Physicochemical Properties of Irradiation Modified Starch Extrudates

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PHYSICOCHEMICAL PROPERTIES OF IRRADIATION MODIFIED STARCH EXTRUDATES

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Abstract

Corn starch samples containing 0, 25, 50 and 70% amylose irradiated with γ-radiation dosages of 0 (native), 5, 10, 20 (containing 0, 2.5 or 5% potassium persulfate, hydrogen peroxide or ceric ammonium nitrate) or 30 kGy were extrusion cooked using a C.W. Brabender single-screw extruder at a barrel temperature of 140 °C, a screw speed of 140 rpm and 18% moisture content. Increasing irradiation dosages from 0 to 30 kGy gave consistently increased expansion ratios from 2.9 to 7.9 for 25% amylose starches and from 6.5 to 14.5 for 50% amylose starches, while the expansion ratios consistently decreased from 6.0 to 2.1 for 0% amylose starches. The expansion ratios for 70% amylose starches remained more or less constant at 10 irrespective of irradiation dosage. Expansion ratios of all the 20 kGy irradiated starch samples treated with chemical agents, however, decreased to 5 or below. The patterns of bulk densities and expansion ratios of the products were generally similar. Increasing irradiation dosages caused darkening of the product color. The water solubility increased from < 1% for native starches to almost 100% for certain irradiated starches processed with chemical additives. Overall, increasing amylose contents of the starches appeared to be resistant to changes that otherwise occurred due to irradiation modifications and chemical treatments. Molecular weights and iodine binding capacities of starches were significantly reduced with irradiation dosages and chemical treatments.

Key Words: Starch, γ-irradiation, irradiation, potassium persulfate, hydrogen peroxide, ceric ammonium nitrate, expansion volume, extrusion, amylose content, bulk density.

Introduction

The expanded snack foods are available on the market are primarily starch or cereal based. he term "expanded" usually refers to products which have low bulk density. The consumer acceptability of these expanded food products largely depends upon the product attributes, such as crispiness, softness and mouthfeel. Low expansion volumes, on the other hand, can make the product harder to chew. The expansion volume of these products is, therefore, a crucial factor in determining consumer acceptability. Extrusion cooking technology has been widely used by the food industries to produce breakfast cereals, and ready-to-eat foods (Andersson et al., 1981; Chinnaswamy and Hanna, 1990). The expansion of starch based foods is a function of several factors including moisture content of the feed (Artz et al., 1990), barrel temperature and the shear rate in the extruder (Chinnaswamy and Hanna, 1988a, b; Kokini et al., 1992). The sample moisture contents, barrel temperatures and shear stress or shear rate not only affected the expansion properties of the extruded products but also affected the functional and sensory qualities which is basically related to changes in molecular properties (Mercier and Feillet, 1975). Chinnaswamy and Hanna (1990) suggested that the average molecular size of the starch as indicated by the fraction I size (void volume peak consisting mostly of branched structures of starch) of the gel permeation chromatographic fractions, may be responsible for the expansion volume of the extruded starch products. Similar observations were also made by Wen et al. (1990).

Adam (1983) reported that γ-irradiation caused a number of chemical and molecular changes in carbohydrates. Adams (1983) further reported that irradiation produced various radiolytic products, such as dihydroxyacetone, formaldehyde, hydrogen peroxide. However, low levels of irradiation can possibly relocate the branch points in the carbohydrate polymers, such as starch, or even create more branching as was reported by Grant and D'Appolonia (1991). They suggested that increased intrinsic viscosities of pentosans treated with low irradiation levels were due to increased branching of the pentosans. Golachowski (1991) suggested that treatment

with 1.5 kGy irradiation treatment changed the functional properties of the potato starches upon storage. Sabularse *et al.* (1991) attributed an increase in the water solubility of the rice starch to the degradation of the starch granular structure from γ-irradiation. Thus, irradiation appears to have promise as a way to modify the molecular size of starches to nullify varietal differences in expansion qualities of starches and cereals. Therefore, it was of interest to study the functional property changes including expansion volumes in starch extrudates due to irradiation modifications of corn starches before and after extrusion cooking.

Materials and Methods

Samples

The corn starches were obtained gratis from American Maize Products Company, Hammond, IN. All starch samples henceforth will be referred to by their respective amylose contents (0% amylose starch for waxy starch, 25% amylose for normal corn starch, 50% amylose starch for amylomaize V, and 70% amylose starch for amylomaize VII). The chemical composition of the starches, as provided by the manufacturer, is given in Table 1. The chemical additives that were used to process starches during extrusion cooking, namely ceric ammonium nitrate (C-3654 lot 129F3471), potassium persulfate (P-9392 lot 28F0841) and hydrogen peroxide (H-1009 lot 30H3542), were purchased from Sigma Chemical Company, St Loius, MO.

Irradiation

Starch samples, each weighing 400 g, were placed in separate plastic containers and subjected to 0 (native), 5, 10, 20 or 30 kGy of γ-radiation dosages, at room temperature, using a ^{60}Co irradiator (Nuclear Materials and Equipment Corporation, Apollo, PA). The dosage rate was standardized by Landuer, Inc, Glenwood, IL at a level of 0.54879 kGy/h. The irradiation dosages for starches were then calculated as:

Levels of irradiation	Time of exposure
5 kGy	9 hours 7 minutes
10 kGy	18 hours 13 minutes
20 kGy	36 hours 27 minutes
30 kGy	54 hours 40 minutes

Chemical treatments

The 0, 25, 50 and 70% amylose starches were treated with a 20 kGy radiation dosage at room temperature, and mixed with 2.5 or 5% potassium persulfate, ceric ammonium nitrate or hydrogen peroxide, on dry weight basis. The control samples had no added chemical additives.

Table 1: Chemical composition of starches[*]

	Starch Amylose (%)			
	0	25	50	70
Protein (% d.b.)	0.2	0.3	0.5	0.8
Phosphorous (mg/100 g)	4.2	14.0	22.8	19.1
Fat (g/100 g)	0.1	0.1	0.4	0.3
Ash (g/100 g)	0.1	0.2	0.1	0.1
Moisture (% d.b.)	10.6	9.5	11.0	10.6

[*]as reported by the manufacturer.

Extrusion

All starch samples were extrusion cooked in a C.W. Brabender (model # 2902) single screw extruder with 3 mm cylindrical die. Extrusion cooking conditions were kept constant throughout the study at 140 °C barrel temperature, 140 rpm screw speed with sample moisture content of 18% (dry basis, d.b.) unless stated otherwise in the text. The process variables of specific mechanical energy, melt pressure, and mass flow rate were monitored using standard procedures (Mercier and Feillet, 1975). The extrudates were divided into two groups. One portion was used for testing the expansion ratio and bulk density. The other portion was ground using Tecator Powdertec 3090 (Tecator, Inc., Germany) to pass through 0.5 mm sieves, and used for physical and chemical analyses.

Pressure

Extrusion pressures (in MPa) were measured using a Dynesco Pressure Transducer Model PT411-10M-6 (Dynasco Inc., Norwood, MA) mounted in the die just before the discharge orifice. Readings were recorded every 5 seconds for at least 60 seconds with an Omnidata polycorder model 516-24 (Omnidata International Inc., Logan, UT) and the averages were reported.

Specific mechanical energy (SME)

SME is the mechanical energy input per unit mass of the extrudate. It was determined by dividing the net power input to the screw by the extrudate flow rate (dry basis). Net power inputs to the screw were calculated from the torque requirements. The torque was measured during extrusion cooking using a torque transducer (BLH Electronics Inc., Waltham, MA) and recorded with the Omnidata polycorder model 516-24. The torque readings were recorded every 5 seconds for at least 60 seconds and the averages were reported. Similarly screw speeds were measured using a stock mechanical pulley with a rotary read-out. The SME was then calculated from below:

$$SME = (M_d \omega / \dot{m}) \ [Wh/kg] \qquad (1)$$

where:
M_d = torque [Nm],
ω = angular velocity [per second] and
$\dot{m}$ = throughput [kg/h]

The angular velocity, ω, was calculated as:

$$\omega = (2 \ \pi \ N) \ / \ 60 \qquad (2)$$

where N = screw rotations per minute (screw speed).

Flow rate

Flow rate was determined by collecting the extrudates continuously for one minute. The sample was then dried in an oven at 105 °C for 12 hours or until equilibrated (Chinnaswamy and Hanna, 1988a). The flow rate was calculated as follows:

$$\dot{m} = \dot{m}_1 \, [(1-M_2) / (1-M_1)] \times 60 \qquad (3)$$

where:

$\dot{m}$ = mass flow rate (kg/h),

$\dot{m}_1$ = sample mass collected for 1 minute at the discharge orifice,

M_1 = moisture content of the starch (feed) and M_2 = moisture content of the extrudate.

Bulk density

The bulk density of the extrudate was determined by a displacement method (Hwang and Hayakawa, 1980; Chinnaswamy and Hanna, in preparation) using the glass beads of 1.00 to 1.05 mm diameter. To find the bulk density of the glass beads, they were added to a 500 ml steel cylinder with sharp edges and tapped gently 60 times on a wooden surface. The cylinder was refilled with beads and leveled off with a ruler and tapped again. This process was repeated until no more shrinkage of glass beads was observed in the cylinder. The mass of the cylinder, completely filled with beads, was then determined. The bulk density of glass beads (ρ_{gb}, in g/cm^3) was calculated as:

$$\rho_{gb} = (W_{gb}) / V_c \qquad (4)$$

where:

W_{gb} = net weight of the glass beads (g), and

V_c = volume of the cylinder in (cm^3).

A 30 cm long piece of extrudate was cut into 12 pieces of about 2.5 cm each. Following the above procedure, the weight of the cylinder with glass beads and the 12 pieces of the extrudate was found. The weight of the glass beads displaced by the extrudate (weight of displaced beads) was determined. The bulk density of the extrudate was then determined as:

$$\rho_{ex} = (W_{ex} \times \rho_{gb}) / W_{gbr} \qquad (5)$$

where:

ρ_{ex} = bulk density of the extrudate (g/cm^3),

W_{ex} = weight of the extrudate (g), and

W_{gbr} = weight of the glass beads replaced by extrudate (g).

Solid density

The solid densities of ground extrudate samples were determined using an air comparison pycnometer (Multivolume pycnometer Model 130-50000-00, Micrometrics, Norcross, GA). The solid volume of a known mass of finely ground sample was determined from pressure readings. An average of the three readings was used for the calculations. The solid densities of the powdered samples were calculated as:

solid density =
sample net weight (g)} / sample volume (cm^3).   (6)

Expansion ratio

The overall expansion volumes were determined as:

Overall expansion ratio =
(solid density / bulk density).   (7)

The solid density and bulk densities were measured using equations (5) and (6) above, respectively.

Shear strength

Shear strength was determined by the Instron testing machine model "TM". A piece of extrudate was sheared by ten blades which sheared 20 cross-sections of the extrudate. The total cross-sectional area of the 20 sections was calculated. The peak force in kg required to shear these 20 cross-sections was recorded (Bhattacharya and Hanna, 1987).

Color

A Hunter colorlab colorimeter (Model D2502, Hunterlab, Inc., Reston, VA) was used to determine color values of the native (unextruded) and ground extruded samples in terms of the L, a and b values. A magnesium oxide block were used for the standard. The standard L, a, b values were 95.49, -0.61 and 0.42, respectively. Color difference, ΔE, was calculated as:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{0.5} \qquad (8)$$

where

ΔL = $L_{standard} - L_{sample}$,

Δa = $a_{standard} - a_{sample}$, and

Δb = $b_{standard} - b_{sample}$.

Water solubility

One to two grams of native and ground extrudate samples were dried in a vacuum oven at 50 °C for 2 to 3 hours. One-half gram of this dried material was weighed in a conical flask. A few drops of ethyl alcohol were added to wet the sample. Then 50 ml of distilled water was added and placed in a shaker water bath at 30 °C for 12 hours. The contents were centrifuged at 5000 rpm for 30 minutes and the filtrate was stored in a separate container. The sediments were then suspended again in 50 ml of distilled water and placed in a shaker water bath at 30 °C for 12 hours. The filtrate was centrifuged and pooled with the previous filtrate. The supernatants were filtered (5 ml) through Whatman # 42 filter paper and the carbohydrate contents were measured using a phenol-sulfuric acid method (Dubois *et al.*, 1956). The standard conversion factor of 0.9 was used for weight conversion of glucose into starch. The water solubility (WS) was then calculated as:

WS (%) =
[{glucose (g/ml) x (0.9)} x 100] / 0.5 g sample
(9)

Gel permeation chromatography (GPC)

Samples of 0 and 50% amylose starches, native (unextruded and extruded) irradiated (unextruded and extruded) with or without addition of 5.0% ceric

A. S. Sokhey and R. Chinnaswamy

Table 2. Data on process variables and some product characteristics.

Radiation (kGy)	Starch Amylose (%)	SME (Wh/kg)	Pressure (MPa)	Flow Rate (kg/h)	Product Characteristics		
					Bulk Density (g/cm^3)	Expansion Ratio	Shear Strength (kPa)
0	0	96.1	9.3	7.3	0.254	6.0	31.4
	25	137.8	13.8	5.1	0.534	2.9	57.9
	50	187.6	26.0	7.5	0.233	6.5	130.4
	70	190.2	21.8	6.2	0.160	9.4	93.2
5	0	125.2	12.4	7.3	0.377	4.0	53.8
	25	79.8	10.1	3.0	0.374	4.0	51.0
	50	190.9	21.5	6.9	0.182	8.3	107.9
	70	198.8	24.0	6.0	0.132	11.4	93.2
10	0	124.2	13.4	6.7	0.522	2.9	64.7
	25	115.9	14.8	3.8	0.398	3.8	39.2
	50	184.4	21.3	6.9	0.184	8.2	75.6
	70	174.2	19.6	5.8	0.160	9.4	67.7
20	0	126.6	14.6	6.6	0.574	2.7	106.9
	25	168.7	12.3	3.6	0.259	5.8	21.6
	50	184.9	21.3	6.7	0.106	14.1	28.4
	70	145.0	18.2	6.6	0.173	8.7	101.0
30	0	155.6	14.6	6.8	0.732	2.1	112.8
	25	124.0	9.8	5.3	0.190	7.9	13.7
	50	175.3	16.6	6.1	0.104	14.5	22.6
	70	146.7	17.8	6.3	0.144	10.5	87.2

ammonium nitrate were dispersed in dimethyl sulfoxide (approximately 0.1%), and 5 mg were 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/h using distilled water containing 0.01% sodium azide as an eluent. Fractions of 4 ml were collected. Aliquots of 2 ml were used for the determination of carbohydrate content using a phenol-sulfuric 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 2 ml fractions were mixed with 0.2 ml of 0.2% iodine solution and 3 ml distilled water and the absorbance of blue color developed was read at 630 and 520 nm. The amylose contents were measured against a standard corn amylose (Sigma Chemical Co.) absorbance and calculated and expressed on a total volume fraction basis. The ratio of amylose contents (blue color values) of each fraction measured at 630 nm to 520 nm was then calculated and reported as 630/520 (nm) ratio. The void volume and total volume of the gel column was determined using Blue Dextran and KCl, respectively. The gel column was also calibrated with dextran standards (Sigma Chemicals, St. Louis, MO) of molecular weight ranges of 2.2×10^6 to 1×10^4 Daltons by a generalized linear model.

Statistical analysis

All values reported are averages of at least two repetitions. Generalized linear model SAS version 6 statistical package was extensively used to analyze the data for curve fitting, and for the statistical validation of the trends and patterns.

Results and Discussion

The values of specific mechanical energy (SME), flow rate, extrusion pressure, bulk densities, expansion ratio and extrudate shear strengths for 0, 25, 50 and 70% amylose starches with or without irradiation modifications are given in Table 2.

Process parameters

The SME varied from 79.8 to 198.8 Wh/kg. Although there are some variations, in general, it appears that the SME increased with increasing irradiation dosage as well as with amylose contents of the starches. The melt pressure inside the barrel as measured at the die-zone showed a similar trend. The extrusion pressure values varied from 9.8 to 26.0 MPa. The flow rate of the extrudates varied from 3 to 7.5 kg/h. In general, it appears that the flow rate increased with increasing amylose contents at low irradiation levels (0, 5 and 10 kGy)
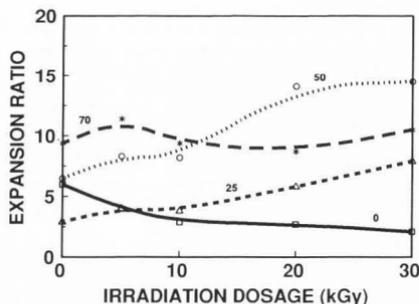
Figure 1. Effect of irradiation dosages on the expansion properties of starches.
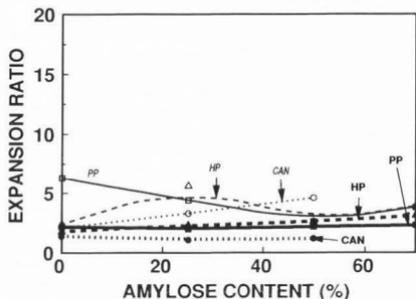

Figure 2. Effect of chemical additives on the expansion properties of the 20 kGy irradiation modified starches. Potassium persulfate (PPS), hydrogen peroxide (HP) and ceric ammonium nitrate (CAN) were mixed with starches at a level of 2.5% (italics, indicated) and 5.0% and then extrusion-cooked.

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while it varied less (6.0 to 6.8 kg/h) for 20 and 30 kGy irradiation dosages, irrespective of starch amylose contents.

Bulk density

The bulk densities of the 0% amylose irradiated starches increased from 0.10 to 0.73 g/cm^3 with increasing dosages of irradiation. The bulk density generally decreased with increasing amylose contents of starches up to 50% amylose and then decreased. Overall, the lowest bulk densities were consistently obtained with 50% amylose starch irrespective of irradiation dosage. A bulk density of 0.10 g/cm^3 was obtained for 50% amylose starch modified with 30 kGy irradiation. This is in agreement with the earlier report of Mercier and Feillet (1975), and Chinnaswamy and Hanna (1988a). It is interesting to note that the bulk densities of 0%

amylose starch increased from 0.25 to 0.73 g/cm^3 with irradiation dosages. The 70% amylose starch bulk density, however, remained in the range of 0.14 to 0.17 g/cm^3, irrespective of irradiation dosages.

Expansion ratio

The overall expansion volume or ratio represents the total increase in volume of the extrudate in all directions (dimensions) in comparison with the volume (powder) of the material. The expansion ratio of 0% amylose starches decreased from 6 to 2.1 as irradiation dosages increased from 0 to 30 kGy (Table 2, Figure 1). The expansion ratio of 25% amylose and 50% amylose starches increased significantly from 2.9 to 7.9 and 6.5 to 14.5, respectively with irradiation dosage. The 70% amylose starches, however, did not exhibit any significant difference in expansion ratio with increasing irradiation dosages. In general the expansion ratios of 0% amylose starches decreased with increasing irradiation dosages. The maximum expansion volume was observed for 50% amylose starch, while the minimum expansion volume was observed for 0% amylose starch, both irradiated at a level of 30 kGy.

As expected, shear strengths, in general had an inverse relationship with expansion ratios. The starches with higher expansion ratios had lower shear strengths. The shear strengths increased from 3 to 4 kPa for 0% amylose starch at 0 kGy irradiation dosage to 112.8 kPa for 30 kGy irradiation dosage. Similar trends are seen for other starches, but with some variations.

Grant and D'Appolonia (1991) reported cross linking in pentosans after γ-irradiation. It was, however, suspected that debranching of the starch molecules may occur at higher irradiation dosages. Free radicals formation on starch by γ-irradiation (Sabularse et al., 1991; O'Meara and Shaw, 1957) could result in degradation and formation of cross links between the adjoining chains of the starch molecules during extrusion. This may perhaps reduce the molecular sizes considerably and allow increased expansion (Chinnaswamy and Hanna, 1990). Free radicals are formed when bonds are imparted high levels of energy by irradiation as explained by Sonntag (1979). These free radicals then loose energy with time, and as soon as the energy level falls below certain level, covalent bonds form. Overall, it appears that the irradiation modifications differed with different amylose content starches partially explaining the differences in their expansion properties.

Further, it was of interest to see whether free radical inducing or enhancing chemicals such as potassium persulfate (PPS), hydrogen peroxide (HP) and ceric ammonium nitrate (CAN), added to the irradiation modified starches, would increase free radical activity during extrusion cooking. Such activity could increase the cross linking of starch molecules, degrade the starch molecules or both. Any of which are known to have implications on the expansion volume. These chemicals were expected to alter the molecular weights and sizes of the starch. It is well documented that free radicals are stable under high temperature and in saturated or super-

heated moisture vapor atmospheres (Fanta and Doane, 1986). Therefore, it was perceived that the free radicals should be stable under extrusion cooking conditions. To test this, irradiation (20 kGy) of modified starches differing in amylose contents were first mixed with chemicals noted previously at 2.5% and 5% on dry weight basis in a Hobart blender for 5-10 minutes before extrusion. All samples were then extrusion cooked.

The expansion ratios of the blends of irradiated starches and chemicals are shown in Figure 2. The expansion ratio of all starches treated with chemicals were reduced to approximately 4, irrespective of amylose contents. Although the objective was to increase the expansion ratio of the poor expanding starch types (0 and 70% amylose starches), the results showed decreased expansion ratios for all starches including the 25 and 50% amylose starches. In other words, the differences in the expansion ratios due to amylose contents were minimized. These may perhaps be due to too much alteration of molecular structures due to combined effects of irradiation modifications and chemical treatments. Among the three free radical inducing/enhancing chemical additives, ceric ammonium nitrate appeared to have the most adverse effect followed by potassium persulfate and then hydrogen peroxide. The expansion ratios decreased with increasing concentrations of chemical additives (Figure 2).

There are no reports available on the effects of ceric ammonium nitrate, potassium persulfate, and hydrogen peroxide on the expansion ratios of the starches. It appears that the high amylose starches were more affected by the addition of chemicals, as indicated by the reduction in the expansion ratios, especially for irradiation modified starches with 2.5% chemical additives (Figure 2). Chinnaswamy and Hanna (1988b) reported similar results with the additions of sodium bicarbonate and urea to starches before extrusion processing. They also reported that sodium chloride caused a slight increase in expansion ratios of 0 and 25% amylose starches, and no change or decreases for 50 and 70% amylose starches. Further study is necessary to understand the finite molecular changes among starches during extrusion cooking with or without chemical additives.

Hunter Color

The extrudates (ground) were analyzed for color changes using a Hunter Lab Color difference meter against magnesium oxide block. The L, a, b and ΔE values for all irradiation modified starches extrusion-cooked with or without chemical additives are given in Tables 3 and 4. In general, for native and irradiation modified starches, the 'L' values varied from 84.5 to 91.2 while 'a' and 'b' values varied from -1.6 to +0.74, and 3.55 to 6.21, respectively. The calculated color difference (ΔE) values varied from 5.51 to 12.2. After extrusion cooking, the 'L' values varied from 71.0 to 86.2, while 'a' and 'b' values varied from -0.12 to 3.08 and 7.83 to 16.1, respectively. The color difference values (ΔE) varied from 13.3 to 28.3. In general, the values of L, a, b increased with increasing

irradiation dosage. Extrusion cooking further increased L, a, b values. The overall trend of increasing color with increasing irradiation dosage remained unchanged even after extrusion cooking. The trend remained unchanged for all starches extrusion cooked with chemical additives at both levels. The color changes after processing may be due to caramelization and Maillard type reactions and formation of complex radiolytic polymer products from starch. Chinnaswamy and Hanna (1988b) reported similar color changes in starches extrusion-cooked with sodium bicarbonate, urea and sodium chloride.

Water solubility

Native ungelatinized starches are normally insoluble in water. Processing can result in changes in the molecular structure of the starches so as to make them more water soluble (Colonna et al., 1989). Therefore, water solubility can be a good indicator of the level of modifications or degradations of starch in the extrudate. The solubility of native starches, and irradiation modified starches before and after extrusion cooking, with or without chemical additives, are shown in Table 5. The water solubilities of native and irradiation modified starches (unextruded) remained below 1% (d.b.) irrespective of amylose content and irradiation dosage. The extrusion processing, however, caused a substantial increase in the water solubilities. It varied from 19.8 to 72.8% (d.b.). In general, the water solubility of extrusion cooked starches decreased from 72.8 to 20.8% with an increase in the amylose content of the starch. This trend is also true, for most part, for native starches, however small the values may be. The water solubility, however, generally increased from 19.8% to 92.4% with increasing irradiation dosage from 0 (extruded) to 20 kGy irradiation dosages and decreased with 30 kGy dosage. Chemical additives further increased the solubility of the 20 kGy irradiation modified starch to almost 100% for 0 and 25% amylose starches while showing only a marginal increase for 50 and 70% amylose starches (Table 5). It is interesting to note that the pattern of water solubility remained unchanged even after extrusion cooking with highly reactive chemicals. High Level of chemical, however, increased the water solubility values of starches. The overall trends of water solubilities are selectively given in Figure 3. The water solubilities of irradiation modified starches extrusion cooked with and without chemical additives increased enormously, indicating that the processing definitely altered the molecular structures of the starches. The type and the extent of such molecular modifications are different for starches varying in amylose contents.

Molecular properties

It was suspected that irradiation modifications induced molecular degradation of starches which might be enhanced with chemical additives. It was thus of interest to assess the molecular status of starch in the extrudates. In this study four different 0% amylose starch samples were selected: (1) native starch, (2) extrusion

Table 3. Color changes in starches due to irradiation and extrusion processing.

Irradiation Dosage (kGy)	Amylose Content (%)	Hunter Color values							
		Before extrusion				After extrusion			
		L	a	b	ΔE	L	a	b	ΔE
0 (Native)	0	84.48	-0.36	5.69	12.21	84.30	-0.35	7.53	13.26
	25	89.60	-1.60	7.82	9.51	86.19	-1.72	10.03	13.42
	50	91.23	-0.65	3.83	5.46	84.82	-0.78	8.13	13.16
	70	89.98	-0.61	4.99	7.16	83.30	-0.12	10.54	15.85
5	0	86.73	-0.36	6.01	10.39	79.71	0.54	9.07	18.03
	25	88.44	0.72	5.03	8.53	80.86	0.77	10.65	17.91
	50	91.23	-0.29	3.35	5.18	80.64	0.51	10.59	18.03
	70	89.13	-0.33	6.21	8.61	80.80	0.75	12.01	18.76
10	0	85.27	-0.21	4.75	11.11	79.58	0.83	9.72	18.48
	25	89.53	0.59	4.85	7.52	77.54	1.86	13.58	22.39
	50	91.15	-0.03	3.35	5.27	80.58	1.10	11.25	18.50
	70	89.96	-0.13	4.47	6.87	78.75	1.33	13.11	21.09
20	0	87.66	-0.41	5.52	9.35	77.58	1.90	13.15	22.12
	25	89.63	0.59	5.41	7.79	70.99	2.90	14.95	28.70
	50	90.92	-0.26	3.49	5.52	77.27	2.00	13.70	22.69
	70	90.34	-0.27	4.53	6.60	75.55	2.37	14.75	24.73
30	0	88.60	-0.48	5.96	8.84	76.52	1.85	13.54	23.20
	25	90.78	0.74	5.97	7.40	73.14	2.65	15.30	26.00
	50	90.69	-0.39	3.95	5.92	74.38	2.61	14.10	25.35
	70	90.07	-0.29	4.59	6.85	72.21	3.08	16.06	28.28

Table 4. Color changes in 20 kGy irradiation modified starches extrusion cooked with chemical additives.

| Chemical Additives	Amylose Content (%)	Hunter Color values							
		2.5% concentration				5.0% concentration			
		L	a	b	ΔE	L	a	b	ΔE
Potassium persulfate	0	82.24	-0.91	10.70	16.75	81.96	-1.06	13.44	18.76
	25	85.18	-1.14	9.16	13.50	82.91	-0.72	15.54	19.65
	50	84.38	-0.82	9.21	14.14	79.33	-0.40	16.41	22.71
	70	78.93	-0.75	11.96	20.16	79.11	-0.98	13.77	21.11
Hydrogen peroxide	0	82.71	-0.61	10.69	16.37	81.48	-0.45	12.58	18.53
	25	79.32	-0.46	12.00	19.86	88.16	-0.91	6.17	9.28
	50	84.67	-0.38	6.67	12.47	85.23	-0.53	6.55	11.93
	70	83.23	-0.32	7.83	14.30	84.94	-0.60	6.19	12.00
Ceric ammonium nitrate	0	79.67	-0.61	12.47	19.86	78.34	-1.05	12.41	20.91
	25	84.85	-0.98	10.39	14.56	80.86	-1.06	9.56	17.32
	50	84.75	-0.83	9.71	14.18	82.51	-1.19	10.93	16.69
	70	85.30	-1.20	11.36	14.94	79.46	-0.36	13.13	20.44

Table 5. Water solubility characteristics of variously processed starches.

| Irradiation Dosage (kGy)	Starch Amylose Content (%)	Chemical agents	Solubility (% d.b.)			
			Before extrusion	After extrusion		
				0	2.5	5.0
0 (Native)	0	-	0.13	72.8	-	-
	25	-	0.13	45.3	-	-
	50	-	0.03	19.8	-	-
	70	-	0.03	20.8	-	-
5	0	-	0.21	70.2	-	-
	25	-	0.15	83.1	-	-
	50	-	0.01	37.0	-	-
	70	-	0.06	19.3	-	-
10	0	-	0.20	73.2	-	-
	25	-	0.13	88.1	-	-
	50	-	0.05	44.7	-	-
	70	-	0.06	20.0	-	-
20	0	-	0.73	92.4	-	-
		PPS	-	-	96.4	100.0
		HP	-	-	100.0	100.0
		CAN	-	-	85.4	99.0
	25	-	0.24	91.6	-	-
		PPS	-	-	100.0	100.0
		HP	-	-	100.0	100.0
		CAN	-	-	82.9	87.1
	50	-	0.12	66.5	-	-
		PPS	-	-	67.8	87.3
		HP	-	-	44.7	51.8
		CAN	-	-	62.3	63.6
	70	-	0.12	25.4	-	-
		PPS	-	-	53.2	62.9
		HP	-	-	28.4	38.7
		CAN	-	-	61.0	73.0
30	0	-	0.97	82.14	-	-
	25	-	0.80	73.07	-	-
	50	-	0.15	72.1	-	-
	70	-	0.18	25.8	-	-

cooked native starch, (3) 20 kGy irradiation modified starch extrusion cooked, and (4) 20 kGy irradiation modified starch extrusion cooked with 5% ceric ammonium nitrate. Each sample was subjected to fractionation on Sepharose CL 2B GPC column and the fractions were analyzed for carbohydrates (starch) using phenol-sulfuric acid method (Dubois et al., 1956). The results are shown in Figure 4. The native starch sample, before extrusion cooking, showed a large void volume fraction with molecular weight ranging between 9.63 x 10^7 and 1.66 x 10^7 Daltons. After extrusion cooking, the void volume fraction size in this molecular weight range decreased for most part. A new peak fraction appeared at

elution volume range of 0.21 to 0.46 Kav (A 0 Kav refers to void volume and a 1 Kav refers to total volume of the gel column) with molecular weight ranging from 1.01 x 10^7 to 1.74 x 10^6 Daltons. This peak second fraction may represent a degraded portion of the original starch molecules. The 20 kGy irradiation modified starches after extrusion cooking gave one peak fraction with average molecular weights ranging from 1.74 x 10^6 to 2.34 x 10^5 Daltons, and between Kav range of 0.46 to 0.75. When extrusion cooked with 5% CAN, the starch exhibited a major peak at the total volume (Kav 1.0) of the gel which had a molecular weight ranges of < 4.05 x 10^4. The original void volume fraction was absent in
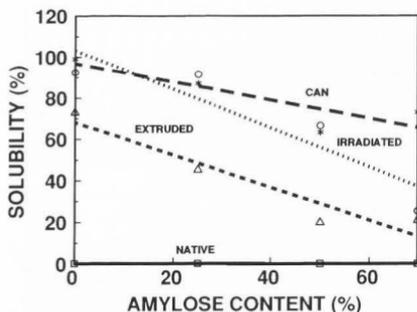
Figure 3. Effect of amylose content on water solubility characteristics of variously processed starches. Native (no treatment), extruded (native starch extrusion-cooked), and irradiated (20 kGy irradiated starch extrusion-cooked), and CAN (20 kGy irradiated starch extrusion-cooked) with 5.0% ceric ammonium nitrate are indicated.
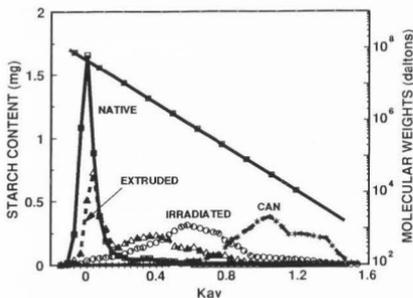
Figure 4. GPC fractionation patterns of variously treated (indicated) 0% amylose starch samples. Notations indicated are as described in Figure 3.

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this sample. It is interesting to note that the average molecular weight of the starches almost halved, when irradiated and extrusion cooked with ceric ammonium nitrate.

This molecular degradation pattern may be true for starches containing 25, 50 and 70% amylose. The degradation pattern of amylose molecules (linear starch fraction) is not clear since the degraded fraction of branched molecules of starch such as void volume fraction, get mixed with the linear amylose molecules (Chinnaswamy and Hanna, 1990). It is also not clear whether branched molecules are formed from linear chains of amylose, degraded branched molecules or combination thereof. Changes in the absorbance of iodine-
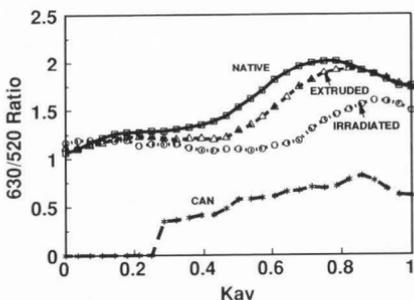
Figure 5. Progressive changes in 630/520 (nm) values of iodine-polysaccharide complexes of GPC fractions of 50% amylose starch. Variously processed 50% amylose starch samples are indicated (explanations as in Figure 3).

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polysaccharide complex fractions at 630 nm (good for amylose or linear fraction) and 520 nm (good for amylopectin, branched or short chained fraction) is indicative of a change in the composition of linear and/or branched fractions of the starch molecules. Therefore, another four sets of 50% amylose starch samples were selected in a similar manner as stated above for the 0% amylose starch. All samples were fractionated using GPC. Each fraction was mixed with 0.2% iodine solution to form iodine-polysaccharide complexes. The absorbance readings at 630 nm and 520 nm were taken for all fractions. The ratios of 630/520 (nm) readings (blue values) were calculated on a 5 mg basis for comparison purposes, the results are given in Figure 5. The 630/520 nm ratios for native starches showed a minimum of 1 for the fraction near the void volume of the gel while the highest value of 1.8 for those fractions eluting in the ranges of 0.6 to 1 Kav. This trend was similar for native 50% amylose starch after extrusion cooking but with slightly lower values as shown in Figure 5. The 20 kGy irradiation modified 50% amylose starch values decreased to about 1.5 in the Kav ranges of 0.7 to 0.8 while the pattern remained otherwise similar but with values of about 1 for the most part. The ratio of 630/520 nm went below 1 substantially for the samples of irradiated 50% amylose starch extrusion cooked with ceric ammonium nitrate. These changes in the absorbance ratios may reflect the changes in the composition of linear and branched fractions; average chain length changes due to degradation or new branching, and a combination thereof. In any case, it appears that the higher amylose starches had different types of changes as compared to 0% amylose or waxy starches with such starch modifications as irradiation, extrusion cooking with or without chemical additives.

Conclusions

Increasing γ-irradiation from 0 to 30 kGy consistently increased the expansion ratios and decreased the bulk densities of 25% and 50% amylose starches. At the same time, increased irradiation dosages consistently decreased the expansion ratios and increased the bulk density of the 0% amylose starches. The 70% amylose starches were not affected by increasing the γ-radiation dosage. The expansion ratios of all starches treated with potassium persulfate, hydrogen peroxide, ceric ammonium nitrate decreased to 5 or less with or without γ-irradiation. The product Hunter color values increased with an increase irradiation dosage. The water solubility increased with γ-irradiation dosages for all starches. Extrusion cooking of starch samples with or without irradiation and/or chemical additives, clearly decreased the molecular weights of starches. Extrusion cooked irradiated starches showed increased degradation of starch as compared to merely extrusion cooked starches. The chemical additives enhanced the degradation of starch molecules during extrusion cooking. The iodine binding abilities of the high amylose starches decreased enormously, indicating molecular reorganizations including degradation, branch formation and combinations thereof.

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Discussion with Reviewers

Reviewer 1: Have you determined the effects of potassium persulfate, hydrogen peroxide and ceric ammonium nitrate on the characteristics of extruded starch in the absence of irradiation?

Authors: No, not yet. The present study is an on going project and the effects of these chemicals on the characteristics of extruded starch in the absence of irradiation will be carried out in future.

Reviewer 1: It would be very instructive if the treated (irradiated, chemically and extruded) starch is exhaustively enzymatically hydrolyzed and the chemical structure examined in detail. This would specifically identified where cross linking had occurred.

Authors: Thank you for your suggestion, we have not done any work in this regard as yet.

E.A. Davis: What levels of γ-irradiation are used commercially to increase shelf life and how does it compare to the levels used in this study.

Authors: The report of the FAO/WHO/IAEA joint committee (1977) recommended that a dosage of 10 kGy was safe for human consumption. Maehler (1985) reported that irradiation dosage of 0.05-0.15 kGy was used to inhibit sprouting in potatoes, onion and garlic, dosages of 0.5-3.00 kGy used for shelf life extension of poultry and meat, and dosages of 10-30 kGy used for decontamination of spices, animals and poultry feed and dried ingredients.

Reviewer V: In the calculation of SME, were the friction loses taken into account? Where exactly was the torque measured?

Authors: Yes, the values were adjusted to zero after the extruder was kept running empty for some time before starch samples were added. The torque was measured on the drive at the drive and screw junction.

Reviewer V: Why couldn't the flow rates through the extruder be maintained constant? Were the screw configuration or barrel length changed?

Authors: The variation in flow rate was probably due to variations in amylose and moisture contents and also due to treatments. We, therefore, had no control over it. The screw and extruder barrel dimensions were kept constant for all samples.