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Physicochemical and Macromolecular Properties of Starch-Cellulose Fiber Extrudates

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PHYSICOCHEMICAL AND MACROMOLECULAR PROPERTIES OF STARCH-CELLULOSE FIBER EXTRUDATES

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Abstract

Three different pure cellulose fibers (James River Corporation, NJ) with lengths of 22, 60 and 110 μm were used at 1, 2, 4, 6, 8 and 10% concentrations with normal corn starch. The fiber-starch mixtures were extruded (C.W. Brabender Laboratory Extruder) at moisture contents of 14, 18 and 22% (db), 140°C barrel temperature and 140 rpm screw speed. The expansion ratio of the starch-fiber extrudates varied from 5.0 to 13.3. The maximum expansion ratio of 13.3 was obtained with 2%-60 μm fiber and 14% (db) moisture content. Increasing fiber concentration and moisture content generally reduced the expansion volumes. Water solubility values varied from 0.7% (db) for 110 μm nature fiber to 9.1% (db) for 2% of 22 μm fiber. Gel permeation chromatography (GPC) fractionation of the starch-fiber extrudates showed extensive degradation of fraction I (amylopectin) with increasing fiber concentrations and fiber lengths. Iodine binding abilities of the fractions varied widely. Water solubility, GPC and iodine binding capacity data generally indicated some chemical reactions among the molecules of starch and fiber.

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Introduction

Extrusion cooking technology has been used extensively by the food industry to produce various products viz candies, breakfast cereals, ready-to-eat foods, expanded products (Andersson et al., 1981). Of these, cereal based products form a sizeable amount (Chinnaswamy and Hanna, 1990c). Extrusion cooking technology still remains more an art than science. This is mainly due to lack of understanding of fundamental changes that take place in structural, molecular, functional and textural characteristics of food product components during extrusion cooking (Sandberg et al., 1986; Payne et al., 1989). During the last two decades the technology has undergone several modifications and has found applications in various food industries. Advances in extrusion technology have also helped to create numerous cereal foods (Artz et al., 1990). Most of these have fiber, starch and proteins as major components. Food industries in the USA and elsewhere developed new high fiber snacks, breakfast cereals, ready-to-eat cereals and soup bases (Anonymous, 1979; Leveille, 1984). Fortification of foods with fiber gave them superior nutritional qualities such as reduced blood cholesterol, good bowel mobility, decreased colon cancer, and reduced calories (Björck et al., 1984a; Bornet et al., 1989; Fairweather-Tait et al., 1989).

Studies of Chinnaswamy and Hanna (1988a,b,c; 1990 a,b,c), Colonna and Mercier (1983), Davidson et al. (1984) and Owusu-Ansah et al. (1983, 1984) clearly established degradation of starch molecules during extrusion processing as well as its effects on expansion volume and other textural and functional qualities. Hsieh et al. (1989) studied some extrudate physical characteristics in relation to extrusion processing variables and fiber contents. Björck et al. (1984b) studied the effect of extrusion cooking on the nutritional properties of dietary fiber. Changes in protein qualities and functional properties during extrusion cooking were summarized in a review by Anonymous (1984) and Stanley (1989). These and other reports warrant a fundamental understanding of the macromolecular changes that take place during extrusion cooking with regard to changes in structural and functional properties of major food components to improve the quality of extruded high-fiber cereal based foods (Mottur and Glass, 1985; Chinnaswamy and Hanna, 1990a). In that context, addition of fibers to starches and their impact on molecular, structural and functional changes are of interest to food and

Table 1. Composition of corn starch[a]

Amylose (%db)	25
Protein (%db)	0.3
Moisture (%db)	10.0
Fat (g/100g)	0.1
Ash (g/100g)	0.1
Phosphorous (mg/ 100g)	4.2

[a]Manufacturer's specifications

cereal industries (Vetter, 1984). Such fibers include hemicelluloses, pectin substances, gums, mucilages, lignins and cellulose. The fiber contents in cereal products vary from 3 to 16.7% (db). Some such fiber sources include corn, wheat, oat, rice bran and soy and differ in fiber content and fiber length. The objective of this study was to determine the effects of fiber length and content on extrudate volume expansion, molecular degradations and complex formations with starch and their impacts on the functional properties of the extrudates.

Materials and Methods

Starch and Fiber Samples

Normal corn starch was received gratis from American Maize Products, Hammond, IN. The chemical composition of normal corn starch is given in Table 1. It is about 99.7% pure starch as isolated from corn using a standard wet milling process. The starch powders were agglomerated.

Pure cellulose fibers with different lengths were obtained gratis from James River Corporation, NJ. The cellulose fibers were 99% pure. The manufacturer's production method involved three stages. In stage 1, green leaves and stems were collected and soaked in water. This produced a pulp without the usual maceration or grinding of the source product eliminating mechanical damage to the fibers. In stage 2, the pulp was bleached. The pulp was then washed with water which removed organics and trace metals to produce virgin cellulose. Finally in stage 3, virgin cellulose was subjected to a dewatering process and fiber

Table 3. Typical chemical analysis of fibers[a]

Moisture %	4 - 7
pH (10% suspension)	5 - 7
Protein %	0
Fat %	0
Starch %	0
Cellulose % (Assay)	97 - 102
Cellulose composition (%)[b]	
Araban	0.2
Xylan	8.0
Mannan	1.7
Galactan	0.8
Glucan	89.3

[a]Manufacturer's specifications
[b]All are % dry basis

sheets were formed which, when subjected to ball milling and/or high speed cutting, produced fiber products with different fiber lengths. Various fiber product physical and chemical properties are given in Tables 2 and 3. Fiber grades BW-300 FCC, BW-40 FCC and UF-900 FCC represent 22, 60 and 110 micron average lengths. It can be seen in Table 2 that water absorption capacity and bulk density increased with fiber lengths from 420 to 950 g/100 g product and 2.1 to 5.1 cc/gm, respectively. These cellulose products contain no protein, starch, fat or other major food component (Table 3). Cellulose composition, however, showed about 8% xylan and 1.7% mannan along with about 89.3% glucan. Henceforth, these three different grade fibers will be referred to in the text by their average lengths of 22, 60 and 110 μm, rather than manufacturers given name, for convenience. The starch-fiber samples were prepared by mixing 0, 2, 4, 6, 8 and 10% fiber on dry weight basis with starch in a Hobert Blender. Sample moisture contents of 14, 18, 22% (db) were obtained by the addition of distilled water. The mixed samples were equilibrated overnight in a sealed containers.

Table 2. Physical characteristics of fibers[a]

Sample	Fiber Length (μm)	Bulk Density (cc/gm)	Water absorption (gm/100gm product)	Screen Analysis		
				% on 35 mesh	% thru 100 mesh	% thru 200 mesh
BW-300 FCC	22	2.1 - 2.3	420	0	100	97[b]
BW-40 FCC	60	2.8 - 3.2	550	0-2	82-94	50-70
UF-900 FCC	110	5.0 - 5.5	950	1-5	60-80	30-40

[a]Manufacturer's specifications
[b]Through 400 mesh

Extrusion Cooking Process

A C.W. Brabender Model 2802 laboratory extruder with a 1.90 cm barrel diameter and 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 held at 150°C, 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). All extrusion cooking experiments were conducted with samples having 18% (db) moisture content and 8% fiber content (22 μm) unless otherwise stated in the text. Samples of about 150 g were collected after attaining a steady-state flow in the extruder. Generally this was done after 2 or 3 mins of extruder operation, with collection taking 1 to 2 mins.

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 (Chinnaswamy et al., 1989).

To determine the water solubility of starch-fiber extrudates, ground (40 mesh) extrudates were vacuum dried at 40°C for 2 to 3 h. About 0.25 g of the dried sample were carefully weighed out. A few drops of distilled water were added to wet the sample. Distilled water (50ml) containing a pinch of sodium azide was added to the samples. The flasks containing sample suspensions were then placed in a Tecator 1024 shaking water bath set at 25°C for overnight. The following day, each sample was carefully transferred into centrifuge bottles. The solutions were centrifuged at 5000 rpm for 30 min in a Sorvall centrifuge. After centrifugation, the supernatants were carefully transferred into bottles. Distilled water (50ml) was again used to transfer the remaining residue in the centrifuge bottle back into its original flask. The entire extraction process was then repeated. Pooled supernatants were used to test the water solubility. About 10 ml sample solutions were filtered again through Whatman #45 μ filters. The filtered solution was used for starch content determinations using phenol-sulfuric acid method (Dubois et al., 1956). The percent water solubilities of the starch-fiber extrudates were then calculated using standard procedures using 0.9 conversion factor to obtain starch equivalents.

Macromolecular Properties of Starches

Native and extruded starch samples were fractionated using gel permeation chromatography (GPC) (Chinnaswamy and Bhattacharya, 1986). Five mg (dry weight) samples were dispersed in dimethyl sulfoxide and fractionated by ascending GPC on Sepharose CL 2B column (Pharmacia Fine Chemicals, Sweden) operating at a flow rate of 30 ml/h and using distilled water containing 0.02% sodium azide as the eluent. Fractions of 5 ml were collected. From them, 2 ml aliquotes were used for determining carbohydrate content by the 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 amylose contents of the fractions were measured from the remaining 3 ml samples after

adding 0.2 ml of 2% iodine solution and reading absorbance at 630 nm against a standard corn amylose (Sigma Chemicals, St. Louis, MO). Amylose contents were calculated and expressed on a total volume fraction basis as iodine polysaccharide content. The absorption maxima (λ_{max}) of the iodine-polysaccharide complexes were also scanned and recorded automatically with a Beckman spectrophotometer (Model DU70). The void and total volumes of the gel column were determined using dextran T 2000 and KCl, respectively. For molecular weight determinations, the column was calibrated with five different dextran standards (Sigma Chemicals, St. Louis, MO) having molecular weights of 2.24 x 10^7, 2.0 x 10^6, 4.8 x 10^5, 6.6 x 10^4, and 1.10 x 10^4 daltons. Each sample was chromatographed at least in duplicate, and the mean values were reported.

Dried starch samples (3.0-10.3 mg) were weighed in differential scanning calorimetry (DSC) sample pans. Sufficient water was added with a Hamilton microsyringe to raise the samples 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 h before analysis. Thermal changes in the starch were monitored with a Perkin-Elmer DSC-2 differential scanning calorimeter interfaced with a thermal analysis data station (TADS). The samples were heated from 25 to 115°C at a rate of 10°C/min. The TADS system calculated the onset temperature (T_o) of the phase transitions, the peak gelatinization of melting temperature (T_p), the temperature of completion of melting (T_m), and the amount of enthalpy change (ΔH) required to bring about the transition. Trimyristin and tristearin standards were used to calibrate the instrument (Chinnaswamy et al., 1989).

A scanning electron microscope (SEM) (AMR 1000, Bedford, MA) was used to study the changes in product microstructures due to extrusion-cooking. Cross sections of samples were cut from the extrudate strands, mounted on SEM stubs using silver colloidal paste, and coated with gold-platinum prior to examination.

Results and Discussion

The relationships among extrusion processing variables, such as sample moisture contents, fiber concentrations and fiber length, and expansion ratios, water solubilities and macromolecular changes have been studied. Structural changes after extrusion-cooking have also been explored.

Expansion Ratio

The expansion ratios of normal corn starch, extrusion cooked with various fibers with different fiber concentrations and different sample moisture contents are given in Table 4. The relationships among the processing variables and expansion ratio, moisture contents, fiber lengths and fiber concentrations are given in Figure 1. The expansion ratio varied from 5.0 to 13.3 among the different samples. Expansion ratios increased from 12 to 13.1 and then decreased gradually to 9.0 with increasing concentration of fiber as shown in Figure 1a for samples extrusion-cooked at 14% moisture content with 110 μm fibers at different concentrations. The trend was the same for the other sets of extrudates with different fiber lengths and moisture contents. The overall maximum expansion volume was obtained with 2% fiber concentration and 14% moisture
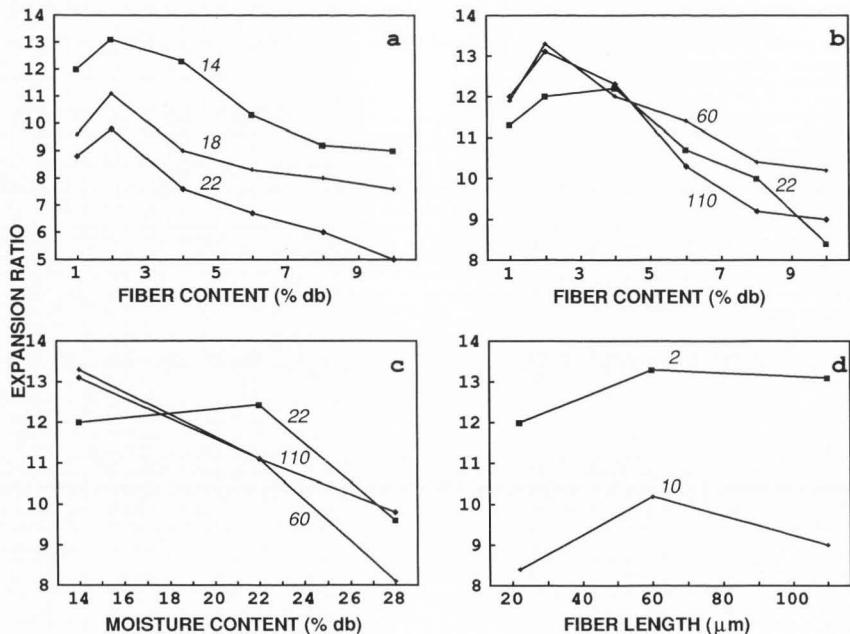
Figure 1. Relationship between expansion ratio and 110 μm fiber contents at different moisture contents (a), different fiber contents and fiber lengths at 14% (db) moisture content (b), different moisture contents and fiber lengths at 8% fiber concentration (c), and different fiber lengths at 2 and 10% fiber concentrations (d).

content among all samples tested (Figure 1b). Fiber enriched extrudates are known to give reduced expansion at high fiber concentrations (Wiedman and Strobel, 1987). Hsieh et al. (1989) reported a decrease in extrudate diameter and a general increase in extrudate length with increasing oat and wheat fiber contents. Since the fibers used in that study were crude in nature, it is difficult to compare them with our results. Effects of moisture content on the expansion ratios of 22, 60 and 110 μm fiber containing starch samples (8% db) are shown in Figure 1c. In general, expansion volume, as expected, decreased with increasing moisture contents for all fibers. Lower moisture contents and the addition of some fiber perhaps increased the molecular degradation of starch adjusting its rheological character in such a way as to yield higher expansion volume (Chinnaswamy et al., 1989; Chinnaswamy and Hanna, 1990a,b). Maga and Fapojuwo (1986) used 17% microcrystalline cellulose with corn meal to produce extruded-expanded snacks. These results are in general agreement with those of Davidson et al. (1984), Colonna and Mercier (1983), and Gomez and Aguilera (1983). When the degradation of starch exceeds a certain level, the expansion volume was reduced (Chinnaswamy and Hanna, 1990b) which was perhaps the case with over 4% fiber

addition. In Figure 1d, it can be seen that expansion increased from 8.4 and 12.0 to 10.3 and 13.3 for a fiber lengths of 22 and 60 μm, respectively, and then decreased to 9.0 and 13.1 for 110 μm fiber length at a fiber concentrations of 2 and 10%. Overall, the samples with 2% fiber and fiber length of 60 μm gave the highest expansion volume. Fiber content, fiber length, or a combination thereof may play a critical role in determining the velocity gradient of starch paste within the extruder which perhaps induces various levels of starch degradation and thus controls expansion volume. In addition, the moisture content of the samples play a critical role along with fiber contents and fiber lengths in determining overall starch molecular degradation which ultimately impacts their respective expanded volumes. Further, the expansion ratio decrease with fiber concentration may be, in part, due to the dilution of the starch content with fiber. Overall, this and other physical and chemical factors determine the expansion ratios.

Water Solubility

Water solubility properties of starch extrudates in this context normally indicate the status of starch gelatinization, rupture of granular structures along with molecular degradations and complex formations. Water solubility

Table 4. Radial expansion ratio of starch-fiber extrudates

Fiber		Moisture Content (%db)		
Length (µm)	Content (%db)	14	18	22
		Expansion Ratio		
22	1	11.3	11.0	7.0
	2	12.0	12.4	9.6
	4	12.2	9.3	9.0
	6	10.7	8.9	8.7
	8	10.0	8.4	7.6
	10	8.4	8.1	5.9
60	1	11.9	10.6	7.2
	2	13.3	11.1	8.1
	4	12.0	16.7	7.1
	6	11.4	8.9	6.4
	8	10.4	8.0	6.2
	10	10.2	7.5	5.8
110	1	12.0	9.6	8.8
	2	13.1	11.1	9.8
	4	12.3	9.0	7.6
	6	10.3	8.3	6.7
	8	9.2	8.0	6.0
	10	9.0	7.6	5.0

Table 5. Effect of fiber content on starch water solubility

Samples	Starch (%db)	Fiber (%db)	Moisture (%db)	Water Solubility (%db)
22[a]	99	1	18	5.6
	98	2		6.1
	96	4		6.8
	94	6		5.8
	92	8		6.7
	90	10		5.4
22	92	8	18	6.7
60	92	8		7.7
110	92	8		6.2
60	92	8	14	3.5
			18	7.7
			22	1.6
22	0	100	18	1.8
60	0	100	18	0.9
110	0	100	18	0.7
Native Starch	100	0	18	0.2
Extruded Starch	100	0	18	9.3

[a]All numbers indicate fiber lengths in µm.

characteristics of the various starch-fiber extrudates, including native fibers, starches and starch extrudates, are given in Table 5. Water solubility values varied from 0.2% (db) for native starch to 7.7% (db) for 8% fiber containing extrudates. Water solubility increased from 5.6% (db) for 1% (db) fiber concentration to 6.8% (db) for 4% (db) fiber concentration. It generally varied with increased fiber concentrations in the extrudate. Water solubility increased from 3.5% (db) for 14% moisture content samples to 7.7% for 18% moisture content and then decreased to 1.6% for 22% moisture extrudates for samples having 60 µm fiber. However, water solubility varied marginally from 6.7% (db) for a fiber length of 22 µm to 6.2% (db) for 110 µm fiber length. This change in water solubility may reflect the status of starch degradation and complex formation between starch and cellulose molecules which in turn reflect the shear and temperature treatments that the paste experienced during extrusion cooking. The water solubility values of starch are generally low as compared to the results reported by other authors including our previous reports. This may reflect the complexing of starch with fibers due to heat and shear induced organic reactions of carbohydrates. Björck et al. (1984b) reported that the fiber content in wheat increased slightly after extrusion cooking. However, Siljestrom et al. (1986) found no appreciable change in wheat fiber content after mild extrusion cooking.

Native starch and native fibers showed very low water solubility values. It is, however, not clear whether the water solubles had both starch and degraded fiber, only starch, or a combination thereof. This needs further study.

Scanning Electron Microscopic Examinations

Extrusion cooking is known to destroy the granular structure of starch and even cleave α (1-4) and (1-6) bonds in starch molecules under severe conditions. Fibers (cellulose) basically have (1-4) linkage of glucose polymers but with β configurations. This makes fibers totally different polymers than starch. The native forms had different average fiber lengths as seen in the micrographs (Figure 2 a, b, c). It was suspected that different fiber lengths may play a critical role in developing a velocity gradient within the extruder for starch paste which may affect the properties of both the starch and the fiber in different ways. Figures 2 d, e, and f show smooth matrices in starch-fiber extrudates. Lue et al. (1990) reported similar results. Extrusion cooking treatments destroyed the fibers' native forms. Starch extrudate properties cited elsewhere suggest heat and shear induced chemical reactions among the starch and cellulose molecules.

DSC examination of native corn starch showed an endothermic peak at 71.6 °C which disappeared after extrusion. Onset temperature (To) and melting completion temperature (Tm) for native starch were 67.5 and 82.2 °C,
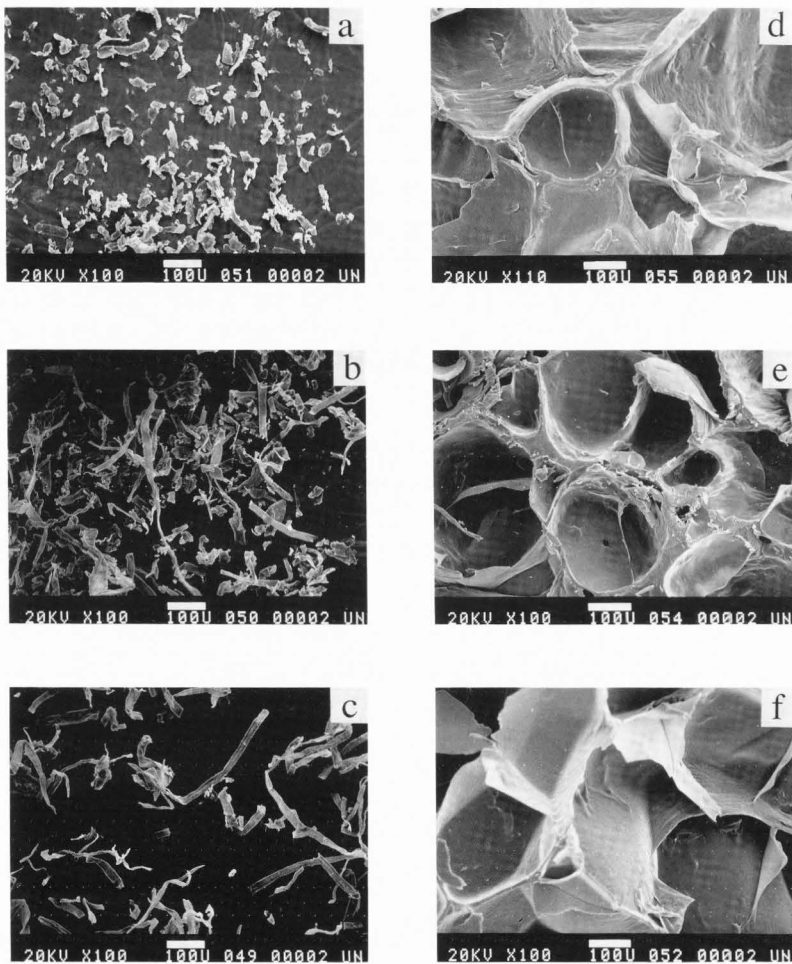
Figure 2. Scanning electron microscopic appearance of native fibers with 22 (a), 60 (b), and 110 (c) μm length and their respective extrudates d, e, and f extruded with 92% (db) starch and at 18% moisture.
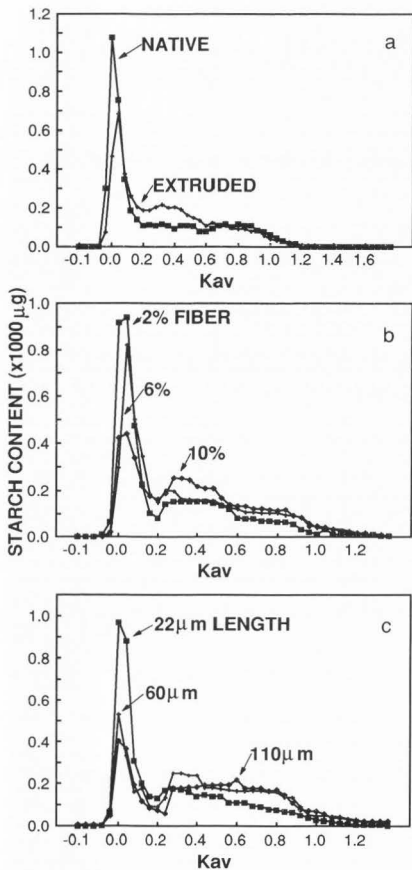
Bars = 100 μm

Figure 3. Gel permeation chromatographic fractionation pattern as measured by phenol sulfuric acid method for starch content (µg), for pure starch before and after extrusion cooking at 18% moisture (a), at different fiber contents (b), and at different fiber lengths at 8% fiber content(c).
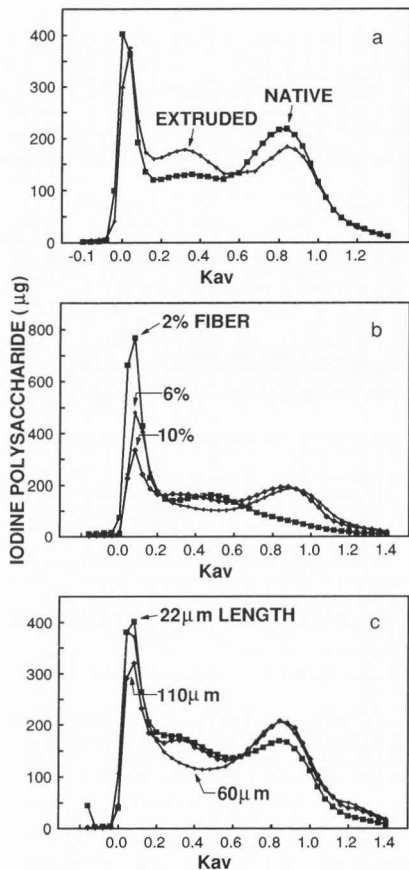

Figure 4. Gel permeation chromatographic fractionation pattern of respective samples in figure 4 as measured by iodine-starch complexing method - (a) starch before and after extrusion cooking, (b) with different fiber contents and (c) with different fiber lengths.

respectively. Extrusion cooked samples with and without fibers showed no typical gelatinization endotherms. This clearly indicated full gelatinization of the starch in the extrudates.

Molecular Properties

Previous studies (Chinnaswamy and Hanna, 1988a,

b, c, 1990a, b, c; Colonna and Mercier, 1983; Davidson et al., 1984) clearly indicate that starch undergoes degradation during extrusion cooking. Depending upon the processing conditions, the starch degradation patterns change drastically, ultimately affect expansion properties. Therefore, the status of the starch degradation in the starch-fiber

Table 6. Properties of starch fractions before and after extrusion cooking.

Fiber		Phenol-Sulfuric Acid Method (μg/5mg of starch)		Iodine Method (μg/5mg starch)		Absorption Maxima (μm)		Molecular Weight (daltons)	
Lengths μm	Content (%db)	Fraction I	Fraction II	Fraction I	Fraction II	Fraction I	Fraction II	Fraction I X10^7	Fraction II x10^6
22	8	2603.5	2396.5	3138.8	1861.2	532	538	2.6	1.69
60		1851.4	3148.7	2372.1	2627.8	--	--	2.6	2.18
110		1405.1	3594.9	2083.7	2916.3	--	--	2.6	5.95
22	2	2816.4	2396.5	2684.4	2315.6	543	575	2.6	1.69
	6	2327.5	3148.7	2511.8	2488.8	582	642	2.6	1.69
	10	1594.5	3594.9	2578.6	2421.4	573	640	2.6	1.69
Native Starch	0	3921.8	1078.3	1449.4	3550.6	576	651	3.33	1.69
Extruded Starch	0	2436.8	2563.1	1471.8	3528.2	570	641	2.6	1.69

extrudates was studied to better understand the functional property changes. Starch extrudates with different fiber contents and fiber lengths were selectively used for this analysis along with native and extruded pure starch samples as references. The samples were dispersed in DMSO and fractionated on a Sepharose CL 2B gel column. Starch fractionation on a GPC column gave two major fractions (Fractions I and II). The Fraction I corresponded to materials that were eluted between 0.0 to 0.2 kav and Fraction II corresponded to all the materials that were eluted after 0.2 kav (Figures 3 and 4). The results are summarized in Table 6. The starch fractionation patterns, as measured by phenol-sulfuric acid method and iodine complexing method, are given in Figures 3 and 4, respectively. These data clearly indicate degradation of starch after extrusion cooking with and without fiber addition. The extent of degradation varied as shown in Table 6. In Figure 3a, it can be seen that extruded pure starch had a lower fraction I content (2.9 mg) than native starch (3.9mg), while fraction II increased from 1.1 mg to 2.5 mg after extrusion cooking for the same starch sample. Addition of 22 μm fiber at a concentration of 2, 6 and 10%(db) lowered fraction I content further. Maximum starch degradation occurred when 10% fiber was added (Figure 3b). The samples with different fiber lengths showed similar starch degradation patterns. The fraction I degradation increased with increasing fiber lengths (Figure 3c).

Fraction I is normally considered to be amylopectin while Fraction II is considered to be amylose (Chinnaswamy and Hanna, 1990b). However after extrusion cooking, the degraded fraction I eluted along with fraction II. Therefore, it was not clear how much degradation occurred in fraction II. Starch extrudates with increasing fiber contents from 2, 6 and 10% showed proportional decreases in fraction I content and consequently fraction II increased (Figure 5). Similar starch degradation patterns were seen with increasing fiber lengths of 22, 60 and 110 μm. Overall, the fraction I decreased and fraction II increased for all extrudates (Figures 3 and 5). Starch fraction I molecular weight decreased from 3.33 x 10^7 Daltons for native starch to 2.6 x 10^7 Daltons for all extruded samples. Fraction II molecular weight, however, varied for samples from 1.69 x 10^5 to 5.95 x 10^5 Daltons. This change in fraction II molecular weight reflected the fraction I degraded product.

Iodine Binding Properties

Starch degradation also affected the iodine binding abilities of fractions I and II of all starches. The pattern is shown in Figure 4. The iodine binding properties of starch perhaps reflects more of its structural difference rather than its molecular weight differences. Linear amylose and/or long branches of amylopectin bind with iodine or other similar molecular systems form coils and trap iodine indicating a difference in iodine values. Thus, the pattern and the values obtained by the phenol-sulfuric acid method and iodine method will differ as the former reflects the content while the latter mostly reflects particular starch structure (linearity of molecules). Differences among the variously extruded starch samples are shown in Figure 4. Shown are decreased values for fraction I and subsequent increased values for fraction II. On close examination, it appeared, however, that there was an increased iodine binding ability for different fractions after extrusion processing. A ratio of values obtained from iodine method (starch structural differences) and phenol-sulfuric acid method (starch content) indicated a non-linear change in the pattern. The results are summarized in Table 7. Native starch had 0.36 for fraction I and 3.29 for fraction II which after extrusion processing changed to 0.60 and 1.38 respectively. Further with fiber contents and lengths it varied from 0.95 to 1.62 for fraction I and 0.67 to 0.9I for fraction II. In any case, these values are much higher than the native starch fractions. All values are expressed on a 5 mg starch basis and, therefore, are comparable. The increase in fraction I value may be due to increased release of long branched structures in the amylopectin molecules during degradation or formation of long structures due to heat and shear induced rearrangement and recombination reactions between starch and fibers or among the molecules of amylopectins and/or amylose or a combination thereof. The decreased values of fraction ratio (Table 7) do not balance exactly for I and II fractions. It appears that this is partly due to the involvement of starch in organic reactions. It could also be due to increase in the reaction rates with increased shear fields, absorption of iodine, or a combination thereof. In any case, it seems that there is a considerable number of reaction mechanisms that operate during extrusion processing in addition to merely cleaving α 1-4, 1-6 or β 1-4 chemical bonds. A detailed study is needed to understand how these macromolecular interactions affect product qualities, safety and nutritional values.
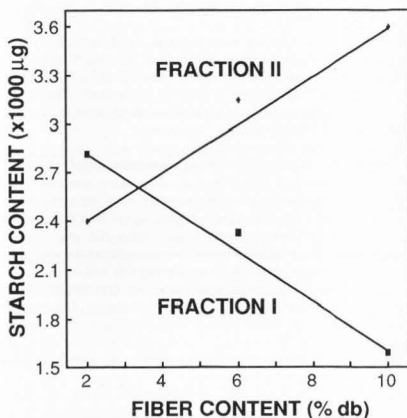
Properties of Starch-Fiber Extrudates

Figure 5. Relationship between starch contents in GPC Fraction I and II as measured by phenol-sulfuric acid method. Different fiber concentrations indicated for 22 μm fiber.

Table 7. Iodine binding abilities of GPC fractions

Sample		Fractions Ratio[a]	
		I	II
Fiber length (μm)	22	1.21	0.78
	60	1.28	0.83
	110	1.48	0.81
Fiber Content (%db)[b]	2	0.95	0.96
	6	1.08	0.79
	10	1.62	0.67
Native Starch	--	0.36	3.29
Extruded Starch	--	0.60	1.38

[a]Ratio of Iodine value to starch content value of fractions on a uniform total 5 mg starch basis
[b]Fiber length 22 μm

Conclusions

Generally it appears that the fiber concentration and/or fiber length affect the velocity gradient (shear flow) within the extruder barrel which influence the starch molecular degradation. Fraction I degradation as seen with GPC analyses increased with increasing fiber concentration and fiber lengths. Starch degradation patterns were generally reflected in extrudate expansion, water solubility and iodine binding properties.

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Discussion with Reviews

I.C. Pang: A vibratory feeder was used in this study. Was
stratification of feed a concern because of the differences
in the particle size between starch and fibers?
Authors: No. Particle size was not a concern. Feeding
samples into the extruder was done routinely using vibrato-
ry feeder to keep all variables constant.

J. Tovar: Although quantitatively important, cellulose is not
the only component of dietary fiber. Some indigestible non-
starch polysaccharides, such as pectin and beta-glucans,
are water soluble and have physicochemical properties
different from those of cellulose. Why did you select
cellulose for the study? Have you investigated the interac-
tion of starch and soluble fibers during extrusion?
Authors: Fiber is a complex system. Recognizing the fact
that it will be very difficult to interpret the data if one uses
regular fiber, we used pure cellulose fibers to simplify
interpretation of the results. Characterization of interac-
tions of starch with soluble fibers during extrusion cooking
needs further fundamental study.

P. Colonna: The residence time distribution is also an
important factor, which must be taken into account. What
would be the influence of the introduction of particles and
solid fibers on the running conditions of such an extruder?
Authors: Residence time distribution (RTD) within the
extruder changes for any change in sample moisture
content and composition, etc. along with other extruder
variables. Particle sizes of different fibers may also have
similar influence on the RTD, but our study does not have
data to report on it as our aims of this paper were on
degradation of starch with respect to cellulose fiber lengths
and concentrations. Nevertheless, it is an important factor
to be considered carefully for further studies.

D.J. Gallant: My own experience in extrusion-cooking has
shown that the less the water content of samples, the more
the shearing strength. In your case, starch and fibers
compete for water. Since the absorption capacity is two
times more for sample 110 (950 g / 100 g) than sample 22
(420 g / 100 g), corn starch granules are less damp in the
first case than in the second one. Consequently, starch
degradation is higher for samples with longer fibers or with
higher concentration of fibers. Does your experience in this
field agree with my observation? However, it is difficult to
understand why the absorption capacity is different be-
tween samples, unless they are different in their hemicellu-
lose composition or content. That is not shown through
the processing described for fibers production and particu-
larly in Table 3. What is your opinion on that?
Authors: Shear force that operates within the extruder
changes with fiber content and/or length. Due to this the
stress placed on the starch molecules changes, which has
direct impact on starch degradation. We have used
manufacturer's data with regard to fiber water absorption
irrespective of fiber composition as it was stated in that
manner by the manufacturer.

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Properties of Starch-Fiber Extrudates

G. Galloway: Are the water solubility and water absorption properties of starches, fibers, and their degraded and complexed products related to each other?
Authors: Water solubilities and water absorption properties are not always linked. However, in this case it may be speculated that more water absorbing fiber fractions are likely to be dissolved more in water when degraded.

D.J. Gallant: How did you measure the average lengths of fibers which seem very homogenous at 110 micrometers but somewhat heterogenous at 22 and particularly much more heterogeneous at 60? Regarding to the bar on each micrograph, average lengths seem much higher than the lengths you have indicated. Could you explain that?
Authors: The fiber lengths were as reported by the manufacturer. Our sample sizes used for SEM were limited which does not represent the average value very well. Therefore, manufacturers value seem to be most appropriate.

D.J. Gallant: Did you take the micrographs (Figs. 2d-f) at the same level of each extrudate strand? Was it at the center or peripheral part of the strands?
Authors: The purpose of our micrographs was to see the fate of fiber length and sizes. Therefore the figures do not represent the same or similar places in the extrudate. After searching various places in the extrudate strands for fiber, a place is selected randomly to make a picture.

D.J. Gallant: In "Results-SEM examinations" you wrote the "when SEM and DSC are put together, they indicate rupture of starch granules, fiber structures and formation of smooth structure". Regarding Figs. 2d-f it is true that we can see some differences, but only in the texture of the strands (sample 110 being more expanded and showing thinner walls than samples 22 and 60). However, it is impossible to say anything on the distribution of the components, how they combined, how the fibers are dispersed, and what is the real behaviour of the starch granules. Concerning the appearance and distribution of the fibers in the starch gel (a part of the starch granules could be only swollen and it is not proved that all starch granules are gelatinized), information would be only given by further cytochemical studies (light microscopy and TEM). Without such studies how could it be possible to assert that "fibers were thoroughly mixed with starch in a nondistinguishable manner? Did you perform such studies?
Authors: SEM magnification was kept constant for pure fibers and extrudates so that they could be compared. We have not performed any such studies to ascertain thorough mixing of fibers and starches..

I. Björck: Data on iodine binding ability of various starch fractions after extrusion might be interpreted in terms of "polymerization". Transglycosidation reactions may take place at low-moist heat treatment of starch and may lead to formation of non-starch linkages of beta-type. Was this possibility considered?
Authors: This is a very good question. Transglycosidation reactions of starch leading to the formation of non-starch linkages of beta-type is very possible.

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