Extrusion-cooking and drum drying of wheat starch . Physical and macromolecular modifications

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Extrusion Cooking and Drum Drying of Wheat Starch. I. Physical and Macromolecular Modifications[1]

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Cereal Chem. 61(6): 538–543

ABSTRACT

Native wheat starch was modified by drum drying under two industrial conditions and by twin-screw extrusion cooking under five barrel temperatures (90–180° C) and five conditions of moisture (19–44%) to produce large gradations in the severity of the treatment. By both technologies, starch granules were transformed into a continuous phase of melted starch, including variable amounts of air bubbles. In comparison with native starch, specific gravity (1.47–1.48 g/cm^3) was not modified; but the surface area of the treated starches was more reduced by extrusion (230–500 cm^2/g) than by drum drying (620–650 cm^2/g). The primary chemical structure, linked by α-1,4 and α-1,6 (3.6–4.0%) bonds, was maintained with total recovery of D-glucose, as enzymic methods show. Extrusion cooking led to a macromolecular degradation of amylose and amylopectin, by random chain splitting, as indicated by intrinsic viscosity, gel-permeation chromatography on Sepharose CL-2B, and average-molecular-weight determinations. In contrast, drum drying, as well as extrusion cooking at 44% moisture and 90° C, degraded starch components very slightly, rendering them less soluble (4.7–24.6%) than other extrudates (56.3–81.6%). For all treated starches, the water-soluble fractions were composed of partly depolymerized amylose and amylopectin, in the same ratio as in native starch, except for the drum-dried samples, which were enriched with amylose. During extrusion cooking, shear completely disperses starch components by decreasing molecular entanglement, whereas during drum drying, the amylose fraction is preferentially solubilized by leaching.

Pregelatinized starches refer to cooked starches (Powell 1967) that are prepared by complete gelatinization and drying. Destruction of the granular structure is the major physical event leading to complete granule fragmentation and to the absence of birefringence. The main properties of cooked starches are increased water absorption and water solubility upon dispersion in cold water; this leads to "instant starch slurries" without heating. Their functional properties are highly dependent upon the cooking and drying conditions.

In spite of its limitations, drum drying is commonly used for the production of pregelatinized starches. However, the more recent technique of extrusion cooking appears to be more versatile, which explains its popularity. In contrast to drum drying, extrusion cooking has been extensively studied mainly for the functional properties of the extruded products (Conway et al 1968, Conway 1971a, Mercier and Feillet 1975, Harper 1981, Linko et al 1981, Faubion and Hoseney 1982, Meuser et al 1983, Gomez and Aguilera 1983). Several investigations have been devoted to the physicochemical changes that occur during extrusion cooking within a large range of treatment conditions (Mercier 1977; Chiang and Johnson 1977; Mercier et al 1979, 1980; Colonna and Mercier 1983; Owusu et al 1983), whereas the effects of extrusion cooking and drum drying have been compared rarely and only on cereals (Anderson et al 1969a, 1969b, 1970; Conway 1971) and on corn-soy-whey mixtures (Aguilera and Kosikowski 1978). Furthermore, drum drying is usually considered to function only as a dryer and not as a process for thermal modifications.

Although various authors (Chiang and Johnson 1977, Gomez and Aguilera 1983, Owusu et al 1983) have suspected macromolecular degradation during the application of these two technologies, amylose and amylopectin depolymerizations have been reported to occur, until now, only during extrusion of tuber starches (Mercier 1977, Colonna and Mercier 1983).

The aim of the present work was to study the morphological changes and chemical transformations of wheat starch as modified by extrusion cooking or drum drying. Knowledge of these modifications should be useful in understanding the functional and nutritional properties of thermally treated starches.

[1] Part of this paper was presented during COST 9 Final Seminar, "Thermal Processing and Quality of Foods," November 14–18, 1983, Athens, Greece.

MATERIALS AND METHODS

Starch

Prime wheat starch, with a moisture content of 13.9% (db), was obtained from Roquette Frères (F-62136 Lestrem, France).

Drum Drying

Drum drying was done on a monoroll rotated at 10 rpm and heated by steam at a pressure of 10 bars (ie, 180° C). The starch slurry, containing 450 g of starch per liter of water, was directly dried in the first assay (D1) or first precooked and then dried in the second assay (D2).

Extrusion

Five experiments were performed on a corotating twin-screw extruder (model BC 45) manufactured by Creusot-Loire (Division Pompes et Extrudeurs, F-42701 Firminy, France) with 500-mm screws. A module with a reverse flight was located on the terminal position of each screw, just before the two dies of 50-mm length and 4-mm diameter. Operating conditions are specified in Table I. The feeding section of the barrel was always cooled with running water while the terminal section was heated by an induction heating belt. The reported temperature is that of the barrel mass just above the reverse flight section. Samples were taken after running for at least 15 min to stabilize temperature, flow rate, and adsorbed power.

Solid-State Analysis

Surface area (S) (cm^2/g) was calculated from the BET equation (Brunauer et al 1938) by argon-adsorption measurements, using the Nelsen and Eggersten (1958) continuous-flow method and a Quantasorb apparatus. Samples (500–1,000 mg) sized to 100–125 μm were predried at 50° C with P_2O_5 to constant weight and out-gassed by heating at 60° C with a purge gas flowing for 1 hr.

Expansion was expressed as the ratio between the diameter of the rod-shaped product and the diameter of the die.

Specific gravity (g/cm^3) was determined by the pycnometer method (volume of approximately 25 ml), using toluene at 25° C. Ground samples, sized to less than 50 μm by sieving, were previously dried for seven days in a vacuum oven at 45° C. Each measurement, done on a 2.5-g sample, was triplicated.

Particle-size analysis for native wheat starch was done on a multichannel Coulter Counter model TA II with an orifice diameter of 100 μm in Isoton II (0.85% w/v NaCl) (Colonna et al 1980).

Small pieces (approx. 7 mm) of pregelatinized starches, after being coated with gold, were viewed with a JSM 50A (Jeol)

scanning electron microscope operating at an accelerating voltage of 20 keV and a very low intensity (8.0×10^{-13} amp) (Colonna et al 1980).

Physicochemical Methods

Starches were fractionated into amylose and amylopectin by selective precipitations with thymol and then *n*-butanol (Banks and Greenwood 1967).

Iodine-binding capacities (IBC) were measured by an amperometric method (Larson et al 1953) at 25° C.

Number-average molecular weights ($\overline{Mn}$) of amylose were determined by measuring their reducing end groups (Hizukuri et al 1981).

Intrinsic viscosities [η] were determined in 0.2 *N* KOH at 25° C with an automatic Ubbelhode viscometer (solvent flow time, 380 sec), using concentrations in the range of 1.5–3 mg/ml. For amylose, the viscosity-average molecular weights ($\overline{Mv}$) were calculated according to the general Mark-Houwinck equation:

$$[\eta] = K_a \overline{M}_v^{a}$$

where Ka (6.92×10^{-3}) and a (0.78) are the parameters determined by Banks and Greenwood (1968).

Gel-permeation chromatography was performed on a column of Sepharose CL-2B, eluted with 0.1 *N* KOH, as described previously (Colonna and Mercier 1983).

Light scattering: weight-average molecular weights ($\overline{Mw}$) of fractionated amylopectins were calculated according to Erlander and Tobin (1968), as modified by Colonna and Mercier (1984).

Enzymic Methods

The percentage of α-1,6 linkages in native and extruded starches was determined by measuring the percentage of reducing power liberated after hydrolysis by isoamylase and calculated as:

$$\% \ \alpha\text{-1,6 linkages} = \frac{\text{Reducing power (glucose equivalents)}}{\text{Polysaccharide in digest (glucose equivalents)}}$$

Debranching by isoamylase in DMSO (20%, v/v), followed by a β-amylolysis to verify the complete hydrolysis of α-1,6 linkages, was performed as by Mercier and Kainuma (1975). All other determinations were done as described previously (Colonna et al 1982).

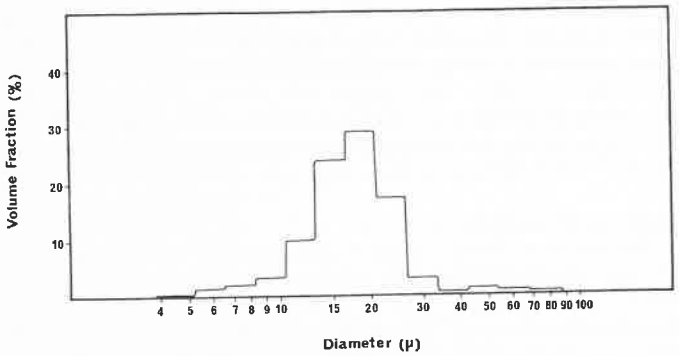

Fig. 1. Particle-size distribution of native wheat starch.

TABLE I
Operating Conditions for Wheat Starch Extrusion Cooking

Sample	Temperature (° C)	Feed Rate (kg/hr) Starch (db)	Water[a]	Screw Speed (rpm)	Amperage (A)
Pa	90	46	36	270	15
hM-lT	125	47	16	270	22
hM-hT	180	47	16	270	18
lM-lT	130	45	11	275	20
lM-hT	180	46	11	270	22

[a] Including starch moisture.

Water-Soluble Fraction

Water-soluble fractions (WSFs) were extracted by shaking for 30 min with a flask-shaker (100 rpm) from 0.25 g of dry starch suspension in 25 ml of distilled water freshly boiled and cooled to 25 and 50° C. WSFs were recovered after being filtered through a filter glass G4 (porosity <16 μm).

RESULTS

Characteristics of Native Wheat Starch

Native wheat starch is in a granular form that is strongly birefringent when viewed under polarized light. Scanning electron microscopic examinations indicate that the granule surface is smooth, with small scars in a few granules. The mean of the granule size distribution, shown in Fig. 1, is 16 μm; the log-normal geometric standard deviation is 1.4 μm. The measured specific gravity is 1.482 ± 0.005 g/cm^{-3} (Table II). Assuming that every starch granule is spherical and has the same density (ρ), a theoretical value for surface area (S) can be calculated from each size fraction (i), defined by Coulter counting, according to the following equation:

$$S = \frac{3}{d} \times \Sigma_i \left(\frac{V_i}{\Sigma_{V_i}} \times \frac{1}{r_i} \right)$$

where for each size fraction, r_i is the radius and V_i the volume fraction of starch granules with radius r_i. By computing, S is found to be 3,030 cm^2/g, whereas by argon adsorption (Table II), S is 3,900 cm^2/g.

Native wheat starch (Table III) has a percentage of α-1,6 linkages of 3.9%, leading to an average chain length ($\overline{CL}$) of 25.6. The IBC, which is of 5.9 mg I_2 bound per 100 mg of polysaccharide, corresponds to an apparent amylose content of 28.5%, as pure amylose has an IBC of 20.7 mg I_2 per 100 mg of polysaccharide. The β-amylolysis limit is 59.6%, and the intrinsic viscosity is 210 ml/g, as measured in 0.2 *N* KOH (Huggin's constant λ_H0.9). The elution profile on Sepharose CL-2B is characterized by a sharp peak located at the void volume (Vo), representing 82.1% of the total polysaccharide, followed by a long tail up to a Kav of 0.84. The material located at the Vo presents a maximum absorption of the iodine-polysaccharide complex (λmax) at a wavelength of 540 nm, which is specific for amylopectin. Along the chromatogram, as Kav increased, the fraction's λmax increased from 540 to 620 nm, expressing a contamination of amylopectin with amylose. Pure amylose is observed only at Kav 0.58. Native starch was fractionated into amylopectin (70.1%) and amylose (26.3%), and the fractionated amylopectin is characterized by an intrinsic viscosity of 97 ml/g (Table IV) with a weight-average molecular weight of 58.3×10^6 g/mole, determined by light scattering.

The intrinsic viscosity of the fractionated amylose is 165 ml/g, leading to a viscosimetric-average molecular weight of 409,000, according to Banks and Greenwood (1968). In contrast, the

TABLE II
Solid Phase Properties of Native and Thermally Modified Starches

Sample	Specific Gravity (g · cm^{-3})	Surface Area (cm^2 · g^{-1})
Native starch	1.482 ± 0.005	3,900
Thermally modified starches		
Extruded		
Pa	1.485 ± 0.004	230
hM-lT	1.469 ± 0.009	500
hM-hT	1.475 ± 0.004	390
lM-lT	1.478 ± 0.009	270
lM-hT	1.480 ± 0.004	480
Drum-dried		
D1	1.471 ± 0.007	650
D2	1.473 ± 0.006	620

TABLE III
Molecular Characteristics of Native and Thermally Modified Wheat Starches

Sample	Iodine-binding Capacity (mg I_2 per 100 mg of polysaccharide)	β-Amylolysis Limit (%)	α-1,6 Linkages (%)	Intrinsic Viscosity		Elution Profile on Sepharose CL-2B		
				[η] (ml/g^{-1})	λH	Material with Kav 0.1 (%)	Kav of Last Fraction with λmax ~540–550 nm	Kav of First Fraction with λmax ~610 nm
Native starch	5.9	59.6	3.9	210	0.9	82.1	0.04	0.21
Thermally modified starches								
Extruded								
Pa	5.3	59.7	3.8	180	0.9	59.5	0.05	0.35
hM-lT	6.0	59.8	3.6	119	0.8	38.5	0.07	0.50
hM-hT	5.8	58.4	3.7	105	0.4	33.6	0.12	0.54
lM-lT	6.1	60.8	3.9	90	0.7	15.2	0.25	0.58
lM-hT	5.4	60.8	4.0	70	0.9	8.5	0.30	0.60
Drum-dried								
D1	5.2	60.3	3.7	188	0.7	77.9	0.05	0.23
D2	5.5	58.4	3.6	182	0.4	64.7	0.06	0.39

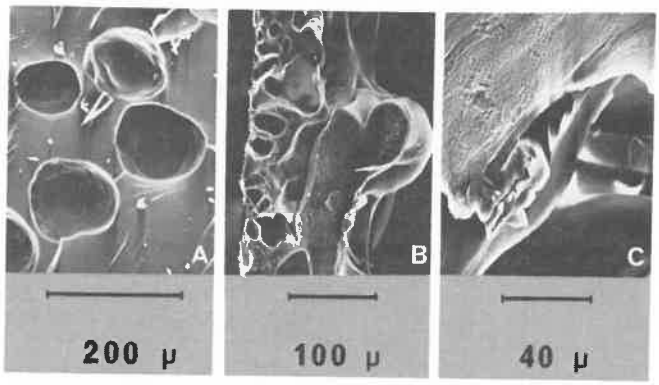

Fig. 2. Scanning electron micrographs of treated starch samples. **A,** Sample Pa; **B,** sample D1; **C,** sample lM-hT.

number-average molecular weight, determined by the end-point analysis, is only of 158,000 ± 3,000.

Modifications of the Solid State

For every sample, the granular shape completely disappears. Starch becomes a continuous phase in which enclosed air bubbles occupy a large part of the volume.

Under the extrusion conditions of sample "Pa" (Fig. 2a), starch forms a cylindrical rope approximately 6 mm in diameter. Only 20–40% of the extrudate volume is occupied by air bubbles of 80–150 μm in diameter; therefore, the expansion is 150%.

Drum-dried samples D1 and D2 look like flakes (Fig. 2b) whose thickness is around 150 μm. Air bubbles are entrapped inside the solid phase and represent 40–60% of the volume of the flakes, but cell size and shape are not uniform throughout the flakes. Two sides can be distinguished: one side in contact with the roll surface is bright, whereas the other one is rippled and dull.

In contrast, the internal structure of the extruded samples is a lattice formed by a melted-starch film (5–10-μm thick) (Fig. 2c), with large air cells whose sizes are in the range 0.5–5 mm. This last feature varies greatly between the four extruded samples and is highly correlated with expansion, ie, 200–400%.

In the sized fraction 100–125 μm, no variation is detectable in the specific gravity (1.47–1.48 g/cm^3) (Table II). However, a major experimental difficulty is the grinding step, which must break all air bubbles entrapped in the starch matrix; this problem is encountered mainly with drum-dried starch samples. In contrast, the surface area for all the thermally modified starches decreases greatly from 3,900 cm^2/g (native starch) to 650–620 cm^2/g for drum-dried and 230–500 cm^2/g for extruded starches (Table II).

Macromolecular Modifications of Starch Components

Macromolecular characteristics of starches, modified by thermal treatment, are reported in Table III.

TABLE IV
Average Molecular Weights (g/mole) of Native and Thermally Modified Wheat Starch Components

Sample	Amylose			Amylopectin	
	$\overline{Mn} \times 10^{-3}$[a]	[η][b]	$\overline{Mv} \times 10^{-3}$[c]	[η][b]	$\overline{Mw} \times 10^{-3}$[d]
Native starch	158	165	409	97	58,300
Thermally modified starches					
lM-lT	99	120	272	46	3,800
lM-hT	93	98	210	36	2,700
D2	153	152	368	75	22,700

[a] Number-average molecular weight.
[b] Intrinsic viscosity (ml/g).
[c] Viscosimetric-average molecular weight.
[d] Weight-average molecular weight.

Starch recovery, as glucose polymer, is complete with the different products as observed by the dual enzymic method amyloglucosidase-glucose oxidase. The content of α-1,6 linkages is still in the range 3.6–4.0%, meaning that the α-1,4/α-1,6 ratio is unmodified. No changes in β-amylolysis limits (58.4–60.8%) and IBC values (5.2–6.1 mg of I_2 bound per 100 mg of polysaccharide) confirm this observation.

In contrast, for every modified starch, intrinsic viscosity is reduced slightly (sample D1: 188 ml/g) or strongly (sample lM-hT:70 ml/g), suggesting a macromolecular degradation of starch molecules. Gel-permeation chromatography, on Sepharose CL-2B, which fractionates molecules in a way opposed to that of hydrodynamic volume, confirms this assumption. The relative amount of excluded material (void volume) decreases from 82.1% for native starch to range from 77.9% (sample D1) (Fig. 3) to 8.5% (sample lM-hT) (Fig. 4). Concurrent with the decrease in intrinsic viscosity, amylopectin, the unique component of this first peak, is present in the chromatograms, up to Kav 0.30, for sample lM-hT. The same behavior is observed for amylose Kav from 0.23 to 0.60. From these chromatograms, samples treated by drum drying (D1 and D2) or extrusion cooking at low temperature (Pa) are only slightly degraded, comparable to native starch. In contrast, the other four samples processed by extrusion cooking at high temperature are extensively modified. To quantify the observed changes, samples lM-lT, lM-hT, and D2 were fractionated into amylose (26.0–27.2% total starch) and amylopectin (69.9–71.0% total starch). Amylopectin $\overline{Mw}$ in the sample D2 decreases only to a value of 22.7 × 10^6; for samples lM-lT and lM-hT, $\overline{Mw}$ are 3.8 × 10^6 and 2.7 × 10^6 g/mole, respectively (Table IV). Similarly, intrinsic viscosity of the amylopectin fraction decreases to the range 75–36 ml/g. For amylose, the two average molecular weights $\overline{Mn}$ and $\overline{Mv}$ decrease only 3–10% for sample D2 in contrast to the sample lM-lT and lM-hT where the reduction is 33–48% (Table IV).

Water Solubility of Modified Starches

Ground thermally modified starches (particle size: 100–125 μm) are partly soluble (Table V). Whereas the three samples Pa, D1, and

D2 display relatively low solubilities (4.7–24.6%) at 25° C, the four other extruded ones (samples hM-lT, hM-hT, lM-lT, and lM-hT) are highly soluble (53.6–81.6%). This solubility is increased at 50° C to the range of 11.9–97.9%. Water solubility is also related to particle size: for the sample lM-hT, solubility increases from 54.0% for the 1,000–1,250-μm fraction to 64.8% for the 400–420-μm fraction and 67.4% for the 100–125-μm fraction. All of these WSFs are highly turbid, but the turbidity disappears completely when 1*N* KOH or NaOH is added. Further determinations were performed, therefore, only on clear solutions that had been treated by 1*N* KOH. Compared to their corresponding total extruded starches, the chromatographic profiles of WSF (Fig. 4) exhibit a reduction of the material eluted at the void volume and a delay in amylopectin fraction disappearance and amylose fraction appearance. This dual shift means that WSFs are enriched into molecules of low molecular weight. This trend is much more pronounced with Pa samples, as only 2.4% of the material is eluted at the void volume and the chromatographic profile is characterized by a broad peak at Kav 0.80. IBC values of WSF from extruded starches and Pa are very close to those of the corresponding total starches, showing a constancy of the amylose-amylopectin ratio.

For the two drum-dried samples, the WSF have higher IBC values, indicating higher amylose contents. As for the Pa sample, the chromatographic profiles are characterized by a small peak (7.5–15.9% of total material), followed by a broad one (Kav 0.80), showing an enrichment in macromolecules of relatively low molecular weight.

DISCUSSION

Argon, which was used for the surface-area determinations, cannot penetrate pores less than 13.8 Å in diameter. However, the disagreement between the experimental and calculated values proves that native starch granules have few mesopores (18 Å < diameter < 500 Å) accessible to argon molecules.

Whatever treatment is considered, starch is melted and becomes a continuous and solid phase. One of the functions of water is to create air bubbles, which leads to differences in expansion (apparent density). The measured specific gravity is not significantly changed, whereas surface area decreases for all the treated starch samples, in comparison with native starch. The decrease is larger for extruded starches than for drum-dried ones, despite the fact that the surface area is measured only on sieved samples between 100 and 125 μm. Assuming square flakes of 10-μm thickness, the calculated surface area should be of 1,400 cm^2/g and at least of 1,600 cm^2/g if the respective particle sizes are 100 or 125 μm.

This decrease in area means that the methodology used is inadequate. The treatments generate thin walls having a smooth surface without mesoporosity or with mesopores, which cannot be measured with the gas-adsorption method, or very small bubbles (<10 μm) remain within the flakes and are readily accessible to the toluene used for specific gravity measurement but not to argon.

Moreover, present methods fail to describe such porous and solid structure in terms of porosity (accessibility to water) and the strength of hydrogen bonds between macromolecules.

Molecular characteristics of native wheat starch components agree with those published previously (Banks and Greenwood 1975, Lii and Lineback 1977, Stacy and Foster 1956). After any thermal treatment, the monomer D-glucose and the two types of linkages α-1,4 and α-1,6 are still the unique features of modified starches, since classic enzymic methods of starch determinations give recoveries of approximately 100%. The retaining of the ratio α-1,4 linkages/α-1,6 linkages explains the stability of the β-

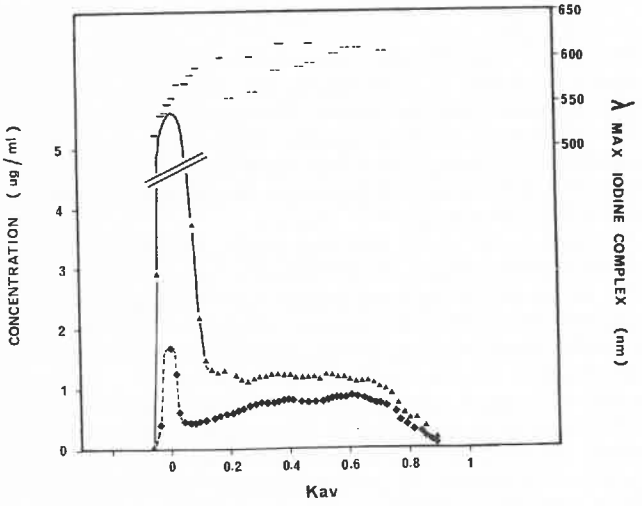

Fig. 3. Elution profiles from Sepharose CL-2B of drum-dried starch (D1) (▲) and its water-soluble fraction (◆).

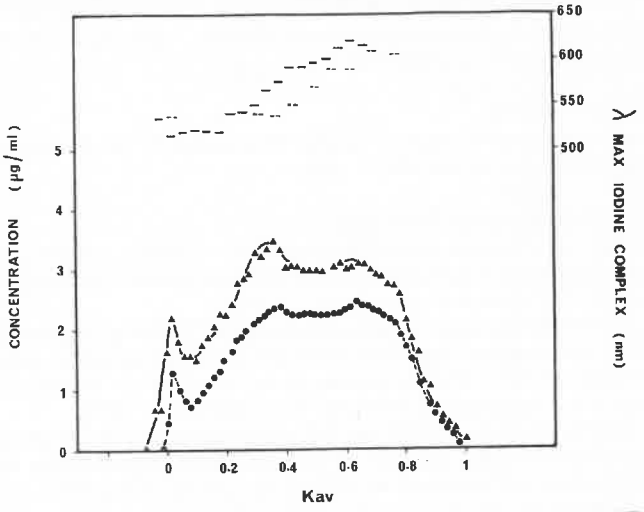

Fig. 4. Elution profiles from Sepharose CL-2B of extruded starch (lM-hT) (▲) and its water-soluble fraction (●).

TABLE V
Quantification and Characteristics of Water-Soluble Fractions from Thermally Modified Starches

Sample	Starch Solubility (%) 25° C	Starch Solubility (%) 50° C	IBC (mg I_2 bound per 100 mg of polysaccharides)	Elution Profile on Sepharose CL-2B: % Material with Kav ≤0.1	Elution Profile on Sepharose CL-2B: Kav of Last Fraction with λmax ~540 nm	Elution Profile on Sepharose CL-2B: Kav of First Fraction with λmax ≥610 nm
Extrusion cooking						
Pa	4.7	11.9	5.0	2.4	ND[a]	ND[a]
hM-lT	56.3	88.9	5.0	29.5	0.35	0.67
hM-hT	81.6	97.9	6.2	22.7	0.29	0.67
lM-lT	77.5	88.3	6.0	14.0	0.39	0.65
lM-hT	67.4	95.9	5.6	6.1	0.42	0.70
Drum drying						
D1	13.6	18.9	11.2	7.5	0.22	0.52
D2	24.6	36.9	7.7	15.9	0.18	0.57

[a] ND = not detectable.

amylolysis limits and partly of the iodine-binding capacities. This last characteristic also proves that, if amylose degradation has occurred, it does not produce a significant amount of material with DP less than 100; otherwise, IBC should decrease (Pfannemuller et al 1971).

In every assay, the intrinsic viscosity of the total starches decreases after any thermal treatment. Since the primary chemical structure is not modified by these processes, the lowering of intrinsic viscosity demonstrates that starch components are degraded into macromolecules of lower molecular weight. Indeed, the profiles obtained by gel-permeation chromatography confirm that both processes induce hydrolytic reactions that affect the starch components. Unfortunately, gel-permeation chromatography cannot be used to determine molecular-weight distributions, since suitable calibration standards with the same chemical structure, are not available commercially, despite the statements of Biliaderis et al (1979). Second, the fractionation range of Sepharose CL-2B is not broad enough for such polydisperse macromolecules. Therefore, starch fractionation and determinations of average molecular weights have been done on four samples: native starch and three treated ones, 1M-1T, 1M-hT, and D2.

For amylose, average molecular weights, $\overline{Mn}$ and $\overline{Mv}$, decrease in every treatment. The polydispersity ratio $\overline{Mv}/\overline{Mn}$ does not change as degradation increases from native amylose to samples D2, 1M-1T and 1M-hT. Amylopectin $\overline{Mw}$ decreases also, but with a higher intensity than do $\overline{Mn}$ and $\overline{Mv}$ of amylose. Furthermore, for amylopectin, it is interesting to study the experimental relation $[\eta] = 0.414\ \overline{Mw}^{0.306}$ with r 0.99. The low value (0.306) of a in this empirical Mark-Houwink-Sakurada equation is attributed to the branched structure of amylopectin (Quivoron 1972). Therefore, intrinsic viscosity measurements would be inefficient for detecting any slight macromolecular degradation. Moreover, no method is available to determine $\overline{Mn}$ for such high molecular weight.

Furthermore, intrinsic viscosity determinations on total starch are not sensitive enough to account for amylopectin degradations: a decrease of 15% for $[\eta]$ (from 210 ml/g to 182 ml/g) corresponds to more than the one-half decrease of the weight-average molecular weight (58.3×10^6 to 22.7×10^6).

These results demonstrate that amylose and amylopectin are more or less degraded by both thermal treatments. The absence of oligosaccharides, which otherwise should appear at the total volume on Sepharose CL-2B, and the stability of amylose dispersity are supporting arguments for a pure random-chain scission (Banks and Greenwood 1975, Jellinek 1978). Yet they do not prove that all chain bonds are of equal susceptibility, regardless of their locations in the macromolecules, especially for amylopectin.

The molecular mechanism of this degradation is still unknown. Lorenz and Johnson (1972) have demonstrated that starch decomposes into carbonyl compounds and fatty acids when starch suspensions (3%) in neutral water are heated at elevated temperatures (120–180°C) over several hours. But drum drying as well as extrusion cooking (van Zuilichem et al 1973, Olkku et al 1980, Colonna et al 1983, Davidson et al 1983) are short processes (less than 30 sec), and the shear must be involved in the physical model. Mechanical shear degradation has been studied for synthetic polymers in solution, but no information is available for melted phase with a low amount of solvent (water).

This macromolecular degradation is a function of the considered process. By comparing drum-drying (D1 and D2) and high-temperature extrusion cooking (hM-1T, hM-hT, 1M-1T, and 1M-hT), extrusion cooking appears to drastically degrade molecules in contrast to drum drying, in which only slight modifications occur. However, sample Pa, produced by extrusion cooking at low temperature and high moisture content, demonstrates that this process results in some molecular degradation, like drum drying. The mechanical degradation by extrusion cooking imposes severe limitations on uses where effectiveness is determined by high molecular weight.

The two processes modify starch by rendering them partly soluble. The high turbidity of the WSFs disappears with chemical (urea, alkali) or thermal agents, proving that these fractions are composed of aggregates of starch molecules linked by hydrogen bonds.

Starches, extruded at high temperature (>120°C), are highly soluble, in contrast to the one produced at low temperature/high moisture (sample Pa) or by drum drying. These results agree with those of Anderson et al (1969a, 1969b, 1970) on corn and sorghum grits, where the range of the water-solubility index is similar, but without chemical identification of soluble materials. For every sample, molecules of low molecular weight are preferentially solubilized. From IBC measurements, it appears that WSFs from extruded starches have the same amylose content as total starches (~28.5%). In contrast, for drum drying, WSF from D1 is composed of 54% of amylose, corresponding to 26% of total starch amylose. The 37% amylose content of WSF from D2 represents 32% of total starch amylose. The higher solubility of the treated starches may be attributed to an increased solubility due to the decrease of molecular weight. This chemical law would justify differences in WSF amount between extruded and drum-dried starches, but is inadequate to explain differences within the four different extruded starches (except Pa).

Two other physical features, based on the conformation of macromolecules in the solid state and on the porosity of the solid state, should be involved, but, until now, no experimental methodology has been available for such a purpose. In extrusion cooking, the shear factor completely disperses the starch components in the melted state, disrupting molecular entanglements. On the other hand, in drum drying, where no shear is applied to the swollen granules, only an amylose leaching occurs before drying. This is confirmed by the higher amylose solubilization in sample D2, which has been submitted to a first precooking before drum drying. This behavior is similar to the gelatinization of wheat starch (Doublier 1981), in which agitation during heating is a major factor for controlling solubilization and swelling of starch pastes.

CONCLUSION

The present results show that the effects of either extrusion cooking or drum-drying on starch must not be interpreted only in terms of gelatinization (physical transformation), but also of macromolecular transformations of both amylose and amylopectin. Such information is necessary for the understanding of the relation between the physical and chemical structures of thermally modified starches and their rheological and nutritional properties.

ACKNOWLEDGMENTS

The authors thank the Roquette staff (F-62136 Lestrem, France), especially M. Dumont, for drum drying the wheat starch. We are very grateful to P. Williams for her excellent technical assistance and to B. Bouchet for the scanning electron microscopy observation.

This investigation was supported by a grant, "Thermal Treatment of Foods," awarded by the French Ministry of Industry and Research.

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[Received November 21, 1983. Accepted May 10, 1984]