

Influence of Drying Temperature, Water Content, and Heating Rate on Gelatinization of Corn Starches

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The gelatinization properties of starch extracted from corn and waxy corn dried at different temperatures were determined at various water contents and heating rates by differential scanning calorimetry. All gelatinization transition temperatures increased with drying temperature and heating rate. Onset and peak temperatures remained relatively constant, whereas end temperature decreased in the presence of excess water. The gelatinization enthalpy (ΔH_g) of corn starch decreased with drying temperature at 50% water; however, it remained constant for waxy corn starch. The effects of water content and heating rate on ΔH_g were dependent on each other. The minimum water levels required for gelatinization of starch extracted from corn dried at 20 and 100 °C are 21 and 29%, respectively. The activation energy (E_a) was calculated using an Arrhenius-type equation and two first-order models; the degree of conversion (α) was predicted using a newly proposed model that produced good results for both E_a and α .

KEYWORDS: Corn starch; waxy corn; transition temperatures; differential scanning calorimetry; gelatinization kinetics

INTRODUCTION

Gelatinization is a phase transition of starch granules from an ordered to a disordered state during heating with excess water (1, 2). The disordered state consists of melting of ordered regions, both on the crystallite level (inner and surface) and on the level of amylopectin double-helical order (3). It is an energy-absorbing process and can be studied with differential scanning calorimetry (DSC) (2). Although gelatinization enthalpy corresponds to overall crystallinity of amylopectin, loss of double-helical order is considered to be responsible for enthalpic transition (4).

Starch gelatinization depends on many factors: water content, heating rate, botanical source of starch, processes applied to starch before gelatinization, and amylose/amylopectin content of starch. High-temperature drying of grains is necessary to achieve high drying rates (5); nevertheless, the effect of drying temperature on the gelatinization of extracted starch has not been studied widely. Some well-known effects of high-temperature drying of corn are high-stress cracking, low resistance to mechanical impact, low starch recovery, loss of solids in steepwater, and poor starch paste viscosity (5–8). An increase in initial gelatinization temperature of corn starch from 72 to 73 and 74 °C has been reported for different corn starches dried at 90 and 100 °C, respectively (9). With an increase in drying temperature, DSC thermograms of starch exhibit an increase in

the gelatinization onset, peak, and end temperatures and endotherm peak width and a decrease in gelatinization enthalpy (10).

At intermediate water levels, two endothermic transitions have been reported for the disorganization of starch crystallites (11). These endothermic effects, associated mainly with melting, are first-order transitions, that is, their rate is proportional to the rate of inducing temperature variations. During gelatinization, hydrogen bonds, which stabilize the structure of double helices, must be broken and possibly replaced by reassociation of the free ends of unwound helices of amylopectin. This leads to the formation of physical junctions and creation of more general amorphous hydrogen-bonded associations, which normally should be attributed to exothermic effects (3).

The kinetic parameters of starch gelatinization, which can be utilized for optimization of industrial-scale processes, have been investigated with a non-isothermal DSC method (12, 13). Resio and Suarez (12) stated that more experimental evidence is needed for modeling gelatinization, whereas Spigno and De Faveri (13) reported that non-isothermal DSC can help to characterize the gelatinization process only if the kinetics of the process are already known.

Our objective was to investigate the effects of corn kernel drying temperature, water content, and heating rate on gelatinization characteristics of starch extracted from corn and waxy corn.

MATERIALS AND METHODS

Materials. One nonwaxy (33A14) corn and one waxy (34H98) hybrid corn were grown on the Agricultural and Biological Engineering

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Table 1. Chemical Composition of Starch Samples

corn variety (type)	drying temp (°C)	total fiber (%)	germ yield (%)	starch (%)	gluten (%)
33A14 (nonwaxy)	20	12.89	5.62	67.67	8.65
33A14 (nonwaxy)	100	14.22	5.96	66.50	8.43
34H98 (waxy)	70	16.09	6.52	59.28	12.40
34H98 (waxy)	100	20.33	5.29	52.75	16.31

Research Farm of the University of Illinois at Urbana–Champaign (UIUC). They were harvested in 2002 at 30% moisture content and subsequently dried at 20, 70, and 100 °C to 15% moisture content. Starches extracted from these corn hybrids were obtained from UIUC. The chemical composition of starch samples as reported by UIUC are given in **Table 1**.

DSC Measurements. Starch samples were weighed in aluminum DSC pans, and water was added to obtain starch pastes of 30, 50, 70, and 90% water content (w/w). The DSC pans were hermetically sealed, and the pastes were scanned using a DSC (TA Instruments, 2920 Modulated DSC, New Castle, DE) from 25 to 100 °C at different heating rates of 1, 3, 5, 7, 10, and 15 °C/min. An empty pan was used as the reference. For each measurement, the overall gelatinization enthalpy ΔH_g (expressed as joules per gram of dry starch) and the onset (T_o), peak (T_p), and end temperatures (T_e) were determined as illustrated in **Figure 1**. T_o is the temperature at which the tangential line from the lower temperature side of the peak intersects with the baseline; T_p is the temperature at the tip of the peak, and T_e is the temperature at which the tangential line from the high-temperature side of the peak intersects with the baseline. ΔH_g is the area under the peak bound by the baseline on the graph. These were calculated using DSC software (Universal Analysis, Thermal Solutions release 2.3, TA Instruments, Inc.). All measurements were done in triplicate.

Kinetic Modeling. In nonisothermal DSC, the rate of reaction is proportional to the peak height at a given time and the extent of reaction is proportional to the total area of the endotherm to that time (14). Non-isothermal DSC measurements for deriving kinetic parameters of starch gelatinization and the degree of conversion (α) at any time t are (13)

$$\alpha = \Delta H_t / \Delta H_g \quad (1)$$

where ΔH_t is the gelatinization enthalpy at any time t . On the basis of this approach, the gelatinization kinetics of starches were evaluated in terms of degree of conversion at the peak temperature (α_{T_p})

$$\alpha_{T_p} = \Delta H_{T_p} / \Delta H_g \quad (2)$$

where ΔH_{T_p} is the gelatinization enthalpy (J/g) at T_p . ΔH_{T_p} was obtained from the area under the peak up to T_p using the DSC software. The conversion at T_p was chosen because that is the temperature of maximum deflection and at which the rate of reaction is maximum (15). Turhan and Gunasekaran (16) proposed a first-order or pseudo-first-order kinetic model for starch gelatinization and used the equation

$$\ln b_t = \ln b_0 - k_r t \quad (3)$$

where b_t is the concentration of ungelatinized starch (%) at time t (s), b_0 is the concentration of ungelatinized starch at the beginning (100%), and k_r is a reaction rate constant (s^{-1}). In eq 3, the ungelatinized part represented by b_t corresponds to $(1 - \alpha_{T_p})$. If t is chosen at T_p , then eq 3 can be modified as

$$\ln\left(\frac{1}{1 - \alpha_{T_p}}\right) = k_r t_{T_p} + C \quad (4)$$

where t_{T_p} (s) is the scanning time from 25 °C to T_p at that heating rate and C is a constant. An Arrhenius-type equation was used to determine the temperature dependency of k_r (16):

$$\ln k_r = \ln A - \frac{E_a}{R} \frac{1}{T_p} \quad (5)$$

In eq 5 A is the pre-exponential factor (s^{-1}), E_a is the activation energy (J/mol), and R is the gas constant (8.314 J/mol·K). E_a for gelatinization was calculated using two methods involving first-order kinetics proposed by Ozawa (15). In the first method, at the peak of the curve, the logarithm of the heating rate (β , °C/min) is linearly correlated with the reciprocal of the absolute value of T_p :

$$\ln \beta = -\frac{E_a}{R} \frac{1}{T_p} + C \quad (6)$$

In the second method, the logarithm of the heating rate divided by the square of the absolute value of T_p is linearly correlated with the reciprocal of the absolute value of T_p (15).

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{R} \frac{1}{T_p} + C \quad (7)$$

Equation 7 is also known as the Kissinger equation (13).

Scanning Electron Microscopy (SEM). The microstructure of starch granules was observed under a field-emission scanning electron microscope (SEM) (Hitachi S900 high resolution, low voltage). Samples were mounted onto carbon stubs and sputter-coated (4-nm) with platinum. The accelerating voltage of the beam was 1.5 kV.

Statistical Analysis. Two-way classification analysis of variance was carried out on the DSC, and significant differences among samples were determined by Duncan's multiple-range test (17).

RESULTS AND DISCUSSION

Effect of Drying Temperature. The effects of drying temperature on T_o , T_p , and T_e of corn and waxy corn starch are summarized in **Tables 2–7**. All transition temperatures increased with drying temperature. T_o values were more sensitive to drying temperature than T_p and T_e , and the increases were more pronounced for corn starch than for waxy corn starch.

All transition temperatures of flint and dent corn reportedly increase with drying treatment at 75% water content and 10 °C/min heating rate. This increase has been attributed to protein remaining in starch possibly reducing the entry of water into granules during gelatinization by inhibiting water–starch interaction because high drying temperatures increase the protein content of the corn starch fraction (9, 10). From **Table 1**, it can be seen that the gluten contents of corn starches dried at 20 and 100 °C are almost the same, but the starch yield is lower for corn dried at 100 °C, meaning there is more gluten per unit of starch. For waxy corn, although the amount of gluten was higher when dried at 100 °C than at 70 °C, the starch yield was lower at 100 °C (**Table 1**). In addition, the presence of proteins, sugar, and salts within the starch inhibits gelatinization by absorbing water, which would otherwise be used for gelatinization (18). Likewise, in our samples gluten may inhibit gelatinization by absorbing most of the available water in the media.

High gelatinization transition temperatures are indicative of a high degree of crystallinity, which provides structural stability and makes starch gelatinization difficult to occur (19). Additionally, T_o is a measure of the perfection of starch crystallites among all granules present; and less perfect crystallites mean a lower T_o (20). Thus, a high degree of crystallinity possibly caused by high drying treatment may account for high transition temperatures, especially the high T_o values we observed.

The endotherm peak width, EPW ($T_e - T_o$) is also influenced by the drying temperature of the corn (10). An increase in EPW of ≈ 1.5 °C for two corn starches, obtained from corn dried at 110 °C, containing 75% water was reported compared to their

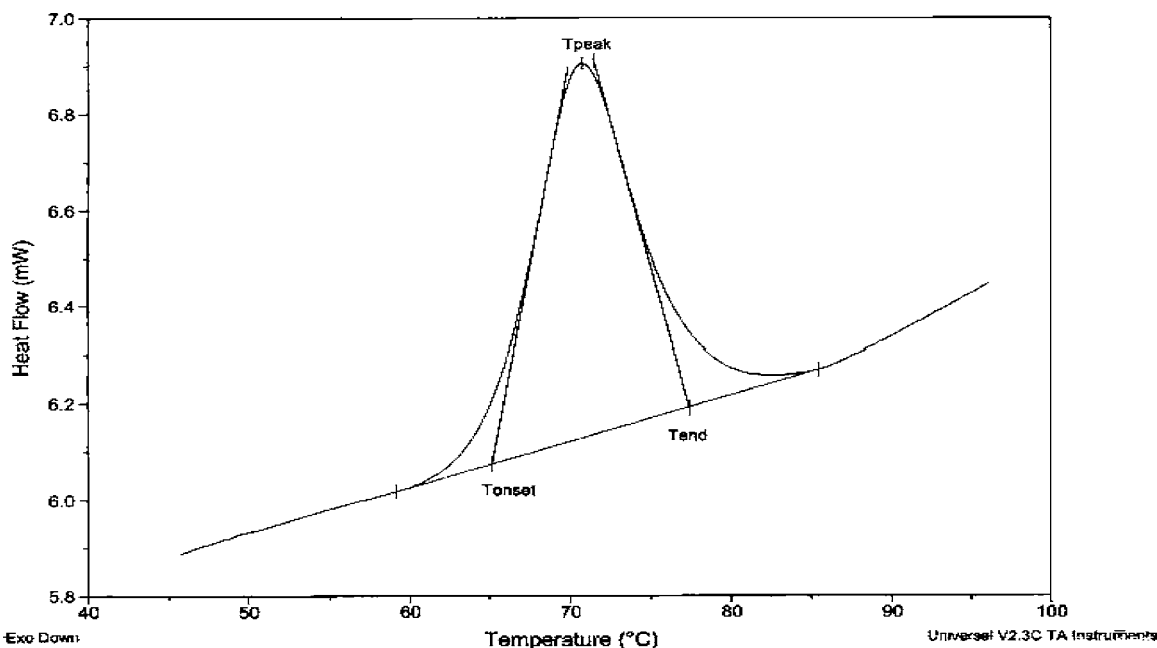


Figure 1. Schematic illustration of transition temperatures (T_o , onset temperature; T_p , peak temperature; T_e , end temperature) on a typical DSC thermogram.

undried counterparts (10). We observed similar increases in EPW of 0.65 and 2.19 °C for starch containing 70% water as the drying temperature increased from 20 to 100 °C for corn and from 70 to 100 °C for waxy corn, respectively. Decreased crystallinity results in narrowing of the DSC peak (21), which suggests that an increase in crystallinity due to high drying temperature may result in widening of DSC peaks. Moreover, there is a possible explanation for a broader gelatinization range for waxy corn than for corn. The EPW of the retrogradation endotherm is broader than the EPW of the gelatinization endotherm for a given sample (22). Assuming a high drying temperature has a kind of “retrogradation-like” effect on amylopectin of waxy corn starch, the starch fraction responsible for retrogradation, may explain the broader gelatinization range for waxy corn starch than for corn starch.

Drying temperature had no effect on ΔH_g of corn starch at 30 and 70% water contents (Table 8). However, the ΔH_g of samples containing 50 and 90% water decreased with drying temperature. The decreases in ΔH_g at these water contents were more pronounced at lower heating rates. Drying temperature did not significantly affect ΔH_g of waxy corn starches (Table 9). It has been stated that difficulty in starch–protein separation due to the negative effect of high-temperature drying may lead to a decrease in ΔH_g (10).

To better understand the effect of high drying temperature on ΔH_g , the relationship between ΔH_g and transition temperatures should also be considered. Singh et al. (23) stated that ΔH_g and transition temperatures are weakly correlated. Conversely, Fujita et al. (24) reported a positive relation between ΔH_g and T_p . Chiotelli et al. (25) demonstrated that T_p , T_e , and ΔH_g increased for sweet potato after acid modification. In Figure 2, it can be seen that all transition temperatures of starch extracted from corn dried at 20 °C are linearly correlated with ΔH_g at heating rates of 1–7 °C/min at 70% water content ($R^2 > 0.98$). For starch obtained from corn dried at 100 °C, this was also true at heating rates of 1–5 °C/min ($R^2 > 0.92$) (Figure 2). Similar relationships for waxy corn starch were obtained (Figure 3). All transition temperatures of starches extracted from waxy corn dried at 70 and 100 °C were linearly correlated with ΔH_g for 70% water content at 1–10 °C/min ($R^2 > 0.86$) and 3–10 °C/min ($R^2 > 0.93$), respectively. Despite these linear

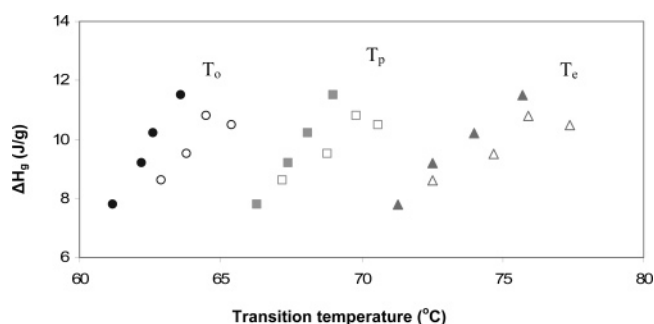


Figure 2. Relationship between gelatinization enthalpy (ΔH_g) and transition temperatures (onset, T_o ; peak, T_p ; and end, T_e) of starches containing 70% water at heating rates between 1 and 7 °C/min. Solid and open symbols show starches extracted from corn dried at 20 and 100 °C, respectively.

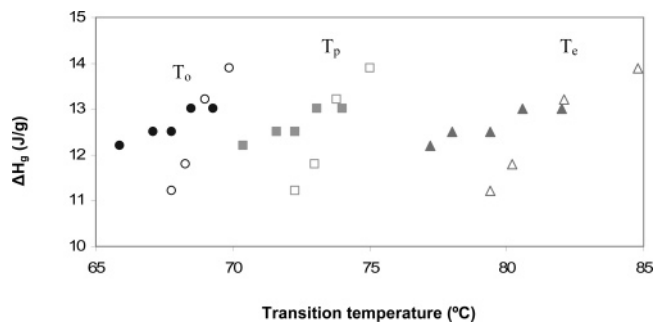


Figure 3. Relationship between gelatinization enthalpy (ΔH_g) and transition temperatures (onset, T_o ; peak, T_p ; and end, T_e) of starches containing 70% water at heating rates between 1 and 10 °C/min for those dried at 70 °C and between 3 and 10 °C/min for those dried at 100 °C. Solid and open symbols show starches extracted from waxy corn dried at 70 and 100 °C, respectively.

correlations between ΔH_g and transition temperatures, it is interesting to note that whereas transition temperatures increased with drying temperature, ΔH_g either remained constant or decreased depending on water content. Moreover, the effect of drying temperature on ΔH_g was dependent on starch type; that is, it had no effect on ΔH_g of waxy corn starch, which contains

Table 2. Gelatinization Onset Temperatures (°C)^a of Starches Extracted from Corn Dried at 20 and 100 °C

water content (%)	drying temp (°C)	heating rate					
		1 °C/min	3 °C/min	5 °C/min	7 °C/min	10 °C/min	15 °C/min
30	20	59.0 ± 0.3 a1	60.8 ± 0.3 b2	62.1 ± 0.4 c2	63.0 ± 0.6 d2	64.9 ± 1.2 e2	66.5 ± 0.4 f12
	100	62.5 ± 0.2 a45	64.3 ± 0.6 b5	64.0 ± 0.5 b34	66.0 ± 0.5 c3	66.9 ± 0.5 d3	68.3 ± 0.4 e4
50	20	59.0 ± 1.1 a1	59.8 ± 0.7 b1	61.0 ± 0.7 c1	62.3 ± 0.3 d1	63.5 ± 0.7 e1	66.6 ± 0.8 f23
	100	62.0 ± 0.6 a34	63.6 ± 0.2 b4	64.2 ± 0.2 b34	65.7 ± 0.6 c3	66.5 ± 0.4 d3	68.5 ± 0.3 e4
70	20	61.2 ± 0.5 a2	62.2 ± 0.2 b3	62.6 ± 0.2 bc2	63.6 ± 0.8 c2	64.5 ± 0.7 d2	67.1 ± 0.4 e3
	100	62.9 ± 0.8 a5	63.8 ± 0.0 b45	64.5 ± 0.2 b45	65.4 ± 0.4 c3	66.7 ± 0.3 d3	68.8 ± 0.5 e4
90	20	61.6 ± 0.5 a23	62.1 ± 0.5 a3	63.7 ± 0.5 bc3	63.2 ± 0.3 b2	64.2 ± 0.5 c2	65.9 ± 0.3 d1
	100	62.9 ± 0.3 a5	64.4 ± 0.3 b5	64.9 ± 0.2 b5	65.9 ± 0.2 c3	66.7 ± 0.4 d3	68.6 ± 0.7 e4

^a Means ± SD (*n* = 3); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different (*p* ≤ 0.01).

Table 3. Gelatinization Onset Temperatures (°C)^a of Starches Extracted from Waxy Corn Dried at 70 and 100 °C

water content (%)	drying temp (°C)	heating rate					
		1 °C/min	3 °C/min	5 °C/min	7 °C/min	10 °C/min	15 °C/min
50	70	65.9 ± 0.3 a1	66.3 ± 0.4 a1	67.2 ± 0.2 b1	68.2 ± 0.5 c1	68.6 ± 0.0 c1	71.2 ± 1.0 d12
	100	66.2 ± 0.2 a12	67.0 ± 0.2 b2	67.8 ± 0.3 c12	68.7 ± 0.4 d12	69.4 ± 0.1 d2	70.7 ± 0.4 e1
70	70	65.9 ± 0.2 a1	67.1 ± 0.3 b24	67.8 ± 0.4 c12	68.5 ± 0.4 c12	69.3 ± 0.3 d2	71.1 ± 0.7 e12
	100	66.6 ± 0.2 a12	67.8 ± 0.6 b34	68.3 ± 0.4 b2	69.0 ± 0.2 c2	69.9 ± 0.6 d23	72.1 ± 0.6 e3
90	70	66.4 ± 0.1 a12	67.1 ± 0.2 b24	67.7 ± 0.7 b12	68.4 ± 0.4 c12	69.9 ± 0.5 d23	71.5 ± 0.5 e2
	100	66.6 ± 0.3 a12	67.8 ± 0.6 b34	68.3 ± 0.0 b2	69.0 ± 0.3 c2	70.4 ± 0.5 d3	71.4 ± 0.4 e12

^a Means ± SD (*n* = 3); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different (*p* ≤ 0.01).

Table 4. Gelatinization Peak Temperatures (°C)^a of Starches Extracted from Corn Dried at 20 and 100 °C

water content (%)	drying temp (°C)	heating rate					
		1 °C/min	3 °C/min	5 °C/min	7 °C/min	10 °C/min	15 °C/min
30	20	63.6 ± 0.5 a1	65.0 ± 0.6 b1	65.9 ± 0.3 c1	67.1 ± 0.6 d1	69.1 ± 1.5 e1	70.6 ± 0.5 f1
	100	65.3 ± 0.2 a2	67.1 ± 0.8 b2	67.2 ± 0.4 b2	69.3 ± 0.4 c2	70.4 ± 0.7 d2	71.8 ± 0.2 e2
50	20	65.9 ± 0.4 a23	67.3 ± 0.1 b23	67.8 ± 0.4 b23	68.9 ± 0.6 c2	70.0 ± 1.0 d2	73.4 ± 1.2 e34
	100	66.3 ± 0.3 a34	68.5 ± 0.4 b45	69.3 ± 0.1 b4	70.8 ± 0.7 c3	71.9 ± 0.3 d3	74.0 ± 0.5 e45
70	20	66.3 ± 0.3 a34	67.4 ± 0.2 b23	68.1 ± 0.4 b3	69.0 ± 0.6 c2	70.1 ± 0.8 d2	73.2 ± 0.8 e3
	100	67.2 ± 0.2 a5	68.8 ± 0.2 b56	68.8 ± 0.2 c4	70.6 ± 0.3 d3	72.0 ± 0.1 e3	74.4 ± 0.7 f5
90	20	66.8 ± 0.2 a45	67.9 ± 0.3 b34	69.3 ± 0.1 c4	69.0 ± 0.4 c2	70.1 ± 0.4 d2	71.8 ± 0.2 e2
	100	67.5 ± 0.5 a5	69.2 ± 0.1 b6	69.6 ± 0.1 b4	71.1 ± 0.3 c3	72.1 ± 0.3 d3	74.3 ± 0.8 e5

^a Means ± SD (*n* = 3); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different (*p* ≤ 0.01).

only amylopectin. This controversy can be clarified by taking into account that crystallinity is a feature of amylopectin (4) and ΔH_g is due to hydrogen bonding rather than crystallinity (19, 20, 23). On these bases, ΔH_g and transition temperatures are and can be highly correlated, although both concepts involve different mechanisms.

All transition temperatures of starch extracted from corn dried at 100 °C deviated from linearity at the 7 °C/min heating rate, probably due to the effect of high drying temperature (Figure 2).

Effect of Water Content. As the water content increased from 30 to 50%, the T_o of the starch extracted from corn dried at 20 °C decreased and then increased with further increase in water content to 70% (Table 2). It appears that drying temperature influenced the effect of water content on the T_o of corn starch. In starch extracted from corn dried at 100 °C the T_o decreased at only the 3 °C/min heating rate as the water content increased from 30 to 50%, whereas it increased only at 1 °C/min for a further increase of water content to 70%, and as the water content increased from 70 to 90%, it remained relatively constant.

The waxy corn starch produced almost undetectable endothermic peaks at 30% water content, indicating the minimum water content required for gelatinization is higher for waxy corn starch than for corn starch. Therefore, no result is listed for waxy corn starch at 30% water content in Table 3. T_o values of waxy corn starch tended to increase slightly as water content increased from 50 to 70% (Table 3). When the water content increased from 70 to 90%, the T_o of the waxy corn starch remained relatively constant.

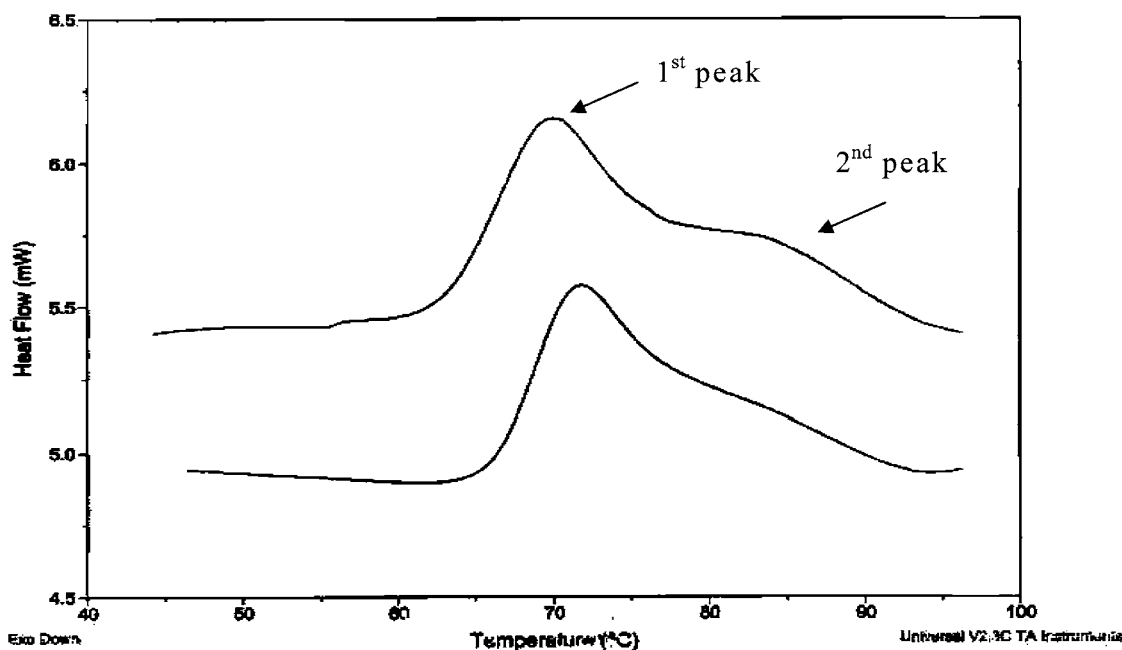
For corn starch, T_p significantly increased when water content increased from 30 to 50% (Table 4). In the presence of intermediate and excess water, the T_p remained relatively constant. For waxy corn starch, the T_p slightly increased as the water content increased from 50 to 70% (Table 5). A further increase in water content did not significantly influence the T_p of waxy corn starch.

Corn and waxy corn starches exhibited two combined (bimodal) endothermic peaks at 50% water content (Figure 4); therefore, their T_e values are not reported. The occurrence of bimodal endothermic peaks is different from normal endothermic peaks; therefore, it was considered that comparison of T_e of the two different types of endothermic peaks to each other

Table 5. Gelatinization Peak Temperatures (°C)^a of Starches Extracted from Waxy Corn Dried at 70 and 100 °C

water content (%)	drying temp (°C)	heating rate					
		1 °C/min	3 °C/min	5 °C/min	7 °C/min	10 °C/min	15 °C/min
50	70	69.6 ± 0.1 a1	70.6 ± 0.1 b1	71.8 ± 0.4 c1	73.0 ± 0.6 d1	73.5 ± 0.1 d1	76.5 ± 1.1 e1
	100	70.4 ± 0.1 a2	71.9 ± 0.1 b23	73.0 ± 0.6 c2	73.7 ± 0.3 c12	74.5 ± 0.2 d23	76.1 ± 0.4 e1
70	70	70.4 ± 0.1 a2	71.6 ± 0.4 b2	72.3 ± 0.6 c12	73.1 ± 0.5 d12	74.0 ± 0.4 e12	76.2 ± 0.5 f1
	100	70.7 ± 0.3 a2	72.3 ± 0.6 b3	73.0 ± 0.6 b2	73.8 ± 0.3 c2	75.0 ± 0.7 d34	77.8 ± 0.8 e2
90	70	70.4 ± 0.3 a2	71.4 ± 0.3 b2	72.0 ± 0.1 b1	73.1 ± 0.5 c12	74.9 ± 0.6 d34	76.8 ± 0.8 e1
	100	71.1 ± 0.1 a2	72.8 ± 0.5 b34	73.0 ± 0.4 b2	73.8 ± 0.3 c2	75.5 ± 0.6 d4	76.6 ± 0.3 e1

^a Means ± SD ($n = 3$); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different ($p \leq 0.01$).

**Figure 4.** DSC thermograms of starch extracted from corn dried at 20 °C (upper curve) and 100 °C (lower curve) with 50% water content at 10 °C/min.**Table 6.** Gelatinization End Temperatures (°C)^a of Starches Extracted from Corn Dried at 20 and 100 °C

water content (%)	drying temp (°C)	heating rate					
		1 °C/min	3 °C/min	5 °C/min	7 °C/min	10 °C/min	15 °C/min
30	20	66.9 ± 0.6 a1	68.4 ± 0.7 b1	69.9 ± 0.4 c1	72.0 ± 0.5 d1	75.0 ± 2.1 e1	79.0 ± 1.3 f2
	100	67.7 ± 0.4 a1	70.2 ± 0.8 b2	71.3 ± 0.7 b2	73.7 ± 0.6 c2	75.4 ± 1.3 d1	77.8 ± 0.2 e1
70	20	71.3 ± 0.1 a2	72.5 ± 0.4 b4	74.0 ± 0.5 c34	75.7 ± 0.5 d3	76.9 ± 0. e2	82.2 ± 0.7 f3
	100	72.5 ± 0.4 a3	74.7 ± 0.5 b5	75.9 ± 0.3 c5	77.4 ± 0.5 d4	79.8 ± 0.7 e4	82.9 ± 0.6 f3
90	20	70.4 ± 0.3 a2	71.4 ± 0.3 a3	73.6 ± 1.0 b3	73.8 ± 0.3 b2	75.6 ± 0.3 c1	78.0 ± 0.9 d12
	100	70.5 ± 0.3 a2	73.5 ± 0.7 b4	74.9 ± 0.3 c45	76.6 ± 0.2 d34	78.2 ± 0.6 e3	81.8 ± 1.1 f3

^a Means ± SD ($n = 3$); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different ($p \leq 0.01$).

was not necessary. The T_e of corn starch significantly increased as water content was raised from 30 to 70%. The T_e of both corn and waxy corn decreased in excess water (Tables 6 and 7).

When the water content increased from 30 to 50%, the decrease in T_o of starch extracted from corn dried at 20 °C can be attributed to the ability of granules to swell. With the availability of water, the swelling of starch granules leads gelatinization to occur at lower temperatures than when water availability is limited. High-temperature drying may have affected the ability of granules to swell; therefore, the decrease in T_o of starch extracted from corn dried at 100 °C can be observed at only one heating rate, whereas the decrease in T_o of starch extracted from corn dried at 20 °C was observable over a wider heating rate range.

There are different accounts of the effect of water content on starch gelatinization. For rice starch, the position of the gelatinization peak is independent of water content (13). On the other hand, the DSC thermograms of wheat and corn starches are strongly water content dependent (26). DSC thermograms for waxy corn starch are strongly influenced by water content in the 30 and 60% ranges (27). For amaranth starch T_o and T_p do not change significantly with water content, whereas T_e decreases dramatically in excess water. The decrease of T_e with water content can be explained by lowering of the temperature at which gelatinization is completed as water content increased (12). Our data are in accordance with the reports of Resio and Suarez (12), Chiotelli et al. (26), and Rolee et al. (27).

The effect of water content on ΔH_g of corn and waxy corn is given Tables 8 and 9, respectively. ΔH_g of corn starch

Table 7. Gelatinization End Temperatures ($^{\circ}\text{C}$)^a of Starches Extracted from Waxy Corn Dried at 70 and 100 $^{\circ}\text{C}$

water content (%)	drying temp ($^{\circ}\text{C}$)	heating rate					
		1 $^{\circ}\text{C}/\text{min}$	3 $^{\circ}\text{C}/\text{min}$	5 $^{\circ}\text{C}/\text{min}$	7 $^{\circ}\text{C}/\text{min}$	10 $^{\circ}\text{C}/\text{min}$	15 $^{\circ}\text{C}/\text{min}$
70	70	77.2 \pm 0.6 a2	78.0 \pm 0.5 a2	79.4 \pm 0.7 b2	80.6 \pm 0.5 c2	82.0 \pm 0.4 d12	85.5 \pm 0.6 e1
	100	77.8 \pm 0.2 a2	79.4 \pm 0.6 b3	80.2 \pm 1.3 b2	82.1 \pm 0.4 c3	84.8 \pm 0.9 d3	88.8 \pm 1.1 e2
90	70	74.2 \pm 0.0a1	75.5 \pm 0.1 b1	76.8 \pm 0.3 c1	78.0 \pm 0.5 d1	81.2 \pm 0.7 e1	85.0 \pm 0.8 f1
	100	75.1 \pm 0.4 a1	77.5 \pm 0.5 b2	77.9 \pm 0.4 b1	80.0 \pm 0.6 c2	82.9 \pm 0.7 d2	84.6 \pm 0.1 e1

^a Means \pm SD ($n = 3$); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different ($p \leq 0.01$).

Table 8. Gelatinization Enthalpies (J/g of Starch)^a of Starches Extracted from Corn Dried at 20 and 100 $^{\circ}\text{C}$

water content (%)	drying temp ($^{\circ}\text{C}$)	heating rate					
		1 $^{\circ}\text{C}/\text{min}$	3 $^{\circ}\text{C}/\text{min}$	5 $^{\circ}\text{C}/\text{min}$	7 $^{\circ}\text{C}/\text{min}$	10 $^{\circ}\text{C}/\text{min}$	15 $^{\circ}\text{C}/\text{min}$
30	20	1.1 \pm 0.2 a1	1.1 \pm 0.3 a1	1.2 \pm 0.1 a1	1.4 \pm 0.1 a1	1.8 \pm 0.3 a1	0.7 \pm 0.1 a1
	100	0.6 \pm 0.1 a1	0.7 \pm 0.1 a1	0.5 \pm 0.2 a1	0.7 \pm 0.1 a1	0.8 \pm 0.1 a1	0.8 \pm 0.3 a1
50	20	5.5 \pm 3.1 a3	10.7 \pm 1.7 c56	10.1 \pm 1.4 c4	10.4 \pm 0.8 c45	9.6 \pm 0.2 c23	7.0 \pm 2.4 b2
	100	2.9 \pm 0.4 a2	4.7 \pm 1.0 b2	5.3 \pm 0.1 b2	7.4 \pm 0.7 c2	8.5 \pm 2.2 c2	8.9 \pm 0.3 c3
70	20	7.8 \pm 0.6 a4	9.2 \pm 0.7 ab4	10.2 \pm 1.4 bc4	11.5 \pm 0.7 c5	10.9 \pm 0.3 c34	10.5 \pm 0.9 c4
	100	8.6 \pm 1.3 a4	9.5 \pm 0.3 ab45	10.8 \pm 1.8 bc4	10.5 \pm 0.5 bc45	11.2 \pm 1.7 c4	9.8 \pm 0.4 abc34
90	20	10.4 \pm 1.8 b5	12.6 \pm 0.9 c6	8.6 \pm 1.2 a3	10.0 \pm 0.9 ab34	9.5 \pm 1.2 ab23	9.6 \pm 1.3 ab34
	100	7.3 \pm 0.7 a4	7.5 \pm 0.4 a3	9.7 \pm 0.2 b34	8.7 \pm 0.4 ab45	9.9 \pm 0.1 b234	8.9 \pm 1.3 ab3

^a Means \pm SD ($n = 3$); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, drying temperature and water content effects) are not significantly different ($p \leq 0.01$).

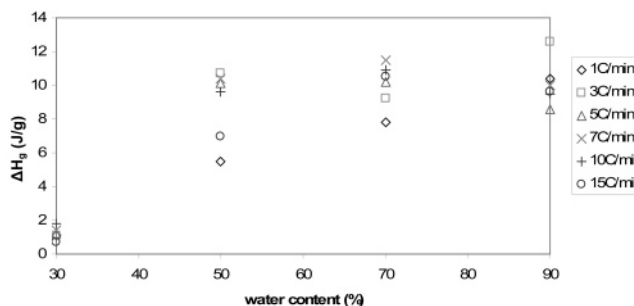
Table 9. Gelatinization Enthalpies (J/g of Starch)^a of Starches Extracted from Waxy Corn Dried at 70 and 100 $^{\circ}\text{C}$

water content (%)	drying temp ($^{\circ}\text{C}$)	heating rate					
		1 $^{\circ}\text{C}/\text{min}$	3 $^{\circ}\text{C}/\text{min}$	5 $^{\circ}\text{C}/\text{min}$	7 $^{\circ}\text{C}/\text{min}$	10 $^{\circ}\text{C}/\text{min}$	15 $^{\circ}\text{C}/\text{min}$
50	70	5.6 \pm 2.9 a1	9.9 \pm 1.1 bc1	11.2 \pm 0.7 c1	10.8 \pm 1.9 c12	12.0 \pm 1.4 c1	7.6 \pm 2.3 ab1
	100	9.7 \pm 0.6 ab2	10.1 \pm 0.3 ab12	12.1 \pm 1.4 b1	10.2 \pm 1.4 ab1	11.5 \pm 0.4 b1	8.7 \pm 0.8 a1
70	70	12.2 \pm 0.8 a2	12.5 \pm 2.0 a12	12.5 \pm 0.9 a1	13.0 \pm 0.9 a23	13.0 \pm 0.8 a1	12.5 \pm 1.7 a2
	100	11.1 \pm 0.8 a2	11.2 \pm 2.4 a12	11.8 \pm 1.9 ab1	13.2 \pm 0.5 ab23	13.9 \pm 1.6 b1	11.5 \pm 1.2 ab2
90	70	10.5 \pm 1.5 a2	11.4 \pm 0.8 ab12	15.0 \pm 1.0 c2	12.1 \pm 1.3 ab123	12.0 \pm 2.0 ab1	13.2 \pm 1.0 bc2
	100	10.9 \pm 3.7 a2	12.7 \pm 1.5 ab2	12.8 \pm 1.7 ab12	14.0 \pm 1.4 b3	11.9 \pm 2.4 ab1	12.1 \pm 1.7 ab2

^a Means \pm SD ($n = 3$); values within each group followed by the same letter (in row; heating rate effect) or numeral (in column, water content effect) are not significantly different ($p \leq 0.01$).

increased with water content between 30 and 70%. With further increase of water content, ΔH_g of starches extracted from corn dried at 20 $^{\circ}\text{C}$ increased at lower heating rates and then slightly decreased at higher heating rates. For starches extracted from corn dried at 100 $^{\circ}\text{C}$, ΔH_g decreased as water content increased from 70 to 90%. For waxy corn starch, ΔH_g increased as water content was raised from 50 to 70%, whereas it remained constant with further increases in water content.

The increase in ΔH_g with water content has been reported by many authors (12, 13, 27, 28). The increase has been reported to be linear until 60% water (13), reaching a constant value above 75% water (12). Furthermore, ΔH_g and the corresponding starch/water ratio could be fitted by linear regression for a water content of $<60\%$ at which the relationship between ΔH_g and water content is linear. Furthermore, by extrapolating the straight line to $\Delta H_g = 0$, we can determine the minimum level of water required for gelatinization. For rice starch, obtained via different extraction treatments and subjected to a 5 $^{\circ}\text{C}/\text{min}$ heating rate, the minimum levels of water for gelatinization have been reported as <1 , 11, and 18% (12). The dependence of ΔH_g of corn starch on water content is depicted in Figures 5 and 6. These figures show that a minimum of 21 or 29% water content is required for gelatinization of starch dried at 20 or 100 $^{\circ}\text{C}$ and subjected to a heating rate of 1 $^{\circ}\text{C}/\text{min}$, respectively. The calculations were made in the water content range of 30–70%, and the regression coefficients were 0.968 and 0.943, respec-

**Figure 5.** Gelatinization enthalpy (ΔH_g) versus water content for starches extracted from corn dried at 20 $^{\circ}\text{C}$ at different heating rates.

tively. The results indicate that starch from corn dried at higher drying temperature needs more water for gelatinization than starch from corn dried at lower temperature.

DSC thermograms of all starches with 50% water at all heating rates exhibit bimodal endotherm peaks, which are assigned to amylopectin double-helix dissociation and melting of crystals (26). DSC thermograms of starches from corn dried at 20 and 100 $^{\circ}\text{C}$ with 50% water content subjected to a heating rate of 10 $^{\circ}\text{C}/\text{min}$ are given in Figure 4. Bimodal peaks at this water content are consistent with published data (3). As the water content increased to 70 and 90%, the two overlapping peaks merged into a single peak as reported by Randzio et al. (3). In addition, when the water content decreased, the lower temper-

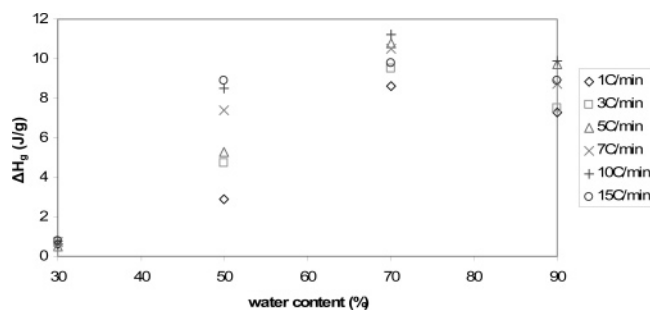


Figure 6. Gelatinization enthalpy (ΔH_g) versus water content for starches extracted from corn dried at 100 °C at different heating rates.

ature peak disappeared and the second peak shifted to higher temperatures (3). On the other hand, Fukuoka et al. (29) stated that the second peak tends to shift to a higher temperature with a decrease in moisture content as reported by Randzio et al. (3), whereas the first peak remains at ≈ 60 °C. We observed only one peak, at about the same temperature, for both 30 and 50% water content samples. Supposedly, the second peak has shifted to a higher temperature that is out of the range of this study.

Effect of Heating Rate. In accordance with published data (12, 13), all gelatinization transition temperatures of corn and waxy corn starch increased with heating rate (Tables 2–7). Furthermore, the endothermic transition broadened with an increase in heating rate. This has been explained by the presence of various crystallite structures in starch granules (12). Moreover, Ozawa (15) pointed out that at high heating rates creation of temperature gradients within the sample leads to broadening of the endotherm peak.

Heating rate had no effect on ΔH_g of corn starch at 30% water content (Table 8). At other water contents, the ΔH_g of starch extracted from corn dried at 20 °C increased as heating rate increased from 1 to 3 °C/min. At heating rates of 3 °C/min and higher, ΔH_g of samples containing 50 and 90% water tended to decrease. For samples containing 70% water, the increase in ΔH_g continued up to 7 °C/min heating rate and then remained relatively constant. There was a slight tendency for ΔH_g to increase in starch from corn dried at 100 °C with heating rate from 1 to 10 °C/min at all water contents other than 30%.

Heating rate did not affect ΔH_g of starch from waxy corn dried at 70 °C at 70% water content (Table 9). At 50 and 90% water contents ΔH_g increased with heating rate up to 5 °C/min and then decreased. The ΔH_g of starch from waxy corn dried at 100 °C remained relatively constant at the lower and intermediate heating rates and then tended to decrease at high heating rates.

There are conflicting reports on the effect of heating rate on ΔH_g : a decrease in ΔH_g with an increase in heating rate (13, 30) and an increase in ΔH_g with heating rate until it reached a maximum value at 10 °C/min (12). Biliaderis et al. (11) stated that heating rate influenced melting thermodynamic parameters of starch dispersions at intermediate water content. This may be the reason for the conflicting reports, because the effect of heating rate on ΔH_g is apparently dependent on water content. Our results are generally in accordance with those of Resio and Suarez (12).

Some slow exothermic phenomena, which are sometimes disregarded, occur at low heating rates. These exothermic transitions are even more pronounced than the endothermic peaks at very low heating rates (3). We observed some exothermic peaks at low heating rates for samples with 70 and 90% water contents (Figure 7). The exothermic peak for

starches extracted from corn dried at 20 °C with 90% water content at 1 °C/min was even higher than the endothermic peak. At 90% water content the exothermic peaks decreased with heating rate from 1 to 3 °C/min (Figure 7); at 70% water content they were observable only at 1 °C/min. For waxy corn starches, exothermic peaks were seen for samples containing 70 and 90% water content at only 1 °C/min. Contrary to our observation with corn starch, exothermic peaks were independent of drying temperature for waxy corn starch. There were few or no exothermic peaks for starches extracted from corn dried at 100 °C, suggesting that high drying temperature may have damaged the bond-forming ability of amylose with amylopectin, which is attributed to the exothermic phenomena (3). At lower water content the exothermic transition starts at higher temperatures (3), which were out of range for this study. This may be why we did not observe exothermic transitions at 30 and 50% water contents.

SEM Observations. SEM observations of starches from corn dried at 20 and 100 °C and from waxy corn dried at 70 and 100 °C are given in Figures 8 and 9, respectively. The micrographs did not show any significant morphological differences, although the wrinkled surface of starch granules is probably due to shrinkage of granules caused by high-temperature drying (Figure 8b). The wrinkled surfaces on waxy corn granules were fewer and smaller size than on corn starch granules (Figure 9b). The magnification was the same for all micrographs; however, the focus of the microscope was changed to show shrinkage on the surface better in Figures 8b and 9b.

Gelatinization Kinetics. The k_r values of corn and waxy corn starches calculated from eq 4 are given in Tables 10 and 11, respectively. The k_r values for all starches increased with water content except for the corn starch sample at 30%, which probably followed a different kinetics for samples with excess water. An increase in k_r values for in situ and in vitro gelatinization with temperature relates to the increasing starch–water reactivity and/or water transferability (16). In addition, higher k_r values indicate a more rapid process of gelatinization (2). On this basis, the increasing k_r with water content can be explained by the increasing water transferability due to more available water to starch–water reactivity, depending on the faster gelatinization. Moreover, it was indicated that the high-temperature drying made gelatinization difficult to occur and transition temperatures increase. It is interesting to note that starch–water reactivity increased with drying temperature for corn starch at 50 and 70% water contents and waxy corn starch at 70 and 90% water contents. These increases point out that corn and waxy corn starches dried at high temperature gelatinize more rapidly probably because of their higher gelatinization temperatures.

The effect of temperature on gelatinization was evaluated using eq 5 (Table 12) over the water content range of 50–90%. Experimental data are represented by eq 5 well. E_a values of waxy corn starch and starches dried at high temperature were higher than those of corn starch and starches dried at low temperature, respectively. The higher the activation energy, the more sensitive is the gelatinization to temperature. In addition, E_a is also an indicator for minimum energy required for gelatinization to occur (16). Accordingly, gelatinization of waxy corn starch and that of starch dried at high temperature were more sensitive to temperature, and gelatinization of these starches requires more energy to overcome resistance of the grain to water transfer.

The E_a values obtained from eqs 6 and 7 for corn and waxy corn starch gelatinization are listed in Tables 13 and 14,

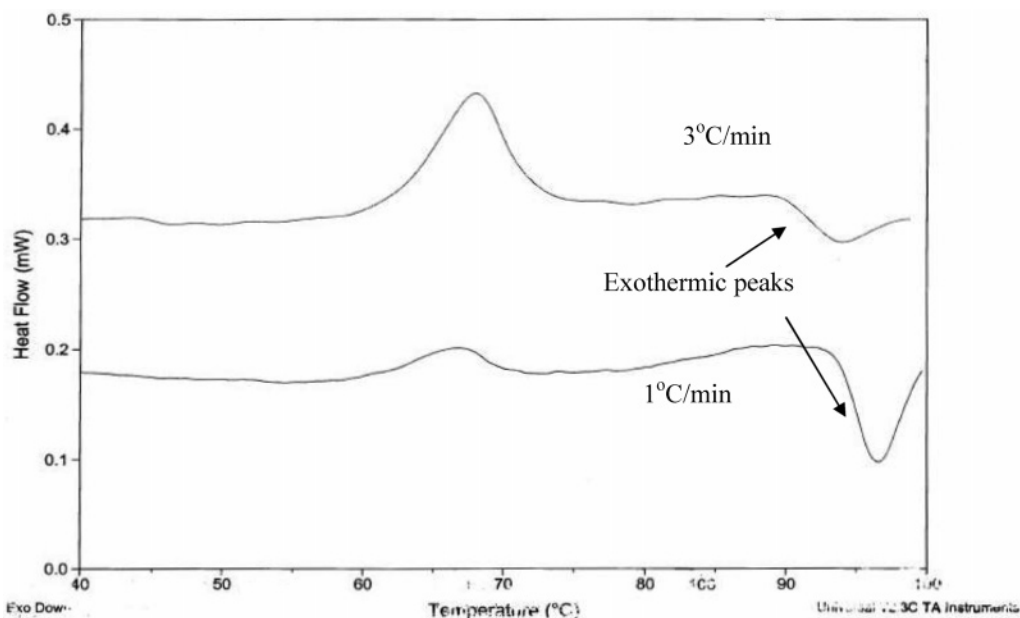


Figure 7. DSC thermograms of starch extracted from corn dried at 20 °C with 90% water at heating rates of 3 and 1 °C/min.

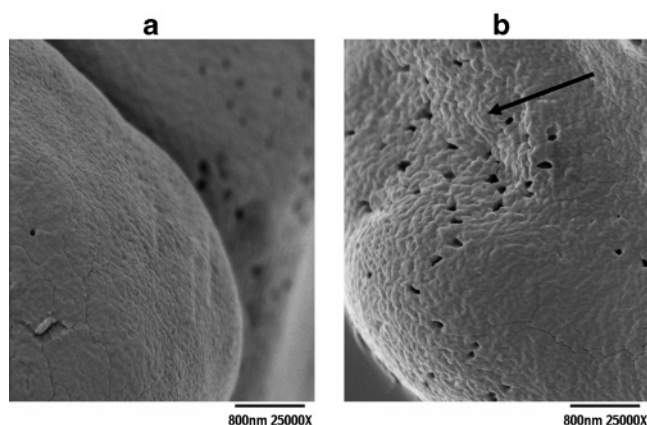


Figure 8. SEM observations of starches extracted from corn dried at 20 °C (a) and 100 °C (b). The arrow points at the shrinkage on the surface. (The magnification was the same for both panels; however, the focus of microscope was changed to show shrinkage better.)

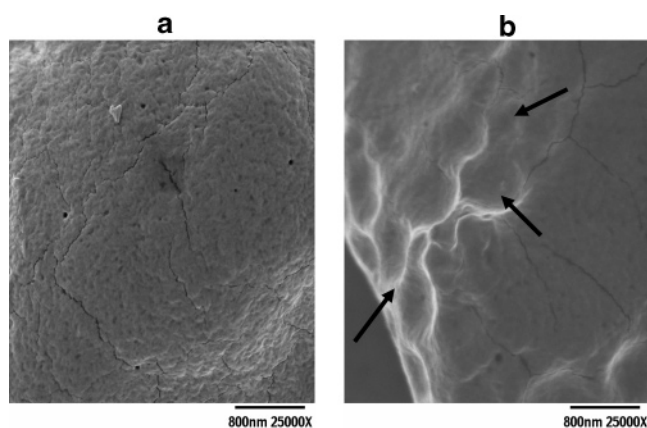


Figure 9. SEM observations of starches extracted from waxy corn dried at 70 °C (a) and 100 °C (b). The arrows point at a number of shrinkage areas on the surface. (The magnification was the same for both panels; however, the focus of microscope was changed to show shrinkage better.)

respectively. Both procedures gave very high R^2 values. Although eq 7 yielded slightly lower values, for a given sample E_a values calculated by both kinetic models were comparable.

Table 10. First-Order Reaction Rate Constant ($k_r \times 10^{-5}, \text{s}^{-1}$)^a for Starches Extracted from Corn Dried at 20 and 100 °C

water content (%)	heating rate range (°C/min)	drying temp	
		20 °C	100 °C
30	3–7	30 (0.957)	10 (0.949)
50	1–5	8 (0.998)	10 (0.993)
70	5–10	10 (0.911)	30 (0.873)
90	3–7	30 (0.905)	30 (0.907)

^a Values in parentheses denote R^2 in the table.

Table 11. First-Order Reaction Rate Constant ($k_r \times 10^{-5}, \text{s}^{-1}$)^a for Starches Extracted from Waxy Corn Dried at 70 and 100 °C

water content (%)	heating rate range (°C/min)	drying temp	
		70 °C	100 °C
50	3–7	6 (0.909)	6 (0.989)
70	5–10	10 (0.612)	20 (0.994)
90	3–7	10 (0.999)	30 (0.981)

^a Values in parentheses denote R^2 in the table.

Table 12. Activation Energy (E_a) for Starches Extracted from Corn and Waxy Corn and Coefficient of Determination (R^2) for Fit of Equation 5

starch	E_a (kJ/mol)	R^2
corn dried at 20 °C	896	1
corn dried at 100 °C	2199	0.903
waxy corn dried at 70 °C	4977	0.946
waxy corn dried at 100 °C	16628	0.998

E_a values of both corn starches increased with water content and reached an almost constant value at 70% for starch from corn dried at 100 °C (Table 13), similar to published data (13). The E_a of starch extracted from waxy corn dried at 70 °C showed a similar increase with water content and then it decreased at 90% (Table 14). In the case of starch extracted from waxy corn dried at 100 °C, E_a values decreased with water content. The E_a of corn starch decreased with drying temperature except at 30% water content, at which it increased. The E_a of waxy corn starch increased with drying temperature at 50 and 90% water contents and decreased at 70% water content. The

Table 13. Activation Energy (E_a , kJ/mol)^a for Gelatinization of Corn Starch for Fit of Equations 6 and 7 in the Heating Range of 3–10 °C/min

kinetic model	30% water		50% water		70% water		90% water	
	20 °C drying temp	100 °C drying temp	20 °C drying temp	100 °C drying temp	20 °C drying temp	100 °C drying temp	20 °C drying temp	100 °C drying temp
eq 6	267 (0.932)	281 (0.850)	412 (0.952)	316 (0.954)	424 (0.962)	371 (0.970)	504 (0.850)	362 (0.912)
Kissinger (eq 7)	261 (0.930)	276 (0.845)	406 (0.951)	310 (0.952)	418 (0.961)	365 (0.969)	498 (0.847)	356 (0.909)

^a Values in parentheses denote R^2 .

Table 14. Activation Energy (E_a , kJ/mol)^a for Gelatinization of Waxy Corn Starch for Fit of Equations 6 and 7 in the Heating Range of 3–10 °C/min

kinetic model	50% water		70% water		90% water	
	70 °C drying temp	100 °C drying temp	70 °C drying temp	100 °C drying temp	70 °C drying temp	100 °C drying temp
eq 6	379 (0.983)	450 (0.999)	491 (0.986)	433 (0.949)	319 (0.906)	372 (0.815)
Kissinger (eq 7)	374 (0.983)	444 (0.999)	486 (0.986)	428 (0.947)	313 (0.903)	366 (0.810)

^a Values in parentheses denote R^2 .

Table 15. Activation Energy (E_a) for Starches and R^2 for Fit of Equation 8

water content (%)		drying temp (°C)	E_a (kJ/mol)	R^2
30	corn	20	221	0.940
		100	249	0.833
50	corn	20	407	0.958
		100	252	0.914
	waxy corn	70	377	0.980
		100	444	0.999
70	corn	20	395	0.973
		100	346	0.952
	waxy corn	70	465	0.987
		100	409	0.939
90	corn	20	412	0.873
		100	331	0.952
	waxy corn	70	273	0.868
		100	304	0.810

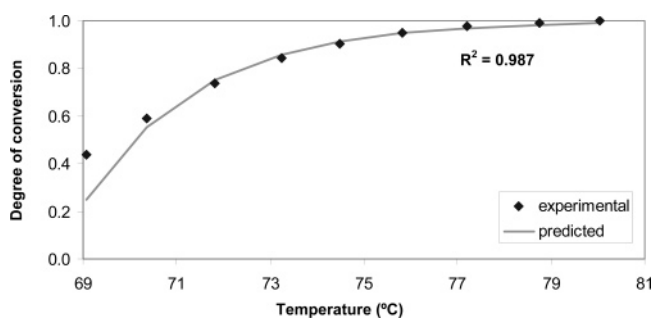
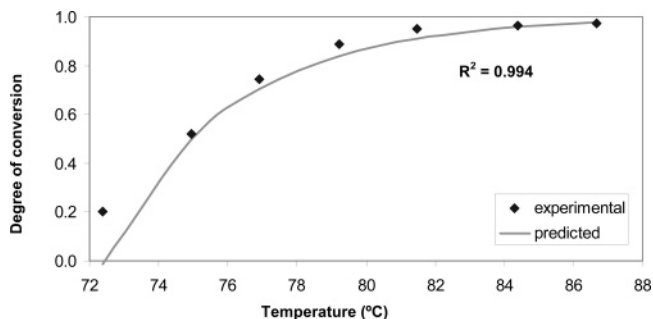
effect of water content and drying temperature on E_a values of starches calculated with eqs 6 and 7 followed the same trends.

On the basis of our findings, $\beta/(1 - \alpha_{Tp})$ is highly correlated with $1/T_p$. Therefore, the left side of eq 4 and eq 6 were combined to express the gelatinization by the following equation:

$$\ln\left(\frac{\beta}{1 - \alpha_{Tp}}\right) = -\frac{E_a}{R} \frac{1}{T_p} + C \quad (8)$$

E_a values of all starches obtained using eq 8 are given in **Table 15**. The following trends can be observed: for starch extracted from corn dried at 20 °C, E_a increased with water content from 30 to 50% and then remained the same; for starch from corn dried at 100 °C, E_a increased with water content up to 70% and then remained relatively constant; for starch extracted from waxy corn dried at 70 °C, E_a increased with water content but with a dramatic decrease at 90% water content; for starch from waxy corn dried at 100 °C, E_a decreased with water content.

Equations 6 and 7 are very well-known models used for characterizing starch gelatinization. Equation 8 we proposed yielded E_a values, and their trend with water content, comparable to those obtained from eqs 6 and 7. Additionally, eq 8 allows for determining the degree of conversion (α) at any time. The α values calculated using eq 8 are compared to the experimental α values obtained from eq 1 in **Figures 10** and **11**. Predicted

**Figure 10.** Degree of conversion (α) of starch extracted from corn dried at 20 °C versus temperature at 70% water content and 10 °C/min.**Figure 11.** Degree of conversion (α) of starch extracted from waxy corn dried at 70 °C versus temperature at 90% water content and 10 °C/min.

results are valid above peak temperatures, because peak temperatures were used in eq 8. Results show that data fit very well for corn starch at 70 and 90% water contents, whereas it is true for waxy corn starch at 90% water content. The model requires T_p and α_{Tp} . With regard to the other parameters, the heating rate is known and E_a can be calculated using other first-order equations, as from the Kissinger equation. Using this model, α at any temperature can be estimated above T_p . It gives more accurate results at >50% water contents, supposedly because the gelatinization kinetics of intermediate and low water levels are different.

In summary, high-temperature drying of corn and waxy corn resulted in an increase of all gelatinization transition temperatures of extracted starches. These increases are attributed to a reduction of water entry into granules due to inhibited interaction between water and starch. Drying temperature had no effect on ΔH_g of waxy corn starch at all water contents and corn starch at 30 and 70% water contents, whereas it decreased with drying

temperature for corn starch containing 50 and 90% water. The difficulty in starch–protein separation due to the adverse effect of high-temperature drying may lead to a reduction in ΔH_g . The minimum level of water for corn starch gelatinization increased with drying temperature; in addition, waxy corn starches needed more water for gelatinization than corn starches. A strong relationship between ΔH_g and T_p was found even though they were affected by high-temperature drying via different mechanisms. The effect of water content on transition temperatures was different and dependent on drying temperature. The T_o of corn starch decreased as water content increased from 30 to 50% and then increased with water content up to 70% water. In these water content ranges, the effect of water content on the T_o of corn starch became limited probably due to the adverse effect of high-temperature drying on the swelling of starch granules. At intermediate water contents, the T_o of waxy corn starch has a tendency to increase, whereas at excess water content the T_o of corn and waxy starches remained constant. T_p and T_e values of corn and waxy corn starches increased with water content up to 70%, and then T_p remained relatively constant while T_e decreased in excess water. The decrease of T_e with water content can be attributed to the lowering of the temperature at which gelatinization is completed as water content increased. At 50% water content, corn and waxy corn starches exhibited bimodal endothermic peaks, which can be assigned to amylopectin double-helix dissociation and crystal melting. As the water content increased, the first peak remained at ≈ 60 °C, whereas the second peak might have shifted to higher temperatures. All transition temperatures of corn and waxy corn starch increased with heating rate, whereas the effect of heating rate on ΔH_g was dependent on water content. At lower heating rates, besides endothermic peaks, exothermic peaks were observed for samples containing 70 and 90% water. Exothermic peaks may have probably shifted to higher temperatures for samples containing lower water contents. SEM observations revealed no significant morphological differences between granules; however, corn and waxy corn starches dried at high temperature exhibited wrinkled surfaces probably due to high-temperature drying. The kinetic modeling of starch gelatinization can be used in controlling parameters and selecting process conditions during processing. E_a values, calculated from an Arrhenius-type equation, of waxy corn starch and starches from corn dried at high temperature increased compared to corn starch and starches dried at low temperatures, respectively. This means that waxy corn starch and starches from corn dried at high temperature are more sensitive to temperature and require more energy for gelatinization. Concurring with published data, E_a values calculated from two first-order models (eqs 6 and 7) increased with water content. We found that $\beta/(1 - \alpha_{Tp})$ highly correlated with $1/T_p$, and using eq 8 an attempt was made to calculate α above T_p . The results were more accurate at >50% water contents for both corn and waxy corn starches than at lower water content.

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