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CORRELATION OF MICROSCOPIC STRUCTURE OF CORN STARCH GRANULES WITH RHEOLOGICAL PROPERTIES OF COOKED PASTES

D. D. Christianson, F. L. Baker, A. R. Loffredo, and E. B. Bagley
Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604

Abstract

The progressive geometric changes that occur in swelling of corn starch granules during heating throughout the range of gelatinization (63-72°C) and at higher temperatures when substantial amounts of soluble starch are released from the granule were observed by scanning electron microscopy (SEM). Corn starch granules begin to swell radially, then undergo radial contraction and random tangential expansion. They form complex geometrical structures at the midpoint range (67-70°C) unlike the more uniform single-dimensional tangential swelling that occurs with lenticular granules of wheat starch. At higher temperatures, when starch begins to solubilize, corn starch granules lose their distinct ridges and appear to melt into thin flat disks. These progressive configurational changes are reflected in the rheological properties of more concentrated starch dispersions cooked for 75 minutes. At the early stages of gelatinization (63-65°C) the granules are relatively rigid and at high enough concentration show dilatant behavior (viscosity increasing with shear rate). At these temperatures, granules remain rigid and maintain their birefringence but are mechanically sheared by stirring during cooking. Once the granules undergo extensive swelling, develop ridges, and lose their birefringence (67-70°C), they are soft enough to exhibit shear thinning behavior (viscosity decreasing with shear rate). The extent of shear thinning depends on concentration, because viscosity and shear stress increase with concentration and the granules become more susceptible to deformation. At high enough concentrations (and associated stresses), the ridges are not as clearly defined as they are at lower concentrations. Granules become more flat and flexible when cooked above 75°C.

Introduction

A major use of processed starch is to give body or thickness to foods where starch is used in relatively low concentrations. Paste viscosity, fluidity, and other physical properties of starch pastes are of major importance in establishing proper food texture and quality. Trends in food product development continue to demand better understanding of the role of starch in foods especially in bakery and snack food application where the starch is used in higher concentration and the water becomes limiting. How the crystalline-amorphous phase transitions and the resultant granule morphology changes that occur during gelatinization affect the development of viscosity and other rheological properties of starch is of particular interest. Sterling (1978) has reviewed several aspects of the textural qualities and molecular structure of starch products.

Although uni-dimensional measurement of granule diameter can demonstrate the swelling of granules during heating (Bean and Yamazaki, 1978), SEM has the advantage over light microscopy in that a greater depth of field can be achieved, which allows observation of geometrical changes in structure and allows closer correlation of structure with properties. Scanning Electron Microscopy (SEM) has been used effectively for the study of the complex geometrical changes that occur in wheat starch granules when dilute suspensions are heated (Bowler et al., 1980).

Starch solubility and the swelling factor (SF) have been correlated with viscosity data (Hoover and Hadziyev, 1981). The exudate (primarily unbranched amylose chains) forms a network that connects the individual granules, thereby increasing viscosity. Hoover and Hadziyev's work is in agreement with earlier work by Miller and co-workers (1973) where they attributed final wheat starch paste viscosity to exudate entanglements with swollen granules. Amylose leaching in potato starch is more extensive at earlier temperatures. Thus viscosity can be more closely correlated with starch solubilization than with the swelling of the granules. Bagley and Christianson (1982) found that in wheat starch the swelling factor can be directly related to viscosity development up to the point where the amount of exudate exceeds 5%
measurements using a Differential Scanning Calorimeter (Donovan, 1979). Although much microscopic information has been obtained on gelatinization and viscosity development of starch pastes, most studies have been carried out using relatively dilute dispersions. In many practical applications, however, starch is used in concentrated dispersions where water becomes limiting and granule morphology contributes to the rheological behavior of batters and doughs. Little attention has been paid to the effect of concentration on extent of swelling and softening of the granule which should affect flow characteristics. In processing starch dispersions, considerable mechanical work is done on the samples. The effect of such work also needs investigation.

This preliminary work was undertaken as part of a study of the whole concentration range from thickeners to doughs to determine what information could be obtained by examining starch granules swollen to different extents and subjected to a range of shearing stresses controlled by the dispersion concentration level. Starch dispersions were cooked in a range of 65-80°C. We were particularly interested in whether the swollen granules were changed in shape or appearance by the shearing stresses applied to them.

**Experimental**

A Globe Pearl Corn Starch 3005 from CPC International was dispersed in distilled water at room temperature and slowly stirred for 10 minutes to ensure absorption equilibrium. Corn starch dispersions prepared at various concentrations (5 to 26%) were heated in a Corn Industries Viscometer (CIV) in the range of 65-85°C. The cooking viscometer was used to shear the granules and to demonstrate effect of mechanical work on the granules. Concentrations were calculated as grams of dry starch per gram of dispersion. Samples were removed from the CIV for viscosity determinations and microscopic examination after the sample had been cooked for 75 minutes at the designated temperature.

Viscosities of the cooked pastes were determined using a Haake Rotovisco viscometer. Samples were run at 60°C and at 23°C after cooling for 2 hours. Flow curves were measured at shear rates from 1 to 500 s⁻¹. All data were obtained using a MV cup (ID 4.201 cm) and MV-II bob (diameter 3.680 cm; length 6.004 cm).

The amount of water absorbed by the granules at various temperatures was separately determined by cooking dilute dispersions (2-5%) in the CIV for 30 and 75 minutes at a specific temperature and measuring the weight of swollen granules after filtering the hot paste. The filtration was carried out using an aspirator and #54 hardened Whatman filter paper. Q (grams of swollen starch per gram of dry starch) found by this procedure is similar to the swelling factor (SF) obtained by centrifuging swollen starch granules and measuring swollen granule weight after decanting supernatant (Leach et al., 1959). Results were reproducible to 5%. Doublier (1981) has shown that preparation method can affect Q values of wheat starch. Our filtration method rather than centrifugation used by Leach appears interchangeable because our results are in harmony with his. The amount of exudate leached from the granules was also determined by measuring the dry solids content of the clear filtrate. Granules remaining on the filter pads were prepared for microscopic examination by methods described below to assess the progressive changes in granule morphology that occur throughout the gelatinization range. These observations served as a reference in the evaluation of granules isolated from pastes cooked at higher concentrations.

Granules to be viewed microscopically were slurried in water (room temperature) and centrifugated at low speed (800 x g, 2 minutes) on a bench-top centrifuge. Pastes were washed several times to remove minor amounts of exudate. The washed granules were resuspended and placed in round-bottom flasks and immersed in an ethanol-dry ice bath. A thin layer of starch was coated on the inside of the flask by swirling in the bath. This layer was then freeze-dried. Methods of freeze fixation and drying of the granules must be evaluated critically to avoid possible artifacts. Studies (Berghofer and Klaushofer, 1976) show that granules prepared by freezing in ethanol-dry ice bath and then drying by lyophilization, as we have adapted for this study, was the preferred method of preparation. Granules isolated from cooked pastes and critical-point dried from ethanol showed no difference in morphological structure than granules prepared by freezing in ethanol-dry ice and lyophilization. Hoover and Hadziyev (1981) prefer using liquid nitrogen as a freeze-fixation method to prevent retrogradation of exudated amylose during drying procedures. These workers can demonstrate that without this precaution retrograded amylose chains from potato starch pastes realign and form a film on the starch granules. The exudate obtained in our corn starch pastes has been removed by washing the granules prior to freeze fixation. Therefore, all granules examined in the SEM in our studies are devoid of exudated amylose even after the paste is cooked at 80°C for 75 minutes.

Dried granules were sprinkled sparsely on specimen support stubs covered with double sticking tape and coated with a layer of gold-palladium (60-40%) 200-300 Å thick. The granules were examined with a Cambridge Steroscan Mark II A scanning electron microscope.

**Results and Discussion**

Initial SEM studies were carried out on the original, uncooked starch and on starch dispersions cooked at low concentrations (5%) for only 15 minutes. This low starch concentration results in low viscosity at short cooking time and minimizes the shear stress placed on the granule during cooking. The
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conditions for granule isolation and preparation for microscopic examination are quite similar to those used earlier for wheat starch (Bowler et al., 1980). Therefore, a comparison can be made.

Raw corn starch granules appear basically spherical, with some granules having faceted sides (Fig. 1A). It is difficult to make interpretations on changes in radial swelling of these granules. Fig. 1B shows granules cooked at 65°C for 15 minutes. For example swelling measurements by filtration of this sample (Fig. 1B) give a swelling Q value of about 3.5, which would correspond to an average diameter change of 50% for spherical particles; yet very little swelling can be seen when these granules are compared to the original granules. At 67°C, swelling continues producing thick ridges (about 3.5 μm) (Fig. 1C and 1D). These ridges become thinner (less than 2 μm) and more numerous, making the granules more complex geometrically at 70°C (Fig. 2A and 2B). The size of the swollen granules is greatly increased at 70°C as compared to 67°C. These granules have been heated to the midpoint of the gelatinization range where most of the granules have lost their birefringence. These progressive shape changes can also be detected in the light microscope using Normanski shadowing even before the granules are freeze dried and, therefore, can not be considered artifacts of freeze drying.

Sterling (1978) has postulated that the molecular structure of the branched and unbranched components is responsible for this radial contraction and tangential expansion. In agreement with his views, it appears that different portions of the granule swell differently depending on the molecular ordering of the starch within the granules. The amorphous regions swell and expand at 67°C. The thick ridges showed birefringence under polarized light which could be due either to unswollen starch or starch in a state of strain. At 70°C, swelling of the more ordered regions occurs, along with the progressive loss of birefringence. At this temperature, the ridges are thinner and indentations are shallower. At 70°C, about 10% of the starch has been solubilized, leaving the more compacted amylopectin as the granule's major structural component. Thus the collapsed regions could result from loss of solubilized amylose. When the ridges are observed under a polarizing light microscope, residual birefringence is seen on the edges of the ridges. Such birefringence can be generated even in an initially isotropic polymer by the diffusion process of solvent entering or leaving the polymer in the sample (Drechsel et al., 1953).

As the cooking temperature is raised to 75°C, the granules develop more ridges (Figs. 2C and 2D). At 80°C, the granules appear to go through a transition of melting or softening.
During this transition, the birefringence or crystallinity of the granule is completely lost and the low molecular weight starch begins to solubilize rapidly (Fig. 4). The granules cooked at 85°C, from which about 20% of the starch has been removed by solubilization, appear smooth and more fluid than the granules cooked at 80°C.

The structural changes observed in corn starch granules are unlike the structural changes that occur with wheat starch granules. At a comparable stage of gelatinization, swelling of lenticular wheat starch granules is maximized in a single direction tangentially; thus, the granules form a flat disk which later folds and refolds until a complex puckered structure is developed between 80 and 90°C (Bowler et al., 1980). On the other hand, corn starch granules swell in an irregular fashion and develop similar looking structures at a much lower temperature (67°C). The equatorial groove present in wheat starch granules remains visually evident along the edges of the deformed granule even at 97°C. It is this groove that apparently influences the progressive changes that occur in wheat starch during gelatinization. Corn starch granules lack any detectable groove, which probably accounts for the different swelling patterns of corn starch seen throughout the gelatinization range. It is apparent from these results that the molecular organization of amylase and amylopectin in corn starch granules differs from that of wheat starch granules. The ridges produced in these granules during heating can be correlated with the ultrastructure of corn starch as proposed by Nikuni (1978).

Before studying the effect of starch concentration on the changes in granule morphology, the extent of swelling (Q, grams swollen starch per gram dry starch) and the extent of starch solubilization were determined. As shown in Fig. 4, corn starch granules swell progressively throughout the range of temperatures studied. Cooking time has no significant effect on the extent of swelling. Swelling equilibrium at each temperature is reached within a short cooking period. Results shown at 30 minute and 75 minute cooks are comparable even though the viscosity data for these cook times are quite different. This is not surprising, since Miller et al. (1973) have noted that "maximum viscosity of a wheat starch suspension heated in an excess of water occurs after most of the granule swelling..."
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Corn starch granules isolated from a 5% dispersion cooked for 15 minutes at 80°C (A) and at 85°C (Band C).

Our results are thus in harmony with this observation. The extent of starch solubilization is doubled from 65 to 69°C (from 5 to 10%) but then levels off at the midpoint range of gelatinization. Once the birefringence is lost (between 70 and 75°C), the amount of solubilized starch production is again doubled over the temperature range of 75 to 85°C.

When corn starch samples are cooked at different concentrations, temperatures, and times, two types of rheological behavior can be observed in the Haake rotational viscometer (Fig. 5). In some cases, the flow curve (viscosity versus shear rate) is typical of shear thinning fluids, where the viscosity decreases with increasing shear rate. Such curves may show a Newtonian region (constant viscosity) at low shear rates. In other samples, dilatant flow may occur, in which the viscosity, in a certain shear rate range, may increase with shear rate.

Dilatant flow occurs when the granules are relatively close packed but too rigid to deform under the stresses applied. The transition from dilatant behavior to shear thinning behavior can occur either with a temperature increase high enough to soften the granules so they are deformed in a shear field or with a concentration high enough so that the stresses imposed on the granules have increased to the stage where they can deform and flow. The large amount of stress applied under these conditions causes the granules to deform in a sinusoidal fashion giving a typical non-Newtonian shear-thinning curve where viscosity decreases with increasing shear rate (Bueche, 1962). The classification of a particle as "rigid" is thus comparative. At a given degree of swelling, the granules may be effectively rigid under low stress while deformed at higher stress levels. The transition will depend on the extent of swelling and degree of plasticization of the granule. Although not detailed in this study, the amount of ordered material in the granules as measured by birefringence clearly plays a significant role in the rheological transitions that occur at various concentrations and temperatures. The majority of the granules must undergo the configurational changes shown in Figure 2C with concurrent loss of birefringence in order for the paste to become shear thinning at any concentration or temperature. Figure 5 illustrates changes in flow behavior of starch dispersions cooked at various concentrations and temperatures; Curve A shows shear thinning behavior; Curve B, dilatant; and Curve C, Newtonian behavior. As shown in Figure 5, a 6% dispersion cooked at 80°C for 75 minutes remains Newtonian up to approximately 100 s⁻¹ (Curve C). Yet a 10% dispersion cooked at 75°C for 75 minutes has excellent shear thinning behavior (Curve A). The wide difference in viscosities of the two pastes plays a significant role in the amount of mechanical stress applied to the granules to deform them. The 10% dispersion cooked at 75°C has a paste viscosity tenfold greater at a shear rate of 10 s⁻¹. Thus the granules in the thicker paste deform under the stress and show shear thinning behavior. Curve B
Fig. 4. Grams swollen starch per gram dry starch (Q) obtained at various temperatures; cooked at 30 minutes △ and at 75 minutes ◊; and grams soluble starch per gram dry starch ○ obtained at various temperatures cooked at 15 minutes.

Fig. 5. Viscosity (cp) vs. shear rate (s⁻¹) for corn starch dispersions cooked at various temperatures and concentrations measured in the Rotovisco at 60°C. A, shear thinning behavior of a 10% dispersion cooked at 75°C for 75 minutes; B, dilatant behavior of a 11% dispersion cooked at 67°C for 75 minutes, and C, Newtonian behavior of a 6% dispersion cooked at 80°C for 75 minutes.

Fig. 6. Corn starch granules isolated from 19% (A) and 26% (B) dispersions cooked at 65°C for 75 minutes and 11% (C) and 16% (D) dispersions cooked at 67°C for 75 minutes. Viscosities of pastes (60°C) at 59 s⁻¹, 87 cps, 8100 cps, 150 cps, and 7500 cps respectively. Rheological behavior: dilatant, shear thinning, dilatant, and shear thinning, respectively.
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Corn starch granules isolated from 10% (A&B) dispersions cooked at 75°C for 75 minutes; from 6% (C&D) and 10% (E&F) dispersions cooked at 80°C for 75 minutes. Viscosities of pastes (60°C) at 59 s⁻¹: 3000 cps, 100 cps and 3500 cps, respectively. Rheological behavior: shear thinning, Newtonian, and shear thinning, respectively.

Fig. 7. Corn starch granules isolated from 10% (A&B) dispersions cooked at 75°C for 75 minutes; from 6% (C&D) and 10% (E&F) dispersions cooked at 80°C for 75 minutes. Viscosities of pastes (60°C) at 59 s⁻¹: 3000 cps, 100 cps and 3500 cps, respectively. Rheological behavior: shear thinning, Newtonian, and shear thinning, respectively.

shows the dilatancy observed with an 11% dispersion cooked at 67°C for 75 minutes. The granules here do not deform at the shear stresses applied but close-pack to increase the viscosity as shear rate increases.

The effect of starch concentration on granule structure that develops during cooking at 65°C and 67°C is illustrated in Figure 6. Figure 6A shows granules from a 19% dispersion cooked at 65°C for 75 minutes and Figure 6B shows granules from a 26% dispersion cooked at 65°C for 75 minutes. At the lower concentration, swelling of some granules is evident; yet the granules remain rigid and show dilatant behavior. Shearing forces (87 cps) are minimal and leave the granules unaffected. At the higher concentration where shear forces (8100 cps) are much greater, the granules undergo deformation. The mechanical stresses applied during stirring are great enough to soften the granules, and the paste becomes shear thinning. The work imposed on the granules dispersed at higher concentration is apparently the only factor that influences the shear thinning behavior at this temperature.

Even at the higher cooking temperature, 67°C, there is still enough particle rigidity to show dilatant behavior when the shear stresses are low (11% concentration) (Fig. 6C). The granules show only slight loss of birefringence at 11%, quite different from the almost complete loss observed at 5%. Also, these granules isolated from both the 5% and 11% cooked dispersion show ridging. In contrast, granules isolated from a 16% dispersion cooked at 67°C for 75 minutes are more geometrical or angular and exhibit more complicated ridging (Fig. 6D). Under these shearing stresses (viscosity, 7500 cps at 59 s⁻¹) the granules undergo softening, lose birefringence, and exhibit shear thinning behavior. Again, the transition to shear thinning can be accomplished by increasing the concentration and thus the shear stress applied during cooking. Granules show ridges at this midpoint temperature of gelatinization somewhat similar to those shown at lower concentrations in Figure 1B and 1D.

At temperatures of 75°C and 80°C, which are above the gelatinization range (62-70°C), granule structure is basically influenced by mechanical
stresses incurred by stirring during the cooking period. The swelling and viscosity equilibria are achieved within a short cooking time therefore differences in morphology at short cook (15 minutes) in Figure 2C and D and long cook (75 minutes) in Figure 7A and B can be attributed to the increased mechanical stress applied to the granule. As seen at the low concentrations (5%), granules cooked at 75°C for 15 minutes develop distinctive and numerous ridges (Fig. 2C and D). If more mechanical stress is applied to the granules by increasing the concentration and lengthening the cooking (with stirring) period to 75 minutes, granules "melt" and deform into structures quite differently than would be anticipated from the low concentration results (Fig. 7A and B, 10% dispersion). In fact, granule structures now look like those obtained at low concentration cooked at 85°C for 15 minutes. Granules isolated from a dispersion cooked at 80°C for 75 minutes have lost their shape completely and now become flat, very flexible disks (Fig. 7C and D). At 6% concentration, the disk-shaped granules are more independent of each other (Fig. 7C and D), whereas at 10% concentration the granules are more fused and adhere to one another (Fig. 7E and F). The residual granule is basically composed of amylopectin, and almost 20% of the granule weight is leached out of the granule during cooking at this temperature. Under our procedures of granule isolation the exudated amylose is removed from the cooked dispersion by washing the residue with water, so it is not observed in the micrograph.

Summary
Corn starch granules heated in the temperature range 65-85°C at various concentrations have been examined microscopically. At 5% concentration and short cook time (15 minutes), granules proceed through a series of progressive morphological changes during heating. These progressive changes differ from those observed in the lenticular granules of wheat starch, indicating differences in the molecular organization of amylose and amylopectin chains within the granule. Granules swell radially at 65°C and retain their original structure. The ridges of the faceted raw corn starch granule become more pronounced at 67°C (midway through the gelatinization stage). At 70°C the granules take on a more angular structure that at higher temperatures melt into thin flat disks once the starch begins to solubilize. Viscometric data were also available for these dispersions. In particular, it was of concern to examine the effect of higher stresses (which occur at high concentration during stirring) on granule morphology. These progressive configuration changes are reflected in the rheological properties of more concentrated starch dispersions. Degree of swelling, extent of loss of birefringence, and the amount of shear stress placed on the granule during extended cooking periods contributes to the rheological properties of the dispersion. At 65°C, where the granules swell but retain their birefringence, they remain relatively rigid and can show dilatant behavior. Although the granules may be effectively rigid under low stress, they become deformable and shear thinning at higher stress levels, that is, when the viscosity of the cooked dispersion is higher. Once the granules begin to lose their birefringence (67-70°C), the granule softens so that even at low dispersion concentration the granules do not closely pack (dilatant) but can undergo sinusoidal deformation giving a typical non-Newtonian shear-thinning curve. At higher temperatures beyond the gelatinization range (above 75°C), the high mechanical stresses (work) imposed on the granules in viscous dispersions cooked for 75 minutes make the granules more fluid, and they "melt" into thin flat disks that adhere to one another.

The methods developed in this study show that shear stresses affect granule morphology. Information is also provided on the relationship of the changes in granule structure during pasting to the rheological properties of the cooked paste.

Acknowledgement
The advice and encouragement of Dr. U. Khoo is gratefully acknowledged, especially her help in interpretation of the relationship of the birefringence to the softening of the granule during pasting.

References
Bowler, P., Williams, M. R., Angold, R. E., A hypothesis for the morphological changes which occur on heating lenticular wheat starch in water. Starke 32(6), 1980, 186-189.
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Discussion With The Reviewers

M. A. Christman: Could you give more detailed description of the corn industries viscometer?

Authors: The Corn Industries Viscometer (CIV) is primarily used as a quality control instrument, similar to the Amylograph, to provide a measure of viscosity of flours and starch during gelatinization. We used this instrument as a mixer in preference to the Amylograph because the CIV has bottom and side scrapers that mix the paste more efficiently than the amylograph especially in dispersions that are shear thinning. We are using the instrument at concentration levels for which it was not designed and are limited to about 23% due to the large torques developed and problems in temperature equilibration.

J. G. Oles: Large amounts of starch are processed at short holding times (5-10 minutes) and swelling is strongly dependent on concentration. Please comment on the effect of these variables.

Authors: We agree and this is precisely why the present work was undertaken. A fundamental understanding of the effect of time, temperature, concentration and processing will be of both practical and scientific interest and more work in this area is needed.

J. G. Oles: Many commercial processes used high temperatures (80°C-115°C) and shorter cook times. Understanding of product microstructure and physical properties would be valuable.

Authors: Again we agree and note that some workers (Evans and Haisman, 1979; and Doublier, 1981) start at the higher temperatures. Our approach differs in that we are trying to understand what occurs solely as a result of granule swelling without the added complication of solubilization of a large part of the starch. Nevertheless, both approaches are needed and again more extensive, detailed and basic investigations will yield valuable information.

M. V. Taranto: In working with wheat starch pastes at high concentrations, Doublier (Starke, 33(12), 415-420, 1981) indicates that a yield stress can be detected and measured. Did you find a yield stress for corn starch pastes at high concentrations? He also points out that the heating rate and speed of rotation used to prepare starch pastes alter their flow properties. A) Would you please give more details on the condition you used to prepare your starch pastes? B) Did you run any experiments to evaluate the effect of the preparation procedure on the morphology of the granules and flow behavior of the final paste?

Authors: In the work of Doublier, as well as the related work of Evans and Haisman (1979) the starch pastes were prepared at higher temperatures than we used. Nevertheless, Evans and Haisman as well as Doublier found yield stresses. Our investigations of yield stresses in wheat starch dispersions have been reported at the Starch Conference at Detmold (April, 1982) and we are in general agreement with both Doublier and Evans and Haisman. We also find yield stresses in corn starch dispersions but there are differences from wheat starch that require further investigation. The results reported by Doublier on effect of heating rate and speed of rotation on the flow properties of his dispersions is not unexpected. Solubilization and effect of shearing on the granules could be even more significant at the higher sample preparation temperatures employed by Doublier than in our work. Our work certainly is in harmony with that of Doublier and reinforces the need for more detailed understanding of variables such as time, temperature, concentration, work input, work input rate on properties of starch dispersions. (See, for example Bloksma, J. Texture Studies 10 261-269, 1980, "Effect of Heating Rate on Viscosity of Wheat Flour Doughs;" Odighoh and Mohsenin, J. Texture Studies 5 441-457, 1975, "Effects of Concentration on the Viscosity Profile of Cassava Starch Pastes During the Cooking-Cooling Process;" Skeggs and Kineeswood, Cereal Chemistry, 58(4), 256-260, 1981, "Mechanical Dough Development-Pilot Scale Studies.") Please also see answer to Dr. Christman.

R. Moss: Is the difference in birefringence between 5% and 11% dispersion at 67°C solely due to lack of water in the 11% dispersion?

Authors: No. Neither concentrations are water limited. The difference we feel is due to the stresses imposed on the granule during flow and hope more work on this subject will be undertaken by others.

R. Moss: Do the authors feel that the washing procedure associated with the preparation of the starch granules for microscopy would alter granule morphology due to leaching of amylose, particularly from those granules that may have been damaged by stirring during heating?

Authors: We do not know what effect granule damage has on the release and solubilization of amylose or other components of the starch granule. We have not investigated this at all.

Reviewer IV: In comparing Figures 2C and 2D with Figures 7A and 7B, both cooked at 75°C but at 15 and 75 minutes respectively, both concentration and cook times are varied. Can we separate the effects of time and concentration?

Authors: At 75°C, swelling is rapid and equilibrium viscosities are essentially achieved within 15 minutes. Thus, the differences are due to the amount of stress imposed on the granules during the longer cooking time and higher concentrations at which the viscosity, and hence, the applied stresses, are higher.
M. Wootton: Would you comment further on the differences in the molecular organization of amyllose and amyllopectin between corn starch and wheat starch granules?

Authors: The differences between corn and wheat certainly show up in the swelling configuration and ridging. While the gross rheological property of viscosity depends on the volume fraction of the swollen granule, the detailed response—i.e., the extent and type of deformations imposed on the granule during shear—would certainly be expected to be different for the two granule types. The single ridge or groove in wheat starch controls the changes in granule shape during heating (Bowler et. al., 1980). However, the corn starch granule lacks this groove which changes the shape of the swelling granule in quite a different way. We have found the paper by Nikuni (1978) useful in understanding the effects of amyllose and amyllopectin in this regard.

R. C. Hosney: Ordered material can produce birefringence even when it is not crystalline. Authors: We agree completely and considerable care should be exercised when interpreting birefringence.

R. C. Hosney: How can we be sure that the swollen granules did not collapse during the drying step in SEM sample preparation?

Authors: While this is always a concern in the interpretation of SEM micrographs, our view for this study is that each sample was treated in the same way. We are looking, then, at differences in samples associated with changes in sample treatment. Consequently, we can say with certainty that, for example, the higher stress levels at the higher concentrations deform the granules. Whether the actual shape or morphology is the same in the dried sample as in the original wet sample is not really pertinent in this work. Further, although not shown, we have looked at the granules in the original dispersions by optical microscopy. These direct observations tend to confirm that the SEM photomicrographs correctly demonstrate the particle structure. However, more detailed study would be worthwhile.

E. A. Davis: Would you expect to see granule integrity when it melts? Does it act as a non-miscible fluid at high temperature?

Authors: At the temperatures we investigated the granule certainly maintains its integrity but as the birefringence disappears the granules become more deformable. The extent to which the particles deform depends on the viscosity level, which determines the shear stresses applied to the granules. These stress levels depend on concentration. In our earlier work on viscosity of these suspensions, we showed that the viscosity depended only on the volume fraction occupied by the swollen granules in the suspension and behave as expected for non-miscible fluids. Certainly, stress levels and temperatures can be reached at which the granules will be torn apart and solubilized. An extreme case is the jet cooker in which the starch is essentially completely solubilized and the starch and water are completely miscible.

E. M. Snyder: There are two large, distinct applications of starch in foods. One is as a thickener where starch is used in relatively low concentrations. The other is bakery products and snack foods. The similarity of the bakery and snack food applications lies in the fact that both are based on very limited water systems (anywhere from 25% to 50% water), and there is not enough water present in either for the starch to hydrate and swell and, in some cases, a large proportion of the product may contain ungelatinized starch. These systems produce what may be considered as a rigid foam and cannot be compared to a system in which starch is pasted. Since the authors refer to paste viscosity, fluidity and other properties of starch pastes, I presume that they are confining their study to the first system where starch is used as a thickener, but they confuse gelatinization of starch with pasting, and never clarify that there is a distinct difference.

Gelatinization is what takes place in an excess of water over an 8–10°C temperature range, reflecting the heterogeneity of the molecular bonding forces from granule to granule within any single species... The hydrated granules do not form a paste until most of the granules have gelatinized (about 69–70°C for corn starch), and this paste does not develop any viscosity until several degrees above that point. Peak viscosity, as measured by a Brabender Amylograph occurs between 89°C and 95°C for corn starch, depending upon concentration. [See Kite, F. E., et al., "Granule Swelling and Paste Viscosity of Thick-Boiling Starches," Bakers Digest, August 1957, and Mazurs, E. C., et al., "Graphical Analysis of the Brabender Viscosity Curves of Various Starches," Cereal Chem. 34(3), 141–152, (1957)].

Yet in the abstract, we find the statement: "At the early stages of gelatinization (63°–65°C) the granules show dilatant behavior (viscosity increasing with shear rate)." Yet in the abstract, corn starch at any concentration has zero viscosity, as not enough of the granules have gelatinized to form a paste. The authors continue: "At these temperatures, granules...maintain their birefringence but are mechanically sheared." ... What evidence is there that they are mechanically sheared? Before a paste can be sheared, a paste must form; granular starch does not shear at all.

Authors: We are not, in fact, confining our studies to the first system mentioned by E. M. Snyder, in which the starch acts as a thickener in relatively low concentrations. Our objective is to span the whole concentration range from thickeners to doughs, or to put it somewhat differently, from systems with excess water to systems that are water limited. The difference in starch granule properties in spanning this range and the reasons for the differences, have not been systematically and quantitatively studied. Next, we are in disagreement semantically with E. M. Snyder's definition of pasting and pastes.
Morphology and Rheology of Corn Starch

To quote H. W. Leach in "Starch, Chemistry and Technology," Vol. 1, Page 300; "the most important practical property of starch is its ability to swell and produce a viscous paste when heated in water." There is no doubt that this is the case. At temperatures of 65-70°C corn starch granules swell and their dispersion viscosities increase dramatically. We therefore disagree with her statement that "hydrated granules do not form a paste until most of the granules have gelatinized." The question of peak viscosity from Brabender measurement is not really that relevant to this work. In Brabender studies, the temperature is not kept constant nor are equilibrium viscosities achieved until the dispersion has been fully heated.

We also disagree completely with the comment that, "At 63-65°C corn starch at any concentration has zero viscosity." Clearly, any suspension of particles in a suspending medium will show a viscosity, \( \eta \), related to the viscosity of the suspending medium, \( \eta_0 \), as:

\[
\frac{\eta}{\eta_0} = f(\phi)
\]

where \( \phi \) is volume fraction. At low concentrations (less than 0.05 volume fraction) the form developed by Einstein is:

\[
\eta = \eta_0 (1 + 2.5\phi)
\]

where \( \phi \) is volume fraction. At higher concentrations the functional relationship becomes more complicated but the principle is clear. For starch, at any concentration, the volume fraction, \( \phi \), of the starch will increase as the water diffuses into the granules to swell them. In the water limited case, \( \phi \) is unity. The effects of \( \phi \) on viscosity at low concentration and temperatures are not observable on the Brabender which was not designed to investigate those regions.

These comments are pertinent to the last two sentences of E. M. Snyder's remarks. Since viscosity is never zero, any shear rate imposed on the dispersion results in shear stresses. The only question to be resolved is how large these stresses and how responsive is the granule to these forces. At low stresses the granules may not be deformable and under some conditions, this granule rigidity shows as dilatant rheological behavior. At larger stresses the same granules can show shear thinning effects which are indicative of granule deformation under shear.

E. M. Snyder: The solubility values obtained by H. W. Leach (1959) are half those reported by the authors. Also, the authors report solubility results reproducible to 5%. This is 5% of what?

Authors: Our examination of Figure 7 of Leach's paper suggests that our results are in harmony with his. At 80° his % solubility is 10% and ours is 12%. Since in Dombier's recent paper (1981, Figure 11) preparation method can affect the results obtained, it is in fact very gratifying that we agree so well with Leach's values. For the reproducibility usually five replications were made and the 'numerical average is reported with \( \pm 2 \) 1/2% variation.
and I agree completely with this. These ridges are quite evident in watching starch gelatinize through the light microscope, and while photos have been published showing this for both corn and potato starch [see Kite, F.E., et al., "Functional Properties of Food Starches," Staerk 15(4), 132-138 (1963) and Elder, A. L. and Schoch, T. J., "Measuring the Useful Properties of Starch," Cereal Science Today 4(7), 202-208 (1959)]. Their case would be strengthened by showing a similar photo for comparison with the SEM. Also, I cannot recall ever seeing photos of pasted starch that had been critical-point dried. They surely would be of interest to those of us struggling with SEM preps from such high-moisture systems. They would definitely be of value.

Authors: We regret giving the impression that we did not admit the possibility of changes during dehydration. This was not our intention. This must always be a concern in sample preparation for microscopy. Remember, however, that the study was undertaken to determine if the shear stress levels affect granule shape. Thus, Figures 6A and 6B, for instance, illustrate that the shear stress level does affect granule configuration. In any event, we were following the preferred procedure described in the literature.

E. M. Snyder: After heating a 5% starch slurry at 65° for 15 minutes, the authors state: "Little swelling is evident, although... measurements...give a Q value of 3.5, which would correspond to a diameter change of 50%." I deduce from this statement that they expected to see all of the granules slightly and uniformly expanded. Not so. The original size range does from about 5 up to about 30 microns (micrometers, if you prefer). At 65°, maybe 30-40% of the granules have gelatinized and swollen many times their original size within seconds, making the original size range even more extreme, so the Q value of 3.5 is an average of a wide-spread range going from marbles to grapefruit, if you will.

Authors: We certainly recognize that the particle size distribution in corn starch is wide. We also recognize that the diffusion is a rate process and particle swelling should depend on time and particle radius. A detailed study of the swelling of granules as a function of time, temperature and granule size would be informative but was not attempted in this study.

E. M. Snyder: If one accepts the premise that the exudate leaching from the swollen granules is the primary reason for viscosity of the starch paste, and that the exudate is primarily amylose, what is responsible for the viscosity of genetically pure waxy maize starch, or any waxy starch, for that matter, that contain no amylose fraction?

Authors: We do not accept the premise that the exudate leaching from the swollen granules is the primary reason for the viscosity of starch pastes. The viscosity of the paste is determined by the volume fraction of the swollen granules and the viscosity of the suspending medium. The viscosity of the suspending medium does, of course, depend on the concentration of material exuded from the granule. 