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Extrusion-Induced Changes to the Chemical Profile and Viscosity Generating Properties of Citrus Fiber

R. J. Redgwell, D. Curti, F. Robin,* L. Donato, and N. Pineau

Nestlé Research Centre, Vers-Chez-Les-Blanc,1000 Lausanne 26, Switzerland

ABSTRACT: Each of 8 variants in extrusion conditions was applied to a commercially available citrus fiber. Extrusion under conditions where the specific mechanical energy (SME) exceeded 400 kJ·kg^{-1} was able to solubilize up to 30% of the fibers. Where the SME was ∼200 kJ·kg^{-1} the degree of fiber solubilization was between 8 and 12%. All extruded fibers showed a loss of water-retaining capacity compared to the reference fiber, and this was attributed to the disruption of the integrated cell wall structure during the extrusion process. Nevertheless, within the 8 extruded variants there was a wide range of viscosity generating capacity which depended on the level of SME to which the fibers were subjected. The SME also had a pronounced effect on the nature of the solubilized fibers in terms of both their monosaccharide composition and their molecular weight profile. Both pectic and hemicellulosic polysaccharides were solubilized. It is concluded that extrusion has promise as a physical process for manipulating both the technological functionality and the health promoting properties of dietary fibers.

KEYWORDS: extrusion, citrus fiber, cell walls, polysaccharides, soluble polysaccharides, pectic polysaccharides, viscosity

INTRODUCTION

The high profile of dietary fiber (DF) as an important part of a healthy diet has put pressure on food companies to incorporate it in their products. There are several obstacles to achieving this aim. The most pressing problem has been, and remains, the maintenance of a desirable sensory appeal in the fiber-enriched products. If a fiber is to be added to products, it would be preferable to use a plant cell wall derived fiber from fruit or vegetables as this is already perceived by the public as the major and natural source of dietary fiber in a normal diet. Research has demonstrated the potential that whole plant cell walls have as agents for texture modulation in processed food products.[1−4] However, these fibers are for the most part insoluble and can confer a gritty, sandy or some other texturally nonappealing in-mouth sensation. Many fibers derived from a range of fruit and vegetables which are commercially available possess just such negative characteristics. Fortunately, recent advances in the processing of a citrus derived fiber have provided a matrix which to a large extent overcomes these negative attributes.

The citrus fiber used in this study can be dispersed in water to give a smooth, high viscosity gel. While this has advantages for some applications, for others the high viscosity means that insufficient amounts of fiber can be added to make a valid claim for DF content. For this reason it was proposed that experiments be conducted to investigate the effect of extrusion on the physical and chemical properties of the citrus fiber. Published work[5−10] with sugar beet pulp, citrus peels, pea hulls or wheat bran indicated that by altering the conditions of extrusion the physicochemical properties of fibers can be varied. Following extrusion the latter work reported an increase in the solubilization of some cell wall polymers, in particular the pectic polysaccharides. An increase in the soluble polymer fraction may have definite advantages in terms of health benefits (e.g., prebiotic activity, serum cholesterol lowering). Extrusion may also have additional advantages. As a general process it was reported to denature undesirable enzymes, to inactivate some antinutritional factors (trypsin inhibitors, tannins and phytates) and to sterilize the finished product.[11]

The current study focuses on the extrusion of a commercially available citrus fiber already in use as a hydrocolloid in processed food. The fiber has a high water-retaining capacity related to the structural integrity of the cell wall particles which are able to absorb and entrap water. It was anticipated that extrusion may degrade this structure and lower the viscosity generating properties of the fiber to a degree commensurate with the specific mechanical energy (SME) of the extrusion process. This would allow the final viscosity generating properties of the fibers to be tailored to the required application. Increased amounts of a low viscosity generating fiber could be added to a product, permitting a valid dietary fiber claim to be made. If as expected extrusion of the citrus fiber was accompanied by an increase in the solubilization of cell wall polymers, additional health benefits may accrue.

The present report details the results of the chemical and viscometric properties of citrus fiber which has been subjected to a range of extrusion protocols designed to transform the hydrated fiber matrix across a broad spectrum of its texture modulating properties.

MATERIALS AND METHODS

Plant Material. Dried and powdered citrus fiber was obtained from Herbafood Ingredients (GmbH), in Werder, Germany (Herbacel AQ plus citrus fiber-N). The citrus fiber is basically a cell wall material derived from citrus peel and is being used as a food component in a range of retail products. In the present study the unextruded citrus fiber will be referred to as the reference. It consisted of 88−93% dietary fiber and 2−5% ash.

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Table 1. Extruder Settings for Each of the 8 Extruded Fiber Samples

extruded sample	temp (°C)	screw speed rpm	moisture (%)	SME[a] (kJ·kg^{-1})
EXF1	80	400	30	406
EXF2	80	400	50	205
EXF3	80	600	30	479
EXF4	80	600	50	248
EXF5	120	400	30	365
EXF6	120	400	50	201
EXF7	120	600	30	411
EXF8	120	600	50	255

[a] Specific mechanical energy.

Extrusion. The extrusion experiments were performed on a corotating double screw extruder (Evolum 25, Clextral Group, Firminy, France), consisting of six independent zones of controlled temperature in the barrel. The length to diameter (L/D) ratio was 24 (D = 25 mm). The screw configuration consisted of conveying and mixing elements.

A die consisting of four cylindrical tubes of 3.2 mm diameter and 6.4 mm length was used to generate extruded cylinders of fiber. The gap between the extruder screw end and front plate was set at 2.5 mm. The extruder was operated with a constant feed rate of 10 kg·h^{-1}. The temperatures in the four first barrel sections were set at room temperature, 30, 40, and 60 °C, respectively. For the last barrel section temperature, screw speed and moisture content in the extruder were adjusted according to an experimental plan design (Table 1). Fibers were introduced into the extruder using a corotating twin screw K-Tron feeder (K-Tron Co, Switzerland). Tap water at ambient temperature (20 ± 2 °C) was injected at a controlled rate with a syringe pump (Teledyne ISCO 500D, Isco, Inc., USA) at 5D distance. The specific mechanical energy (SME) was calculated as follows:

$$SME = \frac{\frac{n_{act}}{n_{max}} \times M - \frac{n_{act}}{n_{max}} \times M_{unload}}{m_{total}} \times P_{max}$$

where M and M_{unload} are the motor torque under load and without load, n_{act} and n_{max} are the actual and maximum screw speed, m_{total} is the mass flow rate and P_{max} is the maximum engine power, which is 27 kW. After stable conditions were established, cylinders of extrudates (~2−3 mm diameter) in pellet form were collected and dried in an air oven at 60 °C for 16 h. Samples of the pellets were frozen in liquid nitrogen and subjected to milling in a cryomill to yield a fine powder. This provided a more convenient form of each extruded fiber for carrying out the chemical analysis.

Design. Data were generated according to a full factorial experimental design to investigate the effect of 3 parameters (two levels each): temperature (80 °C, 120 °C), screw speed (400 rpm, 600 rpm) and moisture (30% and 50%). Eight samples (EXF1−8) were produced according to the design. The two main outcome variables were the SME and fiber solubility. Table 1 summarizes the level of the parameters for each sample and the outcome variable results. The data analysis consists of an analysis of variance (ANOVA) to identify which of the three parameters was responsible for the main changes in the values of the output variables. The least significant difference (LSD) was computed from the ANOVA results for each variable. The LSD is the minimum difference required to consider two mean values as significantly different.

Chemical Methods. Powdered fibers were analyzed for monosaccharide composition following hydrolysis in either 72% H_2SO_4 for 3 h at room temperature and then in 1 M H_2SO_4 for 2 h at 110 °C or 2 M TFA at 110 °C for 1 h. Monosaccharide analysis was carried out by GLC of the alditol acetates.[12] Uronic acid was determined quantitatively by the Blumenkrantz method.[13]

High-Performance Liquid Chromatography. Molecular weight analyses were made with an Agilent 1200 series HPLC instrument equipped with a TSKgel G3000PWXL column (7.8 mm x 30 cm) and a GMPWXL column (7.8 mm × 30 cm) in series with a PWXL guard column (6 mm × 4.4 cm) (Tosco Bioscience). The system was fed with 0.1 M sodium nitrate (sodium azide, 0.02%) at 0.5 mL/min. Signals were measured by refractive index. Samples and pullulan standards (Fluka standard set mp 342−710000 No. 96351) were dissolved in eluant at 5 mg/mL and 3 mg/mL, respectively. They were filtered on nylon syringe filters (0.13 mm diameter, 0.2 μm), before injection (25 μL). Signals were recorded and treated with ChemStation for LC systems (B.04.01 SP1).

Microscopy. Light microscopy was performed on a Zeiss Axioplan 2 equipped with a camera (Axiocam MRc5). A 10× objective was used. A drop of the suspended fiber was mixed with a drop of 1% toluidine blue for visualization.

Determination of Degree of Solubilization. The degree of extrusion induced solubilization of the citrus fibers was determined by 2 separate procedures.

First, a sample of the extruded fiber (0.5−1 g) was suspended in 100 mL of water, with continuous stirring for 2 h at ambient temperature. The suspension was centrifuged at 7000g for 15 min and the supernatant containing the soluble fibers and the residue representing the insoluble fibers was separated and recovered after freeze-drying. Each sample was done in triplicate.

The second procedure used the Megazyme total dietary fiber assay based on AOAC Method 991.43. In summary, the sample to be tested was incubated at 95−100 °C for 35 min in the presence of α-amylase to break down starch and then for a further 30 min at 60 °C in the presence of a protease. The procedure was conducted in a Mes-Tris-buffer at pH 8.2. The fiber suspension was then filtered to separate the insoluble and soluble fractions and the soluble fibers were recovered following precipitation with ethyl alcohol.

Fractionation of Fibers. To determine which of the cell wall polysaccharides had been most affected by the extrusion process, selected samples were fractionated by a procedure designed to distinguish the different types of polysaccharides within the cell wall.[14]

The reference fiber and two extruded samples EXF2 and EXF3 (2 extremes of SME) were subjected to sequential extraction in water, CDTA (*trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid), 0.05 M sodium carbonate, and 4 M KOH. Each fiber (1 g) was suspended in 150 mL of water and stirred at room temperature for 2 h. After centrifugation at 7000g the supernatant was decanted and the residue resuspended in 150 mL of 0.05 M CDTA, pH 6.5 for 6 h at ambient temperature. After centrifugation the residue was resuspended in 150 mL of 0.05 M sodium carbonate containing 20 mM sodium borohydride and stirred overnight at 4 °C and then for 2 h at room temperature. The recovered supernatant was adjusted to pH 4−5 with acetic acid while keeping cool in an ice bath. The residue was extracted further in 4 M KOH containing 20 mM sodium borohydride, and the recovered supernatant was adjusted to pH 4−5 with acetic acid while being kept in an ice bath. All supernatants were dialyzed for several days in a membrane with a molecular weight cutoff of 3.5 kDa.

Rheological Measurements. After extrusion in 8 sets of conditions the 8 variants (EXF1−8) were used in pellet form for all experiments. Suspensions (150 mL) were prepared at different concentrations varying from 5 to 1% w/w for variants EXF1/3/5/7 and from 3 to 1% for variants EXF2/4/6/8 and for the reference. The upper limit was defined as the highest concentration at which the suspension was pourable. Powder was progressively added to Milli-Q water and stirred for 1 h at room temperature. The suspensions were then transferred to a cold room at 4 °C and stirred overnight to permit

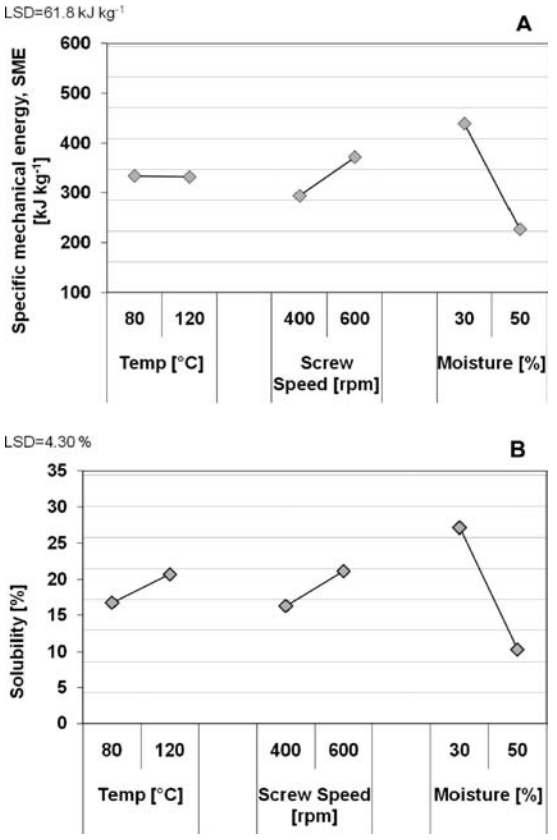

Figure 1. Analysis of variables for SME (A) and fiber solubility (B) (the distance between two grid lines indicates the least significant difference).

complete hydration. Before measurement, samples were equilibrated for at least 1 h at room temperature.

Rheological measurements of fiber suspensions were performed with a strain controlled remoter (ARES, TA Instruments) equipped with a Couette device consisting of two concentric cylinders of 33.96 and 31.95 mm. The temperature was controlled by a water bath at 25 °C. The suspensions were stirred with a magnetic stirrer for 15 s, and then 9 mL of the suspension was transferred to the rheometer. Flow behavior was measured consisting of a preshear rate for 5 sec at 100 s^{-1}. Then an increasing step shear rate ramp from 0.01 s^{-1} to 1 s^{-1} for 2 min and 1 s^{-1} to 100 s^{-1} for 5 min followed by a decreasing shear rate step ramp from 300 to 0.02 s^{-1} in 5 min.

RESULTS

Extrusion. Temperature, screw speed and moisture content were the 3 variables designed to manipulate the SME (specific mechanical energy) of the extrusion process. As shown (Table 1), this allowed the fiber to be extruded over a range of SME between ~200 and 480 kJ·kg^{-1}. It was not possible to lower the water content below 30% during extrusion as this led to blockage of the screw. Some light browning (indicative of some Mailllard reactions) of the citrus fiber was observed following extrusion, and this was more pronounced in the samples extruded at high SME.

Figure 1 shows the analysis of the variables for SME and fiber solubility. The LSD (least significant difference) is the minimum difference required between two values to be declared as significantly different. If the difference between two mean values is greater than LSD, the difference is significant. Thus, for SME moisture has the most pronounced effect (moving from 30% moisture to 50% induced a decrease of the SME by about 200 kJ·kg^{-1}). Screw speed is also significant but to a lesser extent than moisture content, and temperature has almost no impact on SME. For fiber solubility a similar relationship is demonstrated for moisture, but screw speed and temperature are hardly significant factors.

Table 2. Monosaccharide Composition of Citrus Fibers Following Extrusion

	monosaccharide composition (mol %)							
sample	rha	fuc	ara	xyl	man	gal	glc	uronic
original	0.5	1.0	2.8	9.5	6.6	7.1	52.5	19.7
EXF1	0.4	1.0	2.8	9.9	6.5	7.1	52.2	20.0
EXF2	0.4	1.0	2.9	9.7	6.6	7.1	52.3	19.3
EXF3	0.4	1.0	2.8	9.8	6.5	7.1	52.9	19.3
EXF4	0.4	1.0	2.8	9.6	6.5	7.2	52.5	19.6
EXF5	0.4	1.0	2.8	9.8	6.6	7.1	52.9	19.3
EXF6	0.4	1.0	2.8	9.8	6.6	7.2	52.4	19.6
EXF7	0.5	1.0	2.8	9.9	6.6	7.1	52.1	20.0
EXF8	0.6	1.0	2.8	9.3	6.6	7.1	52.4	20.2

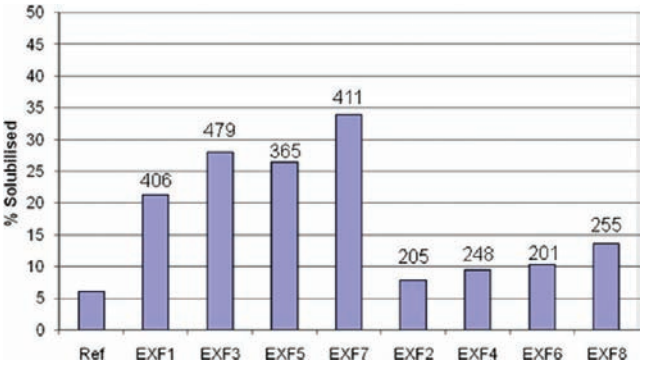

Figure 2. Percentage of extrusion-induced solubilization in water-extracted fibers. EXF1−EXF8 represent fiber samples each extruded at the specific mechanical energy (SME) indicated above each bar (detailed conditions Table 1). Data are mean values of three determinations (SE < 0.2 for all samples).

Samples of the reference citrus fiber and each of the extruded fibers were subjected to compositional analysis (Table 2). There was no significant change in the relative proportions of the monosaccharides. This indicated that no destruction (as opposed to degradation which can take the form of a molecular weight decrease) of the polysaccharides had occurred during extrusion.

Solubilization of Fibers. *Water Extraction.* The amount of fiber solubilized in the extruded samples by a simple water extraction is shown in Figure 2. In the reference sample ~6% w/w of the citrus fiber was solubilized by this procedure. Following extrusion there was a dramatic increase in the percentage of soluble fibers in the extruded samples. There was a good correlation (r^2 = 0.92) between the SME and the degree of solubilization. Thus, samples 1, 3, 5, and 7 which had SMEs of 406, 479, 365, and 411 kJ·kg^{-1} respectively, showed degrees of solubilization of 23, 33, 30 and 36% respectively. In contrast the extruded samples 2, 4, 6, and 8, which were extruded at SMEs of 205, 248, 201, and 255 kJ·kg^{-1} respectively, possessed

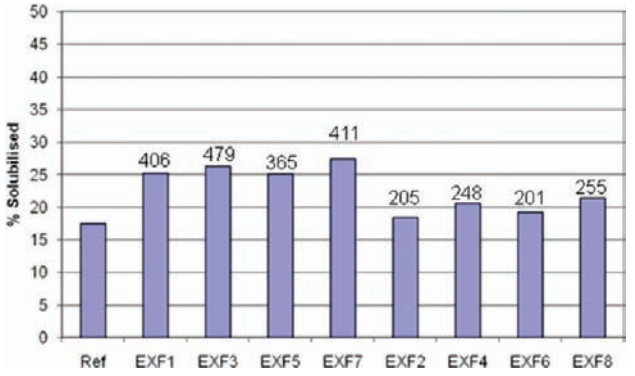

Figure 3. Percentage of extrusion-induced solubilization in AOAC-extracted fibers. EXF1−EXF8 represent fiber samples each extruded at the specific mechanical energy (SME) indicated above each bar (detailed conditions Table 1). Data are mean values of three determinations (SE < 0.2 for all samples).

Table 3. Monosaccharide Composition of Soluble Fibers Isolated by the AOAC DF Determination Method

	monosaccharide composition (μg/mg)								
sample	rha	fuc	ara	xyl	man	gal	glc	uronic	total
ref	16.0	1.5	37.2	5.5	14.7	51.5	5.1	619	751
EXF1	8.6	3.8	18.8	33.6	51.5	86.0	51.6	444	698
EXF3	8.4	4.8	14.6	48,9	58.6	95.1	75.1	417	723
EXF5	9.3	4.4	16.7	42.3	55.3	94.3	63.7	416	702
EXF7	7.8	5.8	13.1	56.7	62.6	106.4	93.5	317	663
EXF2	7.6	1.5	21.9	11.8	22.5	46.7	15.2	546	673
EXF4	9.0	1.9	25.6	14.7	28.9	58.9	21.6	506	667
EXF6	8.8	2.2	26.1	17.5	33.3	57.9	24.7	530	701
EXF8	8.7	2.4	25.9	21.5	37.0	59.0	29.3	590	774

degrees of solubilization between 8.0 and 13.7%. Thus, extrusion at an SME above 365 kJ·kg^{-1} was able to bring about nearly a 6-fold increase in the water-soluble content of the citrus fiber. The increase in solubility of citrus fibers with SME is consistent with previous works performed on other types of dietary fiber.[5−7,9]

AOAC Method. When providing information on the fiber content of products the food industry uses only validated and approved procedures for determining the proportions of insoluble and soluble DF. The second procedure for soluble fiber determination therefore used the AOAC method 991.43. The results of this method when applied to the extruded fibers are shown in Figure 3.

The most obvious difference is the marked increase in the soluble fiber content of the reference citrus fiber determined by the AOAC method (18%) compared to the water extraction (6%). In addition, although the soluble fiber content of the extruded fibers followed the same pattern as for the water extracted samples (i.e., a high SME, resulted in a greater degree of solubilization), the magnitude of the difference was much less marked. This was because the AOAC method solubilized s ignificantly more of the fibers in the reference fiber and samples 2, 4, 6, and 8, which were extruded at low SME. The AOAC method incubates the fibers at high temperatures in an alkaline buffer. Slightly alkaline conditions are known to favor pectin

Table 4. Monosaccharide Composition of Soluble Fibers Isolated by Water Extraction at Ambient Temperature

	monosaccharide composition (μg/mg)								
sample	rha	fuc	ara	xyl	man	gal	glc	uronic	total
ref	12.0	3.4	66.0	101.0	21.4	109.5	26.4	505	845
EXF1	8.9	8.9	47.1	56.8	82.1	116.7	71.6	452	844
EXF3	6.8	11.1	48.1	68.2	76.8	116.4	71.0	448	846
EXF5	11.8	9.7	42.9	58.4	75.8	114.6	79.8	479	872
EXF7	10.3	10.0	38.4	68.7	70.8	103.2	83.0	427	811
EXF2	9.1	4.3	50.8	69.8	55.9	83.4	58.6	519	851
EXF4	8.7	5.1	46.6	69.3	67.0	90.0	65.6	442	795
EXF6	8.7	5.2	43.4	64.2	69.0	84.5	63.9	442	781
EXF8	9.7	9.4	45.6	66.0	80.5	98.5	74.6	436	820

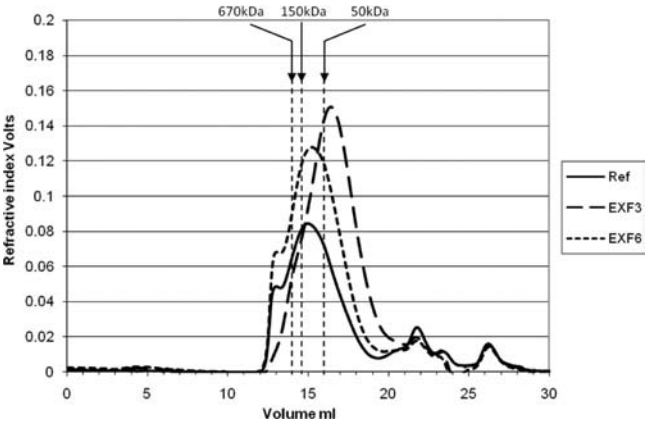

Figure 4. HPLC molecular weight profiles of solubilized fiber fractions from reference fiber and fiber (EXF3) extruded at high SME (479 kJ·kg^{-1}) and fiber (EXF6) extruded at low SME (201 kJ·kg^{-1}).

solubilization. In addition, such conditions are likely to lead to β-elimination of the pectic polysaccharides, resulting in depolymerization of the polymers and their solubilization.

Composition of Soluble Fibers. The soluble fibers in both the AOAC- and water-solubilized fractions were subjected to compositional analysis (Tables 3 and 4).

There were several differences in the composition of the soluble fibers isolated by the different procedures. The water-soluble fiber fraction from the reference fiber contained 20 times the xylose and nearly twice the galactose and arabinose content of the soluble fiber fraction recovered from the AOAC procedure. Since the AOAC method would have been expected to solubilize all the fibers solubilized by the water extraction, it appears that some may have been lost during the alcohol precipitation step. This is most likely to have occurred as a result of some low molecular weight polymers not being precipitated during the alcohol precipitation step.

The increased amounts of extrusion-induced soluble citrus fiber contained high levels of uronic acid (indicative of pectic polysaccharides). Thus, considerable amounts of pectic polysaccharides were solubilized by the extrusion process. In addition there was a pronounced increase in the mannose and glucose content of the soluble fibers, accentuated when the extrusion was done at a high SME (EXF1, -3, -5, and -7). These sugars are located in the hemicellulose polymers of the cell wall which in

Table 5. Principal Monosaccharide Distribution among Hemicellulosic and Pectic Polymers Obtained by Sequential Extraction of Extruded Citrus Fibers

		fiber (mg/g)				
		hemicellulose		pectin		
fraction	% fiber	glc	man	gal	ara	uronic acid
water						
ref	4.9	1.1	0.8	4.4	2.5	22.5
EXF2	6.8	4.3	4.1	6.0	3.3	32.0
EXF3	26.6	25.2	22.4	33.3	11.0	128.7
CDTA						
ref	11.2	0.8	0.6	3.5	2.5	57.8
EXF2	12.2	1.4	1.4	3.9	2.6	54.8
EXF3	8.8	3.5	2.7	3.7	1.2	22.3
Na_2CO_3						
ref	7.7	0.1	0.1	4.7	2.1	34.6
EXF2	6.6	0.2	0.1	4.9	2.0	27.8
EXF3	3.2	0.5	0.2	1.2	0.5	5.2
KOH						
ref	17.8	38.94	17.97	14.5	3.9	8.6
EXF2	17.5	35.49	18.71	13.08	3.70	8.41
EXF3	12.9	28.00	10.74	10.14	2.79	7.43
residue						
ref	58.3	305.7	26.09	25.68	5.54	32.85
EXF2	56.8	323.1	22.19	25.24	5.45	32.90
EXF3	48.3	308.2	12.34	8.73	0.95	3.10

part are hydrogen bonded to the cellulose fibrils. They are insoluble unless strong alkali is used as an extractant. Their solubilization indicates that degradation of these polymers, or much less likely, the cellulose fibrils, has occurred.

Molecular Weight Changes. The molecular weight and size distribution of the soluble fractions from the AOAC extraction procedure were determined using high performance size exclusion chromatography, coupled with multiangle laser light scattering.

Figure 4 shows the results for the soluble fraction from the reference, EXF3, and EXF6, which represent extruded fiber under conditions of high and low SME respectively. The reference and EXF6 showed almost identical profiles consisting of a major peak coinciding with dextran standards of 150 kDa. However there was also a shoulder peak which was greater than 670 kDa. EXF3 showed a marked decrease in molecular weight illustrated by the fact that the peak appeared in a position to the right of the dextran standard of 50 kDa. The high molecular weight shoulder observed in the reference and EXF6 samples had disappeared.

Although not shown in Figure 4, the profiles for EXF1, -5, and -7 (high SME) were comparable to those of EXF3 and those of samples 2, 4, and 8 (low SME) to those of EXF6.

Fractionation of Fibers. The reference fiber and extruded sample EXF2 and EXF3 fibers were subjected to a sequential chemical fractionation which allowed the cell wall polysaccharides to be separated into 4 groups. Following a water extraction the residual material was extracted with 0.05 M CDTA, 0.05 M Na_2CO_3 and 4 M KOH. CDTA is a strong chelator and solubilizes the middle lamella pectin. This group of

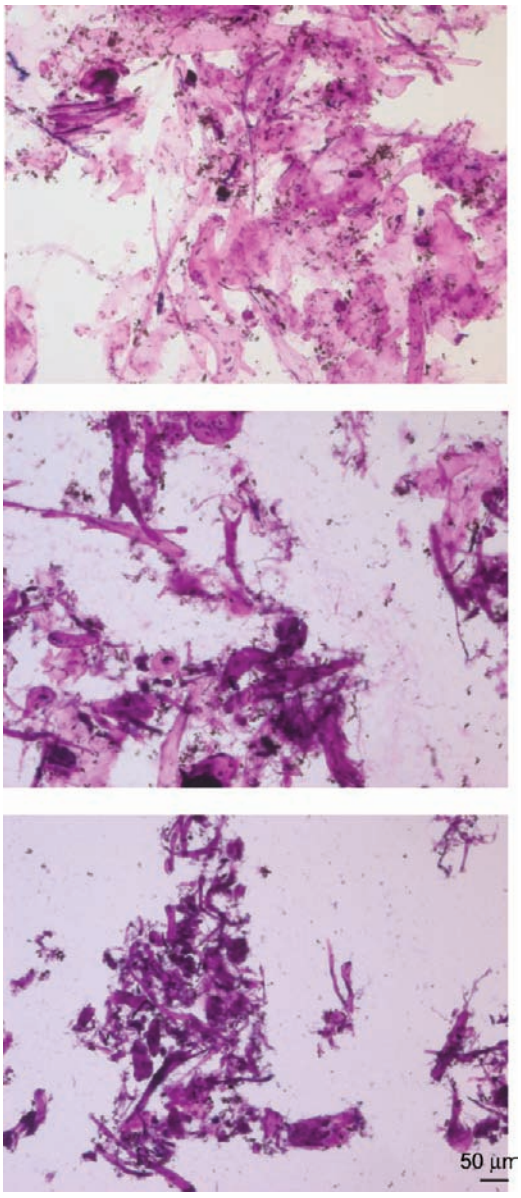

Figure 5. Light microscopy of citrus fibers stained with toluidine blue. Top: Reference fiber. Middle: EXF2, fiber extruded at low SME ($205\ kJ \cdot kg^{-1}$). Bottom: EXF 3, fiber extruded at high SME ($479\ kJ \cdot kg^{-1}$).

polysaccharides are normally mostly homogeneous galacturonans. Sodium carbonate is used to solubilize the primary cell wall pectic polymers which normally carry more neutral side chain sugars than the middle lamella pectin. Finally 4 M KOH is used to break hydrogen bonds and solubilize the hemicellulosic polymers such as xyloglucan, galactoglucomannans and xylans.

By analyzing the amount and composition of each of these fractions it was possible to determine to what degree they contributed to the extrusion-induced solubilization of the cell wall polysaccharides.

For simplicity we have summarized the results for selected monosaccharides which are largely representative of the hemicellulosic (glucose, mannose) and pectic (uronic, galactose, arabinose) polysaccharides (Table 5).

Each of the fractions in the citrus cell wall contributed to the increase in the percentage of the soluble fraction during

extrusion. The Na_2CO_3 and residue fractions showed the greatest loss in uronic acid, indicative of pectic polysaccharides. The EXF2 sample which was extruded at a low SME showed only small changes in its polysaccharide profile for the pectic polymers among the different fractions. However, it was noticeable that the increase in the concentration of glucose and mannose in the water fraction of the EXF2 sample was 4−5-fold that observed for the monosaccharides derived from the pectic polymers. This supports the idea that the hemicelluloses even under relatively mild conditions of extrusion are being degraded into smaller molecular weight fragments which are not able to hydrogen bond to the cellulose fibrils.

Under conditions of high SME, as existed in the EXF3 sample, moderate amounts of the mannose and glucose of the hemicellulose fractions are solubilized. It is possible that the increase in glucose in the water fraction is cellulose derived. However, even in the EXF3 sample there is no indication that the glucose content of the residue (mainly cellulose) has decreased enough to account for the increased glucose content of the water fraction.

Microscopic and Macroscopic Characteristics. When the reference citrus fiber was suspended in water, it rapidly entrapped and absorbed the water within its macrocellular structure. A 1−2% suspension thickened within seconds due to the high water binding properties of the cellular matrix. In contrast, the extruded samples showed little capacity to entrap water. It took 15−30 min before the fibers hydrated to the extent that viscosity generation became apparent. We postulate that the viscosity generating properties of the reference fiber rely on two separate processes. First, the more integrated structure of the reference fiber with its intercellular spaces and channels is mainly responsible for the initial uptake of water that gives rise to the rapid increase in viscosity of the dispersion. This is reinforced by hydration of individual cell wall polysaccharides as the viscosity continues to increase over time. However, following extrusion the extended structure of the reference fiber is disrupted to a greater or lesser extent (depending on the SME of extrusion). The viscosity generation therefore must rely more on the slow hydration of individual cell wall particles and their component polysaccharides. Light microscopy (Figure 5) showed the decreasing levels of integrated cell walls as the SME of extrusion increased.

Depending on the SME of extrusion for the same concentration of fibers it, was possible to generate either a fluid dispersion or a solid gel (Figure 6).

Light microscopy showed not only the breakup of the cellular particulates but also an increase in the color density of the stain in the smaller particles of extruded samples. This is evidence that the material itself is denser, a fact supported by phase separation experiments where the amount of free liquid above a uniform suspension of each of the extruded samples was measured after 10 min. Those samples extruded at the higher SME required a greater concentration of fiber particles if phase separation was to be avoided over a period of 10 min (data not shown).

Viscometry. Figure 7 shows the flow curves determined in distilled water for the reference and EXF3 and EXF4 extruded samples as a function of shear rate. The extruded material showed a much lower viscosity than the reference material. The Newtonian plateau at low shear rate is not apparent for the extruded material, which can suggest that the extruded system consists of a suspension of swollen particles rather than a polymer solution. When the soluble hydrocolloid xanthan gum was extruded it showed the opposite trend.[15] The extruded gum gave a higher viscosity when dissolved in water and also was more easily and rapidly dissolved.

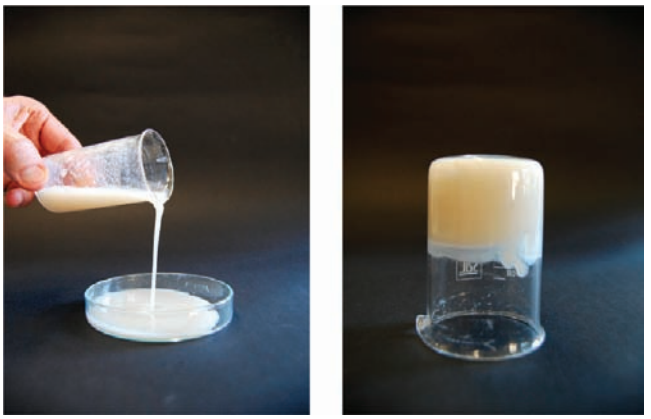

Figure 6. Demonstration of viscosity difference between 6% (w/v) suspensions of fibers extruded at different SME. Left: EXF3, fiber extruded at high SME (479 $kJ \cdot kg^{-1}$). Right: EXF2, fiber extruded at low SME (205 $kJ \cdot kg^{-1}$).

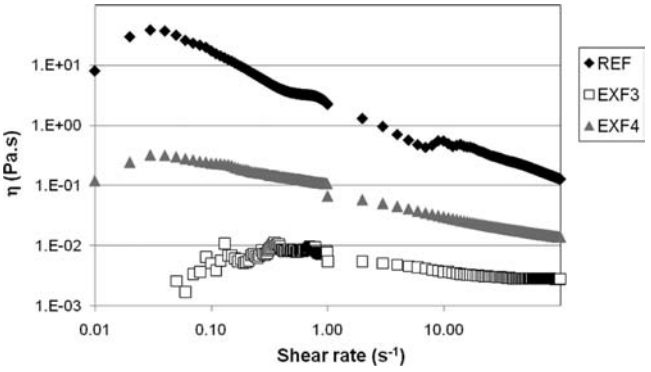

Figure 7. Shear rate effects on the flow behavior of reference fiber and fiber extruded at low (EXF4) and high (EXF3) SME.

Since no low shear Newtonian viscosity (η_o) could be measured, in order to better visualize the effect of concentration for the different variants on the viscosity, selected viscosity at a shear rate of 10.9 s^{-1} was plotted as function of fiber concentration using an exponential function (Figure 8). All systems show the same general behavior. An increase of fiber concentration beyond a certain critical concentration (C_{cr}) where the curve is diverging from the baseline results in a sharp increase in viscosity (Figure 8). Three groups can be identified: reference with higher viscosity and $C_{cr10.9s-1} \sim 0.2\%$, systems with low SME with $C_{cr10.9s-1} \sim 0.3\%$, and system with high SME with $C_{cr10.9s-1} \sim 0.4\%$.

For the reference fiber and fibers extruded at low SME, sedimentation of a dispersion will occur after 10 min. This is probably caused by the fact that the reference fibers and those extruded at a low SME have larger particles which result in a large increase in viscosity after dispersion. However, due to the low concentration of soluble fibers, the particles sedimented earlier compared to systems with high SME, where smaller particles are formed and the higher amounts of soluble fiber raise the viscosity in the nonparticle phase, decreasing the rate of particle sedimentation.

DISCUSSION

Extrusion resulted in a marked transformation of the physicochemical properties of the citrus fiber. The water-retaining properties of the fibers were reduced, and this was attributed to

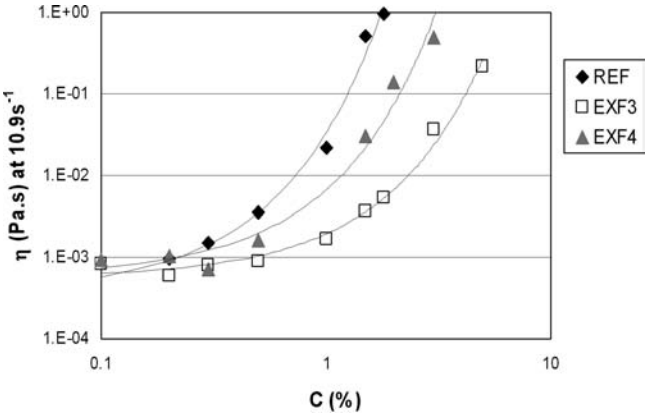

Figure 8. Variation of viscosity (10.9 s^{-1}) as a function of system concentration (%) for reference fiber and fiber extruded at low (EXF4) and high (EXF3) SME.

the fragmentation of much of the cellular structure of the original fiber. The smaller and denser wall fragments were not able to physically entrap or absorb water as rapidly as the reference fiber. This meant that viscosity generation relied on the hydration of the cell wall polysaccharides over a longer period. Fiber extruded at low SME possessed higher viscosities than those extruded at high SME. The latter required 20 times the concentration of fiber to generate the same level of viscosity as fibers extruded at low SME.

The definition of soluble fiber in terms of the validated AOAC method was brought into focus by our experimental approach to the determination of extrusion-induced solubilization. Fiber solubilization, as determined by water extraction, increased markedly in the extruded samples compared to the reference fiber. The differences were not nearly as marked when the AOAC method was used. This is not surprising as the AOAC procedure consists of a thermal extraction (90 °C) at pH 8.2, which would solubilize some pectic polysaccharides in the reference that are not soluble in an aqueous extraction at ambient temperature. It brings into question the relevance of soluble fiber data determined by a procedure, which has little in common with the in vivo digestion process. In addition, the increased solubilization in a simple water extraction has an industrial relevance where the production of soluble fibers is required. The use of acids and alkalis for the solubilization of pectic polymers not only causes degradation of the fibers but also makes the process more expensive.

Compositional analysis of the soluble fiber fractions indicated that both pectic and hemicellulosic polysaccharides were solubilized. Solubilization of the pectic polymers was expected, as to a large extent they are the matrix in which the insoluble cellulose fibrils are embedded and even in the reference fiber they were the major polysaccharides of the soluble fraction. The hemicelluloses, on the other hand, are normally not solubilized by water extraction as they are bound to the cellulose by hydrogen bonds. Their release indicates that either they or the cellulose was cleaved into smaller fragments. This was confirmed by the molecular weight profiles of the solubilized polymers, which showed a 10-fold decrease in size after extrusion at a high SME. It seems likely that the increase in soluble glucose was derived from the hemicellulose fraction, as it paralleled the rise in soluble mannan, suggesting that solubilization of a gluco- or galactoglucomannan had occurred. In addition, the residue fraction (predominantly cellulose) of a fiber sample extruded at high SME showed no indication of glucose depletion which would be expected if the cellulose had been partially solubilized.

The results of this study have shown that the physicochemical properties of suspensions of citrus fiber can be modulated by extrusion to a considerable extent. In the processing food industry there is an increasing focus on functional foods and dietary fiber in particular. Any process which can increase the technological versatility of fiber, and perhaps the spectrum of its health benefit profile, could make a significant impact on the use of fiber in the food industry. The present study shows that extrusion is a physical process capable of doing this. It is to be expected that other physical treatments could also be useful in this regard (e.g., milling by a variety of methods). In the future the consumers' desire for "natural" in processed foods will preclude the use of chemical methods as transforming agents for food ingredients. Physical processes do not face the same degree of consumer resistance and are likely to play an increasing role in food fabrication in the immediate future.

AUTHOR INFORMATION

Corresponding Author

*Tel: +41 21 785 8681. E-mail: frederic.robin@rdls.nestle.com.

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