Gelatinization of Wheat Starch as Modified by Xanthan Gum, Guar Gum, and Cellulose Gum

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ABSTRACT

Amylograph curves and Corn Industry Viscometer curves show that guar, xanthan, and carboxy methylcellulose gum hasten the onset of initial paste viscosity and substantially increase final peak viscosity of wheat starch. The early onset of initial viscosity is attributed to detection of the first stage of swelling and is dependent on media viscosity only. Further development of paste consistency can be attributed to interactions of solubilized starch, gums, and swollen starch granules. Media isolated from starch-guar and starch-xanthan dispersions display synergistic viscosity, which remains stable at room temperature. This viscosity stability suggests that strong associations of soluble starch (amylose) with gums are developed during pasting. Rheological behavior of media isolated from starch-xanthan paste shows pseudoplasticity, whereas media from starch-guar pastes show some resistance to shear at low shear rates. The degree of amylose hydrolysis is reduced with β-amyrase (E.C. 3.2.1.2) if wheat starch solubles isolated from starch-water pastes are reheated with either guar or xanthan gum before enzyme digestion.

Hydrocolloids have been used widely in food products to modify texture, improve moisture retention, control water mobility, and maintain overall product quality during storage (Glicksman 1974). Because wheat starch is a basic ingredient of so many foods, changes in its granule structure and pasting properties in the presence of gums were studied to extend knowledge on the function of starch in cooked and baked products and to expand uses of wheat starch and low-gluten flours in protein-fortified foods (Christianson 1976, Christianson et al. 1974).

Starch granules, including those from wheat, are composed of linear and branched starch molecules associated by hydrogen bonding either directly or through hydrate bridges. The molecules may form radially oriented crystalline areas or be in amorphous regions. Micellar networks formed by association of segments of individual molecules in various patterns impart durability to the granular structure and control the swelling behavior of starch during heating. Heating in water weakens the more crystalline network within the granules by disrupting hydrogen bonds with a concurrent loss of anisotropy. In the more amorphous areas, where the molecules are not as closely associated, progressive hydration and swelling occur more rapidly. Molecules of linear amylose are eventually released into solution. Hydrogen-bonding forces in wheat starch granules relax at two different stages of swelling (Leach et al. 1959). In the first stage, occurring at 55–70°C, granules swell tangentially and simultaneously lose their characteristic polarization crosses. This initial stage is not normally detectable viscometrically. However, Crossland and Favor (1948) noted that the initial gelatinization stages were observable when wheat starch granules were dispersed in carboxymethyl cellulose (CMC) or alginate solutions. They concluded that the changes in the work required to move the swollen granules past each other are magnified in the more viscous media. Sandstedt and Abbott (1964) have shown similar effects with other cereal starches.

An appropriate cause for the large increase in viscosity of wheat starch pastes observed during the second stage of swelling and gelatinization is difficult to assign, even in purely aqueous suspensions. Miller et al. (1973) concluded that the increase in viscosity (after most of the granule swelling ceases, 94°C) is due to the released exudate (soluble amylose) and its entanglement with itself, which enhances the viscometric effects. Addition of CMC or alginate could also contribute to this network formation and result in even greater final paste viscosity.

Other explanations also need consideration. Purely mechanical factors could contribute to the large increase in paste viscosity when starch is heated in gum dispersions. The addition of thickening gums would make the forces exerted on the granules in the shear field much larger than those encountered in starch-water suspensions. These increased forces should significantly affect granule breakdown and the amount of material exuded into the medium. If the gum was not completely dispersed when originally mixed with the starch, viscosity would be increased by improved solubilization of the gum during heating.

To achieve a more complete understanding of the interactions between wheat starch and gums during pasting and gelation, we compared changes that occur in granule structure and in the viscosity of the exudate (starch solubles) when wheat starch is pasted in xanthan, guar, and cellulose gum dispersions.

MATERIALS AND METHODS

Materials

Commercial Aytex wheat starch was supplied by Henkel Corp., Minneapolis, MN. Carbohydrate gums were commercial food grade samples: xanthan (Kelcof, lot KTL2321-75, Kelco Co., San Diego, CA), guar (Supercol U, lot A5228C, Henkel Corp., Minneapolis, MN), and cellulose gum (9H4F, lot 76126, Hercules, Inc., Wilmington, DE). Gum solutions were prepared by sprinkling the gum onto the sides of a water vortex. Stirring was continued at slow speed for 1 hr at room temperature. Viscosities were monitored during stirring to ensure complete hydration. Viscosities (measured by a cone-plate Wells-Brookfield microviscometer, model RVT, shear rate 3.84 sec⁻¹ at 25°C) of each gum at 0.25% concentrations were: xanthan, 128 cp; guar, 35 cp; and cellulose gum, 76 cp. The particular cellulose gum used exhibits shear thinning behavior (Anonymous 1976) and is sodium CMC, a chemically modified cellulose derivative, in contrast to xanthan and guar gums, which are native polysaccharides. The enzyme β-amyrase (α-1,4-glucan maltohydrolase, E.C. 3.2.1.2), obtained from Sigma Chemical Company, was a crude enzyme (type IIIB) from barley.

Pasting Curves

Pasting properties of wheat starch dispersed in prepared aqueous gum media were determined in both the Brabender Visco-Amylograph and the Corn Industry Viscometer. Starch-gum dispersions (6.4% starch db and 0.45% gum db) were prepared by pouring aqueous starch suspensions (1:2, w/v) directly into the gum solution while stirring. Starch granules were well dispersed in this manner. After 0.5 hr of stirring at room temperature, the starch-gum dispersion was placed in the amylograph bowl, heated to 30°C, and held at this temperature until the curve was flat. The dispersion was then heated to 94°C, kept at this temperature for 15

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min (cooking period), then cooled to room temperature. The rates of heating and cooling were 1.5°C/min. Gum solutions without starch were also run under the same amylograph conditions to establish a control viscosity curve and to determine whether the gums were completely dispersed before heating. Both guar and cellulose gum viscosities were depressed slightly (>10 BU variance) during heating but recovered upon cooling. The viscosity of xanthan solutions remained constant. Viscosities were: guar, 20 BU; CMC, 25 BU; and xanthan, 35 BU.

Similar wheat starch-gum dispersions pasted in the viscometer were heated for 30 min in a 94°C water bath. The maximum temperature of the dispersion was 93°C. A cooling curve was produced by exchanging the bath water with cold tap water. The paste was cooled to 22°C. The rate of cooling was not controlled.

**Iodine-Binding Capacity of the Solubles**

Starch-gum dispersions (2.0% db starch and 0.16% db gum) prepared as described for the amylograph studies were heated at 80°C for 30 min in a water bath. A starch-water mixture similarly heated served as a control. Solubles were isolated by centrifugation at 16,000 X g for 15 min, which precipitated the swollen granules. Aliquots containing 40–50 mg of solubilized amylose were potentiometrically titrated against iodine immediately upon isolation to avoid retrogradation. The method of Bates et al. (1943) with modification (Schoch 1957) was followed. Small amounts of iodine bound by the gums were subtracted from the assayed values to determine the iodine-binding capacity of the starch solubles by difference. The data, expressed in milligrams of bound iodine per gram of original starch, demonstrate differences in amounts of amylose released from starch at 80°C in the presence of gums.

**Rheology of Starch Solubles-Gum Complexes**

Solubles were collected from starch-gum dispersions (3–5% starch and 0.25% gum) that had been heated with stirring in a water bath at 80°C for 30 min. Viscosity measurements were made with the Wells-Brookfield microviscometer (4.7-mm cone diameter) at 25°C over a shear rate range of 1.9–384 sec⁻¹. Solubles obtained from starch alone (5%) heated at 94°C for 30 min served as a reference; solubles heated at 80°C for 30 min gave no appreciable viscosity increase. Viscosities of gum solutions (0.25%) were compared with viscosities obtained in the presence of starch solubles.

**Enzyme Digestion of Starch Solubles-Gum Complexes**

Starch-water suspensionsasted in a Corn Industry Viscometer for 30 min at 94°C were centrifuged at 16,000 X g for 30 min to remove insoluble starch. The resulting starch solubles were predominantly linear amylose. Gum solutions (1%) were added directly without further heating to aliquots of solubles to attain a gum concentration of 0.2%. Solubles diluted with a similar volume of water served as controls. β-amylase was added to starch solubles-gum mixtures and to controls at a rate-limiting concentration of 2.5 mg per 5 ml of substrate. Substrates were hydrolyzed for 30 and 60 min at 45°C in a water bath. Hydrolysis was terminated by addition of four drops of 10 N NaOH. Before the reducing sugar analysis, undigested material was removed by low-speed centrifugation (63 X g, 20 min).

Two preliminary studies established the conditions for this experiment. Because fractionated amylose retrogrades rapidly, rates of digestion were measured. The isolated starch solubles were digested with β-amylase after the substrate had stood either at room temperature or at 80°C in a water bath for 1 hr. At the end of that period, the rate and amount of maltose produced by the substrate held in the water bath showed little difference from zero time, but the effect of retrogradation on enzymic maltose production was significant for the substrate held at room temperature. Therefore, in the main experiment, digestion was conducted immediately upon isolation of solubles to avoid retrogradation.

The digestibility of the starch solubles-gum mixture in the presence of gums was also studied. Making the substrate viscous by addition of guar, xanthan, or cellulose gum at 0.2% concentrations did not alter the rate of hydrolysis. Therefore, these starch solubles-gum mixtures could also serve as controls.

To determine whether the gums would associate with the dispersed soluble amylose strongly enough to impede enzyme hydrolysis, starch solubles-gum mixtures were heated for 30 min in an 80°C water bath to initiate complexing. A control of starch solubles in water was heated under the same conditions. Both substrates were subjected to enzyme hydrolysis, and rate curves were run.

**RESULTS AND DISCUSSION**

**Pasting Properties of Starch-Gum Dispersions**

The effects of addition of polysaccharide gums (guar, xanthan, and CMC) on the viscosity of wheat starch dispersions during gelatinization are illustrated in Fig. 1. The viscosities contributed by the gums alone during the heat-cool cycle were subtracted from the original starch-gum amylograms to compare differences in the effect that each gum had on the paste viscosity. The viscosity curves were similar in shape during the first stage (55–70°C), but significant differences were evident at the second stage (80–94°C), during the 15-min cooking period, and finally during the cooling cycle.

Normally, wheat starch fails to show a measurable viscosity during the early stage of granule swelling, as seen in the control curve. However, Crossland and Favor (1948) demonstrated viscometric changes during the early stage by heating wheat starch in viscous media containing CMC or alginate gums. In our experiments, guar and xanthan functioned in a similar manner, but with little interaction occurring between the gums and starch during this initial stage.

Because the viscosity curves (Fig. 1) at the first solubility stage (55–70°C) were uniform in the presence of all three gums, the viscosity of the media after granules were removed was compared with the total viscosity to determine whether or not loss of media water into the granules had increased the gum concentration surrounding the granules. Only slight changes in media viscosity could be shown during this first heating period; hence, changes in the granule structure were the primary cause for the viscosity achieved at this stage.

In a study of wheat and corn starches, Sandstedt and Abbott (1964) found that the shape of normal swelling, solubility, and light transmission curves in aqueous suspensions correspond closely to the shape of amylogram curves of starch-DMC dispersions at this stage of gelatinization. They also could demonstrate the first stage of swelling with corn starch pasted with CMC, but not with waxy corn starch, which does not have two distinct stages of swelling. Recently Bean and Yamazaki (1978) showed that the rapid increase in granule diameter between 58 and 70°C (first-stage swelling of wheat stach) corresponds to the onset of viscosity produced in the wheat starch-CMC amylograph curve.

Although each gum produces similar viscosity changes at this early stage, differences in viscosities produced upon further heating
indicate that each gum interacts with starch differently. At 0.45% gum concentration, the highest peak viscosity is produced with guar, a viscosity almost tenfold greater than that of the control (Table I) and also greater than that obtained with xanthan or CMC at 0.45% concentration. Maximum peak viscosities (94°C) increased proportionally with increasing concentrations of xanthan in the dispersion. These increases in peak height can be directly related to an interaction of xanthan with starch at this temperature, because viscosity increases attributable to the increased gum concentration have been subtracted. On the other hand, peak heights at 70°C for the three gums at 0.45% concentration remain fairly constant. This further establishes that the gum media magnifies the viscosity increases due to changes in granule size or shape during swelling. Studies with guar and cellulose gum and their concentration relationship to paste viscosity are being continued.

When wheat starch is cooked in water, the cohesive forces within the swollen granule weaken, and the viscosity of the paste decreases as the integrity of the granule is lost. The resultant drop in viscosity is most evident in the guar-starch paste, which indicates possible granule breakdown. The viscosity is reduced by 140 BU in comparison with only 40–50 BU for the other gum-starch pastes. Starch pastes made with xanthan or cellulose gum tend to retain their viscosity during the cooking period (Fig. 1). In most cases, the mixture of swollen granules, granule fragments, and molecularly dispersed starch molecules exhibits a pronounced tendency to associate or retrograde when the pastes are cooled, resulting in an increase in viscosity. The “setback” patterns of guar and cellulose gums show a rapid rise in viscosity inconsistent with a much slower rise in the xanthan pattern. Further gelation studies are in progress to determine the significance of these “setback” patterns.

Studies with the Corn Industry Viscometer provide further information on the effect of gums during starch pasting. This viscometer provides both a different stirring apparatus (a scraper on the bottom and sides of the bowl) and a different heating method (a water bath vs radiated heat). Because pseudoplastic gum dispersions heat at a slower rate than aqueous dispersions and are subject to surface overheating in the absence of scrapers, this viscometer reduces the possibilities of overheating the media at the bowl surface. To evaluate superheating effects, these viscosgrams were compared with those obtained with the amylograph. Wheat starch pasted in the presence of gums in this viscometer showed similar patterns of earlier onset of viscosity (first stage) and a large increase in viscosity at the final stage (Fig. 2). The similarity of these results suggests that possible overheating in the amylograph is not a problem. However, if further studies on granule structure changes and starch dispersibility are undertaken, heat transfer in shear thinning mixtures should be considered. The starch-xanthan curve demonstrates that this more viscous media enables detection of the first stage of swelling, as shown by the earlier onset of viscosity. Although guar is at the same concentration as xanthan, the media viscosity is lower and an earlier onset cannot be detected. A specific media viscosity level is needed to demonstrate first-stage swelling. Within 20 min, the viscosity of the starch-gum paste increased fivefold above that obtained with the control. The peak heights were quite similar for both xanthan and guar when starch was dispersed at the same gum concentration although not at the same media viscosity.

### Iodine-Binding Capacity

Table II shows the amount of iodine bound to solubles isolated from starch-gum dispersions. The amount of iodine bound by starch solubles isolated from the control was much less than that obtained by analysis of purified wheat amylase. The lower value is the result of a smaller percentage of the total solubles being extracted from the granule at this temperature (Baldwin et al. 1944).

The shape of the solubles-gum iodine-binding curves (not shown) was typical of standard amylase curves, provided that calculations were made using an electromotive force calibration curve containing the same gum concentration. The shape of the curves of solubles isolated at temperatures lower than 80°C varied, making extrapolation of doubtful significance. The capacity of these solubles-gum mixtures to bind iodine was similar to that of the control solubles, indicating little interference of the gums with

<table>
<thead>
<tr>
<th>Gum</th>
<th>Gum Concentration (%)</th>
<th>Temperature of Initial Viscosity Increase (°C)</th>
<th>Peak Height, BU 70°C</th>
<th>Peak Height, BU 94°C</th>
<th>15-Min Hold</th>
<th>Cooling to 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>83</td>
<td>0</td>
<td>60</td>
<td>40</td>
<td>140</td>
</tr>
<tr>
<td>Xanthan</td>
<td>0.04</td>
<td>72</td>
<td>10</td>
<td>260</td>
<td>240</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>53</td>
<td>110</td>
<td>340</td>
<td>300</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>0.93</td>
<td>54</td>
<td>310</td>
<td>760</td>
<td>750</td>
<td>650</td>
</tr>
<tr>
<td>Cellulose gum*</td>
<td>0.45</td>
<td>54</td>
<td>110</td>
<td>440</td>
<td>400</td>
<td>650</td>
</tr>
<tr>
<td>Guar</td>
<td>0.45</td>
<td>54</td>
<td>110</td>
<td>560</td>
<td>420</td>
<td>560</td>
</tr>
</tbody>
</table>

*The viscosity contributed by the gum itself is subtracted from the original amylogram curve.

**TABLE II**

Iodine-Binding Capacity of Starch Solubles Isolated from Heated Gum Dispersions

<table>
<thead>
<tr>
<th>Wheat Starch</th>
<th>Iodine Binding Capacitya</th>
<th>Bound Iodineb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubles (control)</td>
<td>14.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Solubles with Xanthan</td>
<td>14.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Guar</td>
<td>ND*</td>
<td>9.0</td>
</tr>
<tr>
<td>Cellulose gum</td>
<td>15.9</td>
<td>9.6</td>
</tr>
<tr>
<td>Wheat amylase</td>
<td>19.9*</td>
<td>...</td>
</tr>
</tbody>
</table>

*aAverages of duplicate analysis prepared on three separate occasions.

*bIn milligrams per gram of starch. Calculated from original starch in dispersion. Aliquots of solubles titrated directly with iodine after granules were removed by centrifugation.

*Not determined.

*Value for purified linear amylase from wheat starch (Schoch 1957).
absorption of iodine. We anticipated that the more hydrophobic inner ring of the helix would inhibit hydrophilic gums from displacing iodine, as demonstrated with fatty acids (Osman et al. 1961). However, more iodine was bound to solubles isolated from starch-gum mixtures than to solubles from the control, when calculated on the basis of original starch. The observations reported here require further study. The most obvious conclusion, which is speculative, is that shearing of the granules in these viscous media releases more soluble starch, including branched molecules.

**Rheology of Starch Solubles-Gum Mixtures**

Starch solubles were collected by centrifugation after starch-gum dispersions were heated in a water bath at 80°C for 30 min. The viscosity of the isolated solubles-gum supernatants after cooling to room temperature was measured at various shear rates as shown in Fig. 3. Associations that form with xanthan and guar and solubles when starch is heated in 0.25% gum solutions do not dissociate upon cooling, as evidenced by the synergistic viscosity increase displayed by the isolated solubles-gum supernatants. When larger quantities of starch (5%) were heated in the same gum solution, more solubles were released from the starch. This added amount of solubles in the supernatant (0.6% with guar and 1.0% with xanthan) increased the supernatant viscosity even more and established that the gums do form stable associations with the solubles (Table III). The solubles obtained from cellulose-gum-starch paste showed no increase in viscosity, indicating dissociation at room temperature. However, cellulose gum associations could possible be isolated at higher temperatures. The viscosity increases observed during pasting (Fig. 1) correlate with the increase of media viscosity. However, their contribution is only of minor significance. Other factors, including granule swelling, contributed to the final paste viscosity.

The rheological behavior of the guar-solubles association and the xanthan-solubles association maintains the shear thinning behavior of the original gum solution. Unassociated gum in the media would influence this thinning capacity. However, the guar-solubles association does show some resistance to shear thinning at the low shear rates.

The starch-guar dispersion showed the highest peak height at 94°C (Table II), which can be partially accounted for by resistance of the complex to shear in the amylograph. The lowest peak height of the starch-xanthan paste could also reflect the shear-thinning behavior of the complex.

Viscosity differences in the cooling curves are also influenced by the rheological behavior of these associations. Their stability during cooling and aging is significant for the development of gel structure, especially with respect to changes in water and amylose organization. Gelation studies are being continued.

**Enzyme Digestion of Starch-Gum Complexes**

Further evidence for the interaction of hydrocolloid gums with soluble dispersed starch can be shown by preparing complexes and determining the efficiency of amylolytic hydrolysis with β-amylase. When starch-solubles-gum mixtures were reheated, both xanthan and guar formed associations with soluble amylose strong enough to inhibit the amylolytic digestion (Table IV). The extent of inhibition varied with each gum. The association formed with cellulose gum is must dissociate during digestion because mallow production proceeded basically at the same rate as that of amylose solubles alone.

**SUMMARY**

Viscosity of wheat starch pastes was significantly increased by the addition of a small amount of polysaccharide gums. At the initial stage of gelatinization, gums and their inherent viscosity magnified the effect of swelling so that viscosity increases were apparent in the curves of both the Brabender Amylograph and Corn Industry Viscometer. Some evidence for the formation of soluble starch-gum associations that contribute to the viscosity buildup during the second stage of gelatinization is presented in this article. This preliminary evidence for stable, isolatable soluble starch-gum associations does not preclude other explanations, especially the mechanical effect on the swollen granules and their disruption due to shear forces.

Amylose solubles isolated from starch pastes prepared in water readily associated with the gums by reheating. The associations of the amylose with guar or xanthan reduced the rate of amylolytic digestion of the solubles. The stability of guar and xanthan association suggests differences in rates of starch retrogradation and changes in the physical properties of the resultant gels. Further study of the rate of formation and its effect on gel formation is in progress. These studies encourage further investigation of the interaction of other hydrocolloids with starch during pasting and gelation as a possible means to improve stabilization of starchy types of foods.

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![Fig. 3. Viscosity (25°C) of starch-gum solubles vs speed (rpm) at various soluble concentrations (w/v). Solubles were obtained from 3 or 5% wheat starch pastes heated at 80°C for 30 min in 0.25% gum dispersions. Soluble mix concentration is 1% isolated from starch paste heated to 94°C. A, guar; B, xanthan.](image-url)
ACKNOWLEDGMENTS
We wish to thank Allene Jeanes for her advice and encouragement, Harold Nielsen for technical assistance in the iodine binding studies, and J. Pittsley for assistance in the rheology studies.

LITERATURE CITED

[Received January 27, 1981. Accepted May 18, 1981]