Pressure−Temperature Phase Diagrams of Maize Starches with Different Amylose Contents

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The amylose/amylopectin ratio in starch granules has a distinct impact on the physicochemical properties of starches. In this study the effects of high pressure and temperature combinations on the gelatinization of four maize starches with different amylose contents were investigated in an excess of water (90% w/w). Microscopy was used to determine the loss of birefringence in starch granules. Experiments were undertaken in the pressure range of 0.1−750 MPa and temperature range of 30−110 °C, holding the conditions constant for 5 min. Temperature and pressure stabilities of high amylose starches were found to be significantly higher than those of waxy and normal maize starch. Thermodynamic models are proposed to describe the loss in birefringence as a function of pressure and temperature. From the pressure−temperature phase diagrams constructed it was evident that maize starch gelatinization is not accelerated at pressures below 300−400 MPa. However, at higher pressures the threshold temperature to initiate starch granule hydration and gelatinization is significantly reduced for all starches investigated. This study extends the knowledge of the impact of high pressure on food components and will possibly make the technology more attractive to use as a substitute for or in combination with conventional food-processing methods.

KEYWORDS: Maize starch; amylose content; high pressure; gelatinization; phase diagram

INTRODUCTION

Starch is an important energy source in human nutrition. However, its nutritional value depends on its primary composition and physical structure and subsequent processing. Starch occurs in a wide range of different plants in various tissues and is deposited in the form of granules. The size and shape of granules differ with the type of starch according to its origin. The granules of naturally occurring starches contain two principal types of polysaccharides, amylose and amylopectin. Both are made up of glucose polymers, with amylose predominantly linear and amylopectin as a highly branched molecule. Due to its many branches amylopectin has a molecular mass that is about 1000 times that of amylose. However, any of its branched chains contains only up to 30 glucose units, whereas amylose has a chain length of 500−6000 glucose units depending on its botanical origin (*1*).

Maize starch is widely used in the food industry, often in applications requiring specific viscosity and texture properties. Normal maize starch contains approximately 25% amylose and 75% amylopectin. Other maize types have been produced that contain < 1% amylose, as in waxy maize, or amylose as high as 85%, as in "amylomaize". Such distinct starches not only are of great commercial value due to their different properties (*2, 3*) but also provide an excellent tool to study the roles of amylopectin and amylose in the granule. Normal maize starch granules are medium-sized, polygonal or round, and 10−25 μm in diameter (*4*). Maize starch varieties with high amylose content differ significantly in size, shape, surface coarseness, and relative crystallinity and have a B-type crystal structure in contrast to A-type crystals in normal or waxy maize starches (*4−6*). High amylose maize starches are also characterized by significantly higher phase transition temperatures and lower swelling capacity than normal or waxy maize starches (*7*).

Starch gelatinization is essential for a range of industrial and culinary uses due to its considerable effect on the structural, textural, and physical properties of products. High-pressure processing (HPP) has been found to be an effective physical tool to gelatinize starch granules (*8*). The advantage over the conventional thermal treatment of starches is that a more homogeneous and better defined degree of gelatinization can be achieved through more accurately controlled process parameters (*9*). The detailed mechanism of starch gelatinization under high-pressure conditions is not well understood.

Similar to heat-induced gelatinization, the degree and rate of granule gelatinization under high pressure depend on the treatment temperature and processing time as well as other environmental

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Table 1. Composition of Maize Starches Used in This Study

starch type	amylose (%)[a]	mol mass (kDa)[b]	moisture (%)	protein (%)	fat (%)	ash (%)
waxy maize	<0.5	20787	11.5	0.25	0.17	0.06
normal maize	26	13000	12.8	0.34	0.59	0.08
Gelose 50	50	5115	14.7	0.47	0.91	0.07
Gelose 80	80	673	13.5	0.60	1.08	0.05

[a] Supplied by Penford. [b] Taken from Chen et al. (*4*).

factors (e.g., ion concentration) (*10−15*). Under pressure, starch granules often remain intact or are just partly disintegrated, and the solubilization of amylose is rather poor (*9, 16*). This might be because some crystalline granule structures are prevented from melting due to the stabilization of amylopectin structures by the still present amylose (*16*). This could be a possible reason for the significant difference in, for example, viscosity between starch gels formed at different pressure−temperature conditions and/or the slower retrogradation rate of pressure-treated starch slurries compared with heat-processed starch slurries (*16, 17*). The pressure range in which gelatinization occurs is dependent on the proportion of amylose and amylopectin (*18, 19*) and specific to starch granule-type characterized by its crystalline structure; for example, B-type starches are more resistant to gelatinization under pressure than A- and C-type starches (*8, 11, 20*).

The amylose level has been found to have an impact on the gelatinization temperature and enzymatic digestibility, typically raising the gelatinization temperature and reducing the digestibility or the glycemic index (GI) of starches (*21−23*). The reduced GI is often desirable; however, the higher gelatinization temperature often makes the starch less functional in many food applications.

This study was undertaken to understand the impact of combined pressure−temperature treatments on the phase transition of 10% w/w maize starch slurries with different amylose contents. Thermodynamic models were applied to describe starch gelatinization as a function of pressure and temperature. These models can be used to construct phase diagrams showing the transition of starch granules over a broad range of pressure−temperature combinations tested in this study.

MATERIALS AND METHODS

Materials. The maize starches used in this study, Mazaca 3401X (waxy maize), Avon (normal maize), Gelose 50, and Gelose 80, are commercially available and were kindly supplied by Penford (Australia). The composition of these maize starches was analyzed and is shown in **Table 1**. Moisture, fat, and ash contents were determined using ISO 1666, 3947, and 3593, respectively. Protein contents were analyzed using AACC method 46-30.

The maize starches were suspended in distilled water (10% w/w), taking the water content of the starches into account during all experiments. Starch−water slurries were prepared approximately 2 h prior to processing to enable hydration of amorphous regions of the granule.

Isothermal and Isobaric Treatments and Sample Analysis. Isothermal treatments of maize starches at ambient pressure were investigated between 50 and 110 °C and were carried out by immersing cryo vials (5000-1012, Nalgene, Rochester, NY) containing 1.5 mL of starch slurry in a temperature-controlled water or oil bath. After reaching target temperature (approximately after 2 min), the samples were kept at the selected temperatures for 5 min. Samples were then withdrawn from the bath and immediately cooled in iced water.

Within 60 min of storage in iced water, starch granules were analyzed by detecting the loss of optical birefringence under a microscope (BH2-MJLT, Olympus Optical Co. Ltd., Tokyo, Japan) equipped with a polarization filter. A statistically sufficient number (300−550) of starch granules of each sample were counted, and the number of starch granules that did not completely lose birefringence (N) was determined and used to calculate the degree of gelatinization. The determination of N of Gelose 50 and Gelose 80 was difficult due to very broad particle size distribution,

agglomeration of small particles, and the presence of some very unusually shaped granules. Some of the particles showed very little or no birefringence initially, possibly due to the lower crystallinity of these two starches compared with normal maize starch (*3*). Therefore, the degree of starch gelatinization (D_G) was calculated with eq 1 by dividing the number of granules with birefringence (N_B) by the product of the total number of counted starch granules N, which had to be multiplied by the relative number of granules that did show birefringence initially (N_{Bi}/N_i).

$$D_G = \left(1 - \frac{N_B}{N \times \frac{N_{Bi}}{N_i}}\right) \times 100 \qquad (1)$$

Starch solutions were pressurized in a multivessel HPP equipment (U111, Unipress, Warsaw, Poland) as described previously (*10*). The starch suspension (10% w/w) was transferred into the cryo vial, which was stored in iced water. The cooled samples were then incorporated in the heated pressure vessel. Compression was started when the temperature of the sample reached a level that eventually resulted in the target temperature (±1 °C) due to compression heating during the pressure ramp-up time. The sample temperature was measured with a thermocouple, which was placed directly inside the cryo vial. To minimize the impact of the pressurization and decompression phase on the starch granule's birefringence, the compression and decompression rates were standardized at approximately 20 and 150 MPa/s, respectively. Pressure treatments above 680 MPa were performed in a larger (3.5 L) high-pressure plant (FPG11780B110 High Pressure ISO-LAB System, Stansted Fluid Power Ltd., Essex, U.K.) using compression and decompression rates similar to those used with the multivessel unit. In this unit, the pressure-transmitting fluid was a mixture of water and glycol (ratio 2:1). For a better control and more accurate prediction of the temperature profile of the samples, cryo vials with the starch slurries were inserted in a 0.7 L plastic bottle filled with deionized water and equipped with two thermocouples. The bottle was then preheated to a set temperature that would result in the desired temperature after compression heating and was then placed into the high-pressure treatment chamber. The vessel temperature was preset to the target temperature to minimize temperature loss during the pressure-holding phase.

The 5 min holding was immediately started once the desired pressure−temperature condition had been reached. After pressure release, samples were removed from the vessels within approximately 0.5 min and were stored on ice for at least 15 min. Pressure treatments were performed at 200−750 MPa and temperatures ranging from 30 to 100 °C.

Model Fitting. The behavior of biopolymers is determined by the free volume which results from the conformation of the molecule. In contrast to heating, which causes an increase in free volume through molecular fluctuation, pressure triggers reactions that reduce the relative molecular volume of reactants. It has been shown that starch granule swelling under pressure leads to specific water−starch linkages resulting in a reduction in volume, meaning that starch granule swelling is favored under pressure (*8, 24*).

A useful model describing the occurring phase transition of starch granules subjected to pressure and temperature is based on the transition state theory of Eyring (*25*), suggesting that starch gelatinization is accompanied by the formation of a transition state which exists in equilibrium with the native and gelatinized state. Thus, the equilibrium process between the two distinct states of starch granules (native and gelatinized) can be expressed using the Gibbs free energy (ΔG)

$$\Delta G = G_{gelatinized} - G_{native} \qquad (2)$$
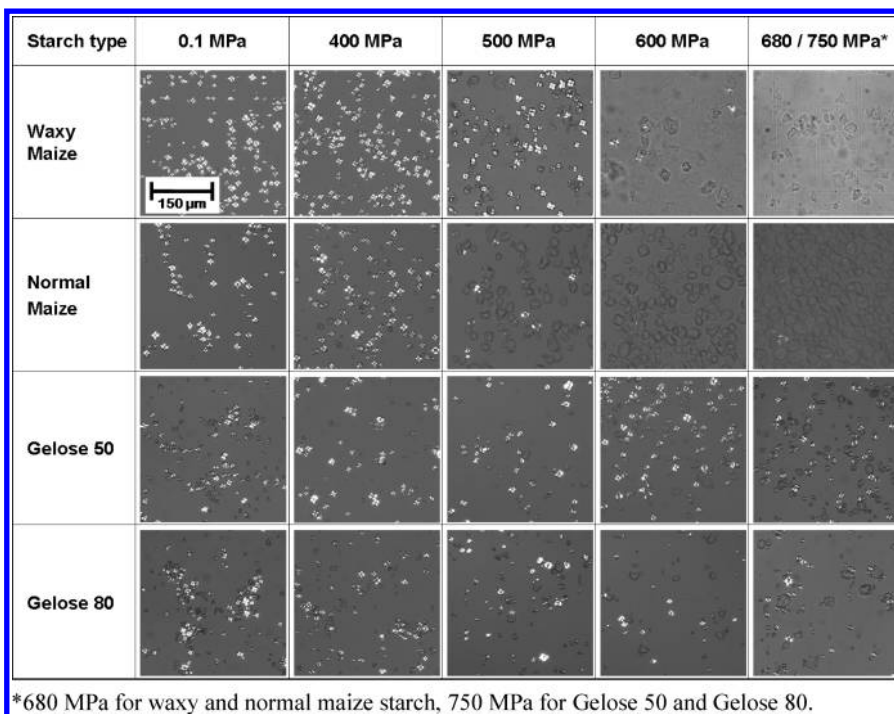
$$\Delta G = -RT \ln K \qquad (3)$$

Figure 1. Granular structure of maize starches with different amylose contents after 5 min of treatment at 30 °C (waxy and normal maize) or 50 °C (Gelose 50 and Gelose 80) and different pressures as observed by light microscopy with polarized light.

where at a given pressure the equilibrium constant K is dependent on the degree of gelatinization D_G:

$$K = \frac{D_G}{100 - D_G} \tag{4}$$

To asses the effects of pressure (p) and temperature (T) on ΔG, Hawley (*26*) proposed an equation coupling ΔV (volume difference) and ΔS (change of the entropy):

$$d(\Delta G) = \Delta V \, dp - \Delta S \, dT \tag{5}$$

Upon integration of this equation from an arbitrarily chosen reference point T_0, p_0, eq 5 can be approximated by the following second-order approximation (*27, 28*):

$$\Delta G(p,T) = \Delta G_0 + \Delta V_0(p - p_0) - \Delta S_0(T - T_0) + (\Delta\beta/2)(p - p_0)^2 -$$
$$(\Delta C_p/2T_0)(T - T_0)^2 + \Delta\alpha(p - p_0)(T - T_0) \tag{6}$$

β is the compressibility factor, C_p the heat capacity, and α the thermal expansion factor; Δ denotes the change of the corresponding parameter during gelatinization. Due to the quadratic approximation of the difference in Gibbs free energy the equilibrium condition will appear as an elliptical line in the pressure−temperature plane (*29*). Since the first publications of Brandts (*30*) and Hawley (*26*) such elliptic phase diagrams have been reported for proteins and starches, for example, cytochrome *c* (*31*) or maize (*10*).

Equation 6 was fitted to the experimental data sets, and the six model parameters were estimated by regression analysis using a statistical program (Table Curve 3D v3 Statistical Package, Systat Software Inc., Richmond, CA).

Although the swelling and gelatinization of starch is not necessarily an equilibrium process, the following thermodynamic relationship for the degree in gelatinization of starch granules as a function of pressure and temperature can be made by combining eq 3 with eq 4 (*32*):

$$D_G(p,T) = \frac{100}{1 + \exp\left(\frac{\Delta G(p,T)}{RT}\right)} \tag{7}$$

RESULTS AND DISCUSSION

Gelatinization of 10% w/w starch slurries with different amylose contents was observed after 5 min of processing at various pressure−temperature combinations. Although other studies have shown that starch granule swelling and gelatinization at high pressures and/or temperatures increased with exposure time, it is assumed that a treatment time of 5 min is the maximum for an economically attractive process and that it is sufficient to fully swell starch granules and often achieve equilibrium conditions (*10, 32, 33*).

Light Microscopy Observations of Starch Gelatinization by Pressure and Temperature. Figure 1 shows the granular structure of maize starches with different amylose contents observed by microscopy under polarized light. Starch slurries have been treated for 5 min at 30 °C (waxy and normal maize) or 50 °C (Gelose 50 and Gelose 80) and at different pressures. It is apparent that starch granules swell with increasing pressure and lose their characteristic Maltese cross of polarized light refraction. The raw granules (0.1 MPa) of the amylose-rich starches (Gelose 50 and Gelose 80) are significantly smaller on average and irregular in diameter and size, and birefringence has a lower intensity than normal or waxy maize starch granules (*4*). About 20% of Gelose 50 and up to 25% of Gelose 80 raw granules (0.1 MPa) do not exhibit Maltese crosses under polarized light. This is most likely due to the significantly lower degree of crystallinity as compared to waxy and normal maize starch granules (*3, 6*) and possibly due to the irregular and angular shapes of Gelose 50 and Gelose 80 granules.

Waxy and normal maize starches show a significant increase in granule size and a drastic loss of birefringence at pressures higher than 400 MPa at 30 °C, whereas both high-amylose starches did not show significant changes in granule size or loss of birefringence up to 500 MPa at 50 °C (**Figure 1**). Waxy maize starch granules are completely disintegrated when pressurized at 680 MPa and 30 °C for 5 min, whereas the granular structure of normal and high-amylose maize starches is preserved, which is in agreement with the results reported elsewhere (*18, 34*).

There is some evidence that, in contrast to heat gelatinization at ambient pressure, amylose leaching and solubilization are generally poor under pressure (*9, 16, 20*). It can be assumed that

crystalline granule components as well as secondary bonds that maintain the granule structure are prevented from melting or being disrupted due to the higher concentration of amylose in the amorphous granule channels. Knorr et al. (*9*) hypothesized that the side by side dissociation and helix unwinding might be suppressed under pressure because van der Waals interactions

and hydrogen bonds are stabilized, which should favor the helix structure. Consequently, starch gelatinization under pressure is interrupted because the disintegration of the crystalline regions remains incomplete even at elevated temperatures.

In this study, starch granule gelatinization was detected using microscopy to observe the loss in birefringence. The method has been found to be suitable to detect very low degrees of starch gelatinization and has been used by several authors (*11, 35−37*). Douzals et al. (*37*) reported that the method often slightly over-estimates the gelatinized fraction in comparison with differential scanning calorimetry (DSC) measurements. However, it is diffi-cult to evaluate the gelatinization degree of high-amylose maize starch with DSC due to an overlapping of peaks of gelatinization and melting of the amylose−lipid complex.

Pressure−Temperature Effects on the Degree of Gelatinization. Tables 2−5 show the determined degrees of gelatinization D_G of waxy, normal, Gelose 50, and Gelose 80 maize starch slurries (10% w/w), respectively, after 5 min of processing at various isothermal−isobaric treatment conditions. For all investigated starches, D_G generally increased with increasing pressure and temperature. Interestingly, the results also indicated that the loss of granule birefringence was lower for some starch samples when processed at the same temperature and at higher pressure (**Tables 2−4**). For example, Gelose 50 starch slurries treated for 5 min at 85 °C and ambient pressure resulted in a D_G of 78%, whereas with treatment at 85 °C and 200 or 400 MPa, the D_G values were 63 and 62%, respectively. A possible explanation is that it takes longer to reach the target temperature at ambient pressure than during high-pressure treatments, when compression heating results in an instant heat transfer throughout the sample. Thus, there is some potential for increased occurrence of gelati-nization during heat-only treatments due to the slightly extended exposure to high temperature. However, pressure-induced stabi-lization of starch granules has been reported in earlier stu-dies (*8, 36, 38*). Similar to pressure stabilization of proteins (*39, 40*), this may be due to high pressures promoting

Table 2. Degree of Gelatinization D_G (Percent) of Waxy Maize Starch Slurry (10% w/w) after 5 min of Isothermal (*T*) and Isobaric (*p*) Treatment

				T			
p (MPa)	30 °C	50 °C	60 °C	65 °C	70 °C	75 °C	80 °C
0.1	0.00	1.0	13.1	37.9	82.0	99.0	100.0
200	nd[a]	9.4	11.1	38.6	58.1	nd	nd
300	nd	3.8	35.2	52.9	nd	nd	nd
400	3.6	37.7	79.3	99.1	nd	nd	nd
500	25.7	85.5	99.9	nd	nd	nd	nd
600	93.2	99.2	100.0	nd	nd	nd	nd
650	nd	100.0	nd	nd	nd	nd	nd
680	100.0	nd	nd	nd	nd	nd	nd

[a] nd, not determined.

Table 3. Degree of Gelatinization D_G (Percent) of Normal Maize Starch Slurry (10% w/w) after 5 min of Isothermal (*T*) and Isobaric (*p*) Treatment

				T		
p (MPa)	30 °C	50 °C	60 °C	65 °C	70 °C	75 °C
0.1	0.0	0.5	15.0	63.5	96.7	99.9
200	nd[a]	0.0	19.6	72.9	85.4	nd
300	nd	15.2	62.1	87.8	nd	nd
400	7.6	76.1	96.4	99.0	nd	nd
500	83.8	99.0	99.9	nd	nd	nd
600	99.5	100.0	100.0	nd	nd	nd
650	nd	100.0	nd	nd	nd	nd
680	100.0	nd	nd	nd	nd	nd

[a] nd, not determined.

Table 4. Degree of Gelatinization D_G (Percent) of Gelose 50 Maize Starch Slurry (10% w/w) after 5 min of Isothermal (*T*) and Isobaric (*p*) Treatment

						T						
p (MPa)	30 °C	50 °C	60 °C	65 °C	70 °C	75 °C	80 °C	85 °C	90 °C	95 °C	100 °C	110 °C
0.1	0.1	2.6	4.7	8.9	20.2	37.4	48.6	78.2	83.6	92.7	99.0	99.6
200	nd[a]	2.3	4.6	9.7	16.3	nd	38.6	63.3	nd	nd	nd	nd
300	nd	nd	6.7	nd	19.18	nd	nd	nd	72.18	nd	nd	nd
400	0.0	9.3	7.1	23.9	26.4	42.1	50.0	61.7	nd	nd	91.9	nd
500	3.9	8.3	15.0	nd	29.0	nd	nd	nd	80.8	nd	nd	nd
600	12.9	13.0	17.0	43.0	53.1	62.5	71.3	84.3	nd	nd	nd	nd
650	nd	nd	36.1	nd	57.2	nd	nd	nd	92.0	nd	nd	nd
680	17.7	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
750	21.1	46.0	38.7	nd	61.5	nd	79.5	nd	nd	nd	nd	nd

[a] nd, not determined.

Table 5. Degree of Gelatinization D_G (Percent) of Gelose 80 Maize Starch Slurry (10% w/w) after 5 min of Isothermal (*T*) and Isobaric (*p*) Treatment

						T						
p (MPa)	30 °C	50 °C	60 °C	65 °C	70 °C	75 °C	80 °C	85 °C	90 °C	95 °C	100 °C	110 °C
0.1	0.2	2.2	0.9	0.0	11.2	14.9	27.0	44.4	49.1	69.7	76.3	89.6
200	nd[a]	2.3	0.0	0.0	14.3	nd	27.6	47.0	nd	nd	nd	nd
300	nd	nd	12.0	nd	17.5	nd	nd	nd	52.0	nd	nd	nd
400	3.7	12.5	18.4	8.4	29.4	nd	36.2	45.5	nd	nd	75.6	nd
500	0.0	10.9	16.3	nd	32.5	nd	nd	nd	59.6	nd	nd	nd
600	18.8	22.1	25.6	33.0	29.8	41.0	49.2	52.5	nd	nd	78.2	nd
650	nd	nd	27.3	nd	41.1	nd	nd	nd	50.2	nd	nd	nd
680	34.5	nd	n.d.	nd	nd	nd	nd	nd	nd	nd	nd	nd
750	27.9	65.7	27.3	nd	39.5	nd	40.7	nd	nd	nd	nd	nd

[a] nd, not determined.

hydrogen bond formation and van der Waals interactions within the molecule, which tend to maximize the packing density and may stabilize the double-helical structure of amylopectin side branches. On the other hand, water associated with starch seems to occupy a smaller volume than water surrounded by other water molecules (*24*), which, according to the principles of Le Chatelier, would enhance starch hydration at increased pressure levels.

Figure 2 shows the influence of temperature for a range of pressure conditions [0.1 and 400 MPa (waxy and normal maize) or 600 MPa (Gelose 50 and Gelose 80)] on the degree of gelatinization of the four maize starches investigated. Starch granule gelatinization of normal and waxy maize was observed between 50 and 65 °C and between 50 and 70 °C, respectively, when processed at ambient pressure (0.1 MPa). This transition temperature range shifted to temperatures below 40 °C for both starches when the pressure was increased to 400 MPa. At this pressure level, complete gelatinization of normal and waxy maize starch slurries (10% w/w) was observed at approximately 60 and 65 °C, respectively. Gelose 50 and Gelose 80 granules began to lose birefringence at approximately 50 and 60 °C, respectively, which is similar to what was found for waxy and normal maize starch granules. However, the gelatinization of Gelose 50 and Gelose 80 granules occurred over a much wider temperature range than what was found for the maize starches with low amylose content. Complete gelatinization of Gelose 50 and Gelose 80 was detected at approximately 100 and 120 °C, respectively, after 5 min of heat treatment at ambient pressure (**Tables 4** and **5**). This is in agreement with DSC studies showing sustained endotherm peaks over a wide temperature range for both starches (*22*). The temperatures at which 50% gelatinization of Gelose 50 and Gelose 80 occurs are shifted from approximately 80 and 90 °C to approximately 72 and 80 °C at 600 MPa, respectively. However, this reduction of the gelatinization temperature is less pronounced at $D_G > 60\%$ because there appears
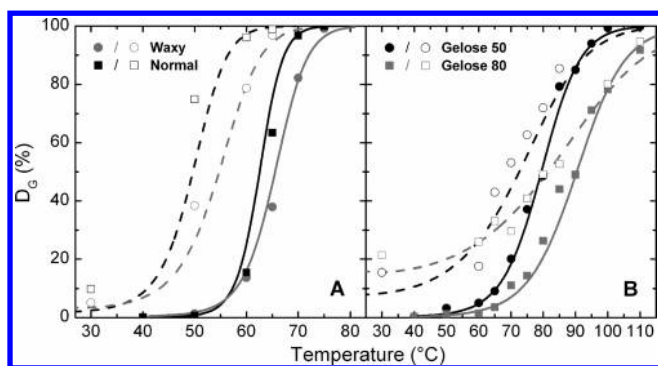
to be a small proportion of thermally resistant Gelose 50 and Gelose 80 starch granules for which the gelatinization temperatures are not affected by pressures as high as 600 MPa. This leads to a flattening of the curve showing D_G as a function of temperature at increased pressure conditions.

Modeling Pressure−Temperature Effects on Starch Gelatinization. The experimental data points shown in **Tables 2−5** have been fitted to a polynomial model based on the change in Gibbs free energy (eq 6). The values derived from the model (**Table 6**) were estimated by nonlinear regression fitting of eq 6 to the experimental data found for the pressure−temperature combinations tested. Inserting eq 6 into eq 7 provides a good functional relationship of the degree of gelatinization with both pressure and temperature. Although different reference pressures and temperatures have been used, the values of ΔG_0, ΔV_0, ΔS_0, $\Delta \beta$, ΔC_p, and $\Delta \alpha$ are on the same order of magnitude as reported for wheat and rice starch (*32, 41*).

The interpolating lines in **Figure 2** are derived from the models denoting a good agreement of the predicted D_G with the observed D_G. A good accuracy of the models can also be derived from the parity plot of the experimental versus the predicted D_G values (**Figure 3**), which indicated no significant heteroscedasticity problems for any of the models. The deviation from the bisector expresses the inaccuracy of the models. A reasonably good correlation of the predicted and experimental D_G values for each starch was found as the coefficient of determination R^2 ranged from 0.91 to 0.97 (**Table 6**).

From **Table 6**, where the tested starches are arranged on the basis of the amylose content, any simple correlation of amylose content and fundamental thermodynamic parameters was not observed evidently. However, some general conclusions can be made: ΔS_0 and ΔC_p were decreased, whereas ΔV_0, $\Delta \beta$, and $\Delta \alpha$ were increased in maize starches with high amylose content (**Table 6**). At the reference pressure and temperature (500 MPa and 30 °C) the volume change during gelatinization was negative

Figure 2. (**A**) Degree of gelatinization of waxy and normal maize starch slurries (10% w/w) after 5 min heat treatments at 0.1 MPa (solid lines/solid symbols) and 400 MPa (dashed lines/open symbols). (**B**) Degree of gelatinization of Gelose 50 and Gelose 80 maize starch slurries (10% w/w) after 5 min heat treatments at 0.1 MPa (solid lines/solid symbols) and 600 MPa (dashed lines/open symbols). Lines are derived from inserting eq 6 into eq 7 and using parameters of **Table 6**.
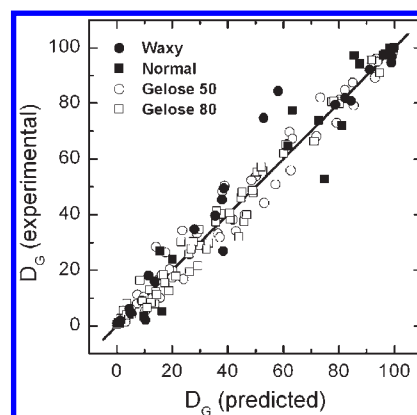

Figure 3. Parity plot for experimental degree of gelatinization D_G of waxy, normal, Gelose 50, and Gelose 80 starch slurries (10% w/w) determined after 5 min of processing at isothermal/isobaric conditions and the gelatinization degree calculated using eq 7 with the parameters of **Table 6**.
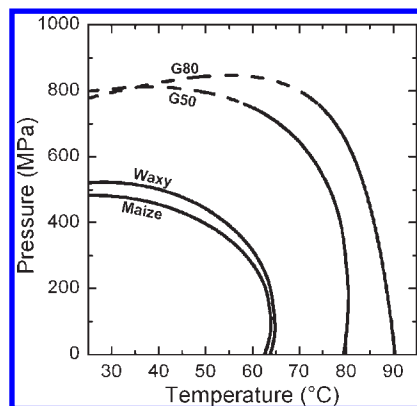
Table 6. Estimated Model Parameter Values for the Gibbs Free Energy ΔG (Equation 7 with p_0 = 500 MPa and T_0 = 30 °C) Describing the Gelatinization of Maize Starch as a Function of Pressure and Temperature

starch type	ΔG_0 (10^3 J mol^{-1})	ΔV_0 (10^{-5} m^3 mol^{-1})	ΔS_0 (10^1 J mol^{-1} K^{-1})	$\Delta \beta$ (10^{-14} m^6 J^{-1} mol^{-1})	ΔC_p (10^3 J mol^{-1} K^{-1})	$\Delta \alpha$ (10^{-7} m^3 mol^{-1} K^{-1})	R^2 [a]
waxy maize	1.75 ± 1.39 [b]	-7.63 ± 1.07	4.26 ± 17.46	-18.90 ± 3.28	7.43 ± 3.24	-0.41 ± 4.51	0.931
normal maize	-2.61 ± 2.22	-13.70 ± 1.74	15.20 ± 28.64	-34.00 ± 6.71	9.73 ± 5.70	0.89 ± 8.34	0.913
Gelose 50	8.56 ± 0.52	-2.36 ± 0.18	5.29 ± 2.99	-2.68 ± 0.64	1.71 ± 0.27	3.03 ± 0.42	0.965
Gelose 80	6.44 ± 0.43	-2.20 ± 0.14	2.27 ± 2.21	0.13 ± 0.54	1.08 ± 0.17	3.22 ± 0.29	0.958

[a] Coefficient of determination of the model. [b] Standard error of regression.

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Figure 4. Phase diagram for 50% gelatinization of waxy, normal, Gelose 50, and Gelose 80 maize starch slurries (10% w/w) after 5 min of processing at isothermal/isobaric conditions. Dashed lines denote conditions outside the range of measurement.

for all starches, indicating that the gelatinized state is favored under the condition. This volume change is smaller for high amylose starches, and thus a higher pressure is required to reach the same degree of gelatinization after 5 min for Gelose 50 and Gelose 80 than for waxy and normal maize starches. This is in agreement with the results shown in **Tables 2−5** and **Figure 2**.

Pressure−Temperature Phase Diagram of Maize Starches. Pressure−temperature phase diagrams with lines indicating constant reaction rates or degree of gelatinization D_G are the most concise way of presenting the combined effect of pressure and temperature in a system. Replacing $\Delta G(p,T)$ in eq 7 by the functional association of eq 6 allows the calculation of pressure−temperature combinations corresponding to a specified D_G. **Figure 4** shows those pressure−temperature combinations that lead to 50% gelatinization of 10% w/w maize starch slurries after 5 min of isothermal−isobaric treatment. Due to the quadratic function of eq 6 the calculated lines for waxy, normal, Gelose 50, and Gelose 80 maize starches were elliptic in the pressure−temperature plane similar to the pressure−temperature phase diagrams reported for other starches (*42*). It is evident that pressure and temperature act synergistically on starch gelatinization in principle. The elliptical shape of the curves also indicates that the pressure stability of waxy, normal, and Gelose 50 maize starch slurries is highest near room temperature. The small but clear antagonistic effect of pressure and temperature on D_G is most pronounced in the pressure region of 100−200 MPa, indicating a stabilization of starch granules against thermally induced gelatinization. Interestingly, Gelose 80 shows slightly increased pressure stability at elevated temperatures (approximately 60 °C). No evidence was found for a pressure-induced increase of the gelatinization temperature of Gelose 80. Normal maize starch granules showed the lowest stability toward pressure and temperature, followed by waxy maize granules with slightly higher pressure−temperature stability. It is apparent from **Figure 4** that Gelose 50 and Gelose 80 starch granules exhibit significantly higher stability against temperature and pressure than normal or waxy maize starch. This is indicated when an equivalent degree of gelatinization (50%) is achieved after 5 min of treatment at ambient pressure; the temperatures required for normal, waxy, Gelose 50, and Gelose 80 maize starch slurries (10% w/w) are about 63, 64, 80, and 90 °C, respectively. At a constant temperature of 30 °C, the pressures required to achieve a D_G of 50% are approximately 490, 520, 800, and 790 MPa for normal, waxy, Gelose 50, and Gelose 80 starch, respectively.

It can be assumed that the difference in amylose content and the accompanying differences in crystalline structure

cause a change in granule stability. The crystalline type of waxy and nonwaxy maize starches is A, whereas high-amylose cereal starches show the B-pattern (*5*). There is some evidence that B-type starches are more pressure and temperature resistant than A-type starches (*6, 16, 20, 38*). Whether the higher number of water molecules in B-type crystals, the nematic (for B-type starches) or isotropic (for A-type starches) intermediate gelatinization phase, or the shorter double helices of A-type starches compared to B-type starches are the reason for the higher pressure resistance of B-type starches can only be assumed (*9, 20, 43*). Melting of the crystal growth ring regions and helix coil transitions of amylopectin are the rate-limiting steps in heat gelatinization and are affected by the crystal structure (*43*). Furthermore, high-amylose starches contain more proteins and lipids than waxy and normal starches (*1, 44*), and it is believed that amylose−lipid complexes restrict swelling of the starch granules in the first stage as they do not dissociate unless temperatures exceed 90 °C (*6, 44*). Although starch gelatinization under pressure is believed to follow slightly different pathways from those described for thermal gelatinization (*9*), it is very likely that high pressures of 600−700 MPa do not solubilize the amylose−lipid complexes sufficiently. Hence, pressure gelatinization of fat- and amylose-rich starches such as Gelose 50 and Gelose 80 will be partial or even rather poor at room temperature, even at pressures as high as 690 MPa (*33*).

Knowledge of the mechanistic background of pressure-induced starch gelatinization is very limited, and pressure−temperature phase diagrams showing the phase transition of starches over a wide range of temperatures and pressures are not widely reported. In this paper, the loss in birefringence has been used as a measure of gelatinization of maize starch slurries (10% w/w) with different amylose contents in response to combinations of pressure (0.1−750 MPa) and temperature (30−110 °C). Using a thermodynamically based model, the degree of starch gelatinization was calculated as a function of pressure and temperature. From this model lines of identical gelatinization degrees can be derived and drawn in a pressure−temperature diagram. Phase transition lines of waxy, normal, Gelose 50, and Gelose 80 maize starch slurries were elliptical in the pressure−temperature plane. The sequence of pressure and temperature stability of maize starch granules in water (10% w/w) followed normal maize < waxy maize < Gelose 50 < Gelose 80. A slightly antagonistic effect of pressure and temperature on starch gelatinization was found at 100−200 MPa, indicating a pressure stabilization of waxy, normal, and Gelose 50 maize starch granules against heat-induced gelatinization. This is possibly because of the strengthening of hydrogen bond and van der Waals interactions within the molecule, which may stabilize the double-helical structure of amylopectin side branches (*9*). More detailed research is required to evaluate and explain the mechanistic background of this phenomenon occurring in the medium-pressure, high-temperature domain.

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