

# Effects of Maturity on Corn Starch Properties

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## ABSTRACT

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The effect of maturity on the quality of starch for two corn hybrids harvested at three different stages of development was measured by differential scanning calorimetry, rapid viscosity analysis, scanning electron microscopy, and image analysis. The onset of gelatinization and peak temperatures were 2–5°C higher for starch from immature grain than starch from mature grain. The gelatinization temperature range was 5°C larger as the grain matured. Peak and trough viscosities decreased with

maturity, while pasting temperature increased. Between the two hybrids, the late maturing hybrid yielded a larger peak viscosity and trough. The early maturing hybrid exhibited a higher pasting temperature. Image analysis data showed that the starch granules from mature grain showed an increase in size compared with the starch granules from grain that were harvested at the late milk line stage for one, but not both hybrids.

Starch is the major storage form of carbohydrates in higher plants. It consists primarily of two components: amylose, an essentially linear polymer, and amylopectin, a predominately branched polymer. Whether modified or in its native state, starches are used for thickening, stabilizing, and gelling abilities in a wide variety of food and nonfood products. Availability makes dent corn the grain of choice for food starch manufacture, thus allowing corn starch to be the most inexpensive food starch available. Approximately 1.8 billion kg per year of corn starch is used in the United States (Moore et al 1984).

Unfavorable weather conditions sometimes interfere with the usual planting practices and maturation period of the corn crop. As a result, immature corn may be produced, marketed, and processed by the wet-milling industry. Consequently, the starch may exhibit functional properties that are unlike starch from fully mature corn. Relatively few reports exist in the literature addressing this issue. Evans (1941) reported a photomicrograph study of granules of yellow dent corn at four stages of development. This study revealed increased diameter and change of shape from circular to polygonal in granules with increased maturity. Wolf et al (1948), reporting on their comparison of corn starches from three corn cultivars at different stages of maturity, found increased starch content and reduced water-binding capacity with maturity and low amylose content in immature corn.

The objectives of this study were to investigate the effects of maturity on the quality of wet-milled corn starch as assessed by thermal and pasting properties using differential scanning calorimetry (DSC) and rapid viscosity analysis (RVA). Scanning electron microscopy (SEM) and image analysis also were used to establish a basis for observed differences in DSC and RVA.

## MATERIALS AND METHODS

### Starches

Corn starches were obtained by wet-milling two corn hybrids at three stages of development as measured by moisture content, milk line, and black layer. (Jennings et al 2002). These harvests were made in approximately two-week intervals from the Iowa State University Agronomy and Agricultural Engineering Research Center near Ames, IA. Pioneer 3525 was an early maturing cultivar (106 days

after flowering [DAF]) and Pioneer 3394 was a late maturing cultivar (111 DAF). The milling procedure used was a modification of the procedure used by Steinke and Johnson (1991) but modified to use starch tabling (Eckhoff et al 1993) as a means of starch and gluten separation.

### DSC

Corn starch thermal properties were measured by using differential scanning calorimetry (DSC-7, Perkin Elmer, Norwalk, CT) coupled with a thermal analysis data station. Approximately 4.0 mg of starch was weighed into an aluminum pan, followed by 8.0 mg of distilled water, and the pan was sealed hermetically. The samples were heated from 30 to 120°C at a rate of 10°C/min (White et al 1990). Onset temperature ( $T_o$ ), peak temperature ( $T_p$ ), and total enthalpy ( $\Delta H_G$ ) were recorded directly from the data station display. The range of gelatinization ( $R_n$ ) was calculated as  $2(T_p - T_o)$  according to Krueger et al (1987). Samples were stored at 4°C and reanalyzed after seven days to determine the level of starch gel retrogradation (%R) as described by White et al (1989). Each sample was run in duplicate.

### RVA Profiles

Peak, trough (holding strength), and final viscosities, as well as breakdown and setback, peak time, and pasting temperature were obtained using the rapid viscosity analysis (model RVA 4, Newport Scientific, Australia) STD2 temperature profile. Samples were prepared by combining 25.0 mL of distilled water and 3.0 g of starch corrected to a moisture content of 14%. The STD2 RVA procedure begins with rapid stirring at 960 rpm for 60 sec to disperse the sample followed by stirring at 160 rpm measuring phase speed. After equilibration at 50°C, the STD2 method heats the sample to maximum temperature of 95°C in 7.5 min, holds the sample at 95°C for 5 min, and then cools it to 50°C in 7.5 min.

Peak viscosity is the maximum viscosity developed during or soon after the heating stage of the test. Trough is the minimum viscosity after the peak. Breakdown is the change in viscosity from peak to the holding strength. Final viscosity is the highest viscosity obtained at the end of the test. Setback is the change in viscosity from holding strength to final viscosity. Peak time is the time that peak occurs. Pasting temperature is the temperature at which viscosity first increases. Each sample was run in duplicate. Values were reported in rapid viscosity units (RVU).

### SEM

Starch samples were dry-mounted to adhesive metal tape attached to a specimen stud. The starch granules were evenly distributed on the tape surface and double-coated with gold palladium (60:40) (Wang et al 1993). The scanning electron micrographs were obtained using a scanning electron microscope (JSM-35, JEOL, Tokyo, Japan) at an accelerating voltage of 10 kV. All micrographs are presented at a magnification of 300×.

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## Image Analysis

Images of the starch granules were acquired by using an X-ray microanalysis system (Delta IV, Kevex, San Carlos, CA) equipped with a video camera (Cohu, Inc., San Diego, CA). The internal scaling feature of the image analysis software was calibrated to measure  $\mu\text{m}^2$ . Particles in contact with one another were not included in the data analysis. The particles were measured to obtain maximum and minimum diameters and Waddell diameter (diameter of an equivalent circle).

## Statistical Analysis

Thermal properties were analyzed by a two-way analysis of variance (ANOVA). The means and Duncan *t*-test were computed using the general linear model program (SAS Institute, Cary, NC).

## RESULTS AND DISCUSSION

### Gelatinization Properties

Means of the DSC thermogram parameters for the corn samples harvested and milled at different stages of maturity are presented in Table I. The thermal parameters ( $T_o$ ,  $T_p$ , and  $R_n$ ) showed significant differences for time of harvest representing differences in maturity. As the starch matured, onset ( $T_o$ ) and peak ( $T_p$ ) temperatures decreased and the gelatinization range ( $R_n$ ) became larger. These functional changes suggest that there are changes in the starch granules in the kernel as it matures. Boyer and Shannon (1987) reported that the endosperm of the developing corn kernel contains cells of varying physiological ages. They also reported that the central crown region begins to accumulate starch 12 days after pollination. The lower region of the endosperm begins synthesis and accumulates much later (Boyer et al 1977). Boyer and Shannon (1987) further reported that the peripheral region of the endosperm forms last and produces small starch granules. Thus, starch within the granule is more homogeneous in the early stages of development and progressively becomes more heterogeneous as the corn kernel matures.

TABLE I  
Thermal Properties<sup>a</sup> for Two Corn Hybrids Harvested at Three Stages of Development<sup>b</sup>

Property	Pioneer 3525	Pioneer 3394	Mean Values <sup>c</sup>
$T_o$ (°C)			
Harvest 1	68.8	69.4	69.1a
Harvest 2	66.5	67.3	66.9b
Harvest 3	65.8	64.6	65.2c
Cultivar mean <sup>d</sup>	67.0a	67.1a	
$T_p$ (°C)			
Harvest 1	71.9	72.7	72.3a
Harvest 2	70.6	71.2	70.9b
Harvest 3	70.9	69.0	70.0b
Cultivar mean <sup>d</sup>	71.1a	70.9a	
$\Delta H_G$ (cal/g)			
Harvest 1	175	201	188c
Harvest 2	224	282	253b
Harvest 3	266	317	292a
Cultivar mean <sup>d</sup>	221b	267a	
$R_n$ (°C)			
Harvest 1	6.4	6.4	6.4c
Harvest 2	8.2	7.8	8.0b
Harvest 3	10.2	8.7	9.4a
Cultivar mean <sup>d</sup>	8.3a	7.6b	

<sup>a</sup>  $T_o$ , gelatinization onset;  $T_p$ , peak temperature;  $\Delta H_G$ , enthalpy of gelatinization;  $R_n$ , gelatinization range.

<sup>b</sup> Harvests 1 and 2 represent corn samples at immature stages in growth. Harvest 3 represents corn at full maturity.

<sup>c</sup> Mean values are pooled across both corn hybrids. Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

<sup>d</sup> Values followed by the same letter in the same row are not significantly different ( $P < 0.05$ ).

Atwell et al (1988) defines starch gelatinization as "the collapse (disruption) of molecular orders within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence, and starch solubilization. The point of initial gelatinization and the range over which it occurs is governed by starch concentration, method of observation, granule type, and heterogeneities within the granule population under observation." Therefore, when the starch granule is more homogeneous, the onset would happen at the temperature at which most of the starch granules begin gelatinization and the range would be relatively smaller. As the granules become more heterogeneous, onset could occur earlier because some granules can begin to gelatinize at that temperature, and the range was wider due to more heterogeneity in the gelatinization times of the granules present. The  $\Delta H_G$  data showed no significant differences in the amount of energy required to gelatinize the starch throughout the study, although there is a trend in the data that indicates that the amount of energy required decreased. These data appear to indicate that, although there may be more heterogeneity in the starch granules present in regard to their time of gelatinization onset with increased maturity, the total amount of energy required to gelatinize the starch does not change significantly.

### Refrigerated-Storage Retrogradation

The transition properties of the retrograded starch samples are shown in Table II. Although there were no statistical differences for harvest date or hybrid among the retrogradation parameter means, the results obtained in our study are in agreement with findings of White et al (1989), who found the  $R_n$  of retrograded samples (seven days at °C) increased while the other parameters decreased considerably compared with the raw starch data. These results suggest, therefore, that all onset and range differences found in the starch granules and attributed to the maturity of the kernel were not evident after retrogradation of the starch. Furthermore, harvesting corn before maturity did not increase or decrease the potential for the starch to retrograde.

TABLE II  
Thermal Properties<sup>a</sup> of Retrograded Starch for Two Corn Hybrids Harvested at Three Stages of Development<sup>b</sup>

Property	Pioneer 3525	Pioneer 3394	Mean Values <sup>c</sup>
$T_o$ (°C)			
Harvest 1	42.0	42.1	42.0a
Harvest 2	42.5	43.0	42.8a
Harvest 3	43.0	43.2	43.1a
Cultivar mean <sup>d</sup>	42.5a	42.8a	
$\Delta H_R$ (cal/g)			
Harvest 1	1.47	1.41	1.44a
Harvest 2	1.38	1.43	1.40a
Harvest 3	1.34	1.20	1.27a
Cultivar mean <sup>d</sup>	1.39a	1.35a	
$R_n$ (°C)			
Harvest 1	17.0	19.6	18.3a
Harvest 2	19.1	18.7	18.9a
Harvest 3	18.3	17.7	18.0a
Cultivar mean <sup>d</sup>	18.2a	18.7a	
R (%)			
Harvest 1	47.0	43.8	45.4a
Harvest 2	45.2	45.2	45.2
Harvest 3	45.2	40.1	40.1a
Cultivar mean <sup>d</sup>	45.8a	43.0a	

<sup>a</sup>  $T_o$ , gelatinization onset;  $\Delta H_R$ , enthalpy of gelatinization;  $R_n$ , gelatinization range; R, retrogradation ( $\Delta H$  of rerun after seven days of storage at 4°C/ $\Delta H$  of initial run)  $\times$  100.

<sup>b</sup> Harvests 1 and 2 represent corn samples at immature stages in growth. Harvest 3 represents corn at full maturity.

<sup>c</sup> Mean values are pooled across both corn hybrids. Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

<sup>d</sup> Values followed by the same letter in the same row are not significantly different ( $P < 0.05$ ).

## RVA

Results from RVA are presented in Table III. The peak viscosity of the late maturing Pioneer 3394 was significantly higher than the early maturing Pioneer 3395. Within the hybrids, peak viscosity for harvest 1 > harvest 2 > harvest 3, which indicates that as the grain matures, the viscosity and starch paste decreases. These observations may be explained in part by the fact that the level of amylose present in a developing corn kernel increases as the kernel matures (Wolf et al 1948; Shannon and Garwood 1984). Therefore, it is conceivable that in immature samples, the highly branched, large polymer amylopectin was most abundant, and its large molecular weight could result in higher viscosities in the starch pastes.

The trough viscosity (holding strength) of the late maturing Pioneer 3394, however, was also significantly higher than the early maturing Pioneer 3395 at  $P < 0.05$ . Within hybrids, the trough values for immature starch were significantly greater than for mature starch. The

**TABLE III**  
Pasting Properties<sup>a</sup> for Two Corn Hybrids Harvested at Three Stages of Development<sup>b</sup>

Property	Pioneer 3525	Pioneer 3394	Mean Values <sup>c</sup>
Peak viscosity (RVU)			
Harvest 1	136	170	153a
Harvest 2	124	154	139b
Harvest 3	118	136	127c
Cultivar mean <sup>d</sup>	126b	153a	
Trough (RVU)			
Harvest 1	50	80	65a
Harvest 2	43	73	58a
Harvest 3	37	55	46b
Cultivar mean <sup>d</sup>	43b	69a	
Breakdown (RVU)			
Harvest 1	86	89	88a
Harvest 2	81	81	81a
Harvest 3	81	81	81a
Cultivar mean <sup>d</sup>	82a	84a	
Final viscosity (RVU)			
Harvest 1	192	191	191a
Harvest 2	191	201	196a
Harvest 3	199	198	199a
Cultivar mean <sup>d</sup>	194a	197a	
Setback (RVU)			
Harvest 1	142	110	126a
Harvest 2	147	128	138a
Harvest 3	162	144	153a
Cultivar mean <sup>d</sup>	150a	127a	
Peak time (min)			
Harvest 1	7	7	7a
Harvest 2	7	7	7a
Harvest 3	7	7	7a
Cultivar mean <sup>d</sup>	7a	7a	
Pasting temp. (°C)			
Harvest 1	75	73	74b
Harvest 2	75	73	74b
Harvest 3	77	74	75a
Cultivar mean <sup>d</sup>	76a	74b	

<sup>a</sup> Rapid Visco Analyser units (RVU).

<sup>b</sup> Harvests 1 and 2 represent corn samples at immature stages in growth. Harvest 3 represents corn at full maturity.

<sup>c</sup> Mean values are pooled across both corn hybrids. Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

<sup>d</sup> Values followed by the same letter in the same row are not significantly different ( $P < 0.05$ ).

**TABLE IV**  
Mean Starch Granule Diameter ( $\mu\text{m}$ ) from Corn Harvested at Different Stages of Development

Harvest	Pioneer 3525	Pioneer 3394	Mean Values <sup>a</sup>
1	9.2	9.0	9.1b
2	8.9	9.5	9.2a,b
3	10.0	9.0	9.5a

<sup>a</sup> Values are pooled across both hybrids. Values followed by the same letter in the same column are not significantly different ( $P < 0.05$ ).

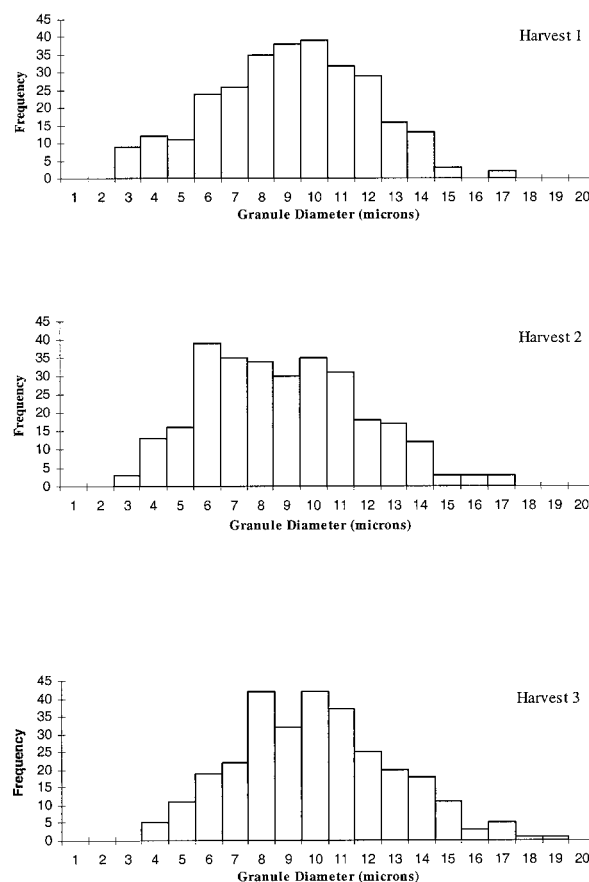
results further validate the results observed in the peak viscosity data. The immature corn samples may have trough values that are larger than the mature samples because amylopectin is a major factor in the structural arrangement of the starch granule (Zobel 1984) and, therefore, with more present, the trough would be greater. More research would need to be done to confirm this hypothesis.

The pasting temperature of the early maturing Pioneer 3395 (76°C) was significantly higher than for the late maturing Pioneer 3394 (74°C) at  $P < 0.05$ . Therefore, the starch from Pioneer 3395 had a higher gelatinization temperature than did starch from the Pioneer 3394. Within hybrids, the starch from the most mature grain (harvest 3) had a higher gelatinization temperature than starch from immature grains. As the corn kernel matures, the starch granules become more compact, losing their circular shape and becoming more polygonal (Evans 1941). Compact granules require more heat to gelatinize than do less compact ones. Therefore, the more immature starch granules required less heat to gelatinize than the mature granules. There were no significant differences observed for breakdown, final viscosity, setback, and peak time in the starch samples for harvest or hybrid.

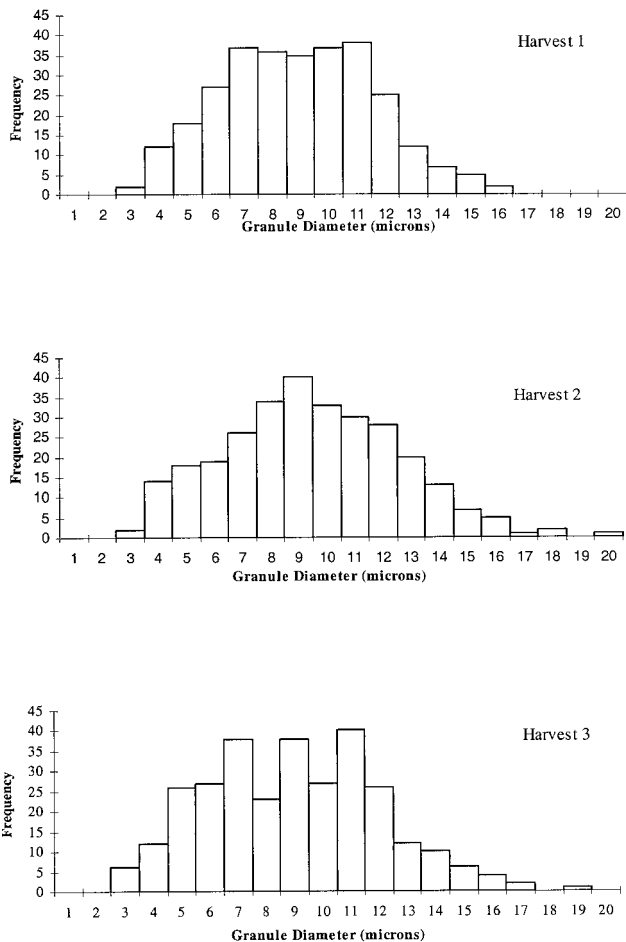
## SEM and Image Analysis

SEM micrographs are instrumental in observing differences in the shape morphology and surface of starch granules. Hypothetically, one would have expected to see larger granules as the grain matured (Wolf et al 1948; Shannon and Garwood 1984). However, the size differences were not evident in the micrographs. This is possibly due to the low magnification of the micrographs.

Mean starch granule diameters for the corn samples are shown in Table IV. No significant differences in granule diameter were observed among starches from different hybrids. Starch granule diameter was significantly affected by harvest for Pioneer 3525 and in the



**Fig. 1.** Starch granule diameters for an early maturing corn hybrid (Pioneer 3525) at three different maturities.



**Fig. 2.** Starch granule diameters for a late maturing corn hybrid (Pioneer 3524) at three different maturities.

mean diameter values; harvest 3 starch showed a larger diameter (9.5  $\mu\text{m}$ ) than harvest 1 (9.1  $\mu\text{m}$ ). This difference was not observed however for Pioneer 3394. Histograms (Figs. 1–2) did not clearly show an increase in granule diameter with maturity as was anticipated.

### CONCLUSIONS

Although effects of both maturity and hybrid were seen in the DSC parameters for this study were significant at  $P < 0.05$ , maturity had the strongest influence. Decreases in  $T_o$  and  $T_p$  with maturity across both hybrids was observed. Gelatinization range ( $R_n$ ) for the starches became higher with maturity, and a significant ( $P < 0.05$ ) difference was observed for hybrid. Although not statistically significant, retrograded starches showed an increase in  $R_n$  and a decrease in the other parameters. RVA results for both hybrid and maturity exhibited significant ( $P < 0.05$ ) differences for peak vis-

cosity, trough (holding strength), and pasting temperature. Although structural and surface differences were not observed in the SEM micrographs, image analysis data did show a significant difference in granule diameters with maturity in Pioneer 3525 and in the mean values. In both RVA and SEM, the starch granules from the mature grain were larger than those from grain harvested at late milk line. The same trend was not observed in Pioneer 3394. Maturity and hybrid clearly influence thermal and pasting properties of corn as demonstrated by the differences observed in DSC, RVA, SEM, and image analysis.

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