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# Critical Reviews<sup>TM</sup> in Food Science and Nutrition

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# CRC CRITICAL REVIEWS in FOOD SCIENCE AND NUTRITION

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**Daryl Lund**, author. B.S., M.S., Ph.D., University of Wisconsin, Madison. Professor of Food Engineering, Departments of Food Science and Agricultural Engineering, University of Wisconsin, Madison, Wisconsin.

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Starch gelatinization phenomena is extremely important in many food systems. This review focuses on factors affecting gelatinization characteristics of starch. Important variables which must be considered in design of processes in which starch undergoes gelatinization are heat of gelatinization and temperature of gelatinization. Major interactions are reviewed for the effects of lipids, moisture content, nonionic constituents and electrolytes on these characteristics. Furthermore, treatment of starch-containing systems prior to heating into the gelatinization temperature range can have a significant effect on ultimate gelatinization characteristics.

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Optimization theories and generally applied optimization techniques are reviewed. The versatility and the complexity anticipated in actual problems are simplified to enable the food practitioners interested in the subject to overcome some of the barriers which prevented full utilization of optimization. The paper summarizes the various mathematical methods available for solving problems of product and process optimization and provides information and advice concerning the advantages and limitations of each technique. A compiled list of optimization subroutines, guidelines and criteria for choosing the proper software are furnished.



**The Role of Collagen in the Quality and Processing of Fish .....301**

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Collagen in the muscles of fish constitutes the main component of the connective tissue membranes joining individual myotomes and is responsible for the integrity of the fillets. The content of collagen in fish muscles is from about 0.2 to 1.4% and in squid mantle about 2.6%. Fish and invertebrate collagens contain slightly more essential amino acids than intramuscular bovine connective tissue collagen. The invertebrate collagens are exceptionally rich in sugars linked mainly O-glycosidically to hydroxylysine residues. During maturation of fish the proportion of collagen to total protein in the muscles increases while the extent of crosslinking does not change significantly. The thermal properties of fish collagens depend significantly on the content of hydroxyproline and proline residues which in turn is correlated to the temperature of the habitat. Generally the shrinkage temperature of fish skin collagens is about 20°C lower than that of mammalian hide collagens. In several species of fish the weakening of the connective tissues post mortem may lead to serious quality deterioration that manifests itself by disintegration of the fillets, especially under the strain of rough handling and of rigor mortis at ambient temperature. Thermal changes in collagen are the necessary result of the cooking of fish, squid, and minced fish products and contribute to the desirable texture of the meat. However, they may lead to serious losses during hot smoking due to a reduction in the breaking strength of the tissues when heating is conducted at high relative humidity. Because of the high viscosity of gelatinized collagen, it is not possible to concentrate the fish stickwaters, a proteinaceous byproduct of the fish meal industry, to more than 50% dry matter. Better knowledge of the contents and properties of fish collagens could be helpful in rationalizing many aspects of fish processing.

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## INFLUENCE OF TIME, TEMPERATURE, MOISTURE, INGREDIENTS, AND PROCESSING CONDITIONS ON STARCH GELATINIZATION

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### I. INTRODUCTION

Cereal grains comprise the largest single food group in the human diet in the world. Cereal grains are used in developed and underdeveloped countries as a primary calorie source and contribute significant and often sole sources of vitamins, minerals, and protein. Processing cereal grain into more desirable food forms (e.g., bread) and improving upon their consumer quality characteristics (flavor, texture, and color) has been practiced for millenia, and references are made to cereal grain processing in the earliest known records.

Currently the food process industry uses starch, the primary constituent of cereal grains, in a variety of ways and a variety of products. With such a long history of use and its importance in food processing, it would be expected that changes in cereal grains and their starches as a function of processing parameters would be well established and characterized. However, this is not the case. Physical and chemical changes in starch as a function of processing conditions have been described and some quantitative information is available for engineering design of processes (e.g., pasting temperatures). The physicochemical fundamentals for these changes and the effect of other constituents on starch cooking phenomena have not been determined.

The purpose of this paper is to review the state of knowledge on starch cooking phenomena. A brief introduction to starch gelatinization will be followed by a review of methods to study gelatinization phenomena. Special emphasis will be given to differential scanning calorimetry (DSC) because of its increased use in studying and monitoring starch gelatinization. The major part of the paper will then focus on the influence of time, temperature, moisture content, ingredients, and processing conditions on starch gelatinization.

### II. GELATINIZATION OF STARCH

Starch granules are insoluble in cold water but swell when heated in an aqueous medium. Initially, the swelling is reversible and the optical properties of the granule are retained (e.g., birefringence). But when a certain temperature is reached, the swelling becomes irreversible and the structure of the granule is altered significantly. The process is called "gelatinization" and the temperature at which gelatinization occurs is called the "gelatinization temperature". At this temperature the granule loses its birefringence and material from the granule diffuses into the water. For a population of granules, the range for gelatinization temperature is usually between 5 to 10°C, indicating that fractions of granules exhibit different gelatinization temperatures.

Aside from swelling during gelatinization, the viscosity of the medium also increases. Both the molecular and granular structures contribute to the increase in viscosity. Initially,

gelatinization occurs in the more accessible and amorphous regions. As the temperature is raised above that for initiation of gelatinization, intermolecular hydrogen bonds which maintain the structural integrity of the granule continue to be disrupted. Water molecules solvate the liberated hydroxyl groups and the granule continues to swell. As a consequence of severe disruption of hydrogen bonds, the granule will be fully hydrated and finally the micellar network separates and diffuses into the aqueous medium. After disruption of the granules, the viscosity decreases. The increase and decrease of viscosity during gelatinization can be followed by a Brabender Amylograph. The increase in viscosity in the early heating stages is due mainly to the release of amylose while, in later stages, the continued viscosity increase is due to interaction of extragranular material and swelling of the granules.

Marchant and Blanshard<sup>43</sup> postulated three constituent processes for starch gelatinization based on nonequilibrium thermodynamics: (1) diffusion of water into the starch granules, (2) a hydration-facilitated helix-coil transition which is a melting process, and (3) swelling as a result of crystallite disintegration (melting). Blanchard<sup>8</sup> reported that total exchange of water between a starch granule and the environment at ambient temperature occurs in about 1 sec. Based on this observation and the temperature dependence of gelatinization, the diffusion process per se is not responsible for starch gelatinization. Using a light-scattering method to further study melting and swelling processes during gelatinization shows that gelatinization may be described as a "semicooperative process". Each starch granule has its own degree of crystallinity with its unique energy characteristics. The imposition of a 2°C temperature rise may result in certain granules being totally gelatinized but, in others, only some of the crystallites will have their gelatinization threshold exceeded. If the temperature increase is applied continuously, eventually the whole population of granules will be gelatinized. Since the amorphous regions hydrate initially, French<sup>22</sup> has proposed that swelling of the amorphous phase which occurs when starch is heated in excess water contributes to the disruption of the crystallite regions by tearing molecules from the crystallites.

Based on changes in characteristics of starch granules (using a Brabender Amylograph) during and after heating in aqueous medium, Olkku and Rha<sup>49</sup> summarized the steps of gelatinization as follows:

1. Granules hydrate and swell to several times their original size.
2. Granules lose their birefringence.
3. Clarity of the mixture increases.
4. Marked, rapid increase in consistency occurs and reaches a maximum.
5. Linear molecules dissolve and diffuse from ruptured granules.
6. Upon cooling, uniformly dispersed matrix forms a gel or paste-like mass.

### III. DETERMINATION OF DEGREE OF GELATINIZATION

Degree of gelatinization can be determined qualitatively and/or quantitatively by physical, chemical, and biochemical methods.<sup>62,65,67</sup>

#### A. Birefringence End Point Method

As was pointed out earlier, loss of birefringence is characteristic of starch that undergoes thermal gelatinization. Watson<sup>62</sup> determined the degree of gelatinization by measuring the percent loss of birefringence with a Koeffler electrically heated microscopic hot stage and a polarizing microscope. In the procedure, 0.1 to 0.2% aqueous starch suspension is prepared and a small drop of this suspension is spotted on a microscope slide and surrounded by a continuous ring of high-viscosity mineral oil. A cover slip is placed on the drop in such a way that air bubbles are not present under the cover glass. A uniformly distributed field of about 100 to 200 granules is usually observed during the examination. The stage is heated uniformly at the rate of about 2°C/min through a variable transformer and the field is watched

to record the temperatures corresponding with loss of birefringence by 2, 10, 25, 50, 75, 90, and 98% of the granules in the field. The 98% point is taken as the gelatinization temperature end-point (BEPT). In practice, usually only initial gelatinization and 98% loss-temperature are recorded. Watson's method was modified by Berry and White<sup>5</sup> to follow the progress of gelatinization by recording the light output on a photocell as a function of hot stage temperature.

### B. Viscosity Method

In common practice — e.g., in industry or commercially — the most widely used method for determining the degree of gelatinization is based on changes in viscosity during gelatinization. A viscoamylograph (or amylograph) records the shear force induced on a spindle as a function of time/temperature when a starch slurry is rotated. The slurry is heated at a rate of 1.5°C/min while the sample holder is rotated at speeds from 30 to 150 rpm; the granules swell and impinge on each other thus increasing the viscosity of the paste. However, when the integrity of the granule is lost, the viscosity decreases. In addition to measuring gelatinization temperature range, the instrument also provides information on temperatures of initial viscosity rise and maximum viscosity, time of cooking, and even viscosity changes during cooling if it is desired.

### C. X-Ray Diffraction Method

In certain cases, X-ray patterns can be used to differentiate between cereal and root starches and to detect changes in crystallinity brought about by physical or chemical treatment of starch granules. The method has been used as a tool to measure the extent of gelatinization.<sup>40,51,61</sup> In principle, there are two methods of recording patterns in an X-ray diffraction unit: (1) the diffractometer method, in which rays scattered from the sample are received by a Geiger-Muller counter tube, the output then amplified and plotted by a chart recorder; (2) the photographic method, in which the pattern is recorded on a photographic film.

X-rays are a form of electromagnetic radiation with a wave length typically between 0.1 and 1.0 nm (1 to 10 Å), which is comparable to the molecular spacing in a crystal. When an X-ray beam impinges on a crystal which is held in a special mount that allows the crystal to be rotated with respect to the incident beam, diffraction occurs. Diffraction is the phenomenon that occurs whenever a wave motion interacts with an obstacle. The diffracted beams are recorded to obtain information on the structure of the crystal and the molecules within the crystal.

In X-ray analysis of starch granules, satisfactory results are obtained if the specimens are properly prepared and mounted. Coarse powder gives less intense patterns. Therefore, the samples have to be less than 200 mesh (74  $\mu\text{m}$ ) in size and packed as densely as possible into a sample holder. The finished surface must be smooth and flush with the face of the sample holder. Upon recording the diffracted beams, the patterns are analyzed based on their interplanar spacings and relative intensities of the diffraction lines.

### D. Amylose/Iodine Blue Value Method

Amylose complexes with iodine to yield a brilliant blue color and this characteristic has been used as an analytical tool to measure amylose content. A quantitative method to determine the amount of amylose present in solution base has been developed by McCready and Hassid<sup>46</sup> and modified by Gilbert and Spragg.<sup>26</sup> The absorbance of the blue color is measured with a spectrophotometer at 600 nm. However, it is suspected that the blue color may not fully develop if retrogradation or incomplete solubilization of amylose is encountered. Under these conditions a more vigorous method of mixing is required. Thus, the method that gives the maximum absorbance should be chosen. In spite of these weaknesses, the iodine blue value method provides a rapid determination of amylose content that is adequate for most purposes.

Application of the amylose/iodine blue complex method has been reported by Roberts et al.<sup>57</sup> as an index of parboiling in rice. Wootton et al.<sup>68</sup> also utilized this method to determine the degree of gelatinization of biscuits. However, the method was not applicable to parboiled rice since gelatinized rice flour was insoluble in water. Birch and Priestly<sup>7</sup> modified this method by dissolving the amylose in alkali solution and then subsequently neutralizing it with acid solution. The alkali treatment dissolves amylose in an aqueous solution. A critical concentration of alkali was found for gelatinized starch (0.2 *N* KOH) while for raw starch it was greater (0.5 *N* KOH). This optimum concentration could be used to distinguish between raw and gelatinized starches. After addition of iodine reagents, the absorbance is measured with a spectrophotometer at 600 nm. The ratio of the absorbance of these two different mixtures (0.2 *N* vs. 0.5 *N* KOH) is proportional to the degree of gelatinization.

### E. Other Methods

Other methods in addition to those previously described are available, e.g., enzymatic digestibility,<sup>59</sup> nuclear magnetic resonance,<sup>37</sup> light-extinction,<sup>12</sup> solubility or sedimentation of swollen granules,<sup>34</sup> and absorption of congo red measurements.<sup>9</sup> However, these methods are less popular due to the difficulties in their procedures or degree of accuracy in measuring the degree of gelatinization.

## IV. DIFFERENTIAL SCANNING CALORIMETRY (DSC) METHOD

Stevens and Elton<sup>60</sup> applied DSC to measure heat of gelatinization of starches, and since then many groups have applied DSC in the study of gelatinization.<sup>24,38,56</sup> Banks and Greenwood<sup>3</sup> suggested this method was valid by considering gelatinization to be the analog of a melting process for a crystal. The DSC method uses a small sample (10 to 20 mg at 10 to 20% total solids) which minimizes the thermal lag within the system. Since the pans containing the sample are hermetically sealed, water will not be lost from the system under normal operating temperatures.

The term "differential scanning calorimetry" was initially a source of some confusion in thermal analysis. The parent technique to DSC is "differential thermal analysis (DTA)" and the indiscriminate use of the terms DSC and DTA resulted in IUPAC proposing definitions of these processes. Several excellent books on thermal analysis provide detailed information on DTA and DSC, including McNaughton and Mortimer,<sup>47</sup> Wendlandt,<sup>64</sup> Pope and Judd (Eds.),<sup>55</sup> and Mackenzie (Ed.).<sup>41,42</sup>

The purpose of differential thermal systems is to record the difference between an enthalpy change which occurs in a sample and that in some inert reference material when both are heated. Systems to accomplish this may be classified into three types: (1) classical DTA, (2) "Boersma" DTA, and (3) DSC.

In the classical and "Boersma" DTA systems, both sample and reference are heated by a single heat source. Temperatures are measured by thermocouples embedded in the sample and reference material (classical), or attached to the pans (Boersma). The instrument measures the temperature difference between the sample and reference as a function of temperature and presents the data as a plot of  $\Delta T$  vs.  $T$ . The magnitude of  $\Delta T$ , at any given  $T$  (or time since the instrument is programmed to heat at a constant rate of temperature change,  $dT/dt$ ) is a function of: (1) the enthalpy change, (2) the heat capacities, and (3) the total thermal resistance to heat flow. The thermal resistance to heat flow is dependent upon the nature of the sample, the way it is packed into the sample pan, and the extent of thermal contact between the sample pan and holder. In "Boersma" DTA, the temperature sensors are attached directly to the pans in an attempt to reduce variations in thermal resistance caused by the sample itself. In either classical or Boersma DTA, the thermal resistance, and hence the calibration constant for the instrument, is a function of temperature. Although data from



DTA provide quantitative information on temperatures of transition, it is very difficult to transform the data to enthalpy changes. To calculate enthalpy changes from DTA data it is necessary to know heat capacities and the variation of the calibration constant with temperature. Consequently DTA systems are not very suitable for calorimetric measurements.

The important difference between DTA and DSC is that in DSC the sample and reference are each provided with individual heaters which allows the determination to be conducted with no temperature difference between sample and reference. Running in this mode allows two important simplifications compared to DTA. First, because the sample and reference pans are maintained at the same temperature, the calibration constant for the instrument is independent of temperature. Obviously this greatly simplifies experimental technique since the calibration constant need only be determined for one standard material. Second, since the sample and reference pan have independent heaters, the difference in heat flow to the sample and reference in order to maintain equal temperature can be measured directly. Thus data are obtained in the form of differential heat input ( $dH/dt$ ) vs temperature (or time, since constant heating rates are used). These data are readily used to obtain temperatures and enthalpy of transitions or reactions.

Like any instrumental technique, there are aspects of the operation which must be carefully attended to in order to obtain data with the desired precision and accuracy. DSC is no exception, especially since a calibration procedure must be used to obtain the calibration constant and fix the temperature scale accurately.

Most of the DSC units currently in use have small sample pans which generally hold 10 to 20  $\mu\ell$  of sample. Obviously, for pure materials, obtaining a representative sample of this size does not present any great difficulty. For optimum peak sharpness and resolution, the contact surface between pan and sample should be maximized, which is usually accomplished by having the sample as thin discs, or films, or fine granules. Frequently, in applications in foods, the sample will be dispersed or soluble in water, which obviates any problem with contact surface. For heterogeneous materials, sampling can present a problem because of the small quantity required. In these cases homogenizing the sample may be required, with care being exercised not to heat the sample during homogenizing (causing some irreversible transitions which are being looked for in DSC).

Generally, the samples are encapsulated in aluminum pans with lids that are crimped into position. For samples containing water, the pan must be hermetically sealed to prevent evaporation of water (with its large enthalpy of vaporization). Generally the pans and crimping devices currently in use will withstand internal pressures to 2 to 3 atm. For higher pressures, there are high-pressure DSC cells available from instrument manufacturers, and flint glass ampules can be used which withstand internal pressures up to 30 atm.

Calibration of the instrument is generally carried out with a high-purity metal with accurately known enthalpy of fusion and melting point. The most commonly used calibrant is indium ( $\Delta H_{\text{fusion}} = 6.80 \text{ cal/g}$ ; mp  $156.4^\circ\text{C}$ ). McNaughton and Mortimer<sup>27</sup> discussed the procedure which should be used to obtain temperature data from the endo/exotherm to within  $\pm 0.2^\circ\text{C}$  and  $\pm 0.1^\circ\text{C}$ .

Determination of enthalpy for the process under study requires measurement of the area of the endo/exotherm. This can present some difficulty because the baseline for the endo/exotherm may not be horizontal (a function of the match of heat capacities of the sample and reference pans) and the peak is generally not symmetrical. An accepted procedure for determining the baseline for the peak is illustrated in Figure 1. First, the baseline on each side of the peak is extrapolated across the peak. The linear portion of each side of the peak is then extrapolated to intercept the extrapolated baseline on its respective side (i.e., right of peak extrapolated to intercept right baseline). The intersections (points  $T_o$  and  $T_c$  on Figure 1) represent the initial and final temperature of the transition. The baseline for determination of the peak area starts at the deviation of the pen from the left-hand baseline

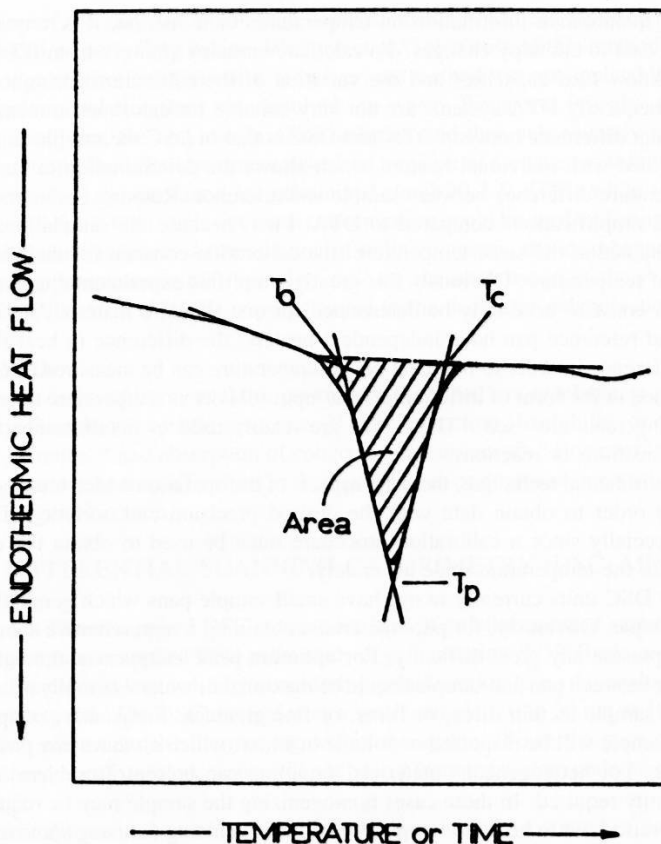


FIGURE 1. Measurement of endotherm area and temperatures of gelatinization on a DSC thermogram.

and terminates at the return of the pen to the right-hand baseline. The area is indicated by the shaded area in Figure 1.

The three basic approaches to determination of the peak area are "cut and weigh", planimeter, and integrator. Each method has some disadvantages and all require experience by the experimenter. For "cut and weigh", it may be necessary to retrace the data onto paper with a uniform density and to allow the paper to reach constant moisture content before weighing. With a planimeter, it may be necessary to enlarge the peak to improve the accuracy of measuring the area. Enlarging can conveniently be done by Xeroxing the original tracing onto a transparency, showing the transparency onto a screen, and tracing the enlarged peak. The magnification factor can be easily determined from the grid on the DSC paper or by marking a known length on the transparency. Electronic integrators would certainly have the required accuracy for use with DSC data; however, it may be necessary to correct the data for a nonhorizontal baseline.

In the last 10 years, DSC has become the analytical method of choice for studying starch gelatinization phenomena. The method can only be applied to separated starch or ground cereal grains because of the nature of the samples. Thus *in situ* starch gelatinization phenomena must be studied by other techniques such as staining and enzymatic digestion susceptibility.



**Table 1**  
**SUMMARY OF GELATINIZATION CHARACTERISTICS OBTAINED**  
**FROM VARIOUS STARCHES AND METHODS**

Type starch	Method	Temperature (°C)				Ref.
		Onset (T <sub>o</sub> )	Peak (T <sub>p</sub> )	Conclusion (T <sub>c</sub> )	ΔH (cal/g)	
Wheat	Hot stage	55	61	66	—	16
	DSC	52	59	65	2.4	16
	Amylograph	54	—	67	—	27
	Turbidity	55	—	95—100	—	3
Potato	Hot stage	59	63	68	—	58
	DSC	57—59	71	94—95	5.1—5.5	60
Corn	Hot stage	65	69	76	—	16
	DSC	65	70.6	77	3.3	16
Rice	Hot stage	72	75	79	—	16
	DSC	70	76.3	82	3.1	16
	DSC	68	74	79	3.0	66

#### V. COMPARISON OF METHODS TO DETERMINE GELATINIZATION CHARACTERISTICS

Several attempts have been made to compare methods for determination of gelatinization characteristics — i.e., temperature and heat of gelatinization. Data from several investigators are presented in Table 1 for gelatinization of starch in excess water. The data show that, in general, the initial temperature (T<sub>onset</sub>) obtained by different methods for the same type of starch are about the same. However, T<sub>peak</sub> and T<sub>conclusion</sub> obtained from DSC are slightly higher than those obtained by other methods. This could be due to a high heating rate that caused overshooting. The end point temperature for wheat starch gelatinization based on turbidity measurement was also much higher than that reported for other methods. This is understandable since the method measures the intensity of light transmitted through the starch solution as it is gradually heated. The largest light transmission was obtained when the starch granules were completely destroyed and dispersed into the medium.

An important observation based on Table 1 is that starches are different in their gelatinization characteristics. Wheat starch has a low temperature of gelatinization (54 to 65°C) and for rice, it is higher (71 to 80°C). Thus the cooking characteristics of the starches differ and will affect the design of industrial processes. Furthermore, the heat of gelatinization (ΔH in Table 1) is dependent on starch source. Wheat has the lowest (2.4 cal/g) and potato the highest (5.3 cal/g) of the four sources in the table. Thus for every gram of potato starch gelatinized in a process, 5.3 cal of heat are required. Since the specific heat of starches is only on the order of 0.2 cal/g°C, the heat of gelatinization requirement can result in a measurable decrease in the rate of heating of a product. Engineers must take this into account when designing heat transfer processes for cooking starch systems which undergo gelatinization.

#### VI. INFLUENCE OF TIME AND TEMPERATURE ON STARCH GELATINIZATION

Most kinetic studies on chemical reactions are performed under isothermal conditions since the temperature can then be considered an independent variable and the time dependence can be determined. In practice, particularly in processing of food constituents, processes to promote desirable reactions are not accomplished isothermally, but the product undergoes a real temperature change (nonisothermal) and there is a significant lag time in the product.

Studies on the kinetics of starch gelatinization are very limited, even though the phenomenon of starch gelatinization has long been recognized. Currently there is no definitive kinetic model for starch gelatinization. Moreover, the phenomenon of gelatinization itself is still not fully understood.

Kubota et al.<sup>31</sup> studied the gelatinization rate of rice starch under isothermal conditions. The viscosity as a function of heating time was measured using a capillary viscosimeter as a measure of the extent of gelatinization. Since they assumed an instantaneous gelatinization at initial mixing between starch and hot water (25:1 water-to-starch ratio), they determined initial viscosity  $K_0$  as the value observed after 1 min of heating. By assuming a first-order reaction model, they calculated the reaction rate constant ( $k$ ) from:

$$\frac{dx}{d\Theta} = k_m (1 - x)$$

where:

$$x = \frac{K - K_0}{K_e - K_0}, \text{ ratio of viscosity } [-]$$

and  $K_0$  = viscosity at zero time (this was approximated by measurement after 1 min of gelatinization, following mixing of the starch with hot water [ $\text{g}^n/\text{cm}^n \cdot \text{sec}^{2n-1}$ ]),  $K_e$  = viscosity at equilibrium time,  $K$  = viscosity at any observed time,  $n$  = flow behavior index  $[-]$ ,  $k_m$  = reaction rate constant [ $\text{min}^{-1}$ ], and  $\Theta$  = time [ $\text{min}$ ].

Use of a  $K_0$  measured after 1 min of gelatinization by Kubota et al.<sup>31</sup> does not appear to be a sound procedure since it does not account for the initial gelatinization process. From their own data, the initial value was very temperature dependent and so was the extent of gelatinization.

Bakshi and Singh<sup>2</sup> also studied the rate of gelatinization using the amylose/iodine blue value method for determining the degree of gelatinization. They used intact rice kernels (brown rice) rather than isolated rice starch. A first-order reaction model was assumed and the rate of gelatinization was expressed in terms of ungelatinized fraction of rice.

$$\ell n(1 - \alpha) = -kt$$

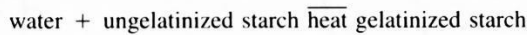
where  $(1 - \alpha)$  = ungelatinized fraction of rice  $[-]$ ,  $k$  = reaction rate constant [ $\text{hr}^{-1}$ ], and  $t$  = time [ $\text{hr}$ ].

In this model, Bakshi and Singh<sup>2</sup> also failed to show the effect of lag time on the extent of gelatinization. Another important observation on their analysis is that according to their results the extent of gelatinization was not temperature dependent, i.e., gelatinization was eventually completed even at temperatures as low as 50°C. On the contrary, the results of Kubota et al.<sup>31</sup> show that the degree of gelatinization is dependent on temperature of heating. Careful observation of the data of Bakshi and Singh<sup>2</sup> also suggests that the extent of gelatinization is temperature dependent. Birch and Priestley,<sup>7</sup> who developed the amylose/iodine blue value method to measure the degree of gelatinization *in situ*, observed that the extent of gelatinization is temperature dependent.

A different approach to studying the kinetics of cooking rice was reported by Suzuki et al. They used a parallel plate plastometer to measure compressibility of cooked rice. To determine the degree of cooking, hence the degree of gelatinization, they used the ratio of thickness of the cooked rice grain between the two parallel plates, after and before the test was conducted. They reported that the deformation ratio with each cooking temperature reached a constant value after some cooking time. Even though it was observed that the final deformation ratio (terminal point of cooking) was not constant and independent of temperature, they used the value of 0.77 as the terminal point and 0.12 as the initial

deformation ratio obtained from uncooked rice that had been soaked in water for 30 min. Assuming that the process is first order, they used a similar model to that of Bakshi and Singh.<sup>2</sup> The uncooked fraction was expressed as  $(1 - \alpha)$ , where  $\alpha$  was equal to  $(x - x_0)/(x_c - x_0)$ , while  $x_0$ ,  $x$ , and  $x_c$  were the deformation ratios at cooking time 0,  $\Theta$ , and the terminal point of cooking, respectively. Again, in this study, the use of one terminal point as the final deformation ratio for every temperature is not consistent with the actual observed data. Furthermore, they also failed to show the effect during cooking of lag time on the deformation ratio, by assuming the initial point as the value obtained from soaking uncooked rice grains for 30 min.

In our laboratory, Wirakartakusumah<sup>66</sup> completed a study on rice starch gelatinization phenomena using DSC to measure the extent of gelatinization. In this study, gelatinization was assumed to obey the following reaction scheme:



The reaction is irreversible, and under isothermal conditions the form of the rate expression is

$$r = -\frac{d[\text{UG}]}{dt} = k[\text{H}_2\text{O}]^m[\text{UG}]^n$$

where  $m$ ,  $n$  = order of reaction for  $\text{H}_2\text{O}$  and  $\text{UG}$ , respectively,  $k$  = the reaction rate constant, and  $\text{UG}$  = ungelatinized starch.

If excess water is present, the reaction rate constant  $k$  and  $[\text{H}_2\text{O}]^m$  can be combined into an apparent or empirical pseudo rate constant  $k_a$ .

$$\frac{d[\text{UG}]}{dt} = -k_a [\text{UG}]^n$$

For  $n = 1$ , a first-order reaction, the integrated form is

$$\ell_n \frac{[\text{UG}_t]}{[\text{UG}_i]} = k_a t$$

where  $\text{UG}_i$  and  $\text{UG}_t$  are the initial and the final amount (at time  $t$ ) of ungelatinized starch, respectively.

The expression  $[\text{UG}_t]/[\text{UG}_i]$  is valued when gelatinization reaches 100% completion provided the time is sufficient at any given temperature. However, if the extent of starch gelatinization is temperature dependent (i.e., the starch is not completely gelatinized at a given temperature even if held an infinite time), the argument  $[\text{UG}_t]/[\text{UG}_i]$  must be modified to describe the extent of reaction.

$$\ell_n \frac{[\text{UG}_t - \text{UG}_f]}{[\text{UG}_i - \text{UG}_f]} = k_a t$$

where  $\text{UG}_f$  is the ultimate amount of ungelatinized starch at the given temperature condition.

Two procedures were used to determine the reaction rate constants. The isothermal method uses data generated by measuring the extent of reaction as a function of time at a given constant temperature condition. The second approach is based on the heat evolution or temperature scanning method using differential scanning calorimetry (DSC) data.

In the isothermal method, the amount of ungelatinized starch was measured by DSC. Since enthalpy of gelatinization ( $\Delta H$ ) is a linear function of degree of gelatinization,  $\Delta H$  can be utilized directly as a measure of the amount of ungelatinized starch for calculations of rate constants.  $\Delta H$  as a function of time at various temperatures is given in Figure 2. It can be seen that the final degree of gelatinization ( $\Delta H$  value) is dependent on the temperature

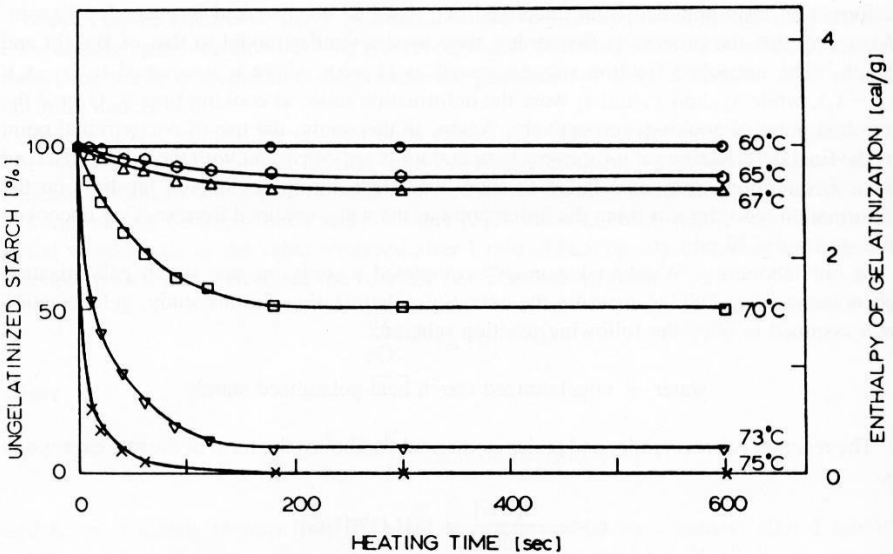


FIGURE 2. Enthalpy of gelatinization of rice starch as a function of time at various heating temperatures.<sup>66</sup>

of heating. Even though only data for observation times up to 40 min are presented, further holding of the starch suspension isothermally for up to 3 hr did not result in further gelatinization. At 75°C, the starch is completely gelatinized within 3 min. The observation that the ultimate extent of gelatinization is dependent on heating temperature agrees with the results reported by Kubota et al.<sup>31</sup> using rice starch suspension and with Birch and Priestly<sup>7</sup> from their investigation using intact kernels.

From Figure 2 it can be seen that during the heating-lag time (about 10 sec), significant gelatinization occurred, particularly at temperatures above 67°C. Thus, in calculating the reaction rate constant from the isothermal data, the initial concentration of ungelatinized starch is that attained at the end of the lag period. Based on this consideration, the rate equation becomes:

$$\ln \frac{[UG_t - UG_l]}{[UG_\infty - UG_l]} = k_a t$$

where  $UG_l$  = the ungelatinized starch content at lag time.

The fraction of ungelatinized starch at the end of the lag time  $[UG_l/UG_\infty]$  and at the end of soaking time  $[UG_s/UG_\infty]$  are presented as a function of temperature in Figure 3. It can be seen that the extent of gelatinization is highly dependent on the temperature of heating and, furthermore, that a significant degree of gelatinization has been accomplished at the end of lag time. At 80°C, 100% gelatinization occurs during the first 10 sec of hearing. Heating to the lag time at 75, 73, and 70°C resulted in 80, 47, and 10% gelatinization, respectively; whereas, virtually no starch was gelatinized after heating to the lag time at 65 and 67°C.

At temperatures greater than 67°C, the first-order rate model adequately described the rate of gelatinization after the lag period. However, it did not describe the rate of gelatinization over the entire range of no gelatinization to maximum extent of gelatinization. This would suggest that the process of gelatinization is complex and not readily described by pseudo first-order kinetics. This makes sense when one considers that there is a population of starch granules, each with its unique degree of crystallinity. The process can be empirically modeled but interpretation of mechanism from the model should be done with great care.

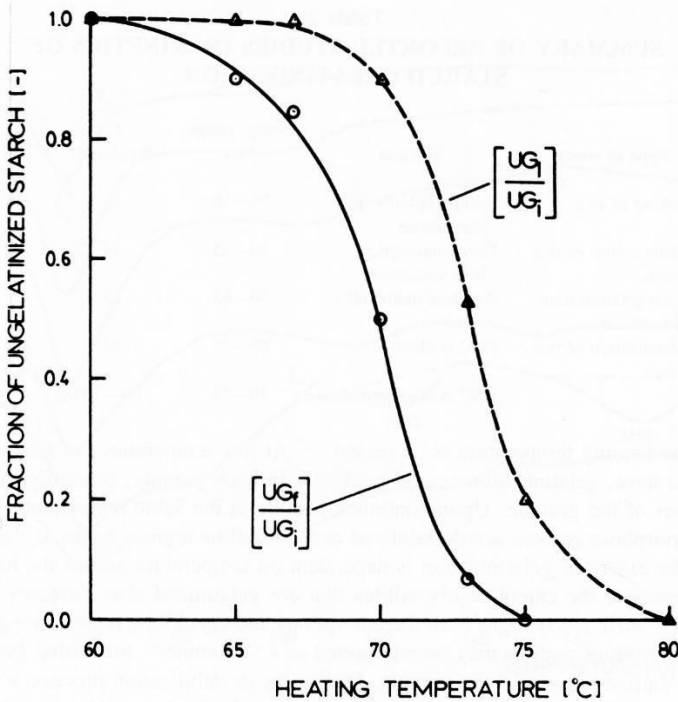


FIGURE 3. Fraction of ungelatinized rice starch at various temperatures of heating.<sup>66</sup>

Even though it is highly questionable to develop a kinetic model for gelatinization, several investigators have done so, and furthermore, they have used the Arrhenius equation to describe temperature dependence of rates of gelatinization. The Arrhenius equation is

$$\ln k = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right)$$

where  $k$  = reaction rate constant [ $\text{min}^{-1}$  or  $\text{hr}^{-1}$ ],  $A$  = the Arrhenius frequency factor,  $E_a$  = activation energy [kcal/mol],  $R$  = gas constant [1.987 kcal/mol/K], and  $T$  = absolute temperature [K].

A summary of the reported studies on kinetics of starch gelatinization together with the values of activation energy is given in Table 2. Suzuki et al., Bakshi and Singh,<sup>2</sup> and Wirakartakusumah<sup>66</sup> (DSC isothermal method) reported similar activation energies (19 to 25 kcal/mol, respectively), while Kubota et al.<sup>31</sup> reported 14 kcal/mol. The difference among these four values was probably due to the difference in the nature of raw material studied and the method of choosing a zero heating time reference.

The  $E_a$ s from the nonisothermal method of Wirakartakusumah<sup>66</sup> are much greater and appear to be dependent on temperature,  $E_a$  increasing with increasing temperature. Each starch granule has its own degree of crystallinity with its own unique gelatinization characteristics. It has been well documented that a starch granule is semicrystalline and consists of amorphous and crystalline regions. Due to its lower order of crystallinity, the amorphous region hydrates initially and is more labile to heat treatment with water present than the crystalline region. Since the amorphous region is an integral part of the starch granule, the destabilization and swelling of the amorphous region during heating at low temperature facilitates further destabilization of the crystalline region by tearing molecules from crys-

**Table 2**  
**SUMMARY OF REPORTED STUDIES ON KINETICS OF**  
**STARCH GELATINIZATION**

Type of study	Method	Temp. range (°C)	E <sub>a</sub> (kcal/mol)	Ref.
Cooking of rice	Compressibility with plastometer	75—100	19	
Gelatinization of rice starch	Flow consistency with viscometer	70—85	14	31
<i>In situ</i> gelatinization of brown rice	Amylose/iodine blue value	50—85	25	2
Gelatinization of rice starch	DSC isothermal	65—75	25	66
	DSC nonisothermal	70—75	44—73	66

tallites as the heating temperature is increased.<sup>6,22</sup> At low temperatures of heating near the onset temperature, gelatinization occurs randomly in each granule, primarily in the amorphous regions of the granule. Upon continued heating at the same temperature, eventually all of the amorphous regions are destabilized and crystalline regions begin to "gelatinize". However, the extent of gelatinization is dependent on temperature and as the heating temperature increases, the extent of crystallites that are gelatinized also increases. When the temperature is sufficiently high, both the amorphous and crystalline regions are gelatinized. Thus, the amorphous regions may be interpreted as a "promoter" for further gelatinization of more crystalline regions of the granule. During the destabilization process, a more open structure of the starch develops. If this is the case, then the isothermal data should represent gelatinization of the more crystalline regions. Generally, the more resistant granules would exhibit a higher E<sub>a</sub>, presumably because of the large number of hydrogen bonds. The high order of crystallinity produces a sharper peak on X-ray diffraction<sup>21</sup> and higher gelatinization temperatures.<sup>14</sup> Donovan and Mapes<sup>14</sup> separated the amorphous regions from the crystalline regions of potato starch using acid hydrolysis. In the present study, the E<sub>a</sub> from the isothermal procedure is 25 kcal/mol, which is lower than the E<sub>a</sub> from the nonisothermal procedure. This may be due to the role that amorphous regions play in destabilizing the crystalline regions during gelatinization, a role which results in lowered activation energy.

In summary, the process of starch gelatinization does not appear to be a first-order process although it can be modeled as a first-order process over limited extents of gelatinization. Rate constants in any model are highly dependent on the starch source and its history. A population of starch granules present a distribution of sensitivities to time/temperature treatment and the temperature dependence does not appear to follow the Arrhenius equation. For purposes of engineering design of starch cooking systems or cereal grain cooking it would appear that experiments must be performed under conditions approximating those anticipated in the actual scaled-up process.

## VII. INFLUENCE OF MOISTURE

At temperature above that for complete gelatinization, several studies show that there is a minimum water-to-starch ratio (w/s) in order to achieve complete gelatinization<sup>17,44,69</sup>

When a rice starch suspension is heated to 150°C, at 10°C/min, up to three endothermic processes are observed depending on the w/s ratio (Figure 4). At w/s ratio ≥ 2:1, only two endotherms are obtained. The first endotherm is observed at an onset temperature (T<sub>o</sub>) of about 71°C. This is the single endotherm which has been characterized as the "gelatinization" phase change.



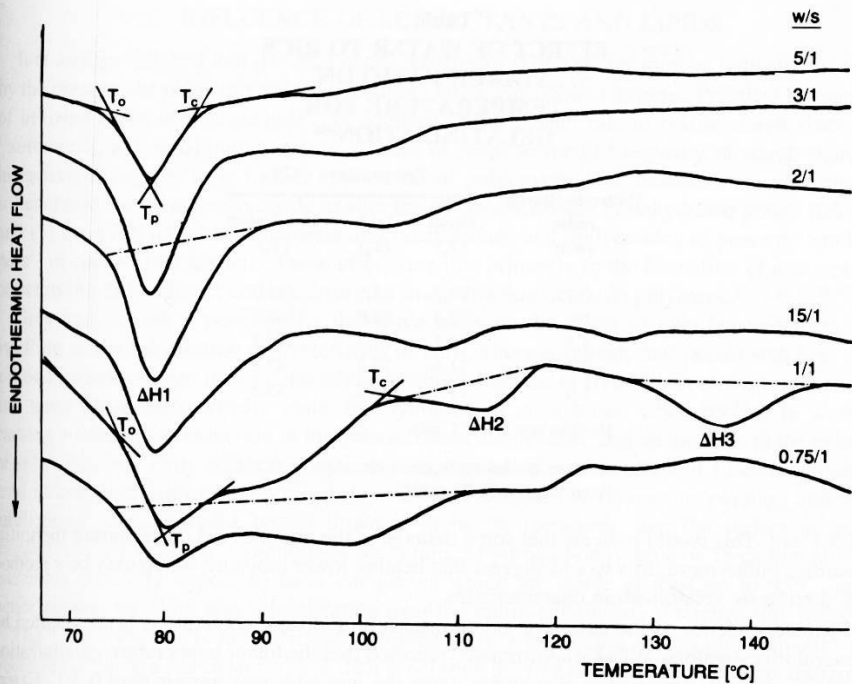


FIGURE 4. Typical endotherms when rice starch suspensions with various w/s ratios are heated to 150°C at 10°C/min.<sup>66</sup>

In addition to the first endotherm, a second endotherm is also obtained in the temperature range between 90 to 110°C. This higher-temperature endotherm is associated with melting of an amylose-lipid complex. A similar type of endotherm which occurred at 100°C was also reported by Kugimiya et al.<sup>32</sup> from maize and wheat starches. When lipids of maize and heat starches were extracted with methanol, the areas of the first endotherm ( $\Delta H_1$ ) were not altered; however, for maize, the second endotherm essentially disappeared after 150 hr of extraction, while for wheat starch the area decreased to about two fifths of the original area.<sup>32</sup> Generally, the lipid content of starches is of the order of 1% or less. However, if this lipid complexes with starch, this may result in 10 to 20% starch-lipid complex by weight.<sup>31</sup>

As the w/s ratio decreases to less than 1.5:1, the gelatinization endotherm ( $\Delta H_1$ ) develops a trailing shoulder with a marked decrease in the area (enthalpy). This shouldering may be due to the destabilizing effect of water and heat treatments on the amorphous and the crystalline regions of starch granules. The onset temperature ( $T_o$ ) and temperature range of gelatinization shift to higher temperatures as the water content decreases as shown in Table 3. As the w/s ratio decreases to less than 1.5:1,  $\Delta H_1$  decreases, and the shoulder peak forms its own endotherm which subsequently shifts to a higher temperature. The second endotherm ( $\Delta H_2$ ) also shifts to a higher temperature. In addition to this shouldering effect with decreasing w/s ratio, a third endotherm ( $\Delta H_3$ ) is observed at temperatures above 130°C. If the heated starch suspension (w/s = 1:1) is cooled from 160 to 10°C immediately, and subsequently reheated back to 160°C using the same heating rate (10°C/min), the gelatinization endotherm disappears, but the second and third endotherms are still present. Wirakartakusumah<sup>66</sup> reported that heating a w/s suspension (1:1) to 100°C at 10°C/min resulted in a lowered and broadened range of temperature of gelatinization in rice starch when the starch was reheated



**Table 3**  
**EFFECT OF WATER TO RICE**  
**STARCH RATIO ON**  
**TEMPERATURE FOR**  
**GELATINIZATION<sup>a66</sup>**

Water-to-Starch ratio (w/s)	Temperature (°C) <sup>b</sup>		
	Onset (T <sub>o</sub> )	Peak (T <sub>p</sub> )	Conclusion (T <sub>c</sub> )
0.75	74.3	81.5	111.3
1.0	72.3	88.0	103.8
1.5	72.1	77.3	94.3
2.0	71.6	77.3	87.8
3.0	71.3	77.2	85.3

<sup>a</sup> Heating rate is 10° C/min.

<sup>b</sup> Average of two replicates with range  $\pm$  0.5° C.  
From Wirakartakusumah<sup>66</sup>.

at 5:1 w/s. This would indicate that some damage to the granules did occur during the initial heating. Furthermore, this would suggest that heating lower moisture starch may be a method of altering its gelatinization characteristics.

The dependence of the extent of gelatinization on moisture content has been reported by several investigators. Wirakartakusumah<sup>66</sup> reported that the lower temperature gelatinization phenomena only occurred in rice starch when the w/s ratio was greater than 0.3:1. Extent of gelatinization attains its maximum value at a w/s ratio of 1.5:1 and remains constant thereafter, no matter how much water is added. From these data it is possible to calculate the molar ratio of water/glucose unit. To start gelatinization of rice starch, more than 3 mol of water/hexose unit are required (>0.25 w/s ratio). To obtain complete gelatinization, approximately 13.5 mol of water are required per mole of glucose unit. These values are in good agreement with the data reported by Donovan<sup>13</sup> on potato starch. About 4 mol water/mole hexose unit and 14 mol water/mole hexose unit were required for initiation of gelatinization and to obtain complete gelatinization, respectively. Collison and Chilton<sup>11</sup> also presented evidence that a critical amount of water was necessary for initiation of gelatinization. Lelievre<sup>35</sup> used the Flory equation for polymer melting to describe the effect of water on starch gelatinization. Application of the Flory equation has provided further evidence that starch gelatinization may be considered as a solvent-assisted, polymer-melting phenomena.

Dependence of gelatinization on moisture content can present problems in starch cooking. If the starch is separated and added to the formulation, then generally a w/s ratio of about 1.5:1 would be required for complete gelatinization (60% moisture, wet basis) and a ratio of 0.3:1 (about 25% moisture, wet basis) would be required for any gelatinization. In isolated form, the imbibition of water into the starch granule would be expected to be very rapid and not rate-limiting in the process. However, if the starch is still in an intact grain (such as cooking rice or whole grains), then *in situ* gelatinization could be limited by water diffusion. This has been shown for rice cooking.<sup>2,31,66</sup> The gelatinization process *in situ* exhibits a temperature dependence similar to that for diffusion coefficients (2 to 10 kcal/mol). Thus for whole grain cooking, it is often necessary to soak the grain prior to applying cooking temperatures in order to facilitate water absorption. At temperatures above that necessary to initiate gelatinization, the diffusion coefficient may actually decrease with increasing temperature. This is due to the fact that as the starch gelatinizes it holds more water and the diffusion coefficient decreases with moisture content. Thus higher temperatures result in greater local moisture capacity, ultimately resulting in a reduced diffusion coefficient across the gelatinized layer.

### VIII. INFLUENCE OF SURFACTANTS AND LIPIDS

It is well established that physical characteristics of starch pastes may be radically altered by the presence of polar substances containing large hydrophobic groups. Practical instances of utilizing these effects include: (1) addition of sulfonated oils to textile starch sizes as "softeners" and antiskinning agents, (2) use of soaps to modify viscosity of starch sizings in paper coatings, (3) the former application of polyoxyethylene monostearate as a bread softener, (4) use of monoglyceride to alter the paste consistency of dehydrated potato flakes, and (5) use of glycerol monostearate and other mono- and diglycerides to prevent "stickiness" in cooked rice kernels. These effects are due primarily to the formation of a complex between the fatty adjunct and amylose, the linear fraction of starch polymers.<sup>18, 19, 24, 29, 33, 45, 48</sup>

Gray and Schoch<sup>31a</sup> performed a definitive study on the effect of nine fatty adjuncts on swelling and solubilization characteristics of corn, waxy sorghum, and potato starches. As a broad generalization, lower polar adjuncts containing four or five carbon atoms (e.g., butyl and amyl alcohols) markedly assist the hydration of corn starch when cooked in water, causing a substantial reduction in the gelatinization temperature and an increase in the extent of solubilization. Fatty adjuncts containing a hydrocarbon residue of about 12 carbon atoms tend to complex with the amylose below 85°C, consequently repressing swelling and solubilization. This complex breaks down at higher temperatures, and the surfactant may thereafter assist swelling. Compounds containing a hydrocarbon residue of 18 carbon atoms (stearate) generally appear to form complexes which are stable at least up to 95°C, and hence repress swelling and solubilization over the entire gelatinization temperature range.

The fatty complex is not efficiently formed merely by adding the requisite amount of potassium soap to a starch slurry, and then generating the free fatty acid *in situ* by neutralizing to pH 5.0 to 6.0. Both elevated temperature and time are necessary to allow diffusion of the adjunct into the starch granule. Without such treatment, the adjunct will complex with the amylose only outside the granule. Gray and Schoch<sup>31a</sup> determined that for a 30% potato starch slurry treated with 1% stearic acid (on a starch dry weight basis), a treatment condition of 50°C for 3 hr was required for maximum reduction in swelling power and solubilization. The concentration of fatty adjunct also affects the swelling power and solubilization. Generally these adjuncts are used at concentrations less than 1% (based on starch dry weight), although Gray and Schoch showed that with stearic acid and potato starch, the swelling power and solubility continued to decrease with stearic acid concentration up to 2.5% (on starch basis).

In summary, fatty adjuncts can be used to influence swelling, solubilization, skinning, and stickiness of starches and cereal grains. When polar adjuncts are used to modify the physical character of starch pastes, the cooking temperatures may produce substantial differences in swelling and solubility in the range 85 to 95°C. The time of addition and time for diffusion of adjunct into the granule are also very important and can cause substantial differences in properties of the cooked starch or cereal grains. If the adjunct is allowed to diffuse into the granule significantly, swelling and solubilization may be greatly reduced. Whereas, if the adjunct is added immediately before cooking, the amylose-lipid complex will largely form extragranularly and the adjunct will have little effect on swelling and solubilization.

### IX. INFLUENCE OF OTHER SOLUTES

Ionic and nonionic constituents affect gelatinization characteristics of starches. Wootton and Bamuniarachchi<sup>70</sup> presented an excellent study on the effect of sucrose and NaCl on wheat starch gelatinization. In spite of the earlier work in this area, the situation regarding the influence of sugar and salt on starch gelatinization is far from clear. From a practical point of view, much of the earlier research dealt with low starch concentrations and, hence, has no direct relation to many baked products. In addition, the range of techniques used makes correlation between the earlier studies difficult and some of these techniques are more

**Table 4**  
**EFFECT OF SUCROSE CONCENTRATIONS**  
**ON THE GELATINIZATION ENDOTHERM**  
**OF WHEAT STARCH**

Sucrose conc. in aqueous phase (%)	$\Delta H_G$ (cal/g)	Extent of gelatinization (%)	Endotherm temp. ( $^{\circ}\text{C}$ )		
			$T_o$	$T_p$	$T_c$
0	4.7	100	50	68	86
15	3.2	68	50	70	86
30	2.8	60	50	73	86
45	2.3	49	50	75	86

From Wootton, M. and Bamunuarachchi, A., *Stärke*, 32, 126, 1980. With permission.

suiting to qualitative, rather than quantitative, interpretation. Thus, although starch makes important contributions to the structural, textural, and functional properties of many heat-processed products, which often contain sucrose and/or salt, quantitative information on the effect of these two ingredients on the gelatinization process is not readily available.

Presented in Table 4 are  $\Delta H_G$ , extent of gelatinization and temperatures at which the endotherms began ( $T_o$ ), reached their peak ( $T_p$ ), and concluded ( $T_c$ ), for wheat starch/water systems containing various levels of sucrose in the aqueous phase. It can be seen that  $T_o$  and  $T_c$  were not affected by increased levels of sucrose while  $T_p$  was increased.

This result agrees with the findings of earlier workers, who indicated that increasing sucrose concentrations caused increases in pasting temperatures corresponding with the changes in  $T_p$ . In a theoretical treatment of starch gelatinization, Leleivre<sup>36</sup> derived an expression relating the composition of starch/water/solute mixtures with the melting (gelatinization) temperature of the starch. From the lack of change in  $T_o$  and  $T_c$ , it appears that while the peak temperature of the gelatinization endotherm rises with increased sucrose concentration, the range over which the process extends is not affected by the concentrations of the solute.

The quantitative effect of various levels of sucrose on the extent of gelatinization of wheat starch is also shown in Table 4. Sucrose has a restrictive effect on the gelatinization process as measured by  $\Delta H_G$ . This effect of sucrose is widely known and several explanations for this phenomenon have been proposed including competition between starch and sucrose for available water, sucrose inhibition of granular hydration, and sucrose-starch interactions.

If change in the level of available water due to moisture binding by sucrose was the only effect operating, then a linear relationship between  $\Delta H_G$  and the sucrose level in the aqueous phase may be expected since such a relationship was found between available water and  $\Delta H_G$ . From the data in Table 4, it can be seen that while  $\Delta H_G$  decreases as the sucrose concentration increases, the relationship between these two parameters is not linear. Thus, the actual mechanism by which sucrose restricts the gelatinization of wheat starch is not simply a lowering of available water in proportion to the level of sucrose present in the system.

Evans and Haisman<sup>20</sup> examined starch gelatinization behavior in the presence of nonionic constituents and found that the effect on temperature and extent of gelatinization could be explained through solute effect on available water and melting point (as expressed by the Flory equation).

The influence of NaCl on starch gelatinization was also studied by Wootton and Bamunuarachchi.<sup>70</sup> Shown in Table 5 are  $\Delta H_G$ , extent of gelatinization, and  $T_o$ ,  $T_p$ , and  $T_c$  observed when various levels of salt were included in the aqueous phase of starch/water (1:2) mixtures.

**Table 5**  
**EFFECT OF SALT CONCENTRATIONS ON**  
**THE GELATINIZATION ENDOTHERM OF**  
**WHEAT STARCH<sup>70</sup>**

Salt conc. in aqueous phase (%)	$\Delta H_c$ (cal/g)	Extent of gelatinization (%)	Endotherm temp. (°C)		
			$T_a$	$T_p$	$T_c$
0	4.7	100	50	68	86
3	2.7	57	58	71	88
6	2.5	53	64	75	88
9	2.6	55	68	78	88
12	2.7	57	65	77	88
15	2.7	57	65	77	88
21	2.8	60	61	80	90
30	3.3	70	59	79	91

From these data it is apparent that salt has a different and more complex effect on starch gelatinization than does sucrose.

Changes in salt concentration affected all three temperatures associated with the gelatinization endotherm. Thus,  $T_a$  rose from 50°C to a maximum of 68°C at a salt concentration of 9% and, with subsequent increments in salt level up to 30%, gradually fell to 59°C.  $T_p$  also rose as salt concentration was increased up to 9%, but then remained relatively constant with further increases in salt level while  $T_c$  rose gradually from 86 to 90°C with increasing salt concentrations. A variation in the temperature range over which the gelatinization endotherm extends also occurred with added salt. Thus, the endotherm had a temperature range of 36°C in the absence of salt, but this range narrowed to 20°C at a salt concentration of 9% and gradually widened to 32°C with subsequent increases in salt level to 30%. This variation was mainly a reflection of changes in  $T_a$ .

Although Wootton and Bamunuarachchi<sup>70</sup> reported that NaCl appeared to exhibit a maximum effect on starch gelatinization at 6 to 9%, Evans and Haisman<sup>20</sup> reported that other salts such as sodium sulfate and sodium hydrogen phosphate (pH 7.0) increased gelatinization temperature, whereas calcium chloride decreased and then increased gelatinization temperature. Oosten<sup>50</sup> proposed a hypothesis to explain these phenomena. His hypothesis is that starch acts as a weak acid ion exchanger and that cations tend to protect and to stabilize the granule structure while anions are the gelatinizing agents by rupturing hydrogen bonds. The effect of NaCl and sodium hydroxide on gelatinization can be used to illustrate his hypothesis.

When some sodium chloride is added to a starch suspended in water, some alcoholic groups in the starch granules are converted to sodium alcoholate groups. The latter are better dissociated, resulting in an increase of the Donnan potential, thus reducing diffusion of chloride ions, the gelatinization-enhancing anion.

The extent of absorption of sodium ions is rather limited in this system since there is no agent to bind the released hydrogen ions. Thus the rise in gelatinization temperature is limited and exhibits a maximum at 6 to 9% NaCl. Adding NaOH to the starch suspension in NaCl results in increased absorption of sodium ions because the hydroxyl ions react with the released hydrogen ions.

In summary, ionic and nonionic soluble constituents influence starch gelatinization. Generally, nonionic constituents result in decreased extent of gelatinization and increased temperature of gelatinization. This effect is explained largely on the basis of the effects of the solute on water activity in the starch granule. The specific effect of electrolytes on starch gelatinization is dependent on the electrolytes and can be explained by the hypothesis that

starch behaves as a weak acid ion exchanger. The influence of ionic and nonionic constituents on starch gelatinization can have real consequences in processing because of their effect on the extent and temperature of gelatinization. Thus, if complete gelatinization at the lowest possible temperature is desirable, it may be best to add all solutes as close to the end of the heat treatment as possible. This would minimize their effect on gelatinization phenomena. Furthermore, the influence of solutes on gelatinization appears to be very rapid since previous studies showed no enhanced effect by extending the contact time. Thus as ionic and nonionic constituents dissolve, they readily interact with the starch granule altering the gelatinization characteristics.

## X. INFLUENCE OF PROCESSING PROCEDURES

Treatment of starch and cereal grains prior to cooking can significantly alter cooking and/or gelatinization characteristics.<sup>15,28,39</sup> Evidence of pretreatment has already been discussed in Section VIII, where it was shown that admixing of starch and lipid (e.g., stearic acid) required a pretreatment of at least 3 hr at 50°C to achieve maximum interaction. In processing of cereal grains, perhaps the most widely known pretreatment is parboiling of rice. It has been well established that parboiling, due to gelatinization of starch, improves the quality of milled rice primarily by increasing the yield of head rice (whole rice kernels). Generally, parboiling consists of two processing operations: soaking and steaming. During soaking, rice is hydrated so that sufficient water is present to allow subsequent gelatinization. During steaming, gelatinization and solubilization of starch occurs which contributes to the final quality of milled rice. Even though steam is the most commonly used method to accomplish gelatinization, other means of heating such as hot sand or continuous soaking in boiling water have also been used in practice.

Parboiling commercial rice results in modification of the starch. Watson and Dikeman<sup>63</sup> reported extensive modification from the aleurone layer through the center of the starchy endosperm when examined using SEM. Furthermore, some vitamins and minerals transfer from the aleurone and germ regions into the starchy endosperm, some lipids disperse from the aleurone and germ layers, and there is inactivation of enzymes and destruction of molds and insects.<sup>23</sup> Those changes are accompanied by a reduction of chalkiness, increase in translucency of the milled rice, and improved digestibility and cooking characteristics. Parboiling strengthens the attachment of the germ and the aleurone to the starchy endosperm and avoids separation of these parts during hulling.

It has been well established that the purpose of soaking is to provide sufficient water necessary for subsequent gelatinization. Different methods are used to obtain faster hydration thus reducing soaking time, including the use of hot water (above 60°C), application of vacuum and/or hydrostatic pressure, and the addition of wetting agents.<sup>23</sup>

Even though higher water temperatures decrease the soaking time significantly, soaking with water above temperatures of gelatinization causes rapid hydration preferentially into the surface layers, leading to early bursting and leaching. Soaking at high temperatures for longer times also increases discoloration of the parboiled milled rice, particularly at temperatures above 70°C and soaking for more than 5 hr.<sup>30</sup> A moisture content of 30% (w.b.) or more is necessary to ensure an even distribution of water throughout the kernel. Without additional treatments (i.e., vacuum or hydrostatic pressure) the optimum temperatures and times of soaking are between 60 to 70°C and 3 to 4 hr, respectively. To avoid excessive discoloration during soaking, sodium bisulfite is commonly used as a bleaching agent or inhibitor of the browning reaction.

When the starch in the endosperm has absorbed sufficient water, it must be heated above its gelatinization temperature to ensure a degree of gelatinization. Saturated steam is a common heating medium to accomplish this because it does not remove moisture during



**Table 6**  
**DEGREE OF GELATINIZATION *IN SITU* OF**  
**LEBONNET VARIETY RICE AS AFFECTED BY**  
**VARIOUS PARBOILING CONDITIONS<sup>66</sup>**

Soaking temperature (°C)	Steaming temperature (°C)	Steaming time (min)	$\Delta H_c^a$ (cal/g)	Degree of gelatinization <sup>b</sup> (%)
63	112	10	1.3	29.1
71	112	10	1.2	35.2
63	121	10	0.8	58.2
71	121	10	0.7	63.2
63	112	15	1.2	36.8
71	112	15	0.9	53.7
63	121	15	0.7	64.6
71	121	15	0.5	74.1
Untreated (uncooked rice)			1.9	0.0

<sup>a</sup> Average of two replicates; range  $\pm$  0.1 cal/g.

<sup>b</sup> (%G) = (100% - %UG), where ungelatinized starch (UG) is obtained from H: (%UG) = 52.9 ( $\Delta H$ ).

heating. Due to condensation and high pressure (usually above atmospheric pressure) the moisture content increases and is equilibrated throughout the kernel. Even at atmospheric pressure, the steam temperature is adequate for gelatinization to occur; however, it may require a longer exposure time. Therefore, there are two parameters that can be controlled during steaming — steam temperature (pressure) and the length of steaming time.

Excessive steaming causes development of dark color and increases cohesion between the germ and the aleurone layer with the starchy endosperm making these parts difficult to remove during milling. The presence of bran and germ produces a lower quality of the milled rice and increases the susceptibility of the grain to rancidity. On the other hand, inadequate steaming results in partial or surface parboiled rice and a defect called "white cores".

Priestly<sup>53</sup> suggested that increasing steaming temperature and time also increased "apparently solubility" (this term designates the solubilized material in the kernel). The increase in apparent solubility improved kernel hardness because apparently the soluble material within the kernel healed the cracks that formed during soaking. The solubilization of starch also facilitated a complex formation between amylose and lipid. This was confirmed by X-ray diffraction as reported by Priestley.<sup>52</sup> Formation of an amylose-lipid complex reduced leaching of amylose (and consequently, stickiness) on re-cooking parboiled rice.<sup>54</sup> Bechtel and Pomeranz<sup>4</sup> reported that based on transmission electron microscope (TEM) examination, parboiling did not affect the structure and crystal lattice and rings of the protein bodies in the endosperm.

Wirakartakusumah<sup>66</sup> completed a study on the influence of soaking temperature (63 and 71°C), steaming time (10 and 15 min), and temperature (112 and 121°C) on extent of gelatinization in rice. Soaking time was constant at 3 hr and soaking temperatures were chosen with one below the gelatinization temperature (63°C) and one above (71°C). Results on the extent of gelatinization (as determined by DSC) are given in Table 6.

An analysis of this 2<sup>3</sup> factorial design is presented in Table 7. It can be seen that all three main effects were significant while the two- and three-level interactions were not. It is apparent from these results that soaking rice at a temperature in excess of that required for gelatinization increased the ultimate degree of gelatinization. Increased steaming time and

**Table 7**  
**CALCULATED EFFECT**  
**AND STANDARD ERRORS**  
**FOR THE 2<sup>3</sup> FACTORIAL**  
**DESIGN OF THE DEGREE**  
**OF GELATINIZATION IN**  
**SITU<sup>66</sup>**

Effect <sup>a</sup>	Estimate ± SE
Average	51.8 ± 1.3
Main effects	
T <sub>so</sub>	9.4 ± 1.3 <sup>b</sup>
T <sub>st</sub>	26.3 ± 1.3 <sup>b</sup>
t <sub>st</sub>	10.9 ± 1.3 <sup>b</sup>
Interaction effects	
T <sub>so</sub> × T <sub>st</sub>	2.1 ± 1.3
T <sub>so</sub> × t <sub>st</sub>	3.8 ± 1.3
T <sub>st</sub> × t <sub>st</sub>	-2.2 ± 1.3
T <sub>so</sub> × T <sub>st</sub> × t <sub>st</sub>	-1.6 ± 1.3

<sup>a</sup> T<sub>so</sub> = temperature of soaking; T<sub>st</sub> = temperature of steaming; t<sub>st</sub> = time of steaming.

<sup>b</sup> Significant difference at = 0.01

temperature also increased degree of gelatinization. Since the starch was not completely gelatinized under any experimental conditions, this would indicate that water may be limiting the process.

The gelatinization characteristics of the remaining ungelatinized starch in the intact rice kernels were altered as a result of the parboiling process. This can be seen by examining the data in Table 8 on the temperatures for gelatinization.

In general, it can be seen that the gelatinization temperatures decreased as the severity of parboiling treatment increased compared to untreated rice. The temperature range also broadened ( $\Delta T$ s are between 12.2 and 13.3°C) compared to the range observed on the untreated sample ( $\Delta T$  is 11.5°C). The broadened temperature range and lower temperature for the endotherms have been interpreted as an indication that the starch granule was damaged and destabilized in the previous parboiling treatment, but the crystalline structure had not been disordered completely. Thus, subsequent reheating with excess water resulted in a lower temperature endotherm and wider temperature due to the lower degree of crystallinity in the granules. Thus, parboiling not only results in *in situ* gelatinization but also alters the temperature for subsequent gelatinization during cooking. Both of these effects can be very important in cooking processes applied to cereal grains.

Steeping is carried out during isolation of starch to soften the grain to facilitate wet milling. For wheat grains, for example, this step is usually done at temperatures up to 50°C for 20 hr. In rice parboiling, the steeping process is also an indispensable step to provide sufficient moisture in the grain for gelatinization. Gough and Pybus<sup>28</sup> observed an interesting characteristic of gelatinization for wheat starch when it was steeped for 72 hr at 50°C. The treatment changed and narrowed the temperature range for gelatinization from 52 to 61°C before steeping to 65.4 to 65.8°C after steeping. The enthalpy of gelatinization also decreased from 3 cal/g to 2.3 cal/g. However, there was no change in the X-ray pattern between the raw and treated starches. A similar study conducted by Lorentz and Kulp<sup>39</sup> for wheat starch steeped at various times and temperatures confirmed the previously reported data. They used a hot stage microscope to determine the temperature for gelatinization. The gelatinization



**Table 8**  
**CHARACTERISTIC TEMPERATURES OF**  
**GELATINIZATION *IN SITU* OF LEBONNET VARIETY**  
**RICE AS AFFECTED BY VARIOUS PROCESSING**  
**CONDITIONS<sup>66</sup>**

Soaking temp. (°C)	Steaming temp (°C)	Steaming time (min)	Gelatinization temp. <sup>a</sup>			
			T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	(T <sub>c</sub> -T <sub>o</sub> ) (°C)
63	112	10	52.2	58.1	65.5	13.3
71	112	10	53.5	60.0	66.0	12.5
63	121	10	49.7	55.9	62.0	12.3
71	121	10	49.0	56.4	61.9	12.9
63	112	15	54.1	58.1	66.5	12.4
71	112	15	49.2	55.5	61.6	12.4
63	121	15	49.3	55.8	61.5	12.2
71	121	15	49.7	56.5	62.0	12.3
Untreated (uncooked rice)			69.0	75.0	80.5	11.5

<sup>a</sup> Average of two replicates; range  $\pm 0.5^\circ\text{C}$ ; determined by DSC at 5:1 w/s ratio and  $10^\circ\text{C}/\text{min}$  heating rate.

temperatures of the starches increased and the range of temperatures narrowed as the temperature and duration of steeping at a specific temperature increased as shown in Table 9.

The occurrence of increasing and narrowing the range of temperature for gelatinization during steeping has been thought to be similar to the annealing process of semicrystalline polymers. In synthetic polymers, exposure to an appropriate temperature and solvent environment causes a spontaneous ordering of the polymer molecules. The ordering process is known as "annealing" and generally occurs at a temperature near the melting point of the polymer. Annealing has been interpreted as being due to a "sliding diffusion" mechanism which entails the movement of complete molecular sequence in crystal lattices or to a partial melting of crystalline material followed by recrystallization at the annealing temperature. Since starch is a semicrystalline material consisting of amorphous and crystalline regions, holding a suspension of granules just below the gelatinization temperature would be expected to give rise to more perfectly ordered crystals with higher melting points. The increase in crystallinity level was confirmed by X-ray examination, according to Ahmed and Lelievre.<sup>1</sup> They also reported that the enthalpy for gelatinization increased after the starch was steeped for 3 days at  $50^\circ\text{C}$  and then freeze-dried. On the contrary, Gough and Pybus<sup>28</sup> had earlier reported that the enthalpy decreased from 3.0 cal/g before steeping to 2.3 cal/g after steeping. However, an additional test using Congo red indicated the occurrence of gelatinization during steeping and consequently could be used to explain the decrease in enthalpy.

Wirakartakusumah<sup>66</sup> investigated the effect of annealing processes on rice starch and some of his results are presented in Table 10. Table 10 shows the effect of holding a 10:1 (water/starch ratio) sample at  $60^\circ\text{C}$  on gelatinization temperature characteristics. As annealing time increased to 24 hr the gelatinization temperatures (T<sub>o</sub>, T<sub>p</sub>, T<sub>c</sub>) shifted to higher values. However, steeping beyond 24 hr did not result in a change in temperatures. The temperature range for gelatinization also narrowed as the starch was annealed for longer times, decreasing from an initial range of about  $12^\circ\text{C}$  to  $6^\circ\text{C}$  after 24 hr. Determination of  $\Delta\text{H}$  of gelatinization from various annealing times resulted in an essentially constant value of 3.0 cal/g. Results from this study confirm results on studies with wheat starch.

**Table 9**  
**GELATINIZATION**  
**TEMPERATURES OF WHEAT**  
**STARCH FOR VARIOUS**  
**STEEPING TIMES AND**  
**TEMPERATURES**

Treatment	Gelatinization temperature (°C)		
	Onset (T <sub>o</sub> )	Peak (T <sub>p</sub> )	Conclusion (T <sub>c</sub> )
Untreated	57.2	60.5	62.6
24 hr @ 25°C	58.0	61.4	63.8
72 hr @ 25°C	58.8	62.0	63.5
24 hr @ 40°C	59.9	62.4	64.4
72 hr @ 40°C	63.0	64.5	65.5
24 hr @ 50°C	66.0	68.4	69.5
72 hr @ 50°C	67.0	69.0	69.5

From Lorentz, K. and Kulp, K., *Stärke*, 32, 181, 1980. With permission.

**Table 10**  
**EFFECT OF ANNEALING**  
**TREATMENT ON**  
**GELATINIZATION**  
**TEMPERATURE OF RICE**  
**STARCH<sup>a66</sup>**

Steeping time at 50°C (hr)	Temperature (°C) <sup>b</sup>		
	T <sub>o</sub>	T <sub>p</sub>	T <sub>c</sub>
Control	71.0	76.8	82.5
1	73.8	77.0	82.3
24	79.1	82.0	85.5
48	79.5	82.5	86.1
72	78.7	81.8	85.3

<sup>a</sup> Heat rate = 10°C/min; w/s = 10:1.

<sup>b</sup> Average of two replicates; range is ±0.5°C.

Changes in gelatinization properties by "annealing" treatments could have significant effects on cooking characteristics of the starch. In situations where it is desirable to reduce the temperature range for cooking and yet achieve gelatinization, an annealed starch may be required. To date, the author is unaware of starch manufacturers who take advantage of annealing treatments in altering starch gelatinization characteristics.

## XI. SUMMARY

Starch gelatinization phenomena are extremely important in many food systems. This review was meant to focus on factors that affect gelatinization characteristics. The characteristics that are very important in designing processes that are applied to foods include heat

of gelatinization and temperature of gelatinization. Since starch granules exhibit a distribution of size and degree of crystallinity it is tenuous at best to suggest a kinetic model for gelatinization. However, empirical models have been developed and they vary from first to second order depending on accountability for gelatinization during thermal lag periods. Using coefficients from these models, the apparent Arrhenius activation energy varies from about 20 to 75 kcal/mol suggesting that, indeed, the distribution of crystallinity in starch granules influences time/temperature response for gelatinization.

Since starch is one of many components in engineered foods, the influence of other constituents on starch gelatinization must be considered. Major interactions were reviewed for lipids, nonionic constituents, and electrolytes. Each can have a significant effect on starch gelatinization characteristics depending on the nature of the starch (e.g., amylose/amylopectin ratio) and the specific constituent (e.g., stearic acid vs. myristic acid). Furthermore, in some instances the time/temperature treatment during mixing and prior to cooking is important. These same constituents can also affect gelatinization *in situ* in intact cereal grains.

Finally, gelatinization characteristics can be influenced by processing conditions applied before the final cooking process. Parboiling and annealing treatments have been used to alter gelatinization, and annealing treatments, in particular, should receive further investigation.

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