Macromolecular and Functional Properties of Native and Extrusion-Cooked Corn Starch[1]

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ABSTRACT

Normal corn starch (25% amylose) was extrusion cooked at different moisture contents (10–30%, db) and barrel temperatures (110–200°C). The expansion ratio was maximum for 14% moisture normal corn starch extrusion cooked at 150°C. The shear strength and slurry viscosity of the extrusion-cooked starches increased while the water solubility decreased with increasing starch moisture content. Gel permeation chromatography fractionation of the extrusion-cooked starches showed that the fraction I content (void volume peak) decreased with decreasing moisture content. Similar attribute pattern changes were seen with extrusion temperature. Corn starches with amylose contents from 0 to 70% were extrusion cooked at 150°C and 14% moisture content. Gel permeation chromatography fractionation showed that the fraction I content of the native starches decreased as the amylose content of the starch increased. Fraction II increased proportionately. Among the starches studied, the maximum expansion ratio of 16.4 was obtained with 50% native amylose starch which had 2.75 mg of starch in fraction I per 5 mg of native starch fractionated. Upon extrusion cooking, the fraction I content decreased further. The changes in the contents of fraction I, however, showed that the branched starch component underwent degradation. The addition of sodium chloride, sodium bicarbonate, and urea further degraded fraction I. Sodium bicarbonate seemed to degrade the starch molecules to a greater extent than did the other chemicals. A new fraction III appeared between fractions I and II in some samples of native starches after addition of chemical agents. Fractionation of pure amylose and amylopectin before and after extrusion cooking indicated that the branched component, amylopectin, degraded to a greater extent than its linear counterpart, amylose.

Extrusion-cooking technology is applied extensively to manufacture cereal or starch-based crispy foods. The texture and mouthfeel of most expanded or puffed extruded snacks depend on their expansion volume (Owusu-Ansah et al 1984). Several studies have investigated the role of extrusion processing variables on the expansion volume of cereals or starches (Owusu-Ansah et al 1983; Meuser et al 1982; Chinnaswamy and Hanna 1988a,b). Among the extrusion variables studied, those that most prominently control expansion volume are the barrel temperature and moisture content of the raw material (Mercier and Feillet 1975; Owusu-Ansah et al 1983, 1984; Chinnaswamy and Hanna 1988a,b). Guy and Horne (1988) extensively reviewed extrusion processing variables and their relationships with cereal product qualities. Other studies further indicate that the qualities of raw materials such as contents of protein, lipid, and starch and their composition and type are also important in controlling expansion volume (Faubion et al 1982, Launay and Lisch 1983, Chinnaswamy and Hanna 1988a). Models have been developed considering mainly the extrusion processing variables (Owusu-Ansah et al 1983, Bhattacharya and Hanna 1987a), but they are inadequate to explain the raw material quality differences and changes that take place during extrusion cooking.

It is generally accepted that extrusion cooking of starch or starchy cereals involves extensive degradation of macromolecules (Gomez and Aguilera 1983, Colonna et al 1984, Davidson et al 1984). Another set of studies indicated that the viscosity changes in starch during extrusion cooking also control expansion (Launay and Lisch 1983). Chinnaswamy and Hanna (1988c) used sodium chloride to promote the expansion volume of starches. The composition of starch, amylose, and amylopectin seemed to influence expansion volume (Chinnaswamy and Hanna 1988a,c).

Extrusion cooking of starches with different amylose contents using different chemicals may alter the effects on macromolecular degradation. Knowing the relationship among the extrusion variables, raw material qualities, molecular degradation with and without chemicals, and expansion volume will allow us to use cereals more effectively to produce tailor-made products to suit consumer needs and will further our understanding of both the extrusion cooking process and product quality. Therefore, the objectives of this study were to characterize the macromolecular and functional property changes in different corn starches, with and without chemical additives, during extrusion cooking under various conditions and to study the interrelationships among various starch property changes during and after extrusion cooking.

MATERIALS AND METHODS

Starch

The corn starches used for this study (waxy [0% amylose], normal [25% amylose], Amylomaize V [50% amylose], and Amylomaize VII [70% amylose]) were obtained gratis from American Maize-Products Company of Hammond, IN. These starches henceforth will be referred to in the text by their respective amylose contents, i.e. 0% amylose starch for waxy, 25% amylose starch for normal corn starch and so on. To study the molecular changes in starch components during extrusion cooking, amylose and amylopectin (practical grade prepared from corn) were purchased from Sigma Chemical Company of St. Louis, MO. The starch, amylose, and amylopectin powders were agglomerated before extrusion cooking to facilitate the flow of the samples into the extruder. Starch powders were agglomerated in rotatory equipment (Reliance Electric Company, IN). The desired sample moisture contents (10–30%, db) were obtained by addition of distilled water and equilibrated overnight in sealed containers. All extrusion cooking experiments were conducted with samples having 14% (db) moisture content unless otherwise stated in the text.

Extrusion

A C. W. Brabender model 2802 laboratory extruder with a 1.90-cm barrel diameter and a 20:1 ratio of barrel length to diameter was used. The extruder screw had a compression ratio of 3:1. The die diameter and length were 3 mm and 15 mm, respectively. The barrel temperatures of the compression and die sections were either held at 150°C or varied from 110 to 200°C, as specified, while the feed section was held constant at 80°C. Starch samples were fed into the extruder at a rate of 60 g/min using a vibratory feeder (model DX, Erie Manufacturing Company, Erie, PA), keeping the screw speed constant at 150 rpm (Chinnaswamy and Hanna 1988b).

To study the effect of some chemical agents on the macromolecular and functional properties of starches during extrusion cooking, NaCl, $NaHCO_3$, and H_2NCONH_2 were mixed with starch

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at a rate of 1 g per 100 g of starch, on a dry weight basis, in a Hobart blender (Chinnaswamy and Hanna 1988c). The mixtures were then adjusted to 14% moisture content before extrusion cooking. Analytical grade NaCl, $NaHCO_3$, and H_2NCONH_2 were purchased from Fisher Scientific Company of Pittsburg, PA.

Functional Properties of Starches

The radial expansion ratios of extrusion-cooked starches were calculated by dividing the cross-sectional area of the extrudates by the cross-sectional area of the die orifice. Each value was an average of 10 readings. The radial expansion ratio henceforth will be referred to in the text simply as the expansion ratio.

To measure the shear strength of starch extrudates, dry strands (<2% db) of extrudates were placed across the width of an Allo-Kramer shear cell (model 550-412 D). The force required to shear the product was recorded with an Instron universal testing machine (model TM) at a crosshead speed of 1 cm/min. Shear stress was then calculated by dividing the shear force by the cross-sectional area of the extrudate sheared (Bhattacharya and Hanna 1987a). Each value was an average of five readings.

To determine the water solubility of starch extrudates, the dry strands were ground to pass through 80-mesh sieve. Distilled water (30 ml) was added to 0.5 g of the ground starch extrudate, and the mixture was agitated for 30 min with a magnetic stirrer at room temperature. The suspension was then centrifuged at 1,500 $\times$ *g* for 15 min. The supernatant liquor was decanted, and the residue was reextracted six times under the same conditions. The sugar (glucose) content of the combined extract was determined by the phenol-sulfuric acid method (Dubois et al 1956) and was expressed as a starch equivalent by multiplying the sugar content by a factor of 0.9.

The aqueous-ethanol-soluble carbohydrate content of the starch extrudates was also determined. To 0.5 g of the ground, extrusion-cooked starch samples, 20 ml of 80% aqueous ethanol was added, and the mixture was agitated for 15 min with a magnetic stirrer at room temperature. The suspension was then centrifuged at 1,800 $\times$ *g* for 15 min. The supernatant was decanted and the residue reextracted under the same conditions until no more carbohydrate was removed. The total sugar content in the combined supernatants was determined by the phenol-sulfuric acid method (Dubois et al 1956).

Apparent viscosity was determined using a coaxial cylindrical Haake Rotovisco viscometer at room temperature (23°C) over an apparent shear rate range of 500/sec. All data were obtained with the MV system cup (4.201-cm i.d.) and MV-II bob (3.68-cm o.d. and 6.004-cm length) according to the method of Christianson and Bagley (1984). Briefly, 20% (db) slurries of the extrusion-cooked and ground samples were made with distilled water in a 100-ml beaker, stirred with a glass rod, and allowed to stand for 15 min. The slurry was again stirred for 30 sec and then poured into the bowl for viscosity measurement.

Macromolecular Properties of Starches

Thermal and macromolecular properties of starches differing in amylose contents and changes due to addition of chemicals, extrusion cooking conditions, etc., were studied using differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Dried starch samples (3.0–10.3 mg) were weighed into DSC aluminum sample pans. Sufficient water was added with a Hamilton microsyringe to raise the sample to 70% moisture (excess water). The pans were hermetically sealed with a Perkin-Elmer volatile sample sealer. The samples were then allowed to equilibrate for at least 2 hr before analysis. Thermal changes in starch were monitored on a Perkin-Elmer DSC-2 differential scanning calorimeter (Norwalk, CT) interfaced with a thermal analysis data station (TADS). The samples were heated at a rate of 10°C/min from 25 to about 125°C. The TADS system calculated the onset temperature of the phase transitions (T_o), the peak gelatinization temperature (T_p), the temperature of completion of melting (T_m), and the amount of energy required to bring about the transition (enthalpy, ΔH). Trimyristin and tristearin standards were used to calibrate the calorimeter.

Native and extruded starch samples were dispersed (approximately 0.1%) in dimethyl sulfoxide, and 5 mg (dry weight) was fractionated by ascending GPC (Chinnaswamy and Bhattacharya 1986) on a Sepharose CL 2B column (Pharmacia Fine Chemicals, Sweden) operating at a flow rate of 30 ml/hr using distilled water containing 0.02% sodium azide as an eluent. Fractions of 5 ml were collected; from these fractions, 2-ml aliquots were used for the determination of carbohydrate content using a phenol-sulfuric acid method (Dubois et al 1956), measured at 490 nm against a glucose standard, and expressed on a starch basis for total volume fraction. The remaining 3-ml samples were read at 630 nm after adding 0.2 ml of 2% iodine solution. The amylose contents of the fractions were measured against a standard corn amylose (Sigma Chemical Co.) absorbance and were calculated and expressed on total volume fraction basis. The absorption maxima (λ_{max}) of the iodine-polysaccharide complexes were also scanned and recorded automatically with a Perkin-Elmer (model 552) spectrophotometer. The void and total volumes of the gel were determined using Dextran T2000 and KCl, respectively. Each sample was chromatographed at least in duplicate and the mean values were reported.

RESULTS AND DISCUSSION

Process Variables

For the best product quality, extrusion cooking of cereals and starches requires control of numerous processing variables, such as moisture content of the ingredients, extrusion cooking temperature, screw speed, and extruder barrel and die configurations (Owusu-Ansah et al 1983; Meuser et al 1982; Guy and Horne 1988; Chinnaswamy and Hanna 1988a,b). Of these variables, screw design and its elements, the moisture content of the ingredients prior to extrusion cooking, and extrusion temperature are known to drastically affect the functional qualities of the products (Mercier and Feillet 1975; Owusu-Ansah et al 1983, 1984; Chinnaswamy and Hanna 1988a,b). Therefore, a systematic study was made to understand the effects of moisture and temperature on the macromolecular properties of extrusion-cooked starches and their relationship to various functional properties.

Starch Moisture

Normal corn starch (25% amylose) was extrusion cooked at moisture contents of 10, 14, 20, and 30% (db) to study the effect of moisture content on the starch functional and molecular properties. The results are presented in Figure 1 and Table I. As reported by Chinnaswamy and Hanna (1988a,b), the maximum expansion ratio was obtained with 14% starch moisture (Fig. 1A). The expansion ratio increased from 7.5 to 14.2 as the moisture content of starch decreased from 30 to 14% and then it decreased sharply. The results were in close agreement with previous reports (Mercier and Feillet 1975; Owusu-Ansah et al 1984; Chinnaswamy and Hanna 1988a,b).

The shear strength of the starch extrudates, water solubility, and apparent viscosities of the extruded ground samples were also studied. Shear strength increased with increasing starch moisture (Fig. 1B) which was in agreement with our previous reports (Chinnaswamy and Hanna 1988a,b). In contrast, the water solubility of the different extrudates decreased with increasing moisture content of starch (Fig. 1C). The highest water solubility of 40.5% was obtained with 10% moisture starch, whereas it was only 13.3% for 30% moisture starch extrudates. In contrast, the apparent viscosities of the variously extrusion cooked starches increased as the moisture content increased from 10 to 30% (Fig. 1D).

To study the macromolecular properties of native and extruded normal corn starch, samples were fractionated by GPC on a Sepharose CL 2B column. Generally, all of the starch samples gave two peaks, one eluting at the void volume and the other eluting at the latter part of the gel. The void volume peak and the second peak will be referred to as fraction I and fraction II, respectively, and any fraction between these two peaks will

be called an intermediary fraction or fraction III. Biliaderis et al (1979, 1981) and Chinnaswamy and Bhattacharya (1986) concluded that fraction I on a Sepharose CL 2B gel is the branched component of starch whereas fraction II is mainly the linear component of starch. Thus, fraction III, if present, is most likely to be a degradation product of fraction I after extrusion cooking.

Figure 1E clearly shows that the GPC pattern varied with different moisture samples. The fraction I content decreased with decreasing starch moisture (Table I). (It should, however, be noted that the GPC patterns and table values of different fractions generally do not match closely, for the reasons stated in the Fig. 1 legend.) The 30% moisture starch gave about 3.2 mg of fraction I per 5 mg of starch fed into the column. This reduced to 2.81, 1.08, and 0.80 for moistures of 20, 14, and 10%, respectively.

TABLE I
Contents of Different Gel Permeation Chromatographic (GPC) Fractions of Normal Corn Starch Extrusion-Cooked at Various Moisture Levels

Starch Moisture Content (%, db)	GPC Fractions[a] (mg/5 mg of starch)		
	I	II	III[b]
10	0.80	3.66	0.54
14	1.08	4.12	...
20	2.81	2.19	...
30	3.20	1.80	...

[a] As measured by phenol sulfuric acid method at 490 nm absorbance and expressed as starch equivalent.
[b] Intermediary fraction between fractions I and II of Sepharose CL 2B gel.

These results clearly indicate that the molecular degradation of the fraction I starch was progressive with moisture reduction in starch. Consequently, fraction II or II and III increased with decreasing moisture contents of samples (Table I). Extrusion cooking of the 10% moisture starch gave an intermediary fraction, or fraction III (Fig. 1E). Although speculation, it is reasonable to guess that as the moisture content of the starch decreased, the resistance to flow increased, which increased the shear within the extruder, which in turn degraded the starch molecules. The mechanical degradation of starch during extrusion was also reported by Vergnes et al (1987).

It was of interest to observe how the iodine-binding properties of these fractions were altered by extrusion cooking and the breaking up of molecules. The GPC peaks of fractions I and II of extrudates of different moisture contents were mixed with an iodine solution and scanned from 500 to 675 nm for maximum absorbance. The absorption maxima are indicative of the chain lengths in the branched sections of starch or linear amylose chains (Banks and Greenwood 1975) and proportions of amylose and amylopectin in the mixture (Chinnaswamy and Bhattacharya 1986, Chinnaswamy et al 1989). The changes in absorption maxima of fraction I and fraction II iodine complexes with regard to different moistures are given in Figure 1F. Both fraction I and fraction II λ_{max} decreased with decreasing moisture contents of starch, indicating that the populations of linear chains (amylose) and long linear-like chains of branched molecules (amylopectin) or the mixtures of these decreased with decreasing moisture contents. Figures 1E and F, when reviewed together, show that not only were the macromolecules degraded but also that the long-chains, or chains that are capable of binding iodine, were

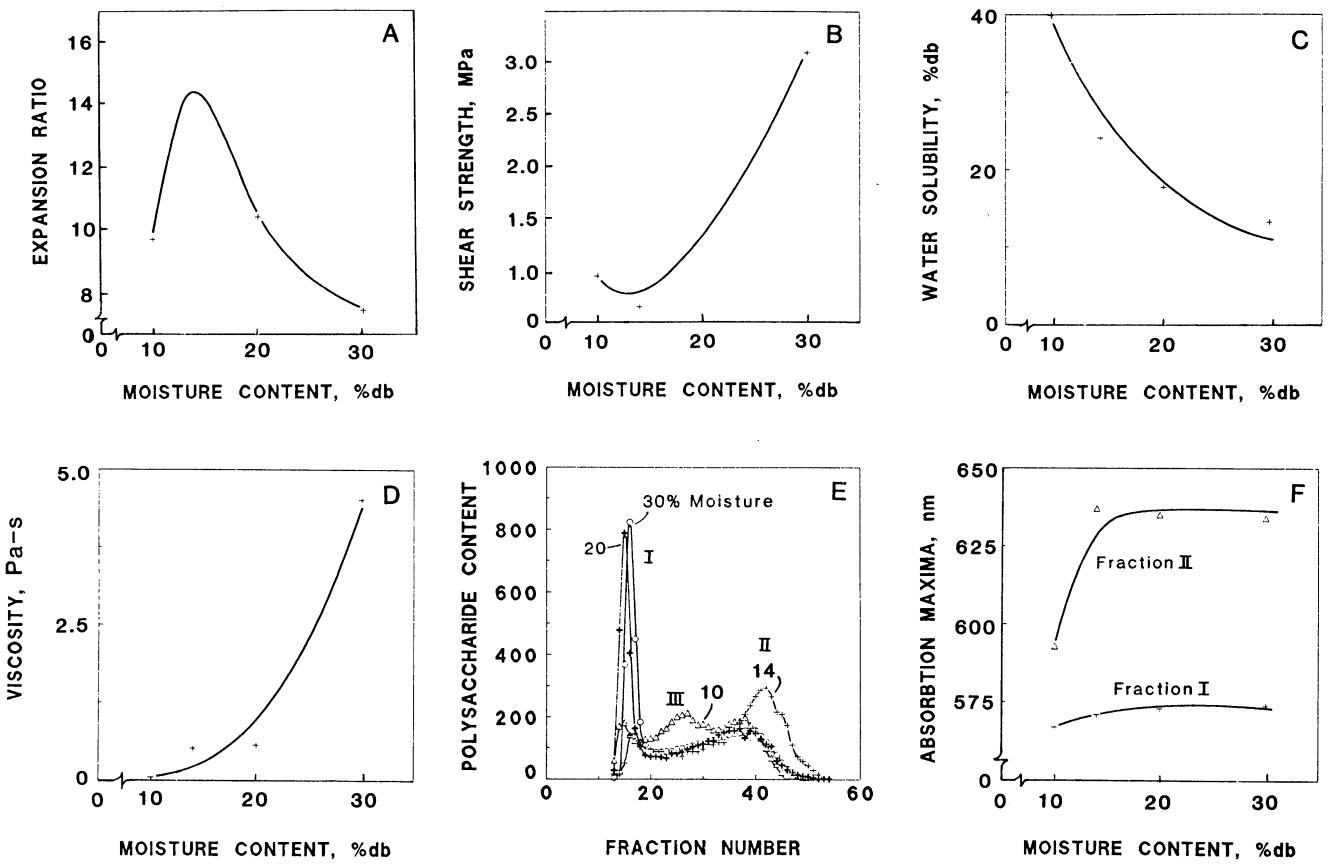

Fig. 1. Relationships between moisture content of starch and the various functional properties of starch extrudates are shown: Expansion ratio (**A**); shear strength of extrudates (**B**); water solubility (**C**); and slurry viscosities of extrudate powders (**D**); gel chromatographic fractionation pattern as determined by iodine fraction complexes at 630 nm, and expressed on a microgram basis (**E**); λ_{max} of iodine fraction I and II complexes (**F**). All gel permeation chromatography values given in this and subsequent figures represent the measurements made from iodine polysaccharide complexes at 630 nm. The corresponding table values, however, were obtained from phenol-sulfuric acid measurements on a starch basis in each volume fraction, and peak fractions I, II, and III represent the patterns (not shown) obtained by the phenol-sulfuric acid method. The number of peaks and pattern do not match closely between these two methods because one represents the starch content (phenol-sulfuric acid) and the other its molecular nature and particularly the iodine-binding abilities.

reduced in fraction I (amylopectin) in general, and particularly for the 10% moisture starch. The data on molecular and iodine-binding changes suggest that some of the starch in the samples was dextrinized. Furthermore, the 10% moisture starch, after extrusion cooking, appeared brownish yellow in color, which perhaps indicates starch dextrinization.

The changes in the macromolecular nature of the starches and their water solubilities, as seen above, were also reflected in their cold slurry apparent viscosities. The most degraded sample (10% moisture), which was comparatively quite soluble (40.5%) in water, had the lowest apparent viscosity (0.048 Pa·sec). The cold slurry apparent viscosities increased with increasing starch moisture up to 4.52 Pa·sec for 30% moisture sample (Fig. 1D). This was due, in part, to less molecular degradation of the starch at higher moisture contents.

Extrusion Temperature

Extrusion cooking temperature (extruder barrel temperature) is also known to affect the expansion properties of starch (Colonna et al 1984; Owusu-Ansah et al 1983; Chinnaswamy and Hanna 1988a,b). Thus, to determine how macromolecular properties changed with temperature, 14% moisture normal corn starch was extrusion cooked at barrel temperatures of 110, 150, and 200°C. Various macromolecular, physiochemical, and functional property changes in those samples are listed in Table II. Fraction I starch was affected the most by changes in barrel temperature. It varied from 2.45 to 3.38 mg per 5 mg of starch as barrel temperatures increased from 110 to 200°C. The λ_{max} of the fraction I and fraction II iodine complexes of the differently extrusion cooked starches also varied from 571 to 588 nm and 607 to 637 nm, respectively, with increasing barrel temperatures. Water solubility increased from 15.7 to 27.3% while apparent viscosity increased from 0.368 to 0.574 Pa·sec with increasing extrusion cooking temperatures. The shear strength of the extrudates varied from 2.07 to 0.68 kPa with increasing temperatures. The alcohol solubility of the extrudates was negligible, indicating that there were essentially no small molecular weight starch components such as oligosaccharides in the extrudates.

TABLE II
Properties of Normal Corn Starch Extruded at Diffeent Barrel Temperatures

Properties	Extrusion Temperature (°C) 110	150	200
Gel permeation chromatography			
Fraction I[a] (mg/5 g of starch)	2.45	1.08	3.38
Fraction II[a] (mg/5 g of starch)	2.55	3.38	1.96
λ_{max} (nm)			
Fraction I[b]	588.00	571.00	585.00
Fraction II[b]	607.00	637.00	627.00
Expansion ratio	11.5	13.4	10.0
Water solubility (%, db)	15.7	29.3	27.3
Apparent viscosity (Pa·sec)	0.368	0.511	0.574
Shear strength (MPa)	1.54	0.68	2.07
Alcohol solubility (%, db)	Trace	Trace	Trace

[a] Content of starch in fractions as measured by phenol-sulfuric acid method (Dubois et al 1956).
[b] Iodine-polysaccharide complex absorbance maxima of gel permeation chromatography separated starch fractions.

Starch Properties

Apart from the extrusion processing variables, the raw material qualities of cereals such as the contents and composition of starch, protein, lipid, and fiber also control the expansion as well as the functional properties (Mercier and Feillet 1975, Faubion et al 1982, Launay and Lisch 1983, Chinnaswamy and Hanna 1988a). Of the several raw material quality parameters studied, the starch amylose-to-amylopectin ratio seems to control the expansion properties most. Chinnaswamy and Hanna (1988a,c) showed that among corn starches of different amylose contents, 50% amylose starch expands best, which was in agreement with Mercier and Feillet (1975) and Bhuiyan and Blanshard (1982). Why the 50% amylose starch expands most was not understood. Thus, we conducted a systematic study to better understand the finite nature of the native starch components (raw material quality) and crystallinity as well as changes that take place during extrusion cooking and the relationship among the various extrudate functional and molecular properties.

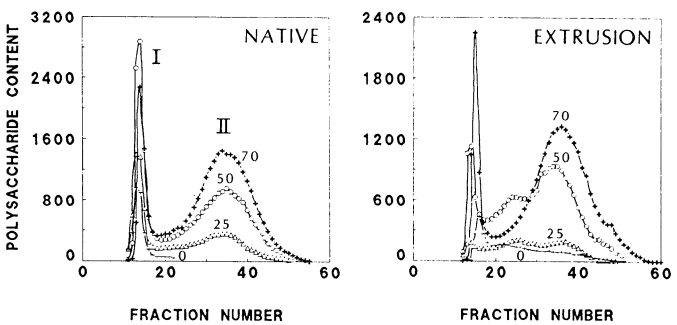

Fig. 2. Gel permeation chromatography fractionation patterns of starches differing in amylose contents before (native) and after extrusion cooking. The polysaccharide contents are expressed on a microgram basis for a total of 5 mg of starch as measured by iodine polysaccharide complex measurements at 630 nm. All subsequent gel permeation chromatography fractionation patterns are shown by similar procedures and expressed as above, unless otherwise mentioned.

TABLE III
Properties of Starches Before and After Extrusion Cooking

Amylose Content (%, db)/ Treatment	GPC Fraction[a] Contents (mg) I	II	III	λ_{max}[b] (nm) I	II	Expansion Ratio	Water Solubility (%, db)	Gelatinization Temperatures[c] (°C) T_o	T_p	T_m	Enthalpy (cal/g)
0%											
Native	5.00	...	...	535	...	...	Trace	63.3	72.5	85.0	3.50
Extrusion-cooked	2.60	2.40	...	537	534	11.8	21.6	...	...	...	...
25%											
Native	3.40	1.60	...	568	636	...	Trace	64.5	71.3	77.1	1.39
Extrusion-cooked	2.81	2.19	...	571	637	13.2	24.1	...	...	...	...
50%											
Native	2.75	2.25	...	574	630	...	Trace	62.7	79.0	90.6	1.87
Extrusion-cooked	1.51	3.49	...	570	610	16.4	7.1	...	...	...	...
70%											
Native	1.68	3.32	...	575	625	...	Trace	65.3	97.0	108.6	1.08
Extrusion-cooked	0.97	1.31	2.72	573	608	7.0	0.9	...	...	...	...

[a] Contents of gel permeation chromatography (GPC) fractions are expressed as equivalents of starch on dry weight basis for 5 mg of total starch as measured by phenol-sulfuric acid method at 490 nm.
[b] λ_{max} of the peak tube of the fractions was measured, after addition of 2% iodine solution, by scanning from 500 to 675 nm.
[c] T_o, T_p, and T_m represent initial, peak, and final gelatinization temperatures of a differential scanning calorimetry endotherm.

Amylose Content

Corn starches having amylose contents of 0, 25, 50, and 70% were extrusion cooked at 150°C, keeping the screw speed and feed rate constant as stated earlier. GPC fractionation patterns of the starches before (native) and after extrusion cooking are given in Figure 2. The starch extrudate properties are given in Table III. The fractionation pattern was essentially the same as that discussed earlier except that 0% amylose starch (waxy starch) gave only one peak (fraction I) at the void volume. All other starches gave two fractions, representing the two major components of starch, amylopectin and amylose, respectively. The fraction II, which represents the linear chains of the starch polymer (amylose), increased from 0 to 3.32 mg per 5 mg of starch as the amylose contents of the starches increased from 0 to 70%. Proportionately, the content of fraction I in terms of polysaccharide (carbohydrate as measured by phenol-sulfuric acid method) decreased. The iodine-binding nature of fraction I, however, generally increased with increasing apparent amylose content, despite its reduction in carbohydrate or starch content (Table III). Chinnaswamy and Bhattacharya (1986) reported similar observations with rice starch fraction I. Why this is so needs further study.

The changes in the macromolecular properties of these starches before and after extrusion cooking are shown in Figure 2 and Table III. The fractionation patterns for the extruded starch samples were similar to those of native starch. The carbohydrate contents of fraction I were reduced from 5.0, 3.4, 2.75, and from 1.68 to 2.6, 2.81, 1.51, and 0.97 mg per 5 mg of starch fed for 0, 25, 50, and 70% amylose starches, respectively, after extrusion cooking (Table III). Fraction II increased proportionately. It should be noted that the initial differences in fractions I and II of the native starches differing in amylose contents are not the same as those found after extrusion cooking.

Other physiochemical properties of native starches were also investigated to determine their relationship with expansion ratio as well as with starch molecular properties. Water solubility, for example, decreased from 3.5 to 1.1% (db) with increasing starch amylose contents (Fig. 3A). The relationship between the starch contents in fractions I and II of the native starches, with their respective native starch amylose contents, is shown in Figure 3B, which shows that as the fraction II increased, fraction I decreased almost proportionately. The λ_{max} of the iodine-polysaccharide complex of fraction I increased from 535 to 565 nm as starch amylose content increased from 0 to 70% (Fig. 3C). Chinnaswamy and Bhattacharya (1986) and Takeda et al (1987) reported a similar relationship between fraction I λ_{max} and the total amylose contents of rice starches.

However, none of these property changes account for the differences in the expansion properties of the different amylose content corn starches. From the results in Figure 3 and Table III, the fraction I contents of the different starches were different not only in their carbohydrate contents but also in their iodine-binding properties. This is an indication of a combined property nature of starch content of fraction I, as well as total starch iodine-binding properties (amylose as measured by iodine-blue

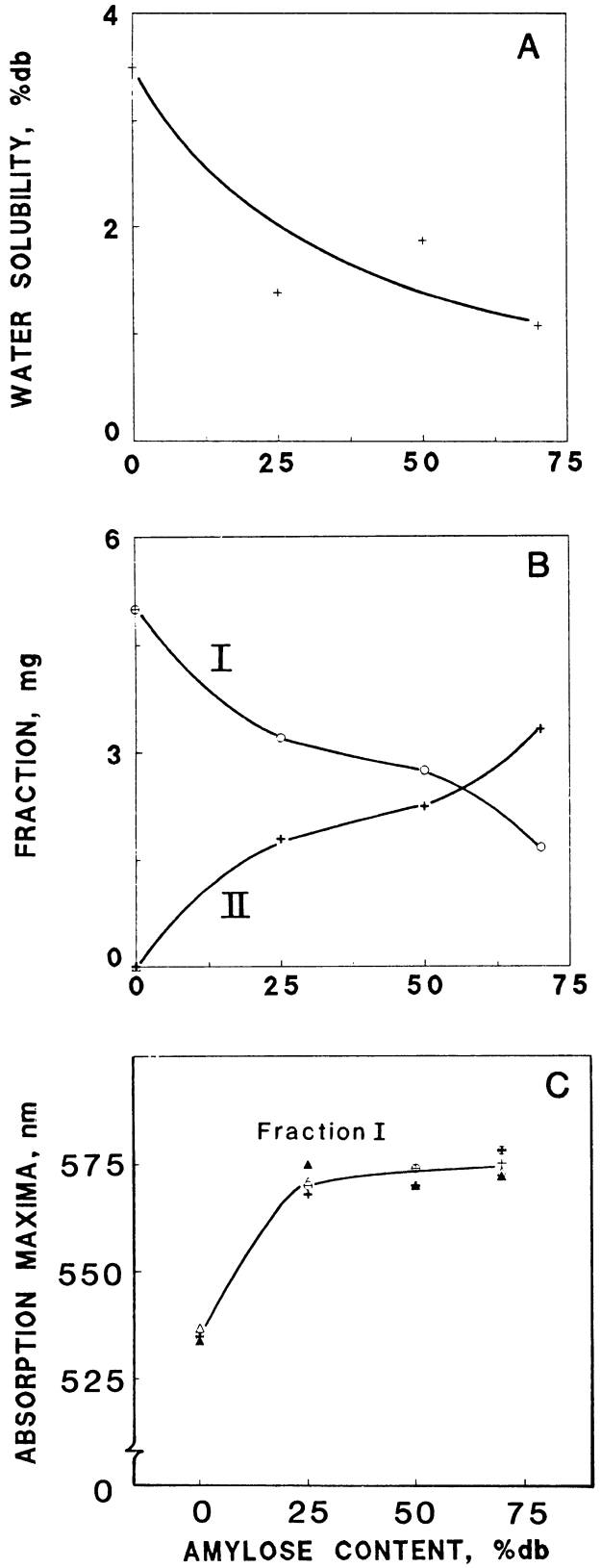

Fig. 3. Relationship between native amylose contents of various starches with its functional properties: water solubility (**A**); gel permeation chromatography fraction starch contents as measured by phenol-sulfuric acid method (**B**); and absorption maxima of fraction I as estimated from the iodine-polysaccharide complex (**C**).

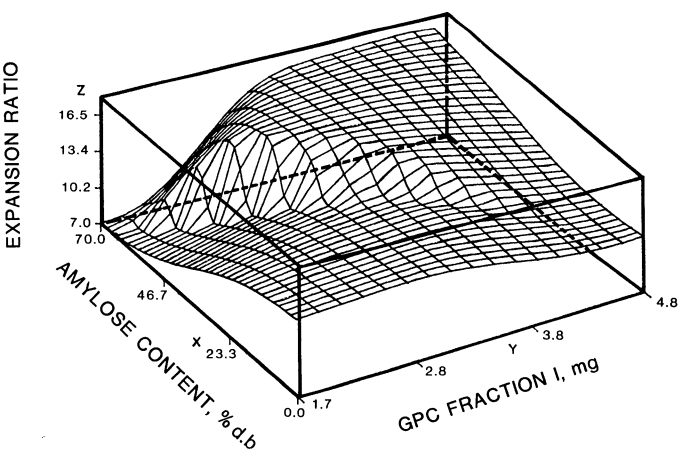

Fig. 4. Interrelationship between starch amylose contents and their respective gel permeation chromatography (GPC) fraction I content (native) with the expansion volume of starch extrudates.

color). Therefore, the expansion ratio was plotted against the respective fraction I contents (Fig. 4) and the apparent amylose contents of native starch as measured by iodine blue color at 630 nm. A combination of 50% amylose and a fraction I carbohydrate content of 2.75 mg per 5 mg of native starch gave the best expansion. However, the relationship shown here is tentative, because the amylose values and fraction I contents represent the same native starch. To further verify this, a separate study would be necessary using native starch samples having the same apparent amylose contents but with different fraction I carbohydrate contents, and vice versa. Chinnaswamy and Bhattacharya (1986) interpreted the fraction I content as being representative of the mean molecular weight of native starch. In other words, the higher the fraction I content, the higher the mean molecular weight of a native starch. In a similar study with rice expansion, Chinnaswamy and Bhattacharya (1986) showed that the fraction I content of native starch (i.e., the mean molecular weight of starch) controlled expansion.

Crystalline Structure

The expansion properties of cereals and starches have also been related to the degree of gelatinization of starch (Chaing and Johnson 1977, Bhattacharya and Hanna 1987b). Thus, a DSC study was made to understand the status of the crystalline nature of starches, before and after extrusion cooking, and its relationship to the expansion ratios of various starches. The gelatinization patterns of native and extrusion-cooked starches are given in Figure 5. The peak gelatinization temperatures (T_P) varied from 71.3 to 97°C among the starches studied (Table III). Generally, the gelatinization temperature of the starches increased with increasing amylose contents. In comparison with the expansion ratio and fractionated starch properties, there seemed to be no relationship between the gelatinization temperature of the starches and the energy (enthalpy) required to bring about the transformations. There were no endotherms present after the starches were extrusion cooked, indicating that all of the native crystalline structures were transformed or that the starches were fully gelatinized (Fig. 5). From the results discussed elsewhere, it appears that the mean molecular weight and the degradation pattern of starch control expansion volume more than does the crystalline nature or the degree of gelatinization. However, it is not clear whether the molecular degradation of starch occurred during extrusion cooking within the barrel or during expansion outside the die or both.

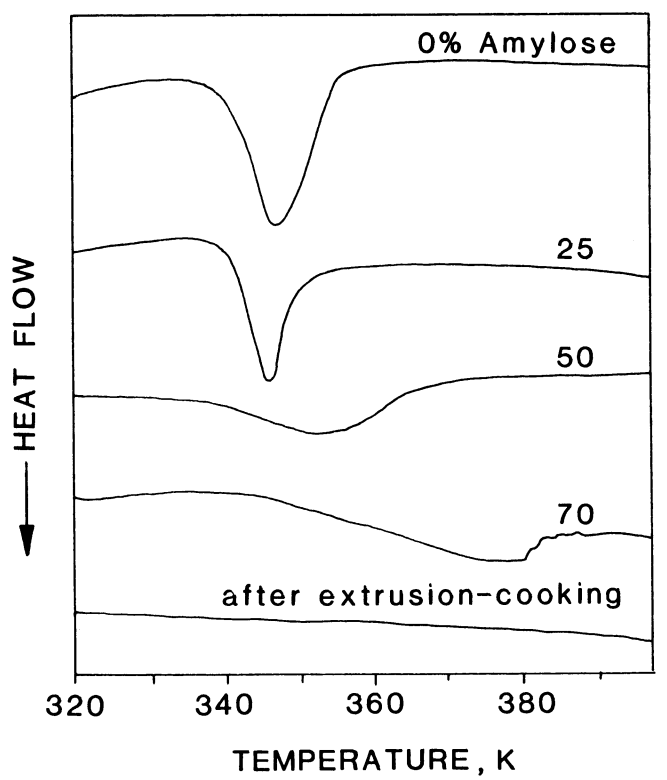

Fig. 5. Differential scanning calorimetric thermograms of starches differing in amylose contents (indicated) before and after extrusion cooking.

Addition of Chemicals

Recently, Chinnaswamy and Hanna (1988a,c) showed that, in

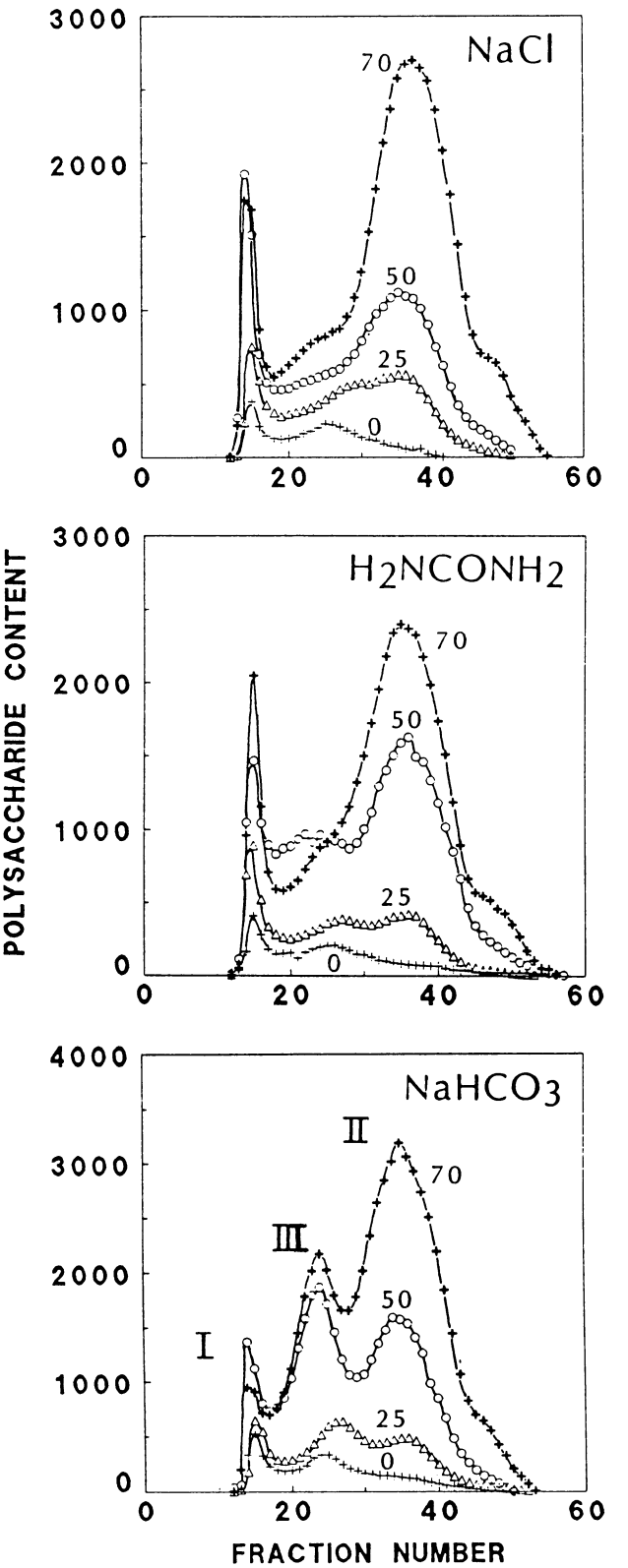

Fig. 6. Gel permeation chromatography fractionation patterns of starches differing in amylose contents after extrusion cooking with sodium chloride, sodium bicarbonate, and urea.

addition to the extrusion process variables and native starch qualities, adding sodium chloride, sodium bicarbonate, and urea altered the expansion properties of starches. Expansion volumes of the poorer expanding starch types such as 0, 25, and 70% amylose native starches were enhanced by 0.5–5.5 units when 1% NaCl (db) was mixed with these starches prior to extrusion cooking. How the expansion properties of these starches were altered chemically was not fully understood. Thus, a study was conducted to understand the macromolecular modifications of these starches in the presence of salts and urea during extrusion cooking and their relationship to the expansion volume of the starches.

Samples of starches treated with sodium chloride, sodium bicarbonate, and urea were fractionated on a Sepharose CL 2B column; the patterns of fractionation, as characterized by polysaccharide-iodine complex color measurements, are given in Figure 6, and selected property changes are cited in Table IV. Overall the chemicals generally reduced the content of fraction I. As seen earlier, extrusion cooking degraded the starch molecules. The broken pieces of fraction I eluted along with normal fraction II as one peak. Of the different starches, the ones most affected were the 50 and 70% amylose starches. Sodium chloride, in general, increased the expansion ratios of all starches from 0.5 to 5.5 units, but sodium bicarbonate and urea decreased the expansion ratio by 1 to 6 units (Tables III and IV). The sodium-chloride-treated starch fractionation patterns showed that the amount of starch in fraction II increased as that in fraction I decreased. The urea and sodium bicarbonate treated samples gave a fraction III. Thus, it is clear that these chemicals altered the degradation patterns of the macromolecules in fraction I during extrusion cooking. Furthermore, the iodine-polysaccharide values and carbohydrate contents in fraction I were not the same, indicating that the differential iodine-binding properties of the various starch fractions were still preserved as in the case of their respective native starches seen elsewhere. In other words, extrusion cooking did not nullify the basic quality differences among starches differing in amylose contents. These chemicals, however, altered the macromolecular degradation patterns enough to control the expansion volume. How these molecular degradations control the expansion volume of starches could be explained if the changes in the viscoelastic properties of the starches and their interaction with the above macromolecular changes were understood.

The relationship between native starch amylose contents, the contents of fractions I, II, and III of the chemically treated starches, and their various functional properties are given in Table IV and Figure 7. The addition of the chemicals generally affected the amount of fraction I in 25% amylose starch less than it did in the 0, 50, and 70% amylose starches. Most affected was fraction I of 0% amylose starch (Fig. 7A). A reciprocal relationship is shown with fractions II and III (Fig. 7B). The water solubility of the sodium bicarbonate treated starches was much higher than the native starches and those extrusion cooked without chemicals (Table IV). The water solubility increased with the addition of sodium chloride, sodium bicarbonate, and urea but decreased with increasing starch amylose content (Fig. 7C). Alcohol solubility increased, in general, with amylose contents of starches (Table IV). Sodium bicarbonate treated samples gave the highest alcohol solubility value of 25.4% (Table IV).

Interrelationships

The above data showed that fraction I of the starches was the major starch quality factor being altered for maximum expansion. The carbohydrate contents of fraction I and the expansion ratios were plotted (Fig. 8) irrespective of the amylose contents of the starches, salts, urea, moisture levels, and barrel temperatures. The maximum expansion of starches occurred at a fraction I content of about 2.75 mg per 5 mg of starch. Thus, it is clear that the expansion ratio of the starches was controlled mainly by the fraction I content. In other words, there was an optimum mean molecular weight of starch for maximum expansion, which perhaps can be altered, to some extent, with processing variables and chemicals.

Degradation of Amylose and Amylopectin

Fractionation of starches, before and after extrusion cooking, on GPC gave two major components for all starch amylose contents and one major void volume fraction for the 0% amylose native starch. After extrusion cooking, fraction I (the branched component) degraded, and the degraded products were eluted along with fraction II (the amylose fraction). It was clear that degradation occurred in fraction I; however, the degradation of fraction II was not clear, as both fraction II and the degraded products of fraction I eluted together as one broad peak for all extrusion-cooked samples. To understand the degradation patterns of both the amylopectin (fraction I) and the amylose (fraction II), amylose and amylopectin (practical grade) were purchased from Sigma Chemical Co. and extrusion cooked under similar conditions. The elution patterns of both the native and the extruded samples of amylopectin and amylose are given in Figure 9 with selected properties given in Table V. Native amylopectin gave only fraction I at the void volume of the gel

TABLE IV
Properties of Starch Extrusion Cooked with Salts and Urea

Amylose Contents (%, db)/ Extrusion Cooked with	GPC Fractions[a] Content (mg)			λ_{max}[b] (nm)		Expansion Ratio	Water Solubility (%, db)	Shear Strength (MPa)	Alcohol Solubility (%, db)
	I	II	III	I	II				
0%									
Salt	1.87	3.13	...	535	541	14.0	33.5	0.447	8.5
Urea	1.49	3.51	...	534	550	7.0	56.1	0.661	6.3
Bicarbonate	1.74	3.26	...	535	545	14.9	42.4	0.518	8.7
25%									
Salt	2.29	2.71	...	570	636	16.9	28.7	0.263	4.8
Urea	3.03	1.97	...	575	617	10.7	29.1	0.638	5.1
Bicarbonate	2.51	2.49	...	568	636	12.0	28.5	0.541	9.4
50%									
Salt	1.43	3.57	...	574	620	17.3	11.1	0.746	5.7
Urea	0.86	1.08	3.06	570	610	10.3	14.4	1.581	8.2
Bicarbonate	0.99	2.01	1.99	570	617	14.9	14.6	1.196	22.4
70%									
Salt	0.95	0.93	3.12	578	615	10.2	5.9	1.248	5.3
Urea	0.32	0.90	3.78	572	616	5.3	6.4	0.409	12.7
Bicarbonate	0.99	1.58	2.43	558	621	11.1	7.4	2.143	25.4

[a] Contents of gel permeation chromatography (GPC) fractions are expressed equivalent of starch on dry weight basis for 5 mg total starch fed as measured by phenol-sulfuric acid method at 490 nm.
[b] λ_{max} of peak tube of fractions was measured after adding 2% iodine solution and scanned from 500 to 675 nm.

(Fig. 9). During extrusion cooking, the amylopectin molecules underwent degradation to give two fractions. The iodine-polysaccharide complex absorbance patterns also show that fraction I of the amylopectin was degraded (Fig. 9). The carbohydrate content calculations show that about 60% of the fraction I was degraded during extrusion cooking. Interestingly, however, the native amylose gave two GPC fractions, as did native starch,

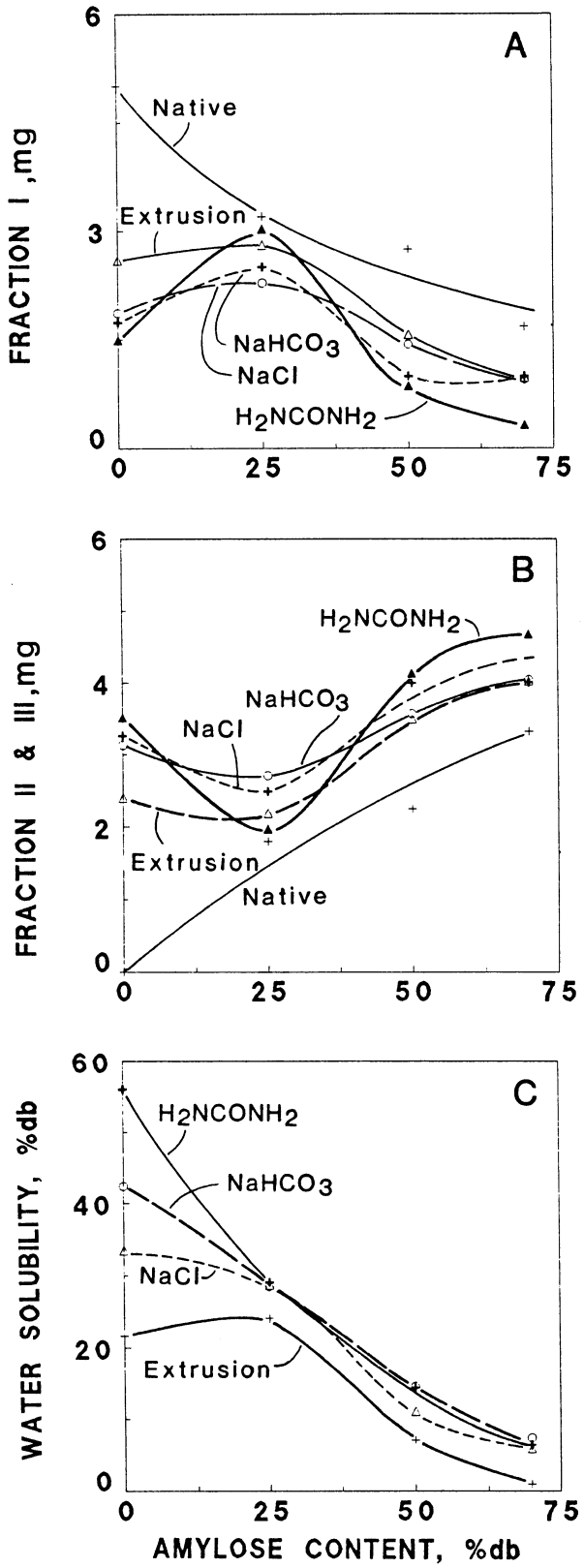

Fig. 7. Relationship between functional and molecular properties of various extrusion cooked starches differing in amylose contents with various chemical additives indicated.

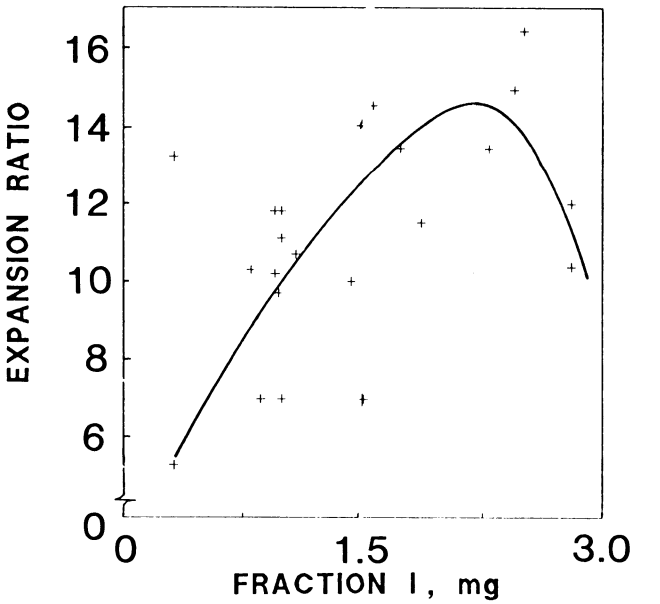

Fig. 8. Relationship between gel permeation chromatography fraction I content and expansion ratio of starch extrudates irrespective of their amylose contents, moisture treatments, chemical treatments, and extrusion temperatures.

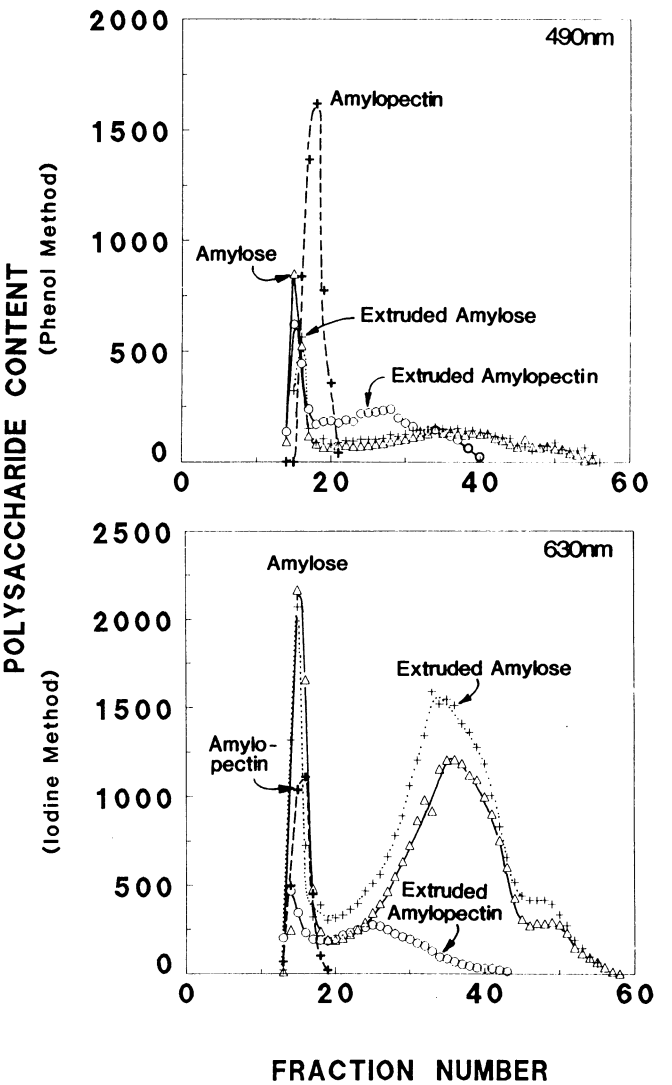

Fig. 9. Gel permeation chromatography fractionation pattern of pure amylose and pure amylopectin before and after extrusion cooking as measured by phenol-sulfuric acid and iodine methods.

TABLE V
Properties of Amylose and Amylopectin Before and After Extrusion Cooking

Properties	Amylose		Amylopectin	
	Native	Extrusion	Native	Extrusion
GPC fraction content[a] (mg)				
I	1.83	1.32	5.0	1.62
II	2.67	3.13	0.0	3.38
λ_{max} of iodine fraction complexes[b] (nm)				
I	578	578	534	539
II	617	617	...	540
Expansion ratio	...	6.3	...	5.3
Water solubility (%, db)	0.82	3.0	1.3	29
DSC gelatinization pattern[c] (°C)				
T_O	65.6	0.0	64.4	0.0
T_P	92.6	0.0	73.6	0.0
T_C	110.2	0.0	83.7	0.0
Enthalpy[c] (cal/g)	1.55	0.0	2.8	0.0

[a] Gel chromatographic fractions are expressed on dry weight basis equivalent of starch for 5 mg of total starch fed into the column as measured by phenol-sulfuric acid method at 490 nm.
[b] λ_{max} of peak tubes of fractions was measured, after adding iodine solution, by scanning from 500 to 675 nm with a spectrophotometer.
[c] T_O, T_P, and T_M represent initial, peak and final gelatinization temperatures of starch, respectively, in differential scanning calorimetry (DSC).

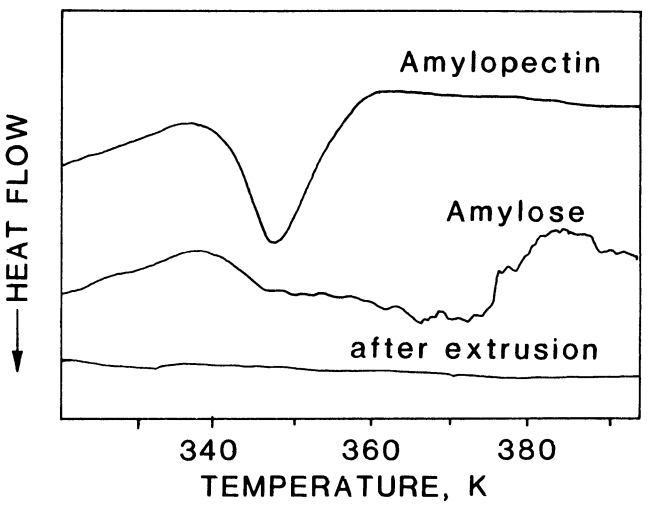

Fig. 10. Differential scanning calorimetry thermograms of pure amylose and pure amylopectins (purchased from Sigma Chemical Co.) before and after extrusion cooking.

and fraction I of the native amylose decreased 26% during extrusion cooking while fraction II increased proportionately. The results, however, raised several questions about the purity of the amylose and amylopectin, since the GPC pattern for native amylose showed two fractions instead of the one fraction expected at the fraction II elution volume. The amylopectin and amylose properties resembled, in some ways, the properties of 0% amylose native starch and 70% amylose native starch (Table V and Figure 9). To test this further, these samples of amylopectin and amylose were subjected to DSC measurements to see whether the samples contained any native crystalline forms. The results are reported in Figure 10 and Table V. The DSC gave an endotherm for native amylopectin and amylose typical of waxy 0% amylose and 70% amylose corn starches (Tables III and V). After extrusion cooking, the endotherms of amylose and amylopectin disappeared and gave a smooth straight line. This may explain why Chinnaswamy and Hanna (1988a) found the expansion ratios of 0 and 70% amylose native starch blends and Sigma amylose and amylopectin mixtures to be almost the same among their identical amylose blends. In other words, the amylose and amylopectin samples seem to have been nothing but 70% amylose and 0% amylose native corn starches. Thus, we are not in a position to say at this time how much the linear components (amylose or fraction II) of the native starches were affected by extrusion cooking. However, it appears that fraction II underwent less degradation than its fraction I counterpart.

CONCLUSIONS

Among the native starches differing in amylose contents, the GPC fraction I content decreased as the fraction II content increased proportionately with increasing native amylose contents. This trend remained the same even after extrusion cooking, with and without salts, which reflected the preservation of the initial raw material quality differences. Native starch having 50% native amylose and 2.75 mg of fraction I in 5 mg of starch expanded the most. Among the starch fractions, fraction I (amylopectin) was degraded to a greater extent with chemical additives in general, and sodium bicarbonate in particular, and the severity of degradation of fraction I of starch increased with decreasing amylose contents. Despite the quality and processing differences such as amylose content, chemical additives, extrusion temperature, and moisture content, the fraction I contents of starches correlated well with the expansion ratios. Extrusion cooking of supposedly pure amylose and amylopectin showed that the branched fraction of starch, amylopectin, degraded more than did its counterpart, amylose. In addition, the fraction I content or degradation of native and variously processed starches seemed to control water solubility, alcohol solubility, and apparent viscosity. DSC showed that all extrusion-cooked starches were fully gelatinized.

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