6), the reaction might also depend on physical contact between the gum and starch. We hypothesize that the alkalinity in the medium facilitated swelling of starch granules so that the gum molecules could more easily impregnate the granules. The medium pH could also affect the phosphate esters groups of potato starch. The more ionized phosphate groups (pH 8) could facilitate granule swelling, but should result in repulsion of the anionic charges on the gum and the phosphate groups.

Heat Treatment in the Presence of CMC

Waxy maize starch. Presence of CMC in the dispersion decreased slightly the peak viscosity of waxy maize starch (CMC and NH, Table I), a result similar to that of alginate. But with heat treatment, peak and final viscosities were raised substantially to values greater than those given by starch heated alone, a result produced at both pH levels. The peak and final viscosities of the pH 6, heat-treated starch-gum mixture were $\approx 2,600$ and 1,800 cP; for the pH 8 treatment, the values were $\approx 3,500$ and 2,300 cP, respectively.

As with alginate, the viscosity produced by pH 6 waxy maize starch heat-treated with CMC was greater than that heat treated at pH 8. Although these viscosity changes were similar to those found with alginate, CMC was more effective in increasing viscosity than was alginate. The actual viscosity increase given by heating with CMC was similar at pH 6 and pH 8 (comparison with both NoGum and CMC samples).

Potato starch. In potato starch (Table II), heat treatment with CMC provided mixed results, but the overall patterns and viscosi-

ties of potato starch heated with CMC were similar to those observed with alginate (viscograms not shown). CMC addition without heating produced a change in the early stage of pasting, but the final viscosity was little changed. The depression of peak viscosity by salt addition before heating was more significant than that produced by sodium alginate. Heat treatment increased the peak viscosity, but decreased the final viscosity (CMC and H, Table II). CMC raised the peak viscosity upon heating, whereas alginate decreased it. Heating with CMC decreased the pasting temperature slightly. Treatment at pH 6 produced a product with shear-thinned paste (breakdown of 540 cP), resulting in a low final viscosity. Treatment at pH 8, however, produced a product with final viscosity almost identical to that of starch heat-treated without gum. Considering the substantial viscosity drops for the NoGum sample heated at both pH values, CMC presence during heating appeared to protect the starch from viscosity decreases. As in alginate, CMC in the dry heat treatment of potato starch was more effective at pH 8 than at pH 6.

Heat Treatment in the Presence of Xanthan

Waxy maize starch. Dispersing starch with xanthan itself made no significant change in the pasting viscogram of waxy maize starch (not shown). However, the paste viscosity was substantially changed by dry heat treatment when xanthan was present in or on granules. Moreover, xanthan rendered a more profound effect on paste viscosity than did alginate or CMC. The effect of xanthan during heat treatment of waxy maize starch on the paste viscosity in water (without buffer) has also been reported (Lim et al 2002). Regardless of the pH of the heated samples, waxy maize starch became resistant to breakdown when heat-treated with xanthan;

the swelling of starch granules became restricted, and no clear peak viscosity (maximum swelling) was visible on the viscogram. The viscosity was maintained during the holding period at 95°C. These changes made the final viscosity significantly higher than the “peak” viscosity. Final viscosity at pH 8 was higher than that at pH 6. The final viscosity loss induced by pH 6 heat treatment without added gum (340 cP for NoGum) was greater than that of waxy maize starch heat treated under same conditions but with xanthan (250 cP). At pH 8, however, the presence of xanthan during heating produced a final viscosity increase of 720 cP; the starch heated without xanthan showed only a 280 cP increase. Therefore, xanthan produced a greater heat-induced viscosity increase at pH 8 than at pH 6, a result opposite to that observed with alginate. The viscograms indicate retarded swelling and shear-stabilization, effects similar to those obtained with chemical cross-linking.

Potato starch. For potato starch, the effect of xanthan during heat-treatment was also greater than that of other gums (Table II). Final viscosity of the heat-treated pH 6 starch-gum mixture (Xan-pH 6) was significantly lower than that of the starch alone treated the same way (NoGum-pH 6). As with CMC, reduced setback resulted in a low final viscosity. At pH 8, however, xanthan made the heat-treated potato starch paste slightly more viscous. Here again (as with waxy maize starch), xanthan appeared to react more at pH 8 than at pH 6, but the reduced breakdown observed with waxy maize starch was not seen with potato starch. At pH 8, the effect of xanthan was similar to that of CMC. The final viscosity remained unchanged by heating when xanthan was present.

It is possible, and likely, that heating under slightly acidic conditions (pH 6.0) removed at least some of the pyruvyl cyclic acetal

TABLE I
Paste Viscogram Data of Waxy Maize Starch Before (NH) and After (H) Heat Treatment with Ionic Gums at pH 6 and 8

Samples	Pasting Temp. (°C)		Peak Temp. (°C)		Peak Viscosity (cP)		Breakdown (cP)		Setback (cP)		Final Viscosity (cP)	
	NH	H	NH	H	NH	H	NH	H	NH	H	NH	H
NoGum-pH 6	77	75	89	85	2,460	1,790	980	830	110	290	1,590	1,250
NoGum-pH 8	76	75	86	84	2,510	2,920	1040	1,250	280	360	1,750	2,030
Algin-pH 6	77	76	88	83	2,200	2,570	740	1,130	80	300	1,530	1,730
Algin-pH 8	77	75	87	84	2,260	3,230	1,080	1,460	360	370	1,530	2,150
CMC-pH 6	77	76	88	82	2,310	2,560	870	880	160	140	1,590	1,830
CMC-pH 8	77	75	86	86	2,230	3,480	1,000	1,490	300	320	1,530	2,310
Xan-pH 6	77	77	86	95	2,600	1,360	1,100	10	250	150	1,750	1,500
Xan-pH 8	75	77	86	95	2,600	2,100	1,420	10	520	340	1,700	2,420

TABLE II
Paste Viscogram Data of Potato Starch Before (NH) and After (H) Heat Treatment With Ionic Gums at pH 6 and 8

Samples	Pasting Temp. (°C)		Peak Temp. (°C)		Peak Viscosity (cP)		Breakdown (cP)		Setback (cP)		Final Viscosity (cP)	
	NH	H	NH	H	NH	H	NH	H	NH	H	NH	H
NoGum-pH 6	71	68	90	91	2,770	1,900	400	380	1,610	1,200	3,980	2,720
NoGum-pH 8	70	68	95	88	2,380	2,410	200	620	1,870	1,650	4,050	3,440
Algin-pH 6	69	68	95	95	2,030	1,650	130	250	1,580	1,030	3,480	2,430
Algin-pH 8	68	67	95	95	2,050	1,840	200	180	1,610	1,520	3,460	3,180
CMC-pH 6	69	66	95	91	1,930	2,290	140	540	1,700	790	3,490	2,540
CMC-pH 8	70	67	95	95	1,770	2,120	70	300	1,370	1,590	3,420	3,400
Xan-pH 6	70	68	95	95	2,880	1,950	460	450	1,680	500	4,100	2,010
Xan-pH 8	66	67	95	95	2,850	3,280	450	780	1,650	1,640	4,100	4,140

TABLE III
Paste Viscogram Data of Waxy Maize Starch Before (NH) and After (H) Heat Treatment with Ionic Gums at pH 6 and 8

Samples	Pasting Temp. (°C)		Peak Temp. (°C)		Peak Viscosity (cP)		Breakdown (cP)		Setback (cP)		Final Viscosity (cP)	
	NH	H	NH	H	NH	H	NH	H	NH	H	NH	H
NoGum-pH 6	77	75	89	85	2,460	1,790	980	830	110	290	1,590	1,250
NoGum-pH 8	76	75	86	84	2,510	2,920	1040	1250	280	360	1,750	2,030
Xan-Algin-pH 6	77	77	87	95	2,260	1,860	800	60	130	110	1,590	1,910
Xan-Algin-pH 8	77	77	87	95	2,220	2,810	1040	1290	150	180	1,520	2,540
Xan-CMC-pH 6	77	76	89	ND ^a	2,310	ND	860	0	130	ND	1,580	1,890
Xan-CMC-pH 8	72	76	89	95	2,140	2,410	850	10	220	470	1,510	2,870

^a Not determined.

groups from xanthan molecules and that some starch polymer molecules were modified with the released pyruvic acid molecules, most likely by esterification, but transacetalation cannot be ruled out.

Heat Treatment in the Presence of Xanthan-Alginate or Xanthan-CMC mixtures

Because of opposite effects on paste viscosity, 1:1 (w/w) mixtures (0.4 g total) of xanthan plus alginate and xanthan plus CMC were used to examine their combined effects on dry-heat-treated waxy maize starch.

Xanthan-alginate mixture. The product of heat treatment of pH 6 waxy maize starch with the xanthan-alginate mixture (1.0% based on total solids) gave a viscogram pattern similar to that found when xanthan alone was used (viscograms not shown), but the peak and final viscosity values were greater by ≈ 400 – 500 cP (Table III). When pH 8 starch was heated with the mixture, the peak viscosity was much higher (950 cP) than that found at pH 6; but in comparison with the starch heated with xanthan alone (Table I), the final viscosity increased by 120 cP, while the peak viscosity increased by ≈ 700 cP, a result of substantial breakdown. This could be a result of lesser reactivity of alginate at pH 8, as found with alginate alone.

Xanthan-CMC mixture. The xanthan-CMC mixture also increased the viscosity over that given with xanthan alone. When a starch-gum mixture at pH 6 was heated, the final viscosity of the mixture was $\approx 1,900$ cP, ≈ 400 cP higher than that of the starch heat-treated in the presence of xanthan alone. When the pH 8 mixture was heated, the treated starch exhibited a final viscosity of $\approx 2,900$ cP, or ≈ 450 cP higher than that obtained by the same treatment with xanthan alone. Comparison of the products from heating at pH 6 and pH 8, with and without the gum mixture, revealed that the viscosity increase was greater as a result of heating at pH 8. Xanthan-CMC provided more viscosity increase than did xanthan-alginate because of the higher reactivity of CMC as compared with alginate.

Waxy maize starch heated with the gum mixtures showed a delay in reaching peak viscosity (restriction in starch swelling) and reduced breakdown. After dry heating at pH 6, the viscosity of the starch product containing xanthan-CMC continued increasing up to the cooling stage, without exhibiting breakdown (ND in Table III). The xanthan-CMC mixture provided more inhibition of swelling and shear-stabilization than did the xanthan-alginate mixture because CMC gave more shear stability than did alginate. Overall, dry heating of waxy maize starch with the xanthan-CMC mixture was more effective than heating with the xanthan-alginate mixture in increasing paste viscosity and shear-stability.

DISCUSSION

Carboxylate/carboxylic acid groups could react with starch hydroxyl groups during dry heating to form ester linkages. Sodium alginate and xanthan contain uronic acid groups. Xanthan contains additional carboxylate groups from the pyruvyl cyclic acetal moiety. Sodium carboxymethylcellulose (CMC) also contains carboxylate groups. Each anionic gum molecule is multi-carboxylated so that more than one starch chain could react with a gum molecule. The number of starch chains esterified to a gum molecule would be an important determinant of pasting behavior. If two or more starch chains are connected to a gum molecule, the gum acts as a granule cross-linking agent. But if one gum molecule is esterified to only one starch molecule, the product is a starch-gum graft copolymer with ionic properties. Viscograms of the heat-treated gum-starch samples indicated that reaction level and type depended on the specific combination of gum and starch used. The pH of the starch-gum dispersion before drying and heating affected reactivity (influenced the paste viscosity of the product). A very small percentage of carboxylic acid groups would be present at pH 6 and essentially none at pH 8, so the greatest effect of pH is probably on the

starch granules. Based on the observed viscogram changes, it is assumed that acidic conditions effected some starch chain cleavages (thinning) and that alkali effected hydrogen-bond disruptions inside granules. An effect of alkali was emphasized when starch alone was heat-treated (Chiu et al 1998, 1999). Reactions of alginate with starch appeared to be more pronounced at the lower pH value, supporting a supposition of esterification. A very low degree of cross-linking of all three gums was indicated at pH 6. More cross-linking was indicated at pH 8. CMC appeared to be almost equally reactive at both pH values. Because all three gums are highly carboxylated, reaction of only a very small percentage of the carboxylate or carboxylic acid groups is required to produce the properties of a lightly cross-linked starch.

Compared with alginate and CMC, xanthan affected the viscosity of the heated starches most. The presence of xanthan during heat treatment gave a product with retarded granule swelling and protected the resulting paste against breakdown, resulting in a subsequent increase in the final viscosity, indicating that cross-linking had occurred. Moreover, reaction with xanthan at both pH values increased the viscosity, but more so at pH 8; whereas alginate seemed to react only at pH 6. So it is still not clear how the reaction with the gums is a function of pH. The pyruvate cyclic acetal groups may have been removed from xanthan molecules as a result of heating in the presence of acid, removing an opportunity for a cross-linking reaction. Reaction with gum molecules must depend on contact with starch molecules, and thus reactivity must also be a function of where and to what degree gum molecules penetrate granules (an aspect under current investigation). A possible explanation for the xanthan reactivity at a high pH is that the alkalinity disrupts intragranular hydrogen bonds, exposing more starch molecule hydroxyl groups.

The different effects of xanthan and the other ionic gums (sodium alginate and sodium CMC) in modifying paste viscosity suggested use of a combination of the gums to control paste properties. Waxy maize starch heated at 130°C for 2 hr with an equivalent mixture (by weight) of xanthan and CMC (0.5% each, based on total solids) displayed excellent shear stability with substantial viscosity increase when either the pH 6 or 8 treatment was used, but especially when pH 8 was used.

The pH of starch-gum mixture is another variable. Efficient impregnation of gum molecules into starch granules is required for efficient reaction between starch and gum, so impregnation could be done at one pH value and heating at another.

CONCLUSIONS

Dry-heating of a granular starch after ionic gum impregnation could be useful for modifying its pasting behavior and paste properties. The process is relatively safe, with no toxic by-product. Reaction between starch and gum can be controlled by gum type and reaction pH. Among the ionic gums tested, xanthan was the best cross-linking agent; alginate and CMC appeared to give primarily noncross-linked products (graft copolymer-type products). Although starch-graft-gum products (through mono-substitution reactions) seemed to be most pronounced at pH 6, degradation of starch may have also occurred during heating in the presence of acid. However, heating at an alkaline pH made the starch granules more reactive with xanthan and the resulting paste more viscous. Therefore, to achieve greater viscosity with good shear stability, use of a mixture of xanthan and another ionic gum is suggested. By using the gum mixture, starch may be modified similarly to a dual chemical modification of substitution and cross-linking. To understand the thermal reactions of ionic gums with starch clearly, more investigations are needed.

LITERATURE CITED

Alloncle, M., Lefebvre, J., Llamas, G., and Doublier, J. L. 1989. A rheological characterization of cereal starch-galactomannan mixtures.

- Cereal Chem. 66:90-93.
- Chiu, C.-W., Schiermeyer, E., Thomas, D. J., and Shah, M. B. 1998. Thermally inhibited starches and flours and process for their production. U.S. patent 5,725,676.
- Chiu, C.-W., Schiermeyer, E., Thomas, D. J., Shah, M. B., Hanchett, D. J., and Jeffcoat, R. 1999. Thermally inhibited non-pregelatinized granular starches and flours and preparation thereof. U.S. patent 5,932,017.
- Christianson, D. D., Hodge, J. E., Osborne, D., and Detroy, R. W. 1981. Gelatinization of wheat starch as modified by xanthan gum, guar gum, and cellulose gum. *Cereal Chem.* 58:513-517.
- Ferrero, C., Matino, M. N., and Zaritzky, N. E. 1993a. Effect of freezing rate and xanthan gum on the properties of corn starch and wheat flour pastes. *Int. J. Food Sci. Technol.* 28:481-498.
- Ferrero, C., Matino, M. N., and Zaritzky, N. E. 1993b. Stability of frozen starch pastes: Effect of freezing, storage, and xanthan gum addition. *J. Food Process. Preserv.* 17:191-211.
- Ferrero, C., Matino, M. N., and Zaritzky, N. E. 1994. Corn starch xanthan gum interaction and its effect on the stability during storage of frozen gelatinized suspensions. *Starch* 46:300-308.
- Goto, F. 1972. Determination of gelatinization property of highly concentrated starch suspensions by Brabender plastograph. IV. Plastograms of heat-treated starches. *J. Jpn. Soc. Starch Sci.* 19:90-99.
- Greenwood, C. T. 1967. The thermal degradation of starch. *Advan. Carbohydr. Chem.* 22:483-515.
- Klaushofer, H., and Berghofer, E. 1978. Starch esters. *Ger. Offen.* 19781012.
- Klaushofer, H., Berghofer, E., and Steyrer, W. 1978. Starch citrates—Production and technical application properties. *Starch* 30:47-51.
- Lim, S., and Seib, P. A. 1993. Preparation and pasting properties of wheat and corn starch phosphates. *Cereal Chem.* 70:137-144.
- Lim, S.-T., Han, J.-A., Lim, H. S., and BeMiller, J. N. 2002. Modification of starch by dry heating with ionic gums. *Cereal Chem.* 79:601-606.
- Liu, H., and Eskin, M. 1999. Interactions of native and acetylated pea starch with yellow mustard mucilage, locust bean gum and gelatin. *Food Hydrocoll.* 12:37-41.
- Rayment, P., Ross-Murphy, S. B., and Ellis, P. R. 1995. Rheological properties of guar galactomannan and rice starch mixtures. I. Steady shear measurements. *Carbohydr. Polym.* 28:121-130.
- Seguchi, M. 1984. Oil-binding capacity of heat-treated wheat starch. *Cereal Chem.* 61:241-244.
- Seguchi, M., and Yamada, Y. 1988. Hydrophobic character of heat-treated wheat starch. *Cereal Chem.* 65:375-376.
- Sekine, M. 1996. Measurement of dynamic viscoelastic behavior of starch during gelatinization in xanthan gum solution. *J. Jpn. Soc. Food Sci. Technol.* 43:683-688.
- Sekine, M., Otobe, K., Sugiyama, J., and Kawamura, Y. 2000. Effects of heating, vacuum drying and steeping on gelatinization properties and dynamic viscoelasticity of various starches. *Starch* 52:389-405.
- Shi, X., and BeMiller, J. N. 2002. Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydr. Polym.* 50:7-18.
- Siljestrom, M., Bjorck, I., and Westerlund, E. 1989. Transglycosidation reactions following heat treatment of starch—effect on enzyme digestibility. *Starch* 41:95-100.
- Sudhakar, V., Singhal, R. S., and Kulkarni, P. R. 1992. Starch-gum interactions—Formulations and functionality using amaranth corn starch and CMC. *Starch* 44:369-374.
- Theander, O., and Westerlund, E. 1987. Studies on chemical modification in heat-processed starch and wheat flour. IV. *Starch* 39:88-93.
- Wing, R. E. 1996. Starch citrate. Preparation and ion exchange properties. *Starch* 48:275-279.

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