Relationship Between Functional Properties and Macromolecular Modifications of Extruded Corn Starch

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ABSTRACT

Corn starch was processed in a semiindustrial, twin-screw extruder under varying conditions for barrel temperature (80–160°C), screw speed (100–200 rpm), and moisture content (20–40%). The relationship between functional properties of extrudates (expansion ratios, water solubility indices, extrudate slurry flow behavior indices) and the extent of molecular degradation of the amylopectin component of corn starch were investigated. A mathematical model was developed that relates the expansion ratios and the extent of molecular degradation of corn starch. Water solubility indices and extrudate slurry flow behavior indices were both also correlated to the extent of molecular degradation.

The effect of extrusion cooking on starch has been extensively studied in the last decade (Colonna and Mercier 1983, Launay and Lisch 1984, Linko et al 1984, Linko 1992). The principal effect of this thermomechanical treatment is to rupture the granular structure of starch. The partial or complete destruction of the crystalline structure of starch is shown by X-ray diffraction patterns (Mercier et al 1980) and scanning electron micrographs (Chinnaswamy et al 1989). The specific functional properties (water solubility and water absorption capacity, expansion ratio, and paste viscosity over a heating and cooling cycle) of the extruded starch have been investigated (Mercier and Feillet 1975, Mason and Hoseney 1986, Kokini et al 1992). Many authors have also studied the changes of starch macromolecular structure due to extrusion (Colonna and Mercier 1983; Colonna et al 1984; Davidson et al 1984a,b; Diosady et al 1985; Ding and Tang 1990; Tang 1991; Davidson 1992). These studies have been reviewed by Wasserman et al (1992) and Mitchell and Aeras (1992).

The connection between the extent of molecular degradation of amylopectin and the changes in expansion ratios, water solubility indices, and flow behavior indices has been studied only qualitatively. Establishing the quantitative connection was the main objective of the work described here.

MATERIALS AND METHODS

Starch

All experiments were conducted using a commercial corn starch donated by an industrial corn producer (Shan bei, Wuxi, P. R. China). Moisture content was 13% (wb) as determined by standard 1666-1973(E) (ISO 1985). Fat content was 0.63% (wb) as determined by standard 3947-1977(E) (ISO 1985). Sepharose CL-2B was produced by Pharmacia Fine Chemicals (Uppsala, Sweden). All other chemicals were of analytical grade.

Extrusion Cooking

Commercial corn starch was extruded in a semiindustrial twin-screw extruder (Creusot-Loire, BC 45) previously described by Reinikainen et al (1986). Five different screw-element combinations were used (Fig. 1). The diameter of the two circular dies was 6 mm. The samples were extruded at various screw speeds (100, 120, 150, 180, and 200 rpm); temperatures (80, 96, 120, 143, and 160°C); and moisture contents (20, 24, 30, 36, and 40%). The constant starch feed rate was 12 kg/hr (before moisture adjustment). The samples of ~1,000 g were collected after steady-state flow in the extruder.

Extrudate Property Measurement

Expansion ratio of the extrudates was calculated by dividing the average cross-sectional area of the extrudates by the cross-sectional area of the die-nozzle orifice, according to Chinnaswamy and Hanna (1988). Each value was the average of 10 readings. The water absorption index (WAI) values and water solubility index (WSI) values were determined as described by Mason and Hoseney (1986) and Gomez and Aguilera (1983). Extruded starch sample was mixed using a glass rod in a thick-walled, tapered centrifuge tube with 30 ml of distilled water at 30°C. The tubes were centrifuged at 1,000 × g for 15 min. The supernatant was carefully decanted and then dried at 110°C. The amount of solubles was expressed as the percent of the original dry sample weight (WSI). The residue in each decanted tube was weighted and WAI was calculated as the ratio of wet residue to starting material.

Paste procedure, originally described by Doublier et al (1986), was modified. The procedure used a heating rate (average rate 3°C/min) from 25 to 95°C in a round-bottom vessel. The starch slurries were heated, and the maximum temperature was held for 30 min. Stirring was obtained by rotating at 80 rpm. Extruded starch slurry concentration was 10% (db). Unprocessed corn starch concentration was 5% (db). Pasted, extruded starch dispersions were hot-filtered through a sintered glass filter to avoid clumps. Starch pastes were then rapidly degassed under vacuum to remove air bubbles.

Viscosity measurement followed that described by Doubler et al (1986). The coaxial cylinder viscometer (Cheng Yi NXS-11, Cheng du, P. R. China) had an internal radius of 19.23 mm, external radius of 20.0 mm, and height of 70 mm. The measurements were made after sample was held at 60°C for 30 min. Samples were submitted to a shear rate of 0–996.1 s^{-1} and back to 0 s^{-1} at the same rate. The flow behavior index (n) can be obtained as:

$$\ln\Omega = (1/n)\ln\tau + \ln[n/2(1/K)^{1/n}(1 - R_b/R_c)^{2/n}] \quad (1)$$

where Ω is the angular velocity of the internal rotating cylinder (s^{-1}); τ is the shear stress (dyne/cm^2); K is the thickness coefficient;

screw conformation								
	length (mm)	200	100	50	200	50	die block	end product
	pitch (mm)	50	35	25	15	−15*		

↑ feed throat

* negative indicates reverse screw

Fig. 1. Chart showing five different screw-element combinations.

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R_b is the internal cylinder radius; R_c is the external cylinder radius. n and K were estimated by linear regression.

Analysis of Structural Characteristics of Extrudates

According to the method of Davidson et al (1984a), the starch sample (1 g) was first dissolved in dimethylsulfoxide and heated to 70°C for 48 hr. Ethanol (95%) was added to form an amorphous precipitate that was recovered by filtration. Filter cake was washed by n-butanol first, and then washed by ethanol and dried at 80°C. Distilled water (20 ml) was added to 40 mg of the dried sample, and the dispersion was boiled for 5 min to produce a solution.

The molecular size distribution of the whole extruded sample was analyzed by applying an aliquot of the solution (6–8 mg of carbohydrate) to a 100- × 1.6-cm column, packed with Sepharose CL-2B, gel beds ~96 cm high. The column was eluted with 0.2M phosphate buffer (pH 7.3) with the aid of a peristaltic pump at a flow rate of ~12–14 ml/hr. Fractions of constant volume (2.8 ml) were collected automatically, and each fraction was analyzed for total carbohydrate according to the phenolsulfuric acid method of Dubois et al (1956). Total carbohydrate was determined from a standard curve prepared using starch solutions of known concentration. An overall mass balance was calculated to ensure that the recovery of carbohydrate from the column was reasonable.

The elution profile presented was based on the method of Davidson et al (1984a): the percentage of total carbohydrate recovered was plotted against the portion coefficient K_a. The K_a value was determined as:

$$K_a = (V_e - V_0)/(V_t - V_0) \quad (2)$$

where V_e is the actual elution volume; V_0 is the elution volume of an excluded substance (void volume); and V_t is the total volume of the gel bed.

RESULTS AND DISCUSSION

The structural features of the extruded and unprocessed samples were characterized by gel-filtration chromatography. Figure 2 is typical gel-filtration chromatography data for the extruded and unprocessed samples. By comparing these distributions, we found the most obvious feature of these chromatograms to be the reduction in the amount of void volume material in all the extruded products, relative to that of unprocessed corn starch. The result was the same as that reported by Davidson et al (1984a): that the relative change in weight fractions of carbohydrate eluted in the Sepharose CL-2B column ($K_a \leq 0.05$) can be used to characterize the extent of mechanical degradation. The term D_{exp} was introduced to express the fraction of macromolecular carbohydrate from the amylopectin component of corn starch that was degraded in the extruder. Measured experimentally it is:

$$D_{exp} = (A_1 - A_2)/A_1 \quad (3)$$

where A_1 and A_2 are the amount of unprocessed starch and extruded sample, respectively, eluted in the Sepharose column. Hence, the fraction $1 - D_{exp}$ is the estimate of the amount of undegraded amylopectin component of corn starch. Expansion ratios (E) of extrudates and the extent of degradation (D_{exp}) are given for the samples shown in Figure 3.

The expansion ratios depended upon the extrusion parameters, but a simple linear relationship between expansion ratios and the extent of macromolecular degradation may not exist.

Although extrudate expansion of starch was studied extensively, many investigators considered that the extrudate expansion was either the function of a single variable (screw speed, moisture content, temperature, or die nozzle dimension) or that it was due to the volume change caused by bubble formation as a result of moisture flash-off (Kokini et al 1992). Davidson et al (1984a,b) explained the expansion ratio from a structural viewpoint (macromolecular degradation). That is, when the extent of macromolecular degradation of starch increased, extrudate expansion decreased. However, these explanations were not quantifiable.

When starch polymer that had been affected by the shearing action of the rotating screw flights was forced through the die nozzle, it became further compressed and it laminated longitudinally. From the structural (molecular) viewpoint, it is believed that extrudate expansion in the die occurs as a result of a disorientation of macromolecules that are oriented within the die by high shear field. From the rheological viewpoint, on the other hand, it is believed that extrudate expansion in the die occurs as a result of the recovery of the melt elastic deformation imposed in the die. It is clear that a deformed element of fluid exhibiting retarded elasticity will not recover its elastic deformation instantly as it flows out of the die (Han 1976). In fact, extruded starch polymer will travel some distance from the exit while recovery is proceeding. The behavior of starch polymer during extrusion can be described as viscoelastic. The existence of normal stress in biopolymeric food doughs can be seen as an increase in the diameter of the product immediately after it leaves the die of the extruder (Harper 1981). It is clear that the extrudate expansion depends upon the rheological properties of starch polymer, which in turn depend upon the molecular parameters of starch polymer (molecular weight, molecular weight distribution, and degree of branching, etc.). Based on these considerations, and making some simplifying assumptions (that starch polymer obeys Hooke's law in shear), we formed our thought regarding the expansion ratios of starch polymer during extrusion:

$$\tau_w = GS_R \quad (4)$$

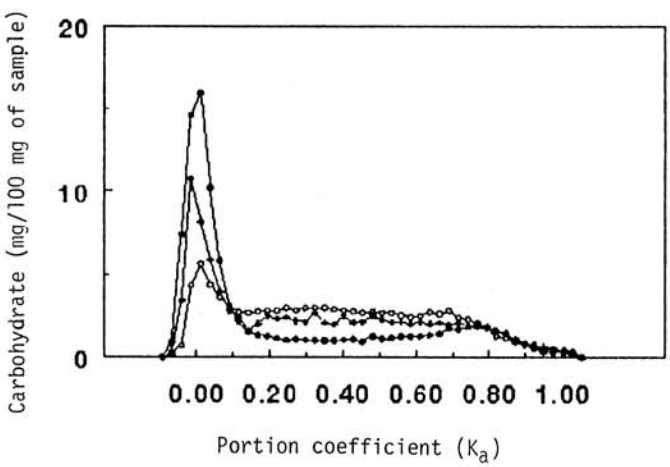

Fig. 2. Distribution of data from the Sepharose CL-2B chromatograms for unprocessed corn starch (•); sample extruded at a screw speed of 180 rpm, temperature of 143°C, and moisture content of 24% (□); sample extruded at a screw speed of 100 rpm, temperature of 120°C, and moisture content of 30% (+).

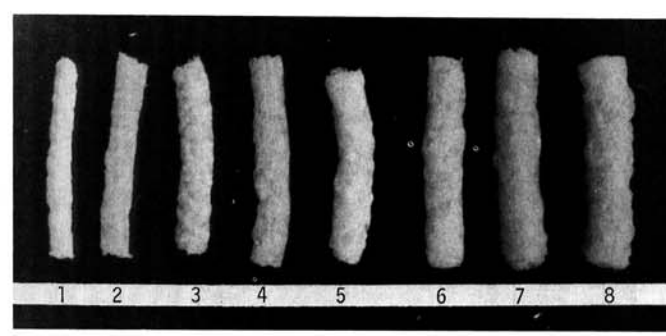

Fig. 3. Physical appearance of corn starch extrudates. Conditions shown are screw speed (rpm), temperature (°C), and moisture content (%), respectively. Extent of degradation (D_{exp}) is shown in parentheses. 1. 200/160/18 (0.90); 2. 150/120/40 (0.22); 3. 200/120/30 (0.55); 4. 180/96/36 (0.37); 5. 180/143/24 (0.67); 6. 150/120/20 (0.62); 7. 180/96/24 (0.46); 8. 120/96/24 (0.32).

where τ_w is the wall shear stress within the die, G is the elastic shear modulus, and S_R is the recoverable shear strain. The elastic shear modulus G is equal to the reciprocal of the elastic shear compliance (Han 1976). It was assumed that the molecular weight and the molecular weight distribution of the amylopectin component of extruded corn starch was monodisperse.

Based on experimental investigations of Davidson (1984a,b), Ding and Tang (1990), and Tang (1991), we assumed the effect of extrusion processing was similar to that from the action of pullulanase. The extruded sample was digested with pullulanase to hydrolyze the branch point, and the digest was fractionated on Sephadex G-50 gel. The distribution of material in these chromatograms was the same as that of the unprocessed corn starch. These results have been reported elsewhere by Tang and Ding (1992). The observations were also similar to the results reported by Davidson (1984a,b). Hence, amylose component of extruded corn starch, which influenced the monodisperse characteristic assumed above, was not taken into account. Therefore, G could be written as (Han 1976):

$$G = 5\rho RT/2M_0 \tag{5}$$

where ρ is fluid density, R is the gas constant, T is the temperature, and M_0 is the molecular weight. According to the Tanner theory (Han 1976), S_R can be written as:

$$S_R = (2E^6 - 2)^{1/2} \tag{6}$$

where E is the expansion ratio. By substituting Equations 5 and 6 for Equation 4, we obtained Equation 7:

$$(2M_0/5\rho RT)\tau_w = (2E^6 - 2)^{1/2} \tag{7}$$

TABLE I
Physical Properties and Rheology Data

Fat content	0.63%
Moisture content	13%
Rheology model data	
K_0 ($P_a \cdot s$)[a]	7.04
α_1[b]	6.59×10^{-4}
α_2[b]	1.12×10^{-1}
α_3[b]	7.28×10^{-3}
α[b]	10.06
E/R (°K^{-1})[c]	4,250

[a] Consistency at reference temperature.
[b] Moisture coefficient (°C^{-1}).
[c] Activation energy/gas constant.

According to Equation 5, if the fluid was incompressible and the initial molecular weight of the amylopectin component of corn starch to be processed was unchangeable, G would be a function of temperature. It was obvious that Equation 5 could not be used directly for modeling the extrusion of starch polymer, because M_0 in Equation 5 was a function of temperature, moisture, and shear stress during extrusion. For this reason, it was assumed that changes to the amylopectin component during extrusion could be expressed as the extent of amylopectin undegradation in corn starch. Assuming that the changes in temperature in Equation 4 were reflected by the changes of M_0 in Equation 5, it was not necessary to isolate it as an independent variable:

$$G \propto 1/(1 - D_{exp})$$

or

$$(1 - D_{exp}) = k_1 G^{-1} \tag{8}$$

Integrating Equation 8 into Equation 7 produces Equation 9:

$$(2E^6 - 2)^{1/2} = k_1 \tau_w (1 - D_{exp}) \tag{9}$$

where, according to Harper (1981), Yacu (1985), and Vergnes and Villemaire (1987), τ_w can be calculated as:

$$\tau_w = \mu_d[\{(3m + 1)/4m\} \times (32Q/\pi d^3)] \tag{10}$$

where μ_d is the product melt viscosity in the die, Q is the volumetric flow rate, d is the die hole diameter, and m is the flow behavior index for extrudate melt in the die. According to Vergnes and Villemaire (1987), μ_d can be calculated as:

$$\mu_d = K_0[\exp(E/RT)\exp(-\alpha MC)]\,(\dot{\gamma}_d)^{m-1} \tag{11}$$

where K_0 is the consistency at reference temperature T_0 and reference moisture content MC_0. E is the activation energy, R is the gas constant, MC is the moisture content (in wt% on a wet basis), T is the temperature (in degrees Kelvin), α is the moisture coefficient, and $\dot{\gamma}_d$ is the shear rate in the die. In the model, some parameters were taken from the literature. It was assumed that the values K_0 and Q were constant (Tayeb et al 1988); this was arbitrary and imperfect in some extent. Density of corn starch was assumed to be 1.5 in the melt form (Tayeb et al 1988).

According to Vergnes and Villemaire (1987), the value of the flow behavior index (m) can be calculated as:

TABLE II
Calculated Values of Pseudoplastic Index and Stress-Measured Values of Expansion Ratios and the Extent of Degradation

Extrusion Conditions (rpm/°C/%)[a]	Flow Behavior Index[b]	Rate of Shear in the Die (s^{-m})	Product Melt Viscosity in the Die ($Pa \cdot s^m$)	Wall Shear Stress in the Die (Pa)	$(1-D_{exp})$	$\tau_w(1-D_{exp})$	Expansion Ratios	$(2E^6-2)^{1/2}$
120/96/24	0.26	3.22	55,560	178,903	0.68	121,654	2.60	24.79
180/96/24	0.26	3.22	55,560	178,903	0.54	96,608	2.45	20.86
180/96/36	0.36	4.74	15,771	74,754	0.63	47,095	1.98	10.81
100/120/30	0.37	4.94	14,557	71,911	0.58	41,708	2.16	14.21
150/120/30	0.37	4.94	14,557	71,911	0.52	37,394	2.00	11.22
150/120/20	0.28	3.48	42,018	146,223	0.38	55,565	2.16	14.12
150/120/40	0.47	7.22	5,043	36,410	0.78	28,400	1.65	6.19
120/143/36	0.51	8.40	4,238	35,599	0.72	25,361	1.40	3.57
180/143/36	0.51	8.40	4,238	35,599	0.62	22,071	1.33	3.02
180/143/24	0.37	4.94	15,122	74,702	0.33	24,652	2.01	11.41
120/143/24	0.37	4.94	15,122	74,702	0.41	30,628	1.87	9.14
150/160/30	0.49	7.79	5,865	45,688	0.69	31,524	1.33	3.04
200/120/30	0.37	4.94	14,557	71,912	0.45	32,360	1.75	7.41
200/160/18	0.34	4.40	19,126	84,154	0.10	8,415	1.23	2.20

[a] Screw speed (rpm)/barrel temperature (°C)/moisture content (%).
[b] For extrudate melt in the die.

$$m(T,MC) = \alpha_1 T + \alpha_2 MC + \alpha_3 T \times MC \quad (12)$$

with T (expressed in °C) and MC as described above. The values of parameters α_1, α_2, and α_3 are listed in Table I. Combining Equation 10 and 11, we could obtain:

$$\tau_w = K_0[\exp(E/RT)\exp(-\alpha MC)] \\ [\{(3m+1)/4m\} \times (32Q/\pi d^3)]^m \quad (13)$$

If the Equation 9 model was correct, then one should be able to determine the expansion ratio $(2E^6 - 2)^{1/2}$ based on the known degree of molecular degradation $\tau_w(1 - D_{exp})$. Equation 9 could be expressed in regression form as:

$$(2E^6 - 2)^{1/2} = k_2\tau_w(1 - D_{exp}) + b_2 \quad (14)$$

where the parameters of straight line k_2 and b_2 can be determined graphically. The physical and rheological properties used in the model are listed in Table I. Table II shows the condition, flow behavior index, calculated shear stress, expansion ratios of extrudates, and the extent of macromolecular undegradation of the amylopectin component of corn starch. Table III lists the analysis of variance for testing significance of regression; the parameter estimates were $k_2 = 2.03 \times 10^{-4}$ (Pa^{-1}), $b_2 = 1.40$, and $r = 0.92$. The proposed model seems to explain the observed relationship between expansion ratios and the degree of molecular degradation. Under a constant feed rate, the expansion ratio of the processed corn starch amylose content depended only upon $\tau_w(1 - D_{exp})$. Although τ_w was calculated by the operational condition, and expansion ratio was easily measured, the measurement of the extent of marcomolecular degradation of amylopectin component of corn starch extrudates was more difficult. However, it could be done using a very tedious gel-permeation or gel-filtration chromatographic technique. According to the deduced model, the extent of marcomolecular degradation in extrudates could be predicted using the expansion ratio. Because operational conditions and expansion ratio could be preset in some commercial extrusion processes, the mechano-chemical effect on extrusion of starch or starch-base materials could be controlled readily in situ by measuring the expansion and by adjusting the operational conditions.

TABLE III
Analysis of Variance for Testing Significance of Regression

Source of Variance	DF[a]	SS[b]	MS[c]	F[d]
Regression	1	499.72	499.72	61.92[e]
Error	12	96.82	8.07	
Total	13	596.54		

[a] Degrees of freedom.
[b] Sum of squares.
[c] Mean square.
[d] *F*-value.
[e] Statistically significant at the 1% level.

TABLE IV
Water Absorption Index (WAI), Water Solubility Index (WSI), and Flow Behavior Index (*n*) for the Extruded Sample

Extrusion Conditions[a] (rpm/°C/%)	WAI[b] (%)	WSI (%)	*n*	D_{exp}[c]
180/143/36	6.22	35.60	0.8365	38.19
180/143/24	5.25	51.76	0.87986	67.43
180/96/36	6.88	27.79	0.7718	37.12
180/96/24	6.69	37.32	0.8257	45.77
120/143/36	6.65	26.56	0.7605	27.94
120/143/24	6.57	45.30	0.8513	59.32
120/96/30	6.47	19.09	0.6722	20.99
120/96/24	6.92	32.61	0.6846	31.76
200/120/30	5.67	51.09	0.8522	54.65
100/120/30	7.00	22.65	0.7041	41.91
150/160/30	6.52	33.97	0.8507	31.48
150/80/30	6.71	27.94	0.7894	26.47
150/120/40	6.61	25.33	0.7675	22.01
150/120/20	5.94	46.16	0.8760	62.24
150/120/30	7.08	31.76	0.8141	47.76
150/120/30	6.67	28.89	0.7886	...
150/120/30	6.64	28.76	0.8343	...
150/120/30	6.89	35.16	0.7859	...
150/120/30	6.87	27.83	0.8068	...
150/120/30	6.70	35.74	0.8501	...
Unprocessed corn starch	...	...	0.5719	...

[a] Screw speed (rpm)/barrel temperature (°C)/moisture content (%).
[b] Grams of gel per grams of sample.
[c] Extent of macromolecular degradation.

WSI, WAI, *n* and the Extent of Macromolecular Degradation

WSI and WAI are important properties of extruded starch. They have been extensively investigated. Table IV lists the WSI,

TABLE V
Analysis of Variance of Response Results for Water Solubility Index (WSI)

Source of variance	DF[a]	SS[b]	MS[c]	F[d]
Linear (R,T,MC)[e]	3	1,272.61	424.20	35.89[f]
Quadratic and interaction	6	105.95	17.66	1.494[g]
Lack of fit	5	120.33	24.07	2.036[g]
Experimental error	5	59.11	11.82	
Total	19	1,558.00		

[a] Degrees of freedom.
[b] Sum of squares.
[c] Mean square.
[d] *F*-values
[e] R = screw speed, T = temperature, MC = moisture content.
[f] Statistically significant at the 1% level.
[g] Not statistically significant at the 10% level.

TABLE VI
Analysis of Variance of Response Results for Water Absorption Index (WSI)

Source of variance	DF[a]	SS[b]	MS[c]	F[d]
Linear (R,T,MC)[e]	3	1.286	0.6087	21.14[f]
Quadratic and interaction	6	1.652	0.2753	9.56[g]
Lack of fit	5	0.385	0.0770	2.67[h]
Experimental error	5	0.144	0.0288	
Total	19	4.007		

[a] Degrees of freedom.
[b] Sum of squares.
[c] Mean square.
[d] *F*-values
[e] R = screw speed, T = temperature, MC = moisture content.
[f] Statistically significant at the 1% level.
[g] Not statistically significant at the 10% level.
[h] Statistically significant at the 5% level.

TABLE VII
Analysis of Variance of Response Results for Flow Behavior Index (*n*)

Source of variance	DF[a]	SS[b]	MS[c]	F[d]
Linear (R,T,MC)[e]	3	0.05164	0.01721	26.89[f]
Quadratic and interaction	6	0.00644	0.00107	1.672[g]
Lack of fit	5	0.0058	0.00116	1.8125[g]
Experimental error	5	0.0032	0.00064	
Total	19	0.06708		

[a] Degrees of freedom.
[b] Sum of squares.
[c] Mean square.
[d] *F*-values
[e] R = screw speed, T = temperature, MC = moisture content.
[f] Statistically significant at the 1% level.
[g] Not statistically significant at the 10% level.

WAI, and n values of various extruded products and of unprocessed corn starch. Data were analyzed using the general linear model, which gave the following response surface:

$$n = 0.814 + 0.0429\ R + 0.03434\ T - 0.0275\ MC,\ r = 0.90 \quad (15)$$

$$\text{WSI} = 31.37 + 5.62\ R + 3.90\ T - 6.81\ MC,\ r = 0.86 \quad (16)$$

$$\text{WAI} = 6.81 - 0.279\ R - 0.19\ T + 0.14\ MC - 0.24\ RT + 0.17\ MC^2,\ r = 0.88 \quad (17)$$

where R, T, MC are screw speed (rpm), temperature (°C), and moisture content (%), respectively. Tables V–VII list the analyses of variance for the regression of WSI, WAI, and n, respectively. WSI increased as the screw speed and the barrel temperature increased, and it decreased as the moisture content increased. WAI decreased as the screw speed and the barrel temperature increased, and it increased as the moisture content increased. These observations were similar to results reported by Anderson et al (1970) and Mason and Hoseney (1986). Flow behavior indices increased as screw speed and temperature increased, and they decreased as the moisture increased. It was well known that extrudates and unprocessed corn starch slurries were both pseudoplastic fluids. Generally, the dispersed phase caused the dispersed medium to be solvated, which caused the dispersed system to behave pseudoplastically. The volume of the colloid particles that were damaged by the shear stress was smaller than the volume of the particles that were not subject to the shear stresses. Flow resistance of particles was reduced and apparent viscosity was decreased. Hence, it could be assumed that the greater the flow behavior index (n), the lesser the extent of the solvation of dispersed medium. Therefore, the extent of solvation of extrudates was less than that of unprocessed starch. The phenomenon had been observed by the determination of the electroviscosity effect of extrudates and unprocessed starch (Tang 1991). The connection between the WSI, n, and the extent of macromolecular degradation could be observed from the data in the Table V. Fifteen points were used to fit the parameters of Equation 18 and 19 by linear regression.

$$\text{WSI} = K_3 D_{\text{exp}} + b_3 \quad (18)$$

$$n = K_4 D_{\text{exp}} + b_4 \quad (19)$$

In Equations 18 and 19, the correlation coefficients were 0.84 and 0.70, respectively. The parameter estimates were: $K_3 = 0.5812$ and $b_3 = 9.83$; $K_4 = 3.17 \times 10^{-3}$ and $b_4 = 0.67$. The correlation of WAI and the extent of macromolecular degradation was not significant.

Although the correlation coefficients for WSI and n were not that ideal, they showed that some relationship between WSI, n, and D_{exp} does exist. The smaller the difference in n between the dispersed fluid of extrudates and that of Newtonian fluid, the greater the extent of macromolecular degradation. For example, when $D_{\text{exp}} = 67.43\%$, $n = 0.8769$; $D_{\text{exp}} = 37.12\%$, $n = 0.7718$; and $D_{\text{exp}} = 20.99\%$, $n = 0.6772$. The inclination of extrudates to solvate was reduced as the extent of macromolecular degradation was increased. This was important to the hydrolysis of extrudates by β-amylase.

CONCLUSIONS

The results of this study showed that the effect of extrusion cooking on starch contributed to macromolecular transformations. The changes in expansion ratios that occurred during extrusion were closely linked to the extent of macromolecular degradation of the amylopectin component of corn starch. The proposed model could be used for predicting the extent of macromolecular degradation by the measurement of expansion ratio. Experimental data of extrudates with different expansion ratios were used to verify the model. The changes in WSI and n could be explained in terms of macromolecular modification. Under some conditions, WSI and n could be used for approximating the extent of macromolecular degradation. The changes of flow behavior index for extrudate solution showed that the amount of extrudates to be solvated generally reduced when extrudates were molecularly degraded.

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