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Physicochemical Changes and Rheological Properties of Starch during Extrusion (A Review)

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Among all flour components, starches play a key role during extrusion. Starch undergoes several significant structural changes, which include gelatinization, melting, and fragmentation. This review focuses on transformations in starch during extrusion and their effect on rheological properties. The effect of extrusion operating parameters, such as residence time distribution, thermal and mechanical energy input and pressure inside the die, and their effect on rheological properties are reviewed. The relationships between rheological properties and extrudate expansion and final extrudate texture are discussed. The dependence of starch viscosity on temperature, moisture content, time-temperature history, shear rate, gelatinization, and fragmentation kinetics during extrusion are reviewed.

1. Introduction

Food extrusion is a continuous cooking and forming process where raw food ingredients undergo many order-disorder transitions, such as starch gelatinization, protein denaturation, and complex formation between lipids and amylose, and are finally shaped at the die. These molecular transformations convert food material into a viscoelastic dough under the presence of heat, moisture, shear, and pressure. Among all flour components, starches play a key role (Leasure and Kokini, 1991). Therefore, this review will focus on starch properties. Starch undergoes several significant structural changes during extrusion that include gelatinization, melting (Chiang and Johnson, 1977a; Owusu-Ansah et al., 1983; Gomez and Aguilera, 1983, 1984; Bhattacharya and Hanna, 1987a; Wang et al., 1991), and fragmentation (Mercier et al., 1979; Faubion and Hosney, 1982; Owusu-Ansah et al., 1982, 1983; Colonna et al., 1984; Davidson et al., 1984a,b; Diosady et al., 1985; Kim and Hamdy, 1987; Wen et al., 1990). The relationship between structural changes in starch and resulting rheological properties is important because the rheological properties of cereal dough, while affecting extrudate expansion and final extrudate texture, also are important for determination of extrusion operating parameters such as residence time distribution, thermal and mechanical energy input and pressure inside the die (which influence final product flavor), appearance, and hydration properties.

The dependence of starch viscosity on temperature, moisture content, time-temperature history, and shear rate has been studied by a number of researchers (Harper et al., 1971; Senouci and Smith, 1988a). A few attempts have been made to model gelatinization and fragmentation kinetics during extrusion (Davidson et al., 1984b; Diosady et al., 1985; Bhattacharya and Hanna, 1987b; Wang et al., 1989) and to model apparent viscosity including reaction

kinetics during extrusion (Morgan et al., 1989; Mackey and Ofoli, 1990; Lai and Kokini, 1990). In addition, the elastic properties of cereal dough during extrusion have also been studied (Jasberg et al., 1981; Jao et al., 1978; Senouci and Smith, 1988b; Padmanabhan and Bhattacharya, 1989). A systematic review of the relationship between structural changes in starch and their observed rheological properties is not available. Therefore, this review attempts to put in perspective the physicochemical changes of starch during extrusion and their effects on rheological properties.

2. Physicochemical Changes in Starch during Extrusion

During extrusion, starches are subjected to relatively high pressure (up to 10^3 psi) (Lai and Kokini, 1990), heat, and mechanical shear forces. Additionally, the food extruder can be regarded as a high-temperature (150–170 °C) short-time (20–200 s) (HTST) bioreactor that can cause starch gelatinization, melting, and fragmentation reactions. The main parameters that influence these reactions, such as shear forces, residence time, and shear rate, are defined by the geometry of the extruder as well as the processing variables, such as temperature, screw speed, feed composition (such as amylose:amylopectin ratio) and moisture content (Meuser and van Lengerich, 1984a,b; Smith and Ben-Gera, 1979; van Lengerich, 1990). Order-disorder transitions usually occur over a range of temperatures. The lowest temperature at which the reaction can be initiated is referred to as the threshold temperature. As a dough's temperature exceeds the transition threshold temperature, the starch molecules begin to undergo various disordering reactions that affect their size and shape. Since rheological properties are related to the size and shape of a fluid's molecules, it seems logical to assume that these molecular changes within starch will greatly affect their rheological properties.

It is well documented that water content in combination with temperature has a significant effect on starch conversion. Starch conversion can take many forms. Under

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Figure 1. "Fringed micelle" model for the crystalline-amorphous structure of partially crystalline polymers. Reprinted with permission from Slade and Levine (1987). Copyright 1987 Van Nostrand Reinhold.

excess water all the crystallites in starch might be pulled apart by swelling, leaving none to be melted at higher temperatures. In a limited water environment, which is the usual condition during extrusion, the swelling forces are much less significant, and the crystallites melt at a temperature much higher than the gelatinization temperature in excess water (Donovan, 1979). Therefore, in this section, the transformation in starch as a function of temperature and moisture in the absence of shear is discussed first. This is necessary to delineate the effect of water and temperature on conversion. Then the effect of shear during extrusion is discussed next.

2.1. Conversion of Starch as a Function of Temperature and Moisture in a Shearless Environment. Slade and Levine (1987) used a "fringed micelle" model illustrated in Figure 1 for conceptualizing a three-dimensional network of starch composed of microcrystalline regions that covalently cross-link amorphous regions of flexible chain segments. For such a partially crystalline polymer as starch, there are three possible characteristic transitions: a glass transition at T_g for the amorphous component, a phase transition at T_m for the crystalline component, and a crystallization transition at T_d for a completely amorphous but crystallizable component, as shown in Figure 2 (Slade et al., 1988). Therefore, the conversion term used in this paper includes both the gelatinization and melting transition.

2.1.1. Gelatinization of Starch. Starch undergoes gelatinization under excess moisture. Wang et al. (1991) define moisture above 63% as excess moisture. This results in a minimum ratio of 14 water molecules to one anhydrous glucose unit required for complete gelatinization (Wang et al., 1990). It is generally accepted that during gelatinization water first penetrates the amorphous region, initiating swelling and resulting in a decrease in birefringence. Additionally, water strips starch chains from the surface of crystallites as the temperature is increased. With increasing temperature, the thermal motion of the molecules and the solvation by the swelling forces lead to decreasing order and disruption of the crystalline regions with uncoiling of the double helices until the granular structure is disrupted nearly completely and a sol is obtained, as shown in Figure 3 (Smith and Ben-Gera, 1979; Donovan, 1979; Lineback, 1986).

Gelatinization of starch can be followed by several methods such as the iodine complexing method (Gomez and Aguilera, 1983, 1984; Owusu-Ansah et al., 1982, 1983),

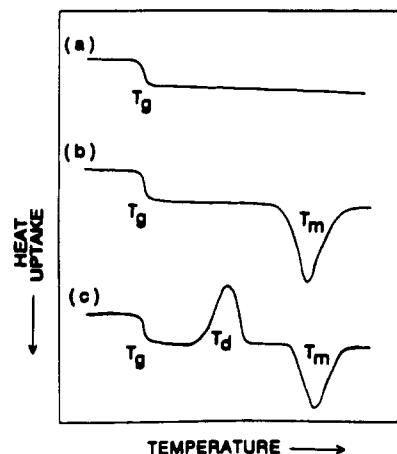


Figure 2. Idealized differential scanning calorimetry (DSC) heat flow curves showing (a) T_g for a completely amorphous material, (b) T_g and T_m for a partially crystalline material, and (c) T_d between T_g and T_m for a completely amorphous but crystallizable material during rewarming following melting and rapid cooling. Reprinted with permission from Slade et al. (1988). Copyright 1988 Marcel Dekker.

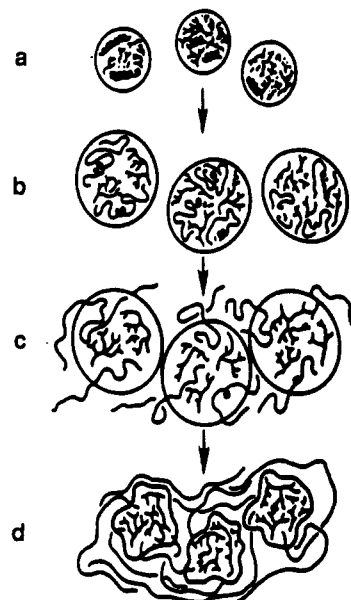


Figure 3. Mechanism of starch gelatinization. (a) Raw starch granules made up of amylose (helix) and amylopectin (branched). (b) Addition of water breaks up amylose crystallinity and disrupts helices. Granules swell. (c) Addition of heat and more water causes more swelling. Amylose begins to diffuse out of granule. (d) Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel. Reprinted with permission from Remsen and Clark (1978). Copyright 1978 Food & Nutrition Press, Inc.

the enzymatic digestion method (Bhattacharya and Hanna, 1987a; Chiang and Johnson, 1977b), measuring changes in viscosity (Lawton et al., 1972), and differential scanning calorimetry (DSC) (Donovan, 1979; Donovan and Mapes, 1980). Iodine staining of granular starch is a routine practice to distinguish between the red-staining waxy varieties and their normal blue-staining counterparts (Synder, 1984; Garcia and Lajolo, 1988). Although only the amylose fraction of starch can react with dilute iodine solution, amylopectin will also react if the concentration of iodine is brought into the range of 10^{-4} M. This minimum concentration of iodine, though adequate for complete reaction of the dissolved starch components, is not high enough to break the associative forces within starch granules (French, 1984). The iodine complexing

Table I. DSC Characteristics of Several Starches

starch	endotherm temp, °C			$-\Delta H_G$, cal/g of starch
	T_0	T_p	T_c	
wheat ^a	50	68	86	4.7
maize	70	78	89	4.3
high-amylose maize	50		133	7.6
waxy maize	68	79	90	4.7
waxy sorghum	68	79	93	4.4
potato	57	72	87	6.6
tapioca	68	78	92	5.5
canna	63	76	92	7.2
corn, commercial ^b	60	67-78	89	3.3
corn, lab	53	63-75	86	2.7
high-amylose corn	71	82-105	114	4.2
waxy corn, commercial	64	71-88	97	4.0

^a Data from Wootton and Bamunuarachchi (1979). ^b Data from Biliaderis et al. (1980).

method is based on the fact that gelatinized starch could solubilize in water more easily and uptake iodine faster than the ungelatinized starch to form an iodine-starch complex. The color of the iodine-starch complex depends on the molecular size.

In enzymatic analysis, the gelatinized starch is digested by glucoamylase, and the resulting glucose can be detected by either reacting with *o*-toluidine to form a green chromogen in glacial acetic acid (Chiang and Johnson, 1977b) or by other glucose measurements. Glucoamylase is an exosplitting enzyme that can split off glucose units from the nonreducing terminal end of starch, and its action is not stopped by the α -1,6-glycosidic linkage in branched molecules such as amylopectin. However, damaged or degraded starch has also been shown to be easily attacked by enzyme action (Evers and Stevens, 1985).

The viscosity method, on the other hand, is based on changes in torque during gelatinization, which can be measured by using the amylograph. The amylographic value (ΔV) is usually used as a rough indication of the degree of gelatinization. The degree of gelatinization is defined as (Lawton et al., 1972)

$$\Delta V = (V_F - V_i) \quad (1)$$

where V_F is the final viscosity of starch suspension, using Brabender units, at a temperature (a typical temperature is 95 °C) higher than the threshold temperature for gelatinization and V_i is the initial viscosity of the starch suspension at 30 °C. A decrease in the amylographic number indicates an increase in the degree of gelatinization (Lawton et al., 1972). In addition to measuring the gelatinization temperature range, information on initial viscosity, maximum viscosity, and time of cooking can also be provided by the amylograph.

Differential scanning calorimetry (DSC) has been widely used to characterize the thermally induced conversion of wheat, maize, Amioca (from corn), and potato starches as a function of moisture content (Donovan, 1979; Donovan and Mapes, 1980; Biliaderis et al., 1980; Eliasson, 1980; Wang et al., 1989). In this method, a sample and an inert material are both heated in a uniform way. The temperature difference between the sample and the reference is then converted to the enthalpy change. The results are then interpreted for starch systems as being related to the breaking of starch-starch hydrogen bonds in favor of starch-water bonds with increased entropy. For cereal starch, the enthalpy values for conversion (ΔH_G) have been reported to range between 2.7 and 7.6 cal/g (Stevens and Elton, 1971; Wootton and Bamunuarachchi, 1979; Biliaderis et al., 1980; Russell, 1987) as shown in Table I, where T_0 represents the initial gelatinization tempera-

Table II. Effects of Heating Rate and Moisture Level on Endotherm Temperatures and $-\Delta H_G$ for Wheat Starch^a

heating rate, °C/min	endotherm temp, °C			$-\Delta H_G$, cal/g of starch
	T_0	T_p	T_c	
8	52	67	78	5.2
16	50	68	86	4.7
32	46	65	85	3.5
water:dry starch ratio	$-\Delta H_G$, cal/g of starch		water:dry starch ratio	$-\Delta H_G$, cal/g of starch
0.50	0.2		1.50	3.6
0.75	0.7		1.75	4.1
1.00	2.0		2.00	4.7
1.25	2.4			

^a Data from Wootton and Bamunuarachchi (1979).

ture, T_p represents the endotherm peak temperature, and T_c represents the temperature at which gelatinization ceased. These characteristic temperatures are significantly affected by the heating rate and the amount of water as well as the extent of starch damage, as shown in Table II. An increase in the extent of damaged starch resulted in a reduced heat of gelatinization. When the gelatinization temperature ranges of different starches obtained by different methods were compared (Lund, 1984), as shown in Table III, the onset temperature of gelatinization for the same type of starch was found to be about the same; however, the peak temperature and conclusion temperature obtained from DSC are slightly higher than those obtained by other methods, an expected result for the high heating rate.

Donovan et al. (1983) investigated the effect of heat and moisture on the degree of gelatinization as measured by differential scanning calorimetry in wheat and potato starch. To get the heat-moisture-treated samples, starches were heated at 100 °C for 16 h at moisture content between 18% and 27% and then cooled as well as dried to a uniform moisture content (about 10%). These treated samples as well as untreated starch were then measured for gelatinization in DSC with excess water. When compared to the untreated starches, the results of treated samples showed a broadening of gelatinization temperature range and a shifting of the endothermal transition toward higher temperatures, as shown in Figure 4. The heat-moisture effects were attributed to either recrystallization and perfection of the small crystalline regions of the granules or new crystallization, because the presence of moisture and the elevated temperature would make polymer chains more mobile and enhance the replacement of interchain hydrogen bonds by water molecules, which results in the growth and perfection of some crystalline regions. Such growth and perfection of crystalline regions will make imbibition of water more difficult and will raise the gelatinization temperature range.

2.1.2. Melting of Starch. When the water concentration is limited, complete gelatinization will not occur at the usual gelatinization temperature range. But as the temperature is increased, the starch granules become progressively more mobile and eventually the crystalline regions will melt. Starch would then be expected to show the usual viscoelastic behavior shown by thermoplastic melts as indicated in Figure 5 (Levine and Slade, 1990).

2.1.2.1. Effect of Moisture. It is well documented that the transition temperature as well as the enthalpy of transition increases with decreasing water concentration for a given starch type. In the DSC thermogram of potato starch obtained at a heating rate of 10 °C/min, Donovan (1979) reported that a single peak was observed when the water level was high (81% in their experiment), and a

Table III. Summary of Gelatinization Characteristics Obtained from Various Starches by Different Methods^a

type of starch	method of analysis	temperature, °C			ΔH , cal/g
		onset (T_0)	peak (T_p)	conclusion (T_c)	
wheat	hot stage	55	61	66	2.4
	DSC ^b	52	59	65	
	amylograph	54		67	
potato	turbidity	55		95-100	5.1-5.5
	hot stage	59	63	68	
	DSC	57-59	71	94-95	
corn	hot stage	65	69	76	3.3
	DSC	65	70.6	77	
rice	hot stage	72	75	79	3.1
	DSC	70	76.3	82	
	DSC	68	74	79	3.0

^a Data from Lund (1984). ^b DSC = differential scanning calorimetry.

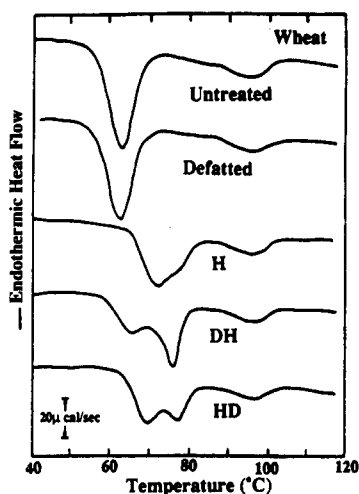


Figure 4. Differential calorimetry runs for untreated, defatted, and heat-moisture (27%) treated wheat starch at 5 °C/min. Sample sizes (dry basis, top to bottom): 2.22, 2.09, 1.92, 2.17, and 1.89 mg, with 12-13 mg of water. H = heat-moisture treated; DH = defatted, then heat-moisture treated; HD = heat-moisture treated, then defatted. Reprinted with permission from Donovan et al. (1983). Copyright 1983 American Association of Cereal Chemists.

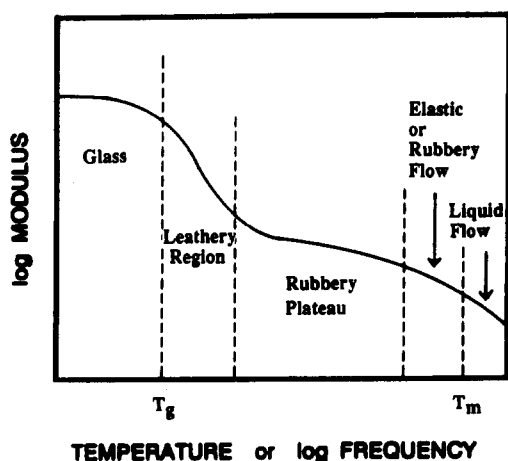


Figure 5. Master curve of the modulus as a function of temperature or frequency illustrating the five regions of viscoelastic behavior characteristic of partially crystalline synthetic polymers. Reprinted with permission from Levine and Slade (1990). Copyright 1990 Van Nostrand Reinhold.

second endotherm developed at higher temperatures when moisture content dropped to 64%. This endotherm became predominant when water concentration was lower

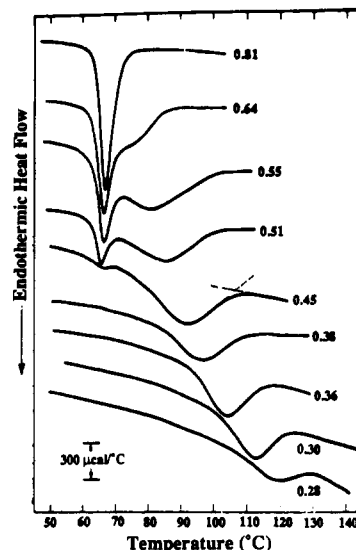


Figure 6. DSC thermograms of potato starch obtained at a heating rate of 10 °C/min labeled with volume fraction of water present. Weight of starch (dry basis) from top to bottom: 1.59, 2.05, 3.19, 2.33, 2.62, 2.05, 2.78, 3.99, and 3.30 mg. The intersection of the straight lines drawn in the 0.45 fraction thermogram shows the method of extrapolation to determine T_m . Molar ratio of water to starch for these experiments, from top to bottom, are 24.8, 10.1, 6.97, 6.12, 4.83, 3.64, 3.27, 2.50, and 2.25. Reprinted with permission from Donovan (1979). Copyright 1979 John Wiley & Sons, Inc.

than 51%, as shown in Figure 6. The responses at low water concentration have been attributed to "melting" of crystallites. Wang et al. (1991) theoretically calculated the necessary amount of water for starch transformation (gelatinization and melting) as

$$A = I - (Sx\alpha 18)/162 \quad (2)$$

$$W = A/[A + S(1 - x)] \quad (3)$$

where A is the unused water concentration of the total starch sample after a specific extent of transformation and a specific stoichiometric ratio of water to glucose (α), I is the initial water concentration, S is the initial starch concentration, x is the percent transformed starch, and W is the unused water concentration of untransformed starch. For high-amylopectin corn starch (Amioca) at a heating rate of 5 °C/min, when moisture content was lower than 61%, lower water content increased the transition temperature as shown in Figure 7. Using corn starch, Takahashi et al. (1982) reported that with moisture content less than 12% there were two endothermic peaks in differential thermal analysis (DTA) as shown in Figure 8. The first peak (A) was remarkable in its sharpness and intensity and was thought to be due to melting of starch involving the collapse of the ordered structure of starch with only a limited breakdown in the main chain of starch molecules. The onset temperature of peak A (fusion temperature) depended on starch type and moisture content, as shown in Figure 9. The finish of the second peak (B) cannot be determined because its endothermic process connected inseparably to an infinite exothermic process. This peak was relatively independent of the moisture content and was supposed to be a thermal decomposition of the glucosyl residues.

The dependence of endotherm temperature (T_m) upon water content can be examined by using the Flory-Hug-

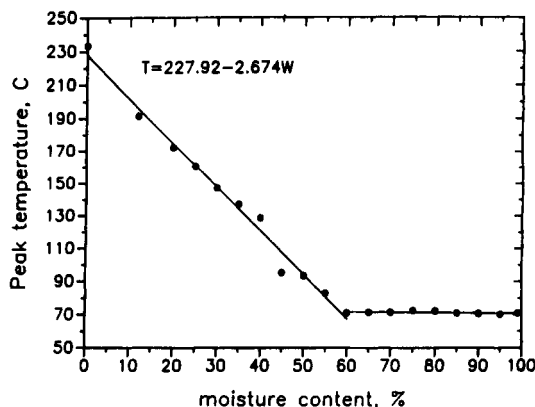


Figure 7. Peak temperature from DSC endotherms for Amioca with various moisture contents. Reprinted with permission from Wang et al. (1991). Copyright 1991 Institute of Food Technologists.

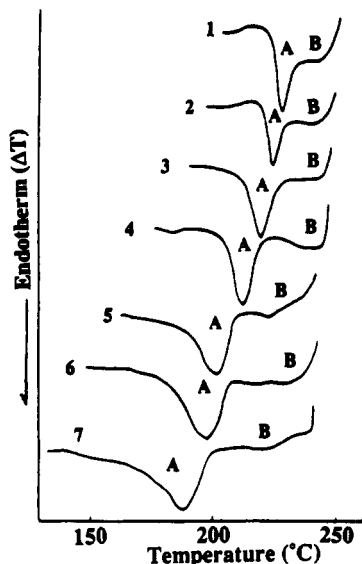


Figure 8. Differential thermal analysis curves for corn starch having different moisture contents. Moisture content (on a dry basis): 1, 5.2%; 2, 6.2%; 3, 7.0%; 4, 7.7%; 5, 8.8%; 6, 9.3%; 7, 10.5%. Reprinted with permission from Takahashi et al. (1982). Copyright 1982 Agricultural Chemistry Society of Japan.

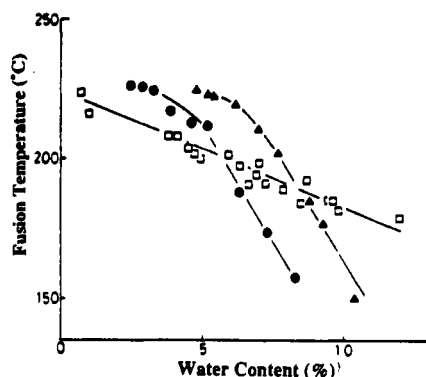


Figure 9. Effects of species and moisture content of starch on the fusion temperature. ●, potato starch; □, kuzu starch; ▲, corn starch. Reprinted with permission from Takahashi et al. (1982). Copyright 1982 Agricultural Chemistry Society of Japan.

gins equation (Flory, 1953):

$$(1/T_m - 1/T_m^0) = (R/\Delta H_u)(V_u/V_f)(\nu_1 - x_1\nu_1^2) \quad (4)$$

where R is the gas constant, ΔH_u is the enthalpy of fusion per mole of crystalline polymer repeat unit, V_u and V_f are

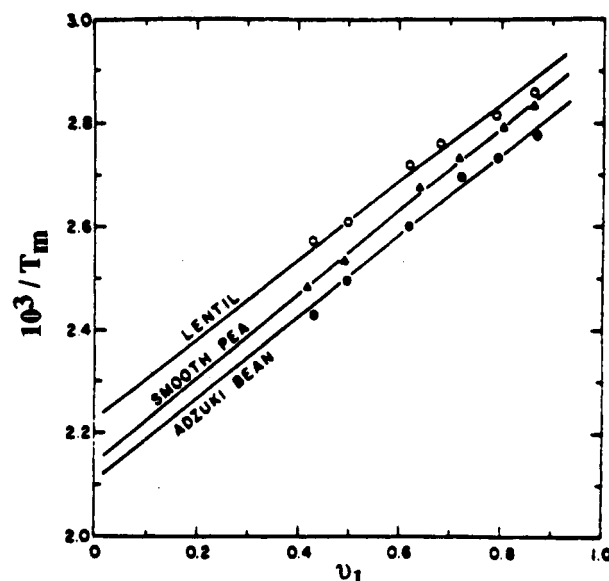


Figure 10. Reciprocal melting point, $1/T_m$ (kelvins) plotted against the volume fraction of water, ν_1 , for three legume starches. Each line is a linear least-squares fit of the experimental data. Reprinted with permission from Biliaderis et al. (1980). Copyright 1980 Institute of Food Technologists.

the molar volumes of repeat units and diluent, x_1 is the Flory-Huggins polymer diluent interaction parameter, T_m (kelvins) is the melting point of the diluent-polymer mixture at the upper temperature limit of the endotherm, ν_1 is the volume fraction of diluent, and T_m^0 is the melting point of the most perfect crystallites of the undiluted polymer. For an ideal solution, x_1 is equal to zero; therefore, the above equation gives a linear relation between ν_1 and $1/T_m$. Figure 10 showed a typical plot of $1/T_m$ against ν_1 for three legume starches (Biliaderis et al., 1980). The intercept at $\nu_1 = 0$ gives $1/T_m^0$, and ΔH_u can be derived from the slope of the line. This equation is based on the assumption of equilibrium melting. Therefore, the presence of water (diluent), which decreases the chemical potential of the system, results in melting point depression.

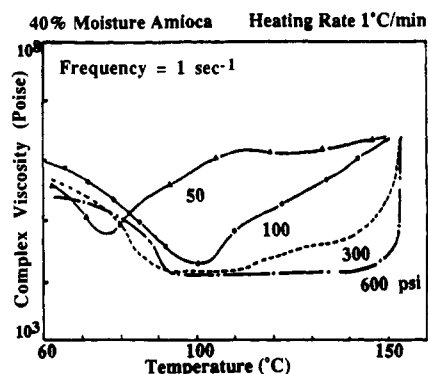
2.1.2.2. Effect of Pressure. Kokini et al. (1990) evaluated the influence of pressure on the DSC profile of Amioca at 20% and 30% moisture. The results are listed in Table IV. At both 20% and 30% moisture, increasing the pressure from 15 to 200 psi induces a 57 °C increase in T_{max} , and at 150 and 200 psi, two thermally induced transitions are observed, in contrast with the monophasic melting at 15 psi. The effect of pressure is also profound in terms of affecting the extent of conversion as measured by using rheological techniques. Herh and Kokini (1990) studied the effect of pressure on starch conversion at both high and low moisture content using a pressure rheometer. At high moisture (64% moisture content), the effect of pressure going from 0 to 300 psig is quite small. However, when the moisture content is 40%, as shown in Figure 11, increasing pressure from 50 to 600 psig results in a shift in the conversion temperature of 40 °C, which is consistent with the results of the pressure DSC study. For polymers such as polyethylene, the change in melting temperature with pressure is of the order of 0.04 K/bar (Wunderlich, 1981). However, the change observed for Amioca corn starch, in the presence of water, is on the order of 1 K/bar, indicating that amylopectin is much more sensitive to changes in pressure than plastic material.

2.2. Transformation of Starch during Extrusion. Extrusion of breakfast cereals and snacks is usually

Table IV. Pressure DSC Scan of Amioca at 20% and 30% Moisture Content^a

pressure, psi (atm)	T_{onset} , °C	T_{max} , °C	pressure, psi (atm)	T_{onset} , °C	T_{max} , °C
20% Water			30% Water		
15 (1)	147	160	15 (1)	137	164
90 (6)	148	195	200 (13.5)	177 ^b	221 ^b
150 (10)	186 ^b	225		135 ^b	150 ^b
	158 ^b	182			
200 (13.5)	158 ^c	217			

^a Data from Kokini et al. (1990). ^b Two transitions. ^c Very broad, possibly two overlapping transitions.

**Figure 11.** Pressure rheometry for Amioca with 40% moisture. Reprinted with permission from Herh and Kokini (1990).

conducted at moisture contents ranging from 12% to 16% wet basis. This water content is much below the amount of water necessary for gelatinization. In addition, the residence time (20–200 s) is so small that heat alone cannot transform starch. However, during extrusion, shear force physically tears apart starch granules and allows faster transfer of water into the interior starch molecules (Burros et al., 1987). The loss of crystallinity during extrusion is no longer caused by penetration of water but by mechanical disruption of the molecular bonds by the intense shear fields within the extruder (Wen et al., 1990). Therefore, under extrusion at low moisture content, a mixture of small amounts of gelatinized and melted states of starch as well as fragmentation exist simultaneously.

2.2.1. Gelatinization and Melting. Studies on the transformation in extruded starch (Anderson, et al., 1970; Mercier and Feillet, 1975; Chiang and Johnson, 1977a; Bhattacharya and Hanna, 1987b; Lai and Kokini, 1990) suggested that the loss of crystallinity was caused by mechanical disruption of the molecular bonds by the intense shear fields within the extruder. Operating conditions such as barrel and die temperature, screw speed, and screw geometry, as well as feed composition such as amylose: amylopectin ratio and moisture content, have a profound influence on mechanical disruption and starch transformation.

Using a response surface design and general linear regression, Owusu-Ansah et al. (1983) investigated the effect of temperature, moisture, and screw speed on gelatinization, cooked starch viscosity, and water absorption index in extruded corn starch and derived regression equations relating these variables to the induced changes. These equations are given in Table V. They found that the interaction between temperature and moisture content was the most important factor affecting conversion during twin screw extrusion. Temperature alone was the next important factor, followed by moisture and then screw speed (Table VI). This finding is consistent with the results of Chiang and Johnson (1977a) for wheat flour, where the interaction between temperature and moisture

content was shown to be the most important factor affecting starch transformation in extruded products during single screw extrusion. When moisture content was between 18% and 27%, increasing the temperature or decreasing the screw speed or the die nozzle size, which affects both the shear rate and residence time, will enhance the extent of transformation, as shown in Figure 12. It was found that moisture content alone did not significantly affect starch transformation (gelatinization in the figure) at low temperature (65 and 85 °C) but enhanced transformation (gelatinization in the figure) significantly at high temperature (95 and 110 °C). Using the iodine combining method, Lai and Kokini (1990) reported that the extent of transformation of extruded high-amylopectin corn starch decreased with increasing moisture content, which confirms the importance of shear stress, but increased with increasing temperature, as shown in Figure 13. This result is consistent with the findings of Bhattacharya and Hanna (1987b) as well as those of Gomez and Aguilera (1984), who conducted amylase digestion as well as iodine methods on extruded corn starch with moisture content between 14.2% and 42.2% at extrusion temperatures between 90 and 164 °C.

Studies on starch conversion during extrusion have also been conducted by using DSC. Gomez and Aguilera (1984) as well as Chinnaswamy et al. (1989) reported that no peak was observed in the temperature range of 25–115 °C for extrudate samples, indicating that the amount of native starch left in extrudates was scarce and undetectable by using a DSC. On the other hand, Wang et al. (S. S. Wang, W. C. Chiang, B. L. Zhao, X. Z. Zheng, and I. H. Kim, personal communication, 1988) and Breslauer and Baumann (personal communication, 1988) successfully used Perkin-Elmer DSC-4 to measure the extent of starch conversion of Amioca extrudate as well as corn meal under a heating rate of 5 °C/min and the temperature range of 20–260 °C. The transition temperature and the enthalpy of transition were found to be influenced by the screw speed of the extruder, moisture content, and final barrel temperature, with temperature and moisture content having the greatest influence. Shifting of the transition temperature or generation of new peaks was observed by extrusion (K. J. Breslauer and G. C. Baumann, personal communication, 1988).

2.2.2. Fragmentation. It is well documented that shear results in fragmentation of the starch granule during extrusion (Wen et al., 1990). Several methods can be used to study the effect of extrusion on starch fragmentation. Starch fragmentation during extrusion was evidenced by partial or complete destruction of the crystalline structure of the raw starch granule, observed by using X-ray diffraction patterns (Charbonnier et al., 1973; Chinnaswamy et al., 1989). Broken or stretched surfaces appear on extruded samples when analyzed by scanning electron microscopy (SEM) (Faubion and Hoseneey, 1982; Owusu-Ansah et al., 1983; Chinnaswamy et al., 1989). In addition, a decrease in viscosity or increase in solubility of starch solutions after extrusion (Colonna et al., 1984; Kim and Hamdy, 1987) and changes in elution profiles as detected by gel-permeation chromatography (GPC) were found (Davidson et al., 1984a; Colonna and Mercier, 1983; Colonna et al., 1984; Klingler et al., 1986; Chinnaswamy et al., 1989; Wen et al., 1990).

Dextrinization is defined as partial hydrolysis of starch which results in products that can be precipitated from aqueous solution by alcohol (Whistler and Daniel, 1984). Gomez and Aguilera (1983) studied the physicochemical properties of starch in corn extrudates. In their study,

Table V. Regression Equations for the Various Responses^a

gelatinization	$Y_g = -22.268 + 1.062X_1 + 24.099X_2 - 4.598X_3 - 0.022X_1^2 - 0.257X_2^2 + 0.016X_3^2 - 0.084X_1X_2 + 0.009X_1X_3 + 0.011X_2X_3$
water absorption index	$Y_a = -4.392 + 0.052X_1 + 1.096X_2 - 0.136X_3 - (8.865 \times 10^{-5})X_1^2 - (1.415 \times 10^{-2})X_2^2 + (3.140 \times 10^{-4})X_3^2 - (3.356 \times 10^{-3})X_1X_2 + (3.720 \times 10^{-4})X_1X_3 + (4.670 \times 10^{-4})X_2X_3$
cold viscosity	$Y_{v1} = -1839.088 + 12.378X_1 + 94.422X_2 + 3.436X_3 - 0.021X_1^2 - 0.373X_2^2 - 0.021X_3^2 - 0.322X_1X_2 - 0.012X_1X_3 + 0.029X_2X_3$
cooked viscosity	$Y_{v2} = -1022.029 + 7.541X_1 + 80.080X_2 - 3.688X_3 - 0.013X_1^2 - 1.300X_2^2 + 0.020X_3^2 - 0.174X_1X_2 - 0.012X_1X_3 + 0.087X_2X_3$

^a Equations from Owusu-Ansah et al. (1983). X_1 = temperature; X_2 = moisture; X_3 = screw speed.

Table VI. Contribution and Significance of Extruder Variables to the Physicochemical Properties of Extruded Corn Starch^a

independent variables	percent contribution to R^2			
	gelatinization	water absorption index	cold viscosity	cooked viscosity
TM	28.08	27.69	7.98	8.29
T^b	25.52	24.59	13.23	19.73
M^c	14.20	14.04	61.89	40.84
S^d	12.02	11.60	1.04	6.22
TS	3.91	3.78	0.13	0.48
M^2	3.89	6.68	0.12	6.24
T^2	2.11	4.02	8.01	10.36
S^2	1.71	0.39	0.05	0.18
SM	0.04	0.04	0.01	0.17
R^2	91.47	92.83	92.46	92.51

^a Data from Owusu-Ansah et al. (1983). ^b T = temperature. ^c M = moisture. ^d S = screw speed.

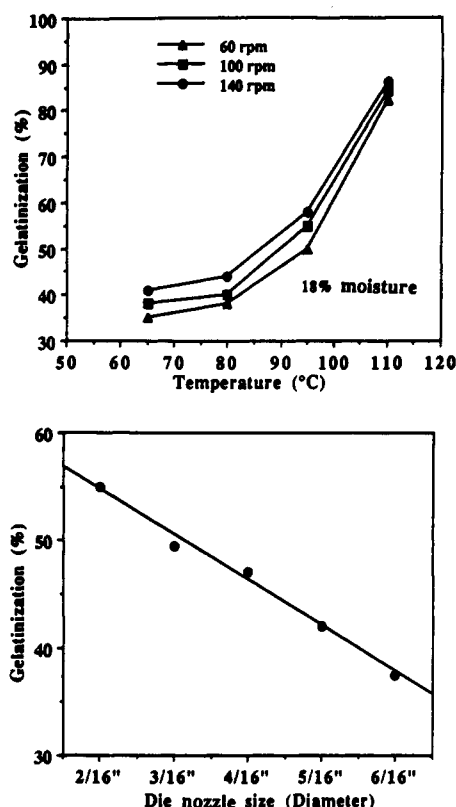


Figure 12. Effects of temperature, screw speed, and die nozzle size on starch gelatinization. Reprinted with permission from Chiang and Johnson (1977a). Copyright 1977 American Association of Cereal Chemists.

the gelatinized starch was obtained by cooking a starch-water suspension (2.5% w/w) at 120 °C for 1 h; the dextrinized starch was prepared by treating a gelatinized suspension with 0.15% α -amylase at pH 6.3, 90 °C, for 2 h. By comparing the physicochemical properties and SEM of raw, gelatinized, dextrinized, and extruded samples, they found that the extruded corn samples can be visualized as a composite of gelatinized and dextrinized

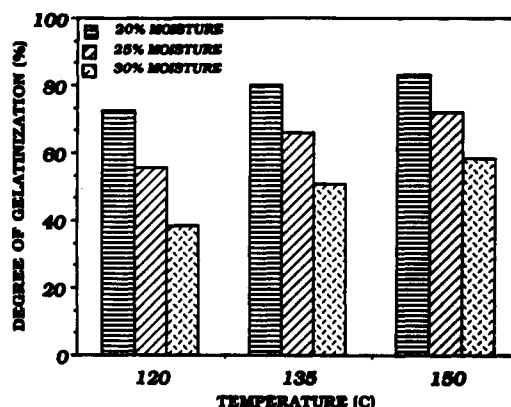


Figure 13. Representative graph of the degree of conversion for Amioca under various extrusion conditions (200 rpm) measured by the iodine combining method. Reprinted with permission from Lai and Kokini (1990). Copyright 1990 John Wiley & Sons, Inc.

materials (Figure 14). Dextrinization appeared to become the predominant mechanism of starch fragmentation during low-moisture and high-shear extrusion. A model of starch fragmentation was presented and is shown in Figure 15 (Gomez and Aguilera, 1984).

The mechanism of fragmentation is reported to be in the form of limited debranching in amylopectin, which causes significant decreases in overall molecular size without measurably changing the percentage of 1→6 bonds as analyzed by the relative number of reducing end groups (Davidson et al., 1984). Fragmentation is thought to be in the form of random chain splitting in amylose (Colonna et al., 1984). Fragmentation in an extruder is also known to be the result of mechanical energy (Meuser et al., 1986; Meuser and van Lengerich, 1984a,b; Klingler et al., 1986). To better characterize mechanical energy, the specific mechanical energy (SME) was defined as (van Lengerich, 1990)

$$SME = M_d \omega / m \quad (5)$$

where SME = specific mechanical energy (W·h/kg), M_d = torque (N·m), ω = rotational speed of screw (s^{-1}), and m = mass flow rate (kg/h). As shown in Figure 16, for SME values up to 200 W·h·kg⁻¹, the decrease in average molecular weight can be described as an exponential function, and the fragmentation due to a constant increase in SME always depends on the remaining concentration of starch with the initial average molecular weight. Both the mechanical and thermal energy transferred to starch dough during extrusion affect the breakdown of the main and secondary valence bonds and hydrogen bonds between neighboring starch polymers in starch structure (Klingler et al., 1986). These structural changes increase the susceptibility of starch to enzyme action, the reduction of hydrogen bonds, and the increase of the free hydroxyl group and affected amylopectin more than amylose. As reported by Colonna et al. (1984), the average molecular weight of amylose and amylopectin decreased by factors of 1.5 and 15, respectively, during extrusion.

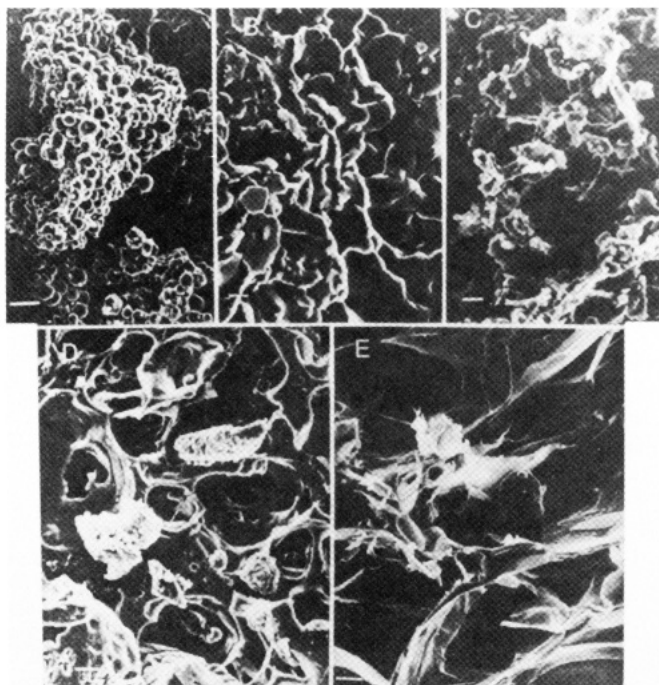
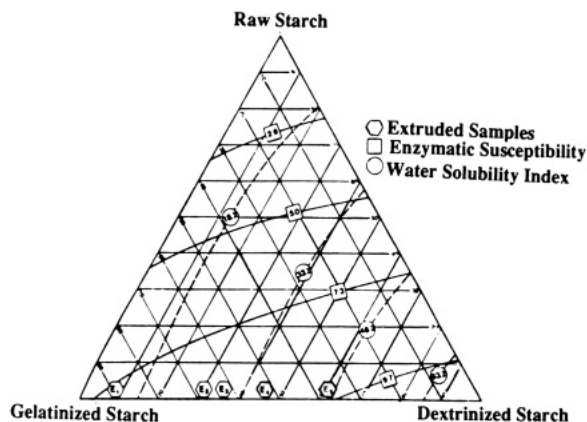


Figure 14. (Top) Response surface of raw, gelatinized, and dextrinized corn blends and extruded corn products. (Bottom) Scanning electron micrographs of corn samples: (A) raw, (B) gelatinized, (C) dextrinized, (D) extruded at 23.7% moisture content, and (E) extruded at 7.6% moisture content. Markers: (A) 30 μm ; (B) and (C) 10 μm ; (D) and (E) 50 μm . Reprinted with permission from Gomez and Aguilera (1983). Copyright 1983 Institute of Food Technologists.

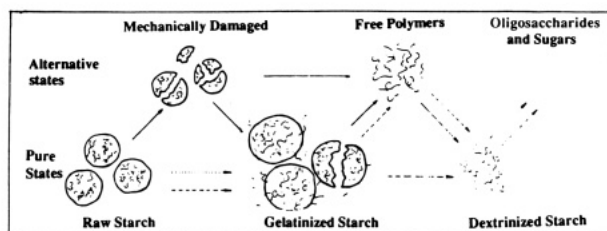


Figure 15. Proposed model of starch degradation during extrusion. \longrightarrow shear; $-\cdot-$ heat; \cdots moisture. Reprinted with permission from Gomez and Aguilera (1984). Copyright 1984 Institute of Food Technologists.

Fragmentation of starch during extrusion depends on the operating conditions of the extruder such as screw speed, temperature, and moisture content (Davidson et al., 1984a) as well as the type of starch used. Davidson et al. (1984a) found that the extent of amylopectin fragmentation decreased with increasing temperature or moisture content and decreasing screw speed, with a

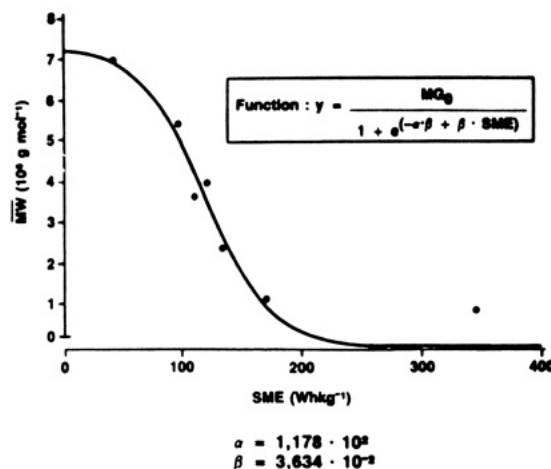


Figure 16. Influence of SME on the medium molecular weight of extruded wheat starch. Reprinted with permission from Lengerich (1990). Copyright 1990 Van Nostrand Reinhold.

moisture range of 20%–25% and temperature range of 121–177 °C. For example, starch fragmentation decreased from 0.62 at 121 °C to 0.43 at 177 °C for 20% moisture and extrusion at 100 rpm, as shown in Figure 17. This is confirmed by Wen et al. (1990) in a study of degerminated yellow corn meal with 20%–30% moisture at 100–200 °C. In a study of cereal starches in a twin screw extruder (Mercier et al., 1979), it was found that, for corn starch with moisture content between 10.5% and 28.5% and barrel temperature between 70 and 250 °C, very little dextrinization occurred as evidenced by no ethanol-soluble fraction formation, indicating that extrusion solubilized the corn starch without fragmenting it into dextrin, as shown in Figure 18. On the other hand it must be kept in mind that this method focuses on fragmentation to a molecular weight below 2000. Consequently, it is possible that fragmentation above this molecular weight level occurred but was not detected. As a matter of fact, the study of Lai (1991) using low-angle laser light scattering clearly showed that fragmentation occurred both in amylopectin- and amylose-based starches, with the degree of fragmentation depending on extrusion conditions. When potato starches were used in the study of Mercier et al. (1979), the extruded potato starch presented an ethanol-soluble fraction, indicating the formation of oligosaccharides smaller than a molecular weight of 2000, as shown in Figure 19. The different behavior between cereal and potato starch was attributed to the difference in the granule structure. It is known that the amylose from potato starch is more easily extracted by hot water than is the amylose from cereal starch. Extrusion may destroy the structure of potato starch so that amylose becomes amorphous and susceptible to shear. In contrast, the butanol-amylose complex, observed in extrudates of cereal starch, protects the amylose fraction, which then cannot be split into oligosaccharides.

2.3. Kinetics of Starch Conversion. Prediction of starch behavior during processing necessitates quantitative characterization of changes through understanding of kinetics of both physical and chemical transformations in limited water as a function of temperature and moisture content, which affect the rate of reaction and extent of shear. In this section, we discuss the kinetics in excess moisture processing without shear and utilize this information for discussion of the kinetics in limited-water, high-temperature, and high-shear processing of starch.

2.3.1. Reaction Kinetics at High Moisture Content. A great deal of research has focused on the kinetics of

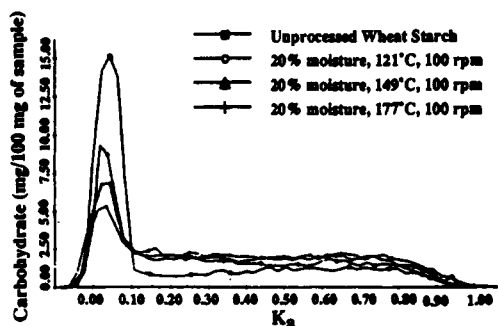


Figure 17. Comparison of the Bio-Gel A-150m chromatograms for unprocessed wheat starch and samples extruded at a feed moisture of 20% and screw speed at 100 rpm. Reprinted with permission from Davidson et al. (1984a). Copyright 1984 Institute of Food Technologists.

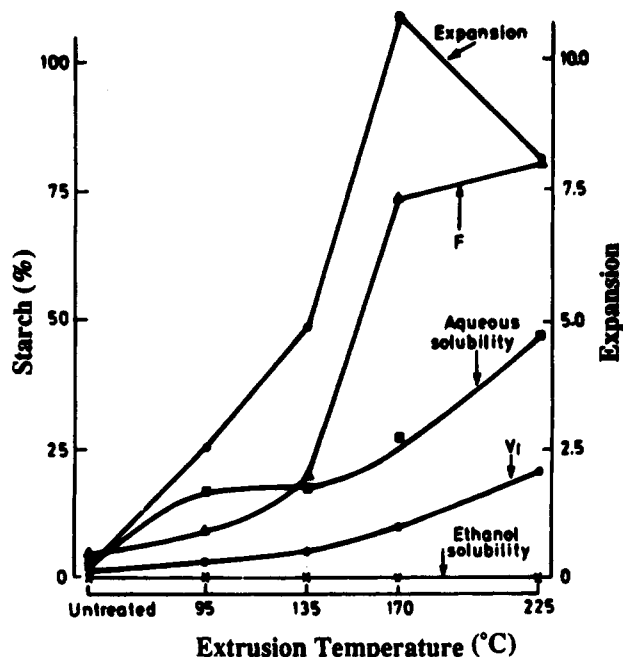


Figure 18. Effects of extrusion temperature (95, 135, 170, and 225 °C) on expansion (○), percentage of water-soluble (■), and ethanol-soluble (×) carbohydrates, V_i (●), and F (▲) (α -amylolysis parameters) of extruded products from corn starch; initial moisture content before extrusion was 22% by weight. Reprinted with permission from Mercier and Feillet (1975). Copyright 1975 American Association of Cereal Chemists.

starch gelatinization in high-moisture systems. Lund and Wirakartakusumah (1984) suggested that the gelatinization kinetics for rice starch follow first-order reaction kinetics when the temperature is greater than 67 °C (as shown in Figure 20):

$$\ln \left(\frac{[UG]_i - [UG]_t}{[UG]_i - [UG]_f} \right) = -kt \quad (6)$$

where $[UG]_i$ was the initial amount of ungelatinized starch, $[UG]_t$ was the final amount of ungelatinized starch at the reaction time t , $[UG]_f$ was the ultimate amount of ungelatinized starch at the given temperature conditions, and k was the reaction rate constant. Using DSC, they found that the activation energy increased with increasing temperature of gelatinization, indicating the temperature dependence of the rate constant did not follow the Arrhenius equation. A distribution of activation energies was proposed and was thought to be related to a distribution of crystalline size and location in the granule, having different responses to time/temperature treatment. The amorphous region with its lower order of crystallinity was

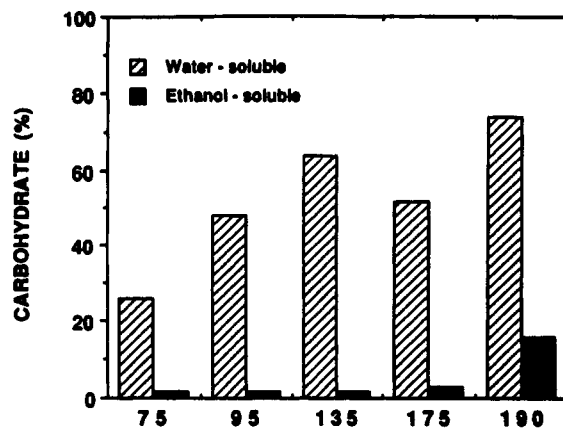


Figure 19. Water-soluble and ethanol-soluble carbohydrate of potato starch extruded at different temperatures with 23% moisture content before extrusion. Reprinted with permission from Mercier et al. (1979). Copyright 1979 Butterworth and Co. (Publishers) Ltd.

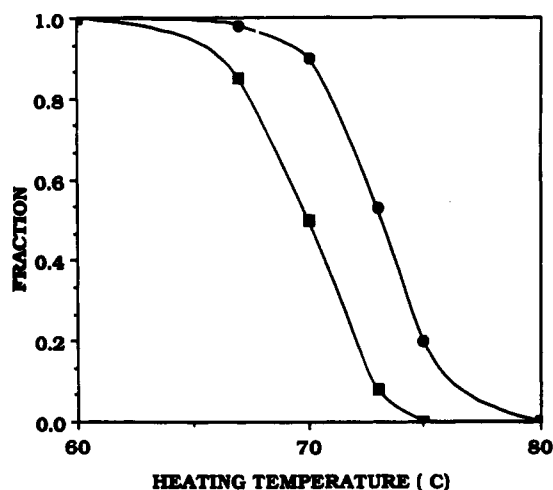


Figure 20. Fraction of ungelatinized rice starch at various temperatures. (■) $[UG]_t/[UG]_i$; (●) $[UG]_f/[UG]_i$. Reprinted with permission from Lund and Wirakartakusumah (1984). Copyright 1984 Elsevier Science Publishing Co., Inc.

thought to hydrate first and was more susceptible to heat treatment with water present than the crystalline region. Therefore, it acted as a promoter for further gelatinization of more crystalline regions of the granules.

Pravisani et al. (1985) determined the kinetics of potato starch gelatinization by using DSC at a heating rate between 1 and 25 °C/min and temperature between 30 and 90 °C. The equation of Ozawa (1970) was used to estimate the activation energy of gelatinization as

$$\ln (\beta / T_p^2) = -E_a / RT_p + \ln (AR/E_a) \quad (7)$$

where β is the heating rate (K/min), T_p is the endothermic peak temperature (K), R is the ideal gas constant, E_a is the activation energy of gelatinization (kcal/mol), and A is the preexponential factor (min^{-1}). A change in the kinetic constant was found at 67.5 °C, as shown in Figure 21. At temperatures lower than 67.5 °C, gelatinization was not complete for long reaction times. The gelatinization of amorphous regions of the granule was also thought to act as a reaction "promoter" of the crystalline zones.

Kinetics can also be studied rheologically. For example, using a parallel plate plastometer to measure the compressibility of cooked rice, Suzuki et al. (1976) showed that the cooking rate of rice, obtained from the ratio of thickness of the cooked rice grain between the two parallel

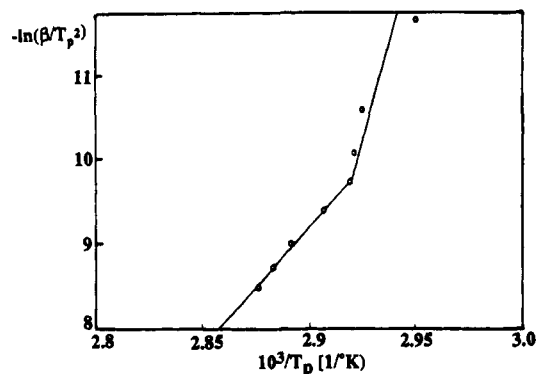
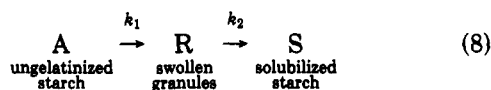


Figure 21. Effect of heating rate, β , on the peak temperature, T_p , shown according to Ozawa (1970). Each represents the average of 8–10 replications. Reprinted with permission from Pravisani et al. (1985). Copyright 1985 Institute of Food Technologists.

plates before and after cooking at different cooking times, followed also first-order kinetics in the temperature range between 75 and 150 °C. The activation energy of cooking changed at 110 °C (Figure 22), indicating a change in the cooking mechanism from being limited by the reaction rate of rice components with water at temperatures below 110 °C to being limited by the rate of diffusion of water through the cooked layer toward the interface of uncooked core where the reaction occurred at temperatures above 110 °C.

Kokini et al. (1990) proposed a kinetic model for starch gelatinization. Assuming that gelatinization of starch in excess water involves a two-stage mechanism, i.e., initial swelling followed by dissolution, the model is



where k_1 and k_2 are rate constants for each step and are assumed to be first order. Since this is a first-order irreversible reaction in series, the concentration of the intermediate R is given as

$$C_R/C_{A0} = [k_1/(k_1 - k_2)](e^{-k_1 t} - e^{-k_2 t}) \quad (9)$$

Different k_1/k_2 values give different shapes of the C_R/C_{A0} vs time curve, as shown in Figure 23. If k_1 is much larger than k_2 , the swelling of starch granules is much more rapid than the solubilization. For this special case, the population density of swollen granules in suspension in the dissolved matrix controls the viscosity of the starch suspension. Since high moisture contents were used in the above studies, moisture content was not limiting. However, this is not necessarily so in processes such as extrusion cooking.

2.3.2. Reaction Kinetics in Limited Water Environments. As mentioned before, several unit operations such as extrusion are usually conducted at too low a moisture level (less than 64%) for complete starch gelatinization. Information on the kinetics of phase transition of starch at low moisture content relevant to extrusion process is very limited. Using DSC, Burros et al. (1987) found that the reaction order of corn starch gelatinization at high temperature (110–140 °C) and low moisture (25%) was smaller (approximately 0.8) than that in excess water (showing first-order kinetics). They suggested a diffusional limitation of the first-order reaction in a restricted water environment that resulted in gelatinization depending on migration of the available water to and into starch granules. In an extruder where mixing

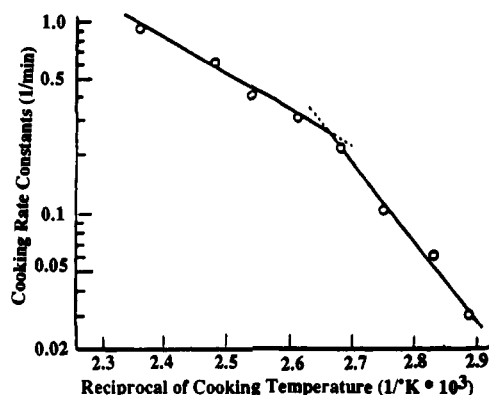


Figure 22. Arrhenius plots of the cooking rate constants of rice (soaking time 30 min). Reprinted with permission from Suzuki et al. (1976). Copyright 1976 Institute of Food Technologists.

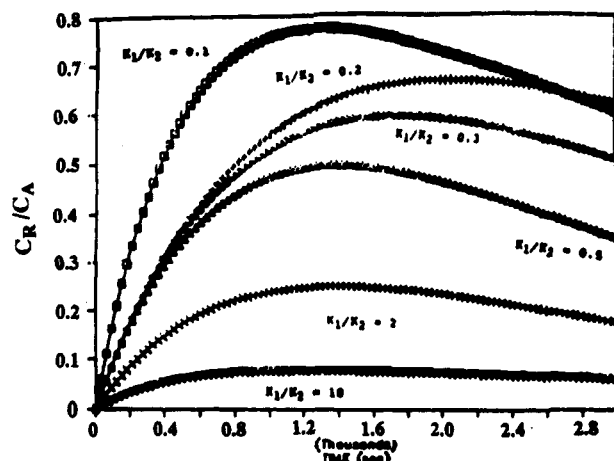


Figure 23. C_R/C_{A0} vs time at different k_1/k_2 ratios. Reprinted with permission from Kokini et al. (1990). Copyright 1990 Elsevier Science Publishing Co., Inc.

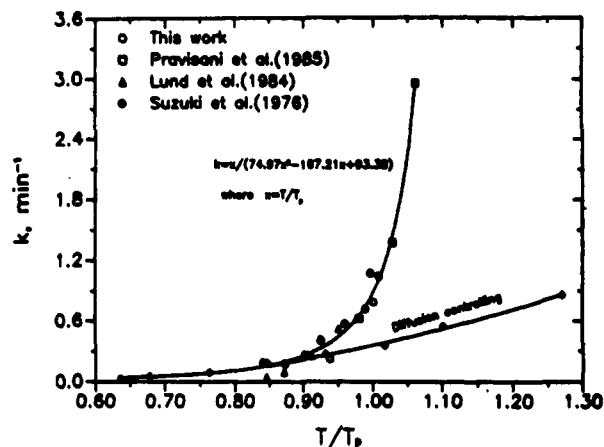


Figure 24. Correlation between rate constants of starch conversion, k , and a nondimensional temperature parameter, T/T_p . Reprinted with permission from Wang et al. (1989). Copyright 1989 Institute of Food Technologists.

and shearing actions are present, convective mass transfer should help in reducing limitation caused by diffusion. To explain the combined effects of moisture and the source of starch on the thermal transition of starch, Wang et al. (1989) use a dimensionless parameter T/T_p , where T is the temperature for reaction and T_p is the peak temperature in a DSC thermogram and is dependent on the source of starch as well as moisture content in the sample. This parameter can be used as an index for judging the effectiveness of thermal effect on starch conversion. The

Table VII. Rate Constants for Starch Gelatinization in Corn^a

temp, °C	k , kg of damaged starch (kg of sample) ⁻¹ s ⁻¹	
	waxy corn	ordinary corn
164	24.14×10^{-3}	10.7×10^{-3}
160	21.94×10^{-3}	8.86×10^{-3}
140	22.41×10^{-3}	9.03×10^{-3}
120	18.94×10^{-3}	7.85×10^{-3}
115	18.65×10^{-3}	6.85×10^{-3}

^a Data from Bhattacharya and Hanna (1987b).

phase transition of waxy corn starch at extrusion temperatures of 145–160 °C and moisture content between 20% and 25% followed pseudo-zeroth-order reaction kinetics, and the diffusion process was not a limiting step, as shown in Figure 24. Pseudo-zeroth-order reaction kinetics is consistent with the findings of Bhattacharya and Hanna (1987b) during single screw extrusion of corn starch with moisture between 17.8% and 42.2% (dry basis) and temperatures between 116 and 164 °C. The rate constants were found to be higher for waxy corn than for high amylose corn and decreased with decreasing temperature, as shown in Table VII.

Shear-induced molecular size reduction has been well documented in polymer systems. Basedow et al. (1979) investigated the mechanical degradation of polyacrylamide and dextran. They reported that shear stress is the controlling factor of molecular size reduction, consistent with other researchers' findings (Casale and Porter, 1978). The rate constant for shear degradation was expressed as an exponential function of shear stress of the form

$$k = C \exp(\Delta E / \tau V_r) \quad (10)$$

as shown in Figure 25, where C is a constant, τ is the shear stress sustained by the polymer molecules, ΔE is the activation energy, and V_r is an "activation" volume of the sheared system, which is assumed to be a constant. The activation energy was found to be a function of molecular weight (Figure 26).

Expanding on this concept, Wang et al. (S. S. Wang, W. C. Chiang, B. L. Zhao, X. Z. Zheng, and I. H. Kim, personal communication, 1988) proposed a concept that allowed inclusion of thermal and shear effects and the interaction between these two effects in a zero-order starch conversion model:

$$k = k_{h0} \exp(-E'_a / RT) + k_{s0} \exp(-E''_a / \nu \tau) + k_{h0} \exp(-E'_a / RT) k_{s0} \exp(-E''_a / \nu \tau) \quad (11)$$

where ν is the molar volume (m³/mol) of anhydroglucose units in the starch-water mixture, τ is the shear stress (N/m²) applied, E'_a is the activation energy for temperature, E''_a is the activation energy for shear stress, and k_{h0} and k_{s0} are rate constants. It was found that the activation energy for shear effect was 3 orders of magnitude smaller than that for thermal effect, indicating that shear stress has a more intense effect than thermal energy on starch conversion.

During single screw extrusion, Davidson et al. (1984a,b) and Diosady et al. (1985) developed a model for shear-induced molecular size reduction of wheat starch to be of first-order reaction kinetics. In their studies, a nominal shear rate ($\pi DN/H$) was used to characterize the deformation rate experienced by the melts, where D is the diameter of the barrel, N is the screw speed, and H is the average screw channel depth over the active volume) in the down channel direction. Since the range of shear stress

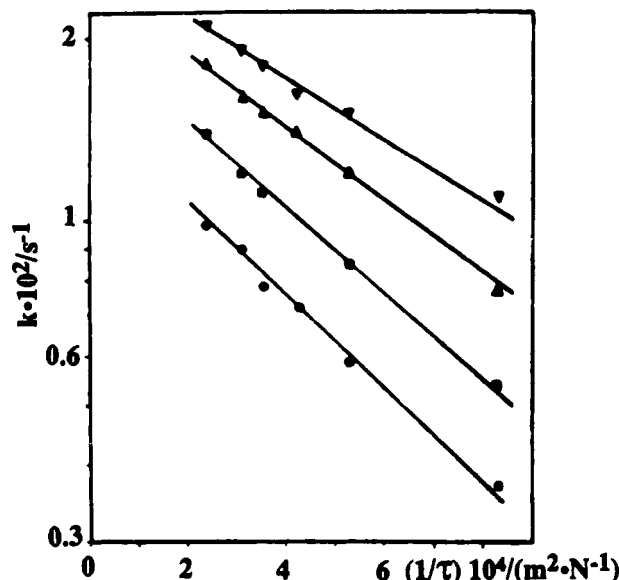


Figure 25. Plot of rate constants of degradation, k , of polyacrylamide as a function of the reciprocal shear stress τ for different molecular weights. ●, MW 5 000 000; ■, MW 6 000 000; ▲, MW 7 000 000; ▼, MW 8 000 000. Reprinted with permission from Basedow et al. (1979). Copyright 1979 Huethig & Wepf Verlag.

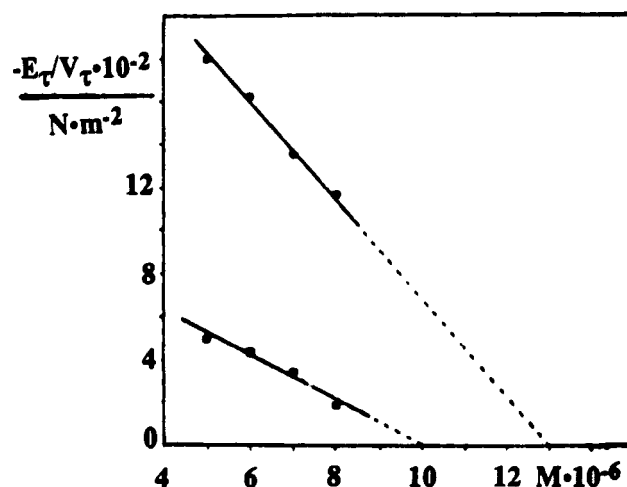


Figure 26. Plot of the quantity $-E_a / V_r$ as a function of molecular weight M for polyacrylamide. ●, solvent water; ■, solvent methanol/water 50% (by weight). Reprinted with permission from Basedow et al. (1979). Copyright 1979 Huethig & Wepf Verlag.

was small, eq 10 was modified to assume the rate constant was a linear function of shear stress:

$$k = k' \tau \quad (12)$$

where k' was the modified rate constant. By assuming that the cooked and uncooked starch components had different intrinsic viscosities, they obtained

$$X_T = f \exp(k \tau t + b) + (1 - f) \quad (13)$$

where X_T was the extent of polymer modification defined in terms of viscosity as $[\eta] / [\eta]_{rs}$, where $[\eta]$ was the intrinsic viscosity of final product and $[\eta]_{rs}$ was the intrinsic viscosity of raw starch, f was the fraction of fully cooked starch, k was the rate constant (m²·N⁻¹·S⁻¹), τ was the mean shear stress (N·m⁻²), t was the mean residence time (s), and b was a constant. This model was tested with wheat starch, and good agreement with experimental data was obtained (Figure 27). However, we have to mention here that

DEGRADATION MODEL

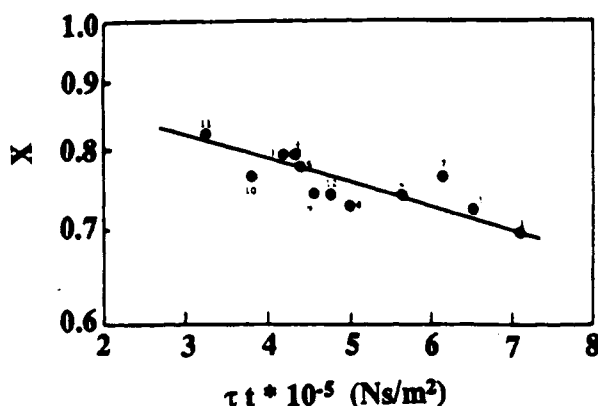


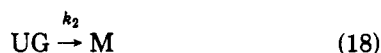
Figure 27. Degradation model: plot of τt against $\log X$ at the following conditions: 1, 25%, 50 rpm, 79 °C; 2, 25%, 100 rpm, 79 °C; 3, 25%, 50 rpm, 100 °C; 4, 25%, 100 rpm, 100 °C; 5, 25%, 50 rpm, 121 °C; 6, 25%, 100 rpm, 121 °C; 7, 30%, 50 rpm, 79 °C; 8, 30%, 100 rpm, 79 °C; 9, 30%, 50 rpm, 100 °C; 10, 30%, 100 rpm, 100 °C; 11, 30%, 50 rpm, 121 °C; 12, 30%, 100 rpm, 121 °C. Reprinted with permission from Diosady et al. (1985). Copyright 1985 Institute of Food Technologists.

intrinsic viscosity is only a measurement of hydrodynamic volume in dilute solutions, which is a function of both molecular size and molecular shape, and is not a direct indication of molecular weight.

In a low-moisture high-shear environment, both shear force and temperature are responsible for breaking hydrogen bonds between linear amylose and branched-chain amylopectin. The extent of hydrogen-bond breaking depends on the intensity of shear and temperature. By considering that melting and gelatinization of starch proceeded in parallel and were followed by continued fragmentation after melting or gelatinization, Kokini et al. (1989) proposed the following mechanistic model for starch during extrusion:



where UG is ungelatinized starch, G is gelatinized starch, M is melted starch, F is fragmented starch, and k_0 , k_1 , k_2 , k_1' , and k_2' are rate constants. Since it has been shown that shear force alone (without thermal effect) could not change the DSC transition of starch to a measurable extent (S. S. Wang, W. C. Chiang, B. L. Zhao, X. Z. Zheng, and I. H. Kim, personal communication, 1988), it is thought that direct fragmentation from ungelatinized starch due to shear is scarce. If it is assumed that fragmentation reactions are catalytic reactions and require a threshold shear stress to proceed, it can be safely argued that a large portion of G and M will not convert to F at relatively high moisture, in which case the mechanism will simplify to



where the first reaction is first order, while the second reaction follows zero-order kinetics. Such information is

important in terms of predicting the molecular changes with respect to time during extrusion.

3. Rheological Properties of Dough Systems during Extrusion

The rheological properties of cereal dough not only control extrudate expansion and texture, as well as final extrudate quality, but also are necessary to describe transport phenomena such as momentum, heat, and mass transfer in an extruder (Bruin et al., 1978; Lai and Kokini, 1990). Cereal doughs portray power law behavior under isothermal conditions and in the shear rate range of 10–1500 s^{-1} , a range pertinent to extrusion (Rossen and Miller, 1973; Lai and Kokini, 1990). However, it is nontrivial to measure the rheological properties of cereal doughs because of the reactive nature and the time-dependent changes in material properties as well as the wide range of temperature and pressure to be considered (Baird and Labropoulos, 1982; Steffe and Morgan, 1987). Capillary and slit dies make rheological measurements during extrusion possible. On the basis of the principle of capillary and slit rheometry, and considering the Rabinowitsch–Mooney correction for power law fluids, one can obtain the shear stress and shear rate, and viscosity is simply the ratio of shear stress to shear rate. On the other hand, the elastic properties of cereal dough can be investigated by analyzing the entrance pressure drop or the exit pressure during extrusion (Han, 1988), since the exit pressure is due to the recoverable elastic energy stored in high molecular weight synthetic or biological polymers. Even though the use of dies modifies the pressure, shear, and temperature history of a material in an extruder, it allows food materials to receive a deformation history pertaining to extrusion cooking that is difficult to achieve in any other rheometer (Fletcher et al., 1985). The rheological properties of cereal doughs are strongly dependent on processing variables such as temperature, moisture content, and screw speed as well as molecular transformations such as gelatinization, melting, and fragmentation.

3.1. Effects of Extrusion Operating Variables and Molecular Transformation on Viscosity. The rheological data from several investigators for maize grits and potato starch during extrusion are summarized in Table VIII. Temperature effects on the viscosity of some Newtonian fluids can be represented by a relationship developed from Eyring kinetic theory:

$$\mu = \mu_{\infty} \exp(\Delta E_v / RT) \quad (19)$$

where μ = Newtonian viscosity, μ_{∞} = viscosity at reference temperature, ΔE_v = molar activation energy of viscosity, R = molar gas constant, and T = absolute temperature. Eyring defined ΔE_v as the molar free energy of activation in a stationary fluid (Bird et al., 1960); it is related to the amount of molecular energy required for a molecule to escape its present surrounding (cage) and move into an adjoining molecular site (hole). Eyring kinetic theory can be used for estimating temperature effects on the consistency coefficient (m) of a pseudoplastic fluid and cereal dough (Metzner, 1959; Harper et al., 1971; Cervone and Harper, 1978; Jao et al., 1978; Bruin et al., 1978; van Zuilichem et al., 1979; Phillips et al., 1984; Fletcher et al., 1985; Bhattacharya and Hanna, 1986, 1987a; McMaster et al., 1987; Senouci and Smith, 1988a) by assuming the flow behavior index (n) to be relatively temperature independent. Shear viscosity was found to decrease with increasing temperature.

In reference to the effect of moisture content, it is clear that water is a necessary component and precursor of most

Table VIII. Summary of Rheological Data for Maize and Potato during Extrusion^a

	temp, °C	moisture content (MC), %	shear rate, s ⁻¹	rheological model	other variables	remarks
cooked cereal dough ^b	67-100	25-30 ^c	10-100	$\eta = m\dot{\gamma}^{n-1} \times \exp[\Delta E/RT] \exp[k(MC)]$	$r = 0.96$ $m = 78.5 \text{ Pa}\cdot\text{s}^n$ $n = 0.51$ $\Delta E/R = 2482 \text{ K}$ $k = -0.079$	single screw extruder + cylindrical viscometer
corn flour dough ^d	90-150	22-30 ^e	10-250	$\eta = m\dot{\gamma}^{n-1} \times \exp[\Delta E/RT] \exp[k(MC)]$	$r = 0.987$ $m = 36.0 \text{ Pa}\cdot\text{s}^n$ $n = 0.36$ $\Delta E/R = 4388 \text{ K}$ $k = -0.101$	single screw extruder (10-100 rpm) + extruder dies
corn grits ^f	177 193 207	13 13 13		$\eta = A\dot{\gamma}^{n-1}$	$n = 0.45-0.55$ $m = 2.8 \times 10^4 \text{ Pa}\cdot\text{s}^n$ $m = 1.73 \times 10^4 \text{ Pa}\cdot\text{s}^n$ $m = 0.76 \times 10^4 \text{ Pa}\cdot\text{s}^n$	single screw extruder + slit die viscometer
corn grits ^g	153-158	15.3-18.7 ^e	82-126	$\eta = m\dot{\gamma}^{n-1} \times \exp[\Delta E/RT] \exp[k(MC)]$	$r = 0.95$ $m = 0.49 \text{ Pa}\cdot\text{s}^n$ $n = 0.68$ $\Delta E/R = 3969 \text{ K}$ $k = -0.03$	single screw extruder + slit die viscometer
corn grits ^h	100-140	20.1-31.5 ^e	45-208	$\eta = m\dot{\gamma}^{n-1}N^{-\alpha} \times \exp[\Delta E/RT] \exp[k(MC)]$	$r = 0.963$ $m = 21.5$ $n = 0.75$ $\alpha = +0.541$ $\Delta E/R = 2834 \text{ K}$ $k = -0.032$ $N = 100-250 \text{ rpm}$	twin screw extruder + slit die viscometer
potato powder ^h	80-140	18-42	21-174	$\eta = m\dot{\gamma}^{n-1}N^{-\alpha} \times \exp[\Delta E/RT] \exp[k(MC)]$	$r = 0.940$ $m = 9.4 \times 10^4$ $n = 0.45$ $\alpha = +0.61$ $\Delta E/R = 860 \text{ K}$ $k = -0.083$ $N = 50-250 \text{ rpm}$	

^a Data from Senouci and Smith (1988a). ^b 80% corn and 20% oat flour; Harper et al. (1971). ^c Wet basis. ^d Pregelatinized; Cervone and Harper (1978). ^e Dry basis. ^f Bruin et al. (1978). ^g Fletcher et al. (1985). ^h Senouci and Smith (1988a).

order-disorder transitions as well as complexing reactions in biopolymers. During extrusion, moisture is relatively more important than barrel temperature in influencing residence time, which is related to viscosity (Phillips et al., 1984). As shown in Table VI, Owusu-Ansah et al. (1983) reported that, for cooked viscosity of corn starch, feed moisture content was the most significant variable. Temperature alone was the next significant variable, followed by the second order of temperature and then the interaction between temperature and feed moisture content. Viscosity of cereal dough was found to be inversely related to moisture (Harper et al., 1971; Cervone and Harper, 1978; Jao et al., 1978; Bruin et al., 1978; van Zuilichem et al., 1979; Phillips et al., 1984; Fletcher et al., 1985; Bhattacharya and Hanna, 1986, 1987a; McMaster et al., 1987; Senouci and Smith, 1988a; Lai and Kokini, 1990). Water was assumed to act as a plasticizer to lubricate and soften the dough and limit swelling of starch granules, therefore decreasing viscosity.

During single screw extrusion, the extruder is flood-fed. An increase in the screw speed is therefore accompanied by a decrease in viscosity due to the shear thinning nature of cereal dough. During twin screw extrusion, on the other hand, viscosities of corn grits, potato powder, and degerminated corn meal are found to decrease with increasing screw speed at constant shear rate, due to the increasing specific mechanical energy introduced, more molecular breakdown, and lower extent of conversion of crystallites (McMaster et al., 1987; Smith and Senouci, 1988a; Wang et al., 1991; Park et al., 1991).

Rheological properties have also been shown to be related to the size, shape, and molecular weight of a fluid's

molecules. Even though mathematical relationships have been developed by using molecular and physical entanglement theories to predict rheological properties of polymers (Ferry, 1980), there are several dissimilarities between polymer and starch transformations in extrusion. Thermoplastic polymers generally undergo reversible melting and irreversible polymerizing reactions during extrusion, but starch undergoes irreversible gelatinization with network entanglement and fragmentation. As mentioned in the previous section, the two most important extrusion variables affecting starch conversion are barrel temperature and material moisture (Lawton et al., 1972; Chiang and Johnson, 1977b; Gomez and Aguilera, 1984; Lai and Kokini, 1990). As the temperature of dough is raised above the conversion temperature range, gelatinization and melting occur. The shear force within an extruder may be strong enough to break these fragile gelatinized and melted granules into small fragments, thereby resulting in a reduction in viscosity (Bhattacharya and Hanna, 1987b). Launay and Lisch (1983) reported that extrusion cooking ruptures the granular structure of starch. At sufficiently high extrusion temperature, starch extrudate becomes almost completely dispersed in cold water. It is thought that the increase in solubility and decrease in intrinsic viscosity is due to depolymerization by random chain splitting (Doublier et al., 1986; Colonna and Mercier, 1983; Davidson et al., 1984a,b). This depolymerization was also evidenced by the variation in the values of the power law index n during rheological measurements in extrusion. For example, for high-amylopectin corn starch, the n values were reported to change from 0.608 with an extrusion temperature of 150 °C and

moisture content of 20% to 0.259 with an extrusion temperature of 100 °C and moisture content of 30%. This change in n indicated a significant change in shear rate dependence of the melt viscosity and in molecular weight (Jao et al., 1978; Davidson et al., 1984a,b; Fletcher et al., 1985; McMaster et al., 1987; Lai and Kokini, 1990). Since this shear modification does not affect amylose and amylopectin to the same degree (Colonna et al., 1984), the change in n values is less pronounced for amylose (Lai and Kokini, 1990). In addition, amylose-rich corn starch has been reported to have higher viscosity than amylopectin-rich corn starch (Bhattacharya and Hanna, 1987b; Lai and Kokini, 1990), due to a strong intermolecular interaction and a much larger effective hydrated volume occupied by the dissolved molecules with the same molecular weight as amylopectin. Therefore, the overall rheological behavior should be interpreted in terms of the physicochemical aspects of starch structure (Colonna et al., 1984).

3.2. Rheological Model for Extrusion Cooking. The dependency of food dough viscosity on temperature, moisture content, and shear rate has been observed by a number of researchers (Harper et al., 1971; Jao et al., 1978; Cervone and Harper, 1978; Bhattacharya and Hanna, 1986, 1987a; Senouci and Smith, 1988a). In all these studies, the viscosity of cereal dough was assumed to have a power function dependency on shear rate, an Arrhenius dependency temperature, and an exponential dependency on moisture:

$$\eta(\dot{\gamma}) = m(\dot{\gamma})^{n-1} \exp(\Delta H/RT) \exp(-k_1 C) \quad (20)$$

The apparent viscosities of cereal doughs during extrusion were shown to be pseudoplastic with n values from 0.25 to 0.75 in the temperature range between 67 and 158 °C and at moisture contents between 13% and 50%.

Mackey and Ofoli (1990), assuming that the increase in viscosity due to the transformation of starch granules was similar to the viscosity increase caused by an increase in the effective polymer molecular weight during a plastic polymerization process, developed a model incorporating the effect of shear rate, temperature, moisture content, time-temperature history, and strain history for starch doughs:

$$\eta = \exp[(\Delta H/R)(1/T - 1/T_r) + b(C - C_r)][(\tau_0/\dot{\gamma})^{n_1} + (\mu_\infty \dot{\gamma})^{n_2-n_1}]^{1/n_1} [1 + A(1 - e^{-k_2 \psi})] [1 - \beta(1 - e^{-d\varphi})] \quad (21)$$

The notation is listed in Table IX. This model allowed for variable power indices, yield stress, and high shear limiting viscosity, and a number of assumptions were made: (1) no elastic effects, (2) no compositional effects other than starch and water, (3) no dependence upon maximum shear rate, (4) no explicit volume fraction dependence, (5) effect of gelatinization on viscosity is additive, may be approximated by first-order reaction kinetics, and has an exponential dependence upon time-temperature history, and (6) homogeneous, isotropic medium.

On the basis of the fact that the activation energy and the moisture dependency constant in eq 20 were not constants but were dependent on the extrusion conditions (Fletcher et al., 1985), Lai and Kokini (1990) developed a simple viscosity model by considering the activation energy as a linear function of moisture, the moisture dependency constant as a linear function of temperature, and a power function dependence of viscosity on gelati-

Table IX. Notation for Equation 29

η	apparent viscosity at temperature T and moisture C (poise)
$\dot{\gamma}$	shear rate, s^{-1}
ΔH	activation energy, cal/mol
R	ideal gas constant, cal/mol·K
T	temperature of food dough, K
b	moisture dependency constant
C	moisture content, % (wet basis)
k_a	reaction constant quantifying effect of gelatinization
T_r	reference temperature, K
C_r	reference moisture, %
τ_0	yield stress, Pa
μ_∞	high shear limiting viscosity (Ofoli model), $Pa \cdot s^{-n_2-n_1}$
n_1, n_2	power indices, dimensionless
A	relative increase in viscosity due to gelatinization, dimensionless
β	index of strain history on viscosity at infinite φ , dimensionless
ψ	integrated time-temperature history = $\int_0^t T(t) \exp[-\Delta E/RT(t)] dt$
φ	weighted average total strain = $\int_0^t \dot{\gamma} dt$
γ	average shear rate for a given cross-sectional area, s^{-1}
α	index of molecular effect on viscosity, dimensionless
d	rate constant quantifying effect of thixotropy

nization as follows for starch dough:

$$\eta(\dot{\gamma}) = m(\dot{\gamma})^{n-1} \exp[(\Delta H_0 + \Delta H_0')/RT] \times \exp[-(k_{10} + k_{10}'T)C](DG)^\alpha \quad (22)$$

This model was tested with a high-amylose and a high-amylopectin corn starch during single screw extrusion, and good agreement between theoretical values and experimental values were obtained.

4. Concluding Remarks

Starch gelatinization in a shearless environment has been studied extensively. However, the conversion of starch during extrusion involves more than gelatinization and includes melting as well as fragmentation. As extrusion cooking involves simultaneous application of heat, pressure, and shear to starch materials, distinction between gelatinization and melting becomes less clear. Additional research should be conducted that will enable accurate estimation of gelatinization and melting during extrusion. Even though qualitatively starch has been reported to undergo fragmentation during extrusion, the quantitative data showing changes in molecular weight as a function of extrusion operating variables are lacking. In addition, reaction kinetic models, considering starch conversion and fragmentation as functions of time, shear, and extrusion operating variables are necessary to predict molecular changes with respect to time during extrusion.

Much progress has been made in modeling the viscosity of food doughs as a function of shear rate, temperature, moisture content, and starch conversion. However, studies on the elastic properties of cereal doughs are very limited, and further research is needed. So far, there is not a single rheological model that incorporates starch gelatinization, fragmentation, and viscoelastic behavior as functions of time, temperature, shear rate, and moisture content. A general rheological model for use in scale-up, quality control, and simplifying the complex process in a cooking extruder is needed.

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Literature Cited

- Anderson, R. A.; Conway, H. F.; Peplinski, A. K. Gelatinization of corn grits by roll cooking, extrusion cooking and steaming. *Starke* 1970, 22 (4), 130.
- Baird, D. G.; Labropoulos, A. E. Invited review: Food dough rheology. *Chem. Eng. Commun.* 1982, 15, 1-25.
- Basedow, A. W.; Edbert, K. H.; Hunger, H. Effects of mechanical stress on the reacting of polymers: shear degradation of polyacrylamide and dextran. *Makromol. Chem.* 1979, 180, 411.
- Bhattacharya, M.; Hanna, M. A. Viscosity modelling of dough in extrusion. *J. Food Technol.* 1986, 21, 167-174.
- Bhattacharya, M.; Hanna, M. A. Textural properties of extrusion cooked corn starch. *Lebensm.-Wiss. Technol.* 1987a, 20, 195-201.
- Bhattacharya, M.; Hanna, M. A. Kinetics of starch gelatinization during extrusion cooking. *J. Food Sci.* 1987b, 52 (3), 764-766.
- Biliaderis, C. G.; Maurice, T. J.; Vose, J. R. Starch gelatinization phenomena studied by differential scanning calorimetry. *J. Food Sci.* 1980, 45, 1669-1674.
- Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport phenomena*; John Wiley and Sons, Inc.: New York, 1960.
- Bruin, S.; van Zuilichem, D. J.; Stolp, W. A review of fundamental and engineering aspects of extrusion of biopolymers in a single-screw extruder. *J. Food Process Eng.* 1978, 2, 1-37.
- Burros, B. C.; Young, L. A.; Carroad, P. A. Kinetics of corn meal gelatinization at high temperature and low moisture. *J. Food Sci.* 1987, 52 (5), 1372-1376.
- Casale, A.; Porter, R. S. *Polymer stress reactions*; Academic Press: New York, 1978; Vol. I.
- Cervone, N. W.; Harper, J. M. Viscosity of an intermediate moisture dough. *J. Food Process Eng.* 1978, 2, 83-95.
- Charbonniere, R.; Duprat, F.; Guibolt, A. Changes in various starches by extrusion cooking. II. Physical structures of extruded starches. *Cereal Sci. Today* 1973, 18, 286.
- Chiang, B. Y.; Johnson, J. A. Gelatinization of starch in extruded products. *Cereal Chem.* 1977a, 54 (3), 436-443.
- Chiang, B. Y.; Johnson, J. A. Measurement of total and gelatinized starch by glucoamylase and o-toluidine reagent. *Cereal Chem.* 1977b, 54 (3), 429-435.
- Chinnaswamy, R.; Hanna, M. A.; Zobel, H. F. Microstructural, physicochemical, and macromolecular changes in extrusion-cooked and retrograded corn starch. *Cereal Food World* 1989, 34 (5), 415-422.
- Clark, J. P. Dough rheology in extrusion cooking. *Food Technol.* 1978, 32 (7), 73-82.
- Colonna, P.; Mercier, C. Macromolecular modification of manioc starch components by extrusion-cooking without lipids. *Carbohydr. Polym.* 1983, 3, 87-108.
- Colonna, P.; Doublier, J. L.; Melcion, J. D.; deMonredon, F.; Mercier, C. Extrusion cooking and Drum drying of wheat starch. I. Physical and macromolecular modification. *Cereal Chem.* 1984, 61 (6), 538-543.
- Davidson, V. J.; Paton, D.; Diosady, L. L.; Larocque, G. Degradation of wheat starch in a single screw extruder: characteristics of extruded starch polymers. *J. Food Sci.* 1984a, 49, 453.
- Davidson, V. J.; Paton, D.; Diosady, L. L.; Rubin, L. T. A model for mechanical degradation of wheat starch in a single-screw extruder. *J. Food Sci.* 1984b, 49, 1154.
- Diosady, L. L.; Paton, D.; Rosen, N.; Rubin, L. J.; Athanassoulas, C. Degradation of wheat starch in a single-screw extruder: mechano-kinetic breakdown of cooked starch. *J. Food Sci.* 1985, 50, 1697-1699.
- Dolan, K. D.; Steffe, J. F. Back extrusion and simulation of viscosity development during starch gelatinization. *J. Food Process Eng.* 1989, 11, 79-101.
- Donovan, J. W. Phase transitions of starch-water system. *Biopolymers* 1979, 18, 263.
- Donovan, J. W.; Mapes, C. J. Multi-phase transitions of starches and nageli amyloextrin. *Starke* 1982, 32, 190.
- Donovan, J. W.; Lorenz, K.; Kulp, K. Differential scanning calorimetry of heat-moisture treated wheat and potato starches. *Cereal Chem.* 1983, 60 (5), 381.
- Doublier, J. L.; Colonna, P.; Mercier, C. Extrusion cooking and Drum drying of wheat starch. II. Rheological characterization of starch pastes. *Cereal Chem.* 1986, 63 (3), 240-246.
- Eliasson, A. C. Effect of water content on the gelatinization of wheat starch. *Starch/Starke* 1980, 32 (8), 270.
- Evers, A. D.; Stevens, D. J. In *Advances in cereal science and technology*; Pomeranz, Y., Ed.; American Association of Cereal Chemists, Inc.: St. Paul, MN, 1985; pp 321-349.
- Faubion, J. M.; Hoseney, R. C. High-temperature short-time extrusion cooking of wheat starch and flour. I. Effect of moisture and flour type on extrudate properties. *Cereal Chem.* 1982, 59 (6), 529-533.
- Ferry, J. D. *Viscoelastic properties of polymers*, 2nd ed.; John Wiley and Sons, Inc.: New York, 1980.
- Fletcher, S. I.; McMaster, T. J.; Richmond, P.; Smith, A. C. Rheology and extrusion of maize grits. *Chem. Eng. Commun.* 1985, 32, 239-262.
- Flory, P. J. *Principles of polymer chemistry*; Cornell University Press: Ithaca, NY, 1953.
- French, D. In *Starch: Chemistry and Technology*; Whistler, R. L., Bemiller, J. N., Paschall, E. F., Eds.; Academic Press, Inc.: New York, 1984.
- Garcia, E. G.; Lajolo, F. M. Starch transformation during banana ripening: The amylase and glucosidase behavior. *J. Food Sci.* 1988, 53 (4), 1181-1186.
- Gomez, M. H.; Aguilera, J. M. Changes in the starch fraction during extrusion-cooking of corn. *J. Food Sci.* 1983, 48, 378-381.
- Gomez, M. H.; Aguilera, J. M. A physicochemical model of corn starch. *J. Food Sci.* 1984, 49, 40-43.
- Han, C. D. In *Rheological measurement*; Collyer, A. A., Clegg, D. W., Eds.; Elsevier Applied Science: London and New York, 1988.
- Harper, J. M.; Rhodes, T. P.; Wanninger, L. A. Viscosity model for cooked cereal doughs. *Am. Inst. Chem. Eng. Symp. Ser.* 1971, No. 108.
- Harper, J. M. *Extrusion of food*; CRC Press Inc.: Boca Raton, FL, 1981a; Vol. I.
- Harper, J. M. *Extrusion of food*; CRC Press Inc.: Boca Raton, FL, 1981b; Vol. II.
- Herh, P. K.; Kokini, J. L. The effect of pressure on gelatinization of starch using small amplitude oscillatory measurements under pressure. Presented at the Institute of Food Technologists 51st annual meeting, Anaheim, CA, 1990.
- Jao, Y. C.; Lewandowski, D.; Erwin, W. W. Engineering analysis of soy dough rheology in extrusion. *J. Food Process Eng.* 1978, 2, 337-342.
- Jasberg, B. K.; Mustakas, G. C.; Bagley, E. B. Effect of extruder retention time on capillary flow of soy dough. *J. Food Process Eng.* 1981, 5, 43.
- Kim, K.; Hamdy, M. K. Depolymerization of starch by high pressure extrusion. *J. Food Sci.* 1987, 52, 1387-1390.
- Klingler, R. W.; Meuser, F.; Niediek, E. A. Effect on the form of energy transfer on the structural and functional characteristics of starch. *Starch/Starke* 1986, 38 (2), 40-44.
- Kokini, J. L.; Baumann, G. C.; Bresslauer, K.; Chedid, L. L.; Herh, P.; Lai, L. S.; Medeka, H. A kinetic model for starch gelatinization and effect of starch/protein interactions on rheological properties of 98% amylopectin and amylose rich starches. In *Engineering and Foods, Advanced Process*; Spiess, Schubert, Eds.; Elsevier/Applied Science Publishers: New York, 1990; Vol. 1, pp 109-121.
- Lai, L. S. Effects of amylose/amylopectin ratio and extruder operating variables on the rheological properties of corn starches. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 1991.
- Lai, L. S.; Kokini, J. L. The effects of extrusion operating conditions on the on-line apparent viscosity of 98% amylopectin (Amioca) and 70% amylose (Hylon 7) corn starches during extrusion. *J. Rheol.* 1990, 34 (8), 1245-1266.
- Launay, B.; Lisch, L. M. Twin-screw Extrusion Cooking of Starches: Flow Behavior of Starch Pastes, Expansion and Mechanical Properties of Extrudates. *J. Food Eng.* 1983, 2, 259.

- Lawton, B. T.; Henderson, G. A.; DerLatska, E. J. The effects of extruder variables on the gelatinization of corn starch. *Can. J. Chem. Eng.* 1972, 50 (4), 168.
- Leasure, L.; Kokini, J. L. The effect of starch/protein interaction on rheological properties of amylopectin and amylose based cereal system. *Cereal Chem.* 1991, submitted for publication.
- Levine, H.; Slade, L. Influences of the glassy and rubbery states on the thermal, mechanical and structural properties of doughs and baked products. In *Dough Rheology and Baked Product Texture*; Faridi, H., Faubion, J. M., Eds.; Van Nostrand Reinhold: New York, 1990; pp 157-330.
- Lineback, D. R. Current concepts of starch structure and its impact on properties. *J. Jpn. Soc. Starch Sci.* 1986, 33 (1), 80-88.
- Lund, D. Influence of time, temperature, moisture, ingredients and processing conditions on starch gelatinization. *CRC Crit. Rev. Food Sci. Nutr.* 1984, 20 (4), 249-273.
- Lund, D. B.; Wirakartakusumah, M. A model for starch gelatinization phenomena. In *Engineering and Food*; McKenna, B. M., Ed.; Elsevier/Applied Science Publishers: New York, 1984; Vol. 1, pp 425-429.
- Mackey, K. L.; Ofoli, R. Y. Rheological modeling of corn starch doughs at low to intermediate moisture. *J. Food Sci.* 1990, 55 (2), 417-423.
- McMaster, T. J.; Senouci, A.; Smith, A. C. Measurement of rheological and ultrasonic properties of food and synthetic polymer melts. *Rheol. Acta* 1987, 26 (3), 308-315.
- Mercier, C.; Feillet, P. Modification of Carbohydrate Components by Extrusion Cooking of Cereal Products. *Cereal Chem.* 1975, 52, 283-298.
- Mercier, C.; Charbonniere, R.; Gallant, D.; Guilbot, A. Structural modification of various starches by extrusion cooking with a twin screw French extruder. In *Polysaccharides in Foods*; Blanshard, J. M. V., Mitchell, J. R., Eds.; Butterworths: London, 1979; p 153.
- Metzner, A. B. Flow behavior of thermoplastics. In *Processing of thermoplastic materials*; Bernhardt, E. C., Ed.; Van Nostrand Reinhold Co.: New York, 1959.
- Meuser, F.; van Lengerich, B. In *Thermal Processing and Quality of Foods*; Zeuthen, P., Ed.; Elsevier/Applied Science Publishers: London, 1984a; p 175.
- Meuser, F.; van Lengerich, B. In *Thermal Processing and Quality of Foods*; Zeuthen, P., Ed.; Elsevier/Applied Science Publishers: London, 1984b; p 180.
- Meuser, F.; Klingler, R. W.; Niediek, E. A. Characterization of mechanically modified starch. *Starch/Stärke* 1978, 30 (11), 376-384.
- Morgan, R. G.; Steffe, J. F.; Ofoli, R. Y. A generalized viscosity model for extrusion of protein doughs. *J. Food Process Eng.* 1989, 11, 55-78.
- Owusu-Ansah, J.; van de Voort, F. P.; Stanley, D. W. Effect of extrusion variables on product moisture and extrusion crystallinity of corn starch. *Can. Inst. Food Sci. Technol. J.* 1982, 15 (4), 257-261.
- Owusu-Ansah, J.; van de Voort, F. P.; Stanley, D. W. Physico-chemical changes in cornstarch as a function of extrusion variables. *Cereal Chem.* 1983, 60 (4), 319-324.
- Ozawa, T. Kinetic analysis of derivative curves in thermal analysis. *J. Thermal Anal.* 1970, 2, 301.
- Padmanabhan, M.; Bhattacharya, M. Analysis of pressure drop in extruder dies. *J. Food Sci.* 1989, 54 (3), 709-713.
- Park, T. S.; Roshdy, T. H.; Chang, Y. K.; Kokini, J. L. Influence of specific mechanical energy during twin-screw extrusion on the rheological properties of corn flour biopolymer. *J. Food Eng.* 1991, submitted for publication.
- Phillips, R. D.; Chhinnan, M. S.; Kennedy, M. B. Effect of feed moisture and barrel temperature on physical properties of extruded cowpea meal. *J. Food Sci.* 1984, 49, 916-921.
- Pravisani, C. I.; Califano, A. N.; Calvelo, A. Kinetics of starch gelatinization in potato. *J. Food Sci.* 1985, 50, 657-660.
- Remsen, C. H.; Clark, J. P. A viscosity model for a cooking dough. *J. Food Process. Eng.* 1978, 2, 39-64.
- Rossen, J. L.; Miller, R. C. Food extrusion. *Food Technol.* 1976, 27 (8), 47-53.
- Russell, P. L. Gelatinization of starches of different amylose/amylopectin content. A study by differential scanning calorimetry. *J. Cereal Sci.* 1987, 6, 133-145.
- Senouci, A.; Smith, A. C. An experimental study of food melt rheology. I. Shear viscosity using a slit die viscometer and a capillary rheometer. *Rheol. Acta* 1988a, 27 (5), 546-554.
- Senouci, A.; Smith, A. C. An experimental study of food melt rheology. II. End pressure effects. *Rheol. Acta* 1988b, 27 (6), 649-655.
- Slade, L.; Levine, H. Polymer-chemical properties of gelatin in foods. In *Advances in Meat Research, Vol. 4, Collagen as a Food*; Pearson, A. M., Dutson, T. R., Bailey, A., Eds.; Van Nostrand Reinhold: New York, 1987; pp 251-266.
- Slade, L.; Levine, H.; Finley, J. W. Protein-water interactions: Water as a plasticizer of gluten and other protein polymers. In *Protein Quality and the Effects of Processing*; Phillips, D., Finley, J. W., Eds.; Marcel Dekker: New York, 1988; pp 9-124.
- Smith, D. B.; Ben-Gera, I. The application of high temperature short time extrusion in the food industry. In *Food Process Engineering*; Linko, P., Malkki, Y., Olkku, J., Larinkari, J., Eds.; Applied Science Publishers Ltd.: New York, 1979; Vol. 1.
- Steffe, J. F.; Morgan, R. G. On-line measurement of dynamic rheological properties during food extrusion. *J. Food Eng.* 1987, 10, 21-26.
- Stevens, D. J.; Elton, G. A. H. Thermal properties of the starch-water system. I. Measurement of the heat of gelatinization by differential scanning calorimetry. *Stärke* 1971, 23, 8.
- Suzuki, K.; Kubota, K.; Omichi, M.; Hosaka, H. Kinetic studies on cooking of rice. *J. Food Sci.* 1976, 41, 1180-1183.
- Synder, E. M. Industrial microscopy of starches. In *Starch: Chemistry and Technology*; Whistler, R. L., Bemiller, J. N., Paschall, E. F., Eds.; Academic Press, Inc.: New York, 1984.
- Takahashi, K.; Shirai, K.; Wada, K. Structural changes in starch granules of low moisture content during heating. *Agric. Biol. Chem.* 1982, 46 (10), 2505-2511.
- Wang, S. M.; Bouvier, J. M.; Gelus, M. Rheological behavior of wheat flour dough in twin-screw extrusion cooking. *Int. J. Food Sci. Technol.* 1990, 25, 129-139.
- Wang, S. S.; Chiang, W. C.; Yeh, A. I.; Zhao, B. L.; Kim, I. H. Kinetics of phase transition of waxy corn starch at extrusion temperatures and moisture contents. *J. Food Sci.* 1989, 54 (5), 1298-1301.
- Wang, S. S.; Chiang, W. C.; Zhao, B. L.; Zheng, X. Z.; Kim, I. H. Experimental analysis and computer simulation of starch-water interaction during phase transition. *J. Food Sci.* 1991, 56 (1), 121-124.
- Wen, L. F.; Rodis, P.; Wasserman, B. P. Starch fragmentation and protein insolubilization during twin-screw extrusion of corn meal. *Cereal Chem.* 1990, 67 (3), 268-275.
- Whistler, R. L.; Daniel, J. R. Molecular structure of starch. In *Starch: Chemistry and Technology*; Whistler, R. L., Bemiller, J. N., Paschall, E. F., Eds.; Academic Press, Inc.: New York, 1984.
- Wootton, M.; Bamuniarachchi, A. Application of differential scanning calorimetry to starch gelatinization. II. Effect of heating rate and moisture level. *Starch* 1979, 31, 262-264.
- Wunderlich, B. In *Thermal Characterization of Polymeric Materials*; Turi, E. A., Ed.; Academic Press: New York, 1981; pp 92-234.
- van Lengerich, B. Influence of extrusion processing on in-line rheological behavior, structure and function of wheat starch. In *Dough Rheology and Baked Product Texture*; Faridi, H., Faubion, J. M., Eds.; Van Nostrand Reinhold: New York, 1990; pp 421-472.
- van Zuilichem, D. J. Single screw extrusion of starch and protein rich materials. In *Proceedings of the 2nd international symposium on engineering and food*; Elsevier/Applied Science Publishers: New York, 1979; pp 745-756.

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