

Amaranth starch-rich fraction properties modified by extrusion and fluidized bed heating

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Abstract

Today amaranth is a promising food source yet its technological properties are not well known. The modification of some properties of an amaranth starch-rich fraction by a controlled heating is studied. This fraction was obtained by the differential milling of *Amaranthus cruentus* grains.

Tests were performed by both fluidized bed and extrusion heating, according to a factorial experimental design of two variables: temperature and moisture, at three levels 150–170–200 °C and 120–160–200 g/kg wb, respectively. Effects were evaluated by the ANOVA method. As responses, solubility and water absorption, amylographic and dynamic rheological properties, crystallinity, granular integrity and resistant starch content were evaluated. Flours obtained from samples heated by fluidized bed gave aqueous dispersions with high consistencies when cooked, and they had low solubility in water and preserved part of the starch crystalline structure. Flours obtained from extrusion-heated samples gave very high solubility in water but had lower consistency of the aqueous dispersions when cooked, and they showed a complete loss of the crystalline and granular structure.

By applying each of the two heating processes, it was possible to modify, according to selected targets, the amaranth starch-rich fraction, what would allow to obtain pre-cooked amaranth flours with a wide range of hydration and rheological properties.

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1. Introduction

Although amaranth has been produced in America and Africa for centuries, only recently their remarkable nutritional properties have been recognized (Bressani, Kalinowskw, Ortiz, & Elias, 1987). The grains contain about 150 g/kg proteins and 630 g/kg starch which has waxy characteristics (Betschart, Irving, Shepard, & Saunders, 1981; Lehman, 1996; Sanders & Becker, 1984;

Teutonico & Knorr, 1985). Due to the particular amaranth grain structure and morphology (Irving, Betschart, & Saunders, 1981), it is possible to separate its anatomical parts mechanically and thus obtain milling fractions with different compositions. Taking this into account, a differential dry milling technique, able to separate distinct grain pieces of different compositions in a selective way was developed at the Centro de Investigación y Desarrollo en Tecnología de Alimentos ((CIDTA), Facultad Regional Rosario, Universidad Tecnológica Nacional) (Tosi, Ré, Lucero, & Masciarelli, 2000). The amaranth differential milling may produce three fractions: a protein rich one containing more than 40% protein, another one rich in dietary fibre and the starchy fraction containing about

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79% starch (Tosi et al., 2000). This starchy fraction, which is formed essentially by the nearly spherical entire degermed and dehulled grain or endosperm, was named “amaranth groats”, and can be considered a good raw material to produce pre-gelatinized amaranth flours.

During starch dry cooking, the major changes are the disruption of the crystalline regions followed by the loss of granule integrity. The degree of the structural changes promoted depends on the processing variable values.

The loss of crystalline structure is evidenced by both the disappearance of the characteristic X-ray pattern and the loss of birefringence or by the decreasing of the gelatinization enthalpy, measured by differential scanning calorimetry (DSC). Another effect is a redistribution of the starch molecules in a continuous phase. These last changes can be followed by measuring the solubility in water of the treated material (González, Torres, De Greef, & Gordo, 1986; Mercier & Feillet, 1975).

Resistant starch is associated to some structures formed by starch components in natural food or during processing that are refractory to the enzymatic attack (Asp, 1994). Resistant starch has been recognized to having potential physiological benefits as lowering the glycemic index of the food, reducing blood lipids, and it might decrease the risk for the development of diabetes and possibly, colon cancer (Jenkins et al., 1998). Resistant starch content (RSC) depends on the characteristics of the starch present in food, type of granule, amylose/amylopectine ratio, crystallinity, presence of other chemical species able to interact with starch. Food processing conditions, thermal treatments, gelatinization, cooling and storing time, among others (López, Ros, Perigo, & Rincón, 1994) have influence on food RSC.

Dry-heating processes like fluidized bed heating (FBH) using hot air, and extrusion heating (EH) are suitable for food treatment due to their valuable characteristics of uniformity and short-time treatments and both can be used to modify the starch granular structure and, consequently, to produce pregelatinized flours (Koepe et al., 1987; Mendoza & Bressani, 1987; Tosi, Ré, Ciappini, & Masciarelli, 1996). Changes produced in starch materials due to extrusion cooking have been extensively studied in cornstarches and grits (González et al., 1986; González, De Greef, Torres, & Gordo, 1987; Kokini, Chang, & Lai, 1992; Mason & Hosney, 1986; Mercier & Feillet, 1975). On the other hand, changes produced by FBH, depend on the characteristics of the starch-rich fraction or amaranth groats and it is affected by temperature, moisture content and treatment time.

As FBH and EH processes are based on different ways of energy transference, the present work aims to compare the effects produced by these two heating processes on the functional and structural characteristics of the starch-rich fraction obtained by the differential milling of amaranth grains with the purpose of obtaining precise tailored pre-cooked amaranth flours.

2. Materials and methods

2.1. Materials

The raw material was the amaranth starch-rich fraction constituted by the entire degermed and dehulled grain or endosperm. These tiny sphere-like particles, with less than 1 mm diameter, were obtained by the differential milling (Tosi et al., 2000) of *Amaranthus cruentus* grains, from farms of Río Cuarto, Córdoba province, Argentine Republic. This starchy fraction was named “amaranth groats”. The proximal composition (in dry basis) of this fraction, determined according to AACC methods (AACC, 1994) was: moisture 103 ± 5 g/kg, starch 770 ± 7 g/kg, protein ($N \times 6.25$) 67 ± 3 g/kg, ash 1.7 ± 0.7 g/kg and oil 4.3 ± 0.8 g/kg.

2.2. Methods

2.2.1. Extrusion and FBH

Thermal processing tests on the amaranth groats were performed by extrusion or FBH, according to a factorial experimental design of two variables at three levels (3^2), with a duplicate central point. Eleven experiments were carried out for each heating process. Both the extruder barrel temperature and the fluidizing air temperature (which was assumed as the bed temperature), together with the initial moisture content of the amaranth groats were chosen as processing variables or factors and their values were selected according to the experimental design. Temperature (T) and moisture (M) ranges were 150–175–200 °C and 120–160–200 g/kg wb, respectively. Treatment time was fixed to be 18 s for both heating processes. Time, that in discontinuous or batch FBH at the given experimental conditions, caused a sudden expansion of the treated particles and, consequently, a significant decrease in their density; as a consequence, they were dragged out of the bed set in a fluidized state. In EH this fixed time was elapsed by the material moving across the barrel of the extruder to reach the discharge end at the rotational speed adopted. FBH was carried out by using a pilot-scale fluidized bed equipment (Tosi, Ré, Cazzoli, & Masciarelli, 1982; Tosi et al., 1996). EH was carried out on a 10 DN Brabender extruder (Duisburg, Germany), with a 3:1 compression ratio screw at 173 rpm using a 3 mm diameter die. After the treatment, all samples were kept in a constant relative humidity atmosphere until their final moisture content ranged 110 ± 2 g/kg wb. Then, the treated samples were milled until a 200-mesh granulometry. They were named “amaranth flour”, and kept at -18 °C until they were analysed. Untreated samples were moisture stabilized, milled and kept in a same way as the control samples.

2.2.2. Evaluated properties

On treated samples, several hydration, amylographic consistencies, dynamic rheological and structural charac-

teristics were measured. They were: solubility in water and water absorption (WA); initial, peak and retrogradation consistencies; the storage modulus at the end of the heating period, the storage modulus and at the end of the cooling period, and the temperature at which the storage modulus showed a sharp increase, enthalpy of gelatinization transition, crystallinity degree and RSC, all of them were selected as responses corresponding to the factorial experimental design.

2.2.3. Hydration properties

Solubility in water (S) and WA were determined according to González et al. (1986, 1987) and González, Torres, and De Greef (2002b). S was expressed as soluble solids per kilogram of amaranth flour (dry basis). This was done by dispersing 2.5 g of amaranth flour in 50 ml water at 30 °C, agitating 30 min intermittently and centrifuging at 2000g for 10 min. Soluble solids were obtained from supernatant evaporation at 105 ± 1 °C. WA was obtained according to the Baumann method, modified by Torgensen and Toledo (1977) and it was expressed as milliliters of water per gram of dry sample.

2.2.4. Amylographics properties

Initial consistency (IC), peak consistency (PC) and retrogradation consistency at 30 °C (RC) were determined according to González et al. (1986, 1987, 2002b). Amylograms were performed with an aqueous suspension of 0.086 g amaranth flour/g suspension, in a VISCO/amylo/GRAPH (Brabender Instruments Inc., South Hackensack, NJ, USA) using the 250 gcm head. IC was taken at 150 rpm, while the other amylographics characteristics, PC and RC were taken at 75 rpm.

2.2.5. Dynamic rheological properties

The determined dynamic rheological properties were: storage modulus values reached both at the end of the heating period (G'_h) and at the end of the cooling period (G'_c) and the temperature at which G'_h showed a sharp increase (TG'_{inc}). They were measured with a Paar Physica Controlled Stress Rheometer MCR 300 (Gaz, Austria), equipped with parallel plate geometry. Measurements were made in the linear region. Strain and frequency were set at 0.01% and 1 Hz, respectively. The temperature of the bottom plate was controlled with a Peltier system (Viscotherm VT2, Paar Physica) (Gaz, Austria), liquid paraffin was applied to the exposed sample surfaces to prevent evaporation. Amaranth flour aqueous suspensions (0.20 g flour/g) were heated from 20 to 90 °C at a rate of 10 °C/min, kept at 90 °C for 10 min, time enough to allow the storage modulus (G') equilibrium, then cooled to 20 °C at 10 °C/min and held for 15 min at this temperature. From the dynamic measurements G'_h , G'_c and TG'_{inc} were evaluated.

2.2.6. Structural characteristics

Treated and control samples were analysed by DSC and X-ray diffraction (XRD) to determine structural changes. DSC studies were performed in a Thermal Analysis System Mettler Toledo DSC821 (Schwerzenbach, Switzerland). The samples (13–20 mg wet weight, at 20:80 sample:water ratio) were placed in the DSC hermetic aluminium pans. Afterwards, they were run from 25 to 110 °C at a rate of $\beta = 10$ °C/min. The equipment was calibrated with Indium, as reference an empty double pan was used. The analysis by X-ray diffraction was performed in a powder diffractometer Shimadzu DX-1 (Kyoto, Japan) with CuK α radiation, to 30 kV and 40 mA and 0.5°/min run velocity from 5° to 30° (2 θ).

2.2.7. Resistant starch content

RSC was evaluated according to the method proposed by Goñi, Garcia-Dig, Mañas, and Saura-Calixto (1996).

2.2.8. Statistical analysis

All determinations were carried out in duplicate and the Statgraphic Plus 4 (Statistical Graphics Corp., Maryland, USA) software was used to obtain the response surfaces and the ANOVA. The effects of the variables T and M , and their respective interactions $T \times T$, $M \times M$, and $T \times M$ were evaluated by a second grade polynomial adjustment whose terms were defined as T , M , T^2 , M^2 , and $T \times M$. The statistical significance or P values corresponding to each polynomial term of the regression models for each heating process was evaluated. Data analysis was carried out by using the response surfaces graphics but they were not included.

3. Results and discussion

3.1. Hydration properties

Hydration properties of the starch-rich fraction treated by FBH and EH are summarized in Table 1. Table 2 shows ANOVA results.

3.2. Solubility in water (S)

According to the statistical significance of the model coefficients (Table 2) S is influenced only by EH treatments. A unique $P < 0.05$ value corresponding to M was found, but the significance of $M \times M$ and $T \times M$ effects is not small. As the lack of fit is not significant and the regression coefficient R is good, the model is feasible. The solubility values ranged between 54 and 73 g/kg. These high solubility values for EH samples are even higher than those of other extruded waxy type cereals. González, Torres, and Añón (2000a) suggested that amaranth endosperm is less resistant than that of other waxy cereals and they proposed solubility as a direct indicator of the degree of cooking in extruded cereals, because solubility is related to the degree of rupture of the granular structure.

Table 1

Solubility in water and water absorption of amaranth flours as function of treatment temperature and initial moisture content for fluidized bed and extrusion heated samples

Treatment temperature (°C)	Moisture content (g/kg wb)	Solubility in water (g dry solid/kg)		Water absorption (ml water/g dry solid)	
		FBH	EH	FBH	EH
150	120	7.42±0.40	54.07±3.2	2.11±0.35	1.75±0.26
150	160	6.77±0.40	72.58±3.5	3.60±0.37	2.07±0.19
150	200	7.26±0.33	70.90±3.1	2.70±0.38	2.85±0.21
175	120	7.11±0.35	57.35±3.0	3.45±0.33	1.94±0.25
175	160	8.68±0.36	67.57±3.4	3.70±0.30	2.16±0.20
175	160	7.72±0.35	68.35±3.3	3.50±0.31	2.37±0.25
175	160	8.25±0.34	64.97±3.7	4.20±0.42	2.47±0.28
175	160	7.65±0.32	71.86±4.1	5.11±0.33	3.09±0.31
200	120	7.58±0.40	67.31±3.6	5.45±0.36	2.35±0.23
200	160	7.40±0.37	70.91±3.1	6.18±0.38	2.78±0.16
200	200	9.97±0.35	71.57±3.0	6.74±0.43	3.49±0.22
Without treatment		8.50±0.35		2.42±0.30	

Table 2

Statistical significance to each coefficient of model equation for solubility in water and water absorption, for fluidized bed and extrusion-heated samples

Polynomial terms	Solubility in water		Water absorption	
	FBH	EH	FBH	EH
T^a	0.097	0.106	0.001	0.032
M^b	0.143	0.015	0.053	0.012
$T \times T$	0.613	0.116	0.222	0.549
$T \times M$	0.118	0.071	0.567	0.721
$M \times M$	0.739	0.065	0.773	0.247
Lack of fit	0.233	0.207	0.229	0.993
R^c (%)	63.8	88.3	92.2	98.3

^aTreatment temperature.

^bAmaranth groat initial moisture content.

^cRegression coefficient.

According to Colonna, Tayeb, and Mercier (1989), increases in the W for extruded samples might be related to the lower molecular weight of starch components released from the granules. Solubility values for FBH are in the same order of that of the untreated sample.

3.3. Water absorption (W)

W model coefficients values (Table 2) show highly significant effects for T ($P < 0.001$) in FBH treatments and M ($P < 0.05$) in EH treatments. The significance of other terms, such as M in FBH ($P = 0.053$) or $T \times M$ and $M \times M$ in EH ($P = 0.065$ and 0.071 , respectively) is not small. In both cases the lack of fit is not significant and the regression coefficients are very good. The model for FBH treated samples is practically linear and predicts the highest values at 200 °C and 200 g/kg wb. T effect becomes more important as M increases. Compared with EH samples, which are characterized by high solubility and low WA values, FBH gives higher WA, being these values almost

the double than EH for the same T and M , which is attributable to a high preservation degree of the starch granule integrity.

3.4. Amylographic consistencies

Amylographic consistencies of the starch-rich fraction treated by FBH and EH are summarized in Table 3. Table 4 shows ANOVA results. Fig. 1 shows typical amylograms corresponding to both processes compared to the sample untreated. The most noticeable differences in amylograms corresponding to EH and FBH processes were their shape and consistency values.

3.5. Initial consistency (IC)

T and M in both heating processes (Table 3) significantly influence on the IC , but values of extruded samples are the highest ones. According to ANOVA (Table 4), the model is practically linear and the M effect is the most significant. For FBH treatments, the regression models show that the lack of fit is significant. Their IC values are ranging that of the untreated samples. Only at 200 °C for 160 and 200 g/kg wb, a noticeable significant IC increase was observed. The higher IC values for extruded samples are attributable to their high solubility, which makes their dispersion much more viscous than FBH samples.

3.6. Peak consistency (PC)

Only two extruded samples show a very small amylographic peak at M equal to 120 g/kg wb for treatments at 150 and 175 °C. All FBH samples show higher PC values than the untreated ones, except for the sample treated at 200 °C and 200 g/kg wb moisture. Significant effects of the terms M and $M \times T$ were found on FBH treatments. The highest values of PC were obtained at the lowest M and higher T . A possible explanation to this behaviour is that

Table 3

Initial consistency, peak consistency and retrogradation consistency of amaranth flour as function of treatment temperature and initial moisture content for fluidised bed and extrusion heated samples

Treatment temperature (°C)	Moisture content (g/kg wb)	Amylographic consistencies					
		Initial consistency (BU ^a)		Peak consistency (BU)		Retrogradation consistency (BU)	
		FBH	EH	FBH	EH	FBH	EH
150	120	54 ± 7	185 ± 15	2500 ± 16	90 ± 10	2500 ± 22	70 ± 15
150	160	56 ± 7	455 ± 17	2484 ± 18	np ^b	2100 ± 18	240 ± 18
150	200	67 ± 8	651 ± 24	2576 ± 20	np	2206 ± 16	360 ± 19
175	120	59 ± 7	247 ± 21	2912 ± 22	100 ± 14	2268 ± 20	287 ± 17
175	160	84 ± 1	540 ± 16	2576 ± 20	np	2400 ± 21	330 ± 20
175	160	70 ± 8	570 ± 15	2742 ± 18	np	2217 ± 19	369 ± 21
175	160	84 ± 1	630 ± 17	2864 ± 22	np	2664 ± 22	370 ± 17
175	200	98 ± 1	825 ± 23	2632 ± 19	np	2128 ± 20	430 ± 23
200	120	84 ± 1	420 ± 15	3640 ± 20	np	2534 ± 18	310 ± 15
200	160	336 ± 14	610 ± 14	2814 ± 18	np	2226 ± 17	337 ± 15
200	200	588 ± 18	793 ± 22	1750 ± 18	np	1778 ± 17	375 ± 16
Without treatment		70 ± 0.70		1890 ± 18		2072 ± 20	

^aBrabender units.

^bnp = not present.

Table 4

Statistical significance corresponding to each model coefficient for initial, peak and retrogradation consistencies of amaranth starch-rich flours for fluidized bed and extrusion heated samples

Polynomial term	Amylographic consistencies				
	Initial consistency		Peak consistency ^a	Retrogradation consistency	
	FBH	EH	FBH	FBH	EH
T^b	0.002	0.042	0.211	0.774	0.113
M^c	0.005	0.006	0.024	0.283	0.033
$T \times T$	0.007	0.348	0.321	0.606	0.079
$T \times M$	0.004	0.417	0.021	0.560	0.639
$M \times M$	0.828	0.388	0.968	0.704	0.261
Lack of fit	0.046	0.434	0.316	0.703	0.296
R^d (%)	94.1	96.7	90.63	49.0	88.3

^aEH samples have not measurable peak consistency.

^{b,c,d}Refer to Table 2.

interactions occur between starch granules and proteins during FBH, resulting in an increase of the particle size of the swollen granules, which produce higher consistencies of the cooked aqueous suspension. Such interpretation is based on the known fact that a substantial number of proteins are located on the starch surface (Baldwin, 2001). Considering that the amaranth groats is the entire endosperm, during the dry heat treatment some protein fractions may interact among themselves and with the starch granules surface, giving increased-volume structures.

3.7. Retrogradation consistency (RC)

According to ANOVA values (Table 4), a $P < 0.05$ value for RC was found ($P = 0.033$ for M) only in EH samples. The lowest RC values were obtained by EH (Table 3).

Differences of consistency among EH samples are related to the size of the particle dispersed in the continuous phase, and are characterized by an almost complete loss of the granular structure. EH samples show the typical inverse relationship between retrogradation consistency and solubility found for extruded starchy materials (González et al., 1987, 2002b), but the variability of amylographic consistency of amaranth starch samples is narrower than that of corn. This is attributable to the corn strong endosperm (González, Torres, De Greef, Tosi, & Ré, 2002a). FBH produces higher RC values than the untreated sample; such higher RC values were obtained at the lowest M . However, the damage degree caused to the starch granular structure for FBH at 200 °C and 200 g/kg wb moisture would be enough to give lower peak and retrogradation consistencies than those of the untreated sample. According to Holm,

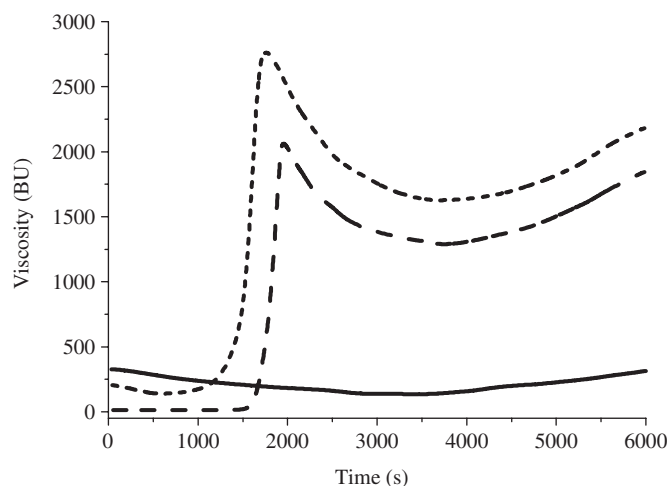


Fig. 1. Typical amylograms for samples corresponding to each treatment in comparison with the sample without treatment. Extrusion (200 and 0.16 g water/g wb) (—), fluidized bed heating (200 °C and 0.16 g water/g ws) (---), and native (without treatment) (-.-.-).

Björck, and Eliasson (1988) during high-temperature treatments, a more extensive starch fragmentation occurs in popped products, compared to their extruded counterpart.

3.8. Dynamic rheology

Table 5 shows the results of dynamic rheology tests corresponding to FBH samples. T_{gel} is the temperature at which the elastic modulus (G') starts to increase during the heating period. It is worth mention that FBH decreases T_{gel} , meaning that the swelling process starts earlier than for the untreated samples ($TG'_{inc} = 66.2$ °C), probably due to the structural changes which allow not only an increase in WA at room temperature but also a starting of the swelling process of the starch amorphous region at lower temperature (lower TG'_{inc}). As it is shown later, the crystalline structure was partially lost during FBH, so an increase in WA was promoted. G'_h and G'_c values show wide variations among samples (Table 5), being the values corresponding to the untreated or control sample in the middle of these ranges ($G'_h = 476.8$ Pa and $G'_c = 743.2$ Pa). The lowest G'_h and G'_c values correspond to samples submitted to extreme conditions (150 °C, 120 g/kg wb and 200 °C, 200 g/kg wb).

Table 6 shows the ANOVA results of the dynamic rheology tests. It is observed that G'_h and G'_c are significantly affected by both T and M , but the lack of fit is also significant and regression coefficients are very low. The regression models are unsuitable. The low TG'_{inc} for the sample treated at 150 °C and 120 g/kg wb is difficult to explain because one of the samples shows high crystallinity as it is indicated later. Nevertheless, it is clear that TG'_{inc} is an indicator of the hydration and swelling process of the amorphous region and that this starting temperature depends on the changes on the granule structure promoted

Table 5

Temperature at which storage modulus increases, storage modulus reached at the end of the heating period and storage modulus reached at the end of the cooling period for fluidized bed heated samples

Treatment temperature (°C)	Moisture content (g/kg wb)	Temperature at which storage modulus increases (°C)	Storage modulus at the end of heating (G'_h) (Pa)	Storage modulus at the end of cooling (G'_c) (Pa)
		FBH	FBH	FBH
150	120	40.4 ± 1.5	222.4 ± 22.7	343.5 ± 17.2
150	160	59.0 ± 1.8	222.0 ± 27.7	340.7 ± 16.5
150	200	52.6 ± 1.6	668.4 ± 29.6	426.0 ± 16.9
175	120	66.1 ± 1.6	658.4 ± 34.3	450.8 ± 17.6
175	160	53.0 ± 1.7	535.0 ± 27.3	838.0 ± 18.1
175	160	54.0 ± 1.5	551.5 ± 27.5	856.0 ± 18.5
175	160	55.0 ± 1.5	570.0 ± 27.2	870.0 ± 17.9
175	200	65.5 ± 1.6	246.7 ± 28.6	354.8 ± 18.0
200	120	56.1 ± 1.7	577.8 ± 28.5	716.4 ± 17.5
200	160	62.7 ± 1.8	360.0 ± 31.2	492.5 ± 16.5
200	200	66.2 ± 1.7	280.5 ± 29.4	428.0 ± 16.3
Without treatment		66.2 ± 1.7	476.8 ± 27.9	743.2 ± 17.3

Table 6

Statistical significance of each model coefficient of the storage modulus reached at the end of the heating and the storage modulus reached at the end of the cooling for fluidized bed heating

Polynomial term	Storage modulus at the end of heating G'_h	Storage modulus at the end of cooling G'_c
T^a	0.1332	0.0055
M^b	0.0256	0.0165
$T \times T$	0.0069	0.0036
$T \times M$	0.0022	0.0074
$M \times M$	0.1132	0.0031
Lack of fit	0.0073	0.0046
R^c (%)	60.9	64.7

^{a,b,c}Refer to Table 2.

by FBH. G'_h will depend not only on the swelling degree but also on the particles and molecules entanglements. Similarly, G'_c is an indicator of the gelation occurring upon cooling.

Only the results corresponding to FBH samples are reported as significant, because there were no interesting changes for EH samples during the test. Both G'_h and G'_c values for EH are much smaller than those for FBH treated samples. Their values range between 6 and 23 Pa for G'_h and 19 and 55 Pa for G'_c , there is no significant gelatinization or gelation phenomena observed on these samples.

3.9. Structural characteristics

Table 7 shows the gelatinization transition enthalpy (ΔH) and the crystallinity degree (CR) obtained with DSC and XRD methods respectively, corresponding to FBH samples. The loss of crystallinity increases as T increases, indicating that some other changes occurring in the granule

Table 7

Gelatinization transition enthalpy, crystallinity degree and resistant starch content for fluidized bed heated samples

Treatment temperature (°C)	Moisture content (g/kg wb)	Gelatinization transition enthalpy (J/g wb)	Crystallinity degree (%)	Resistant starch content (g/kg db)
150	120	-9.66 ± 0.13	35.9 ± 2.1	59.5 ± 1
150	160	-9.54 ± 0.15	36.4 ± 2.3	48.5 ± 1
150	200	-9.42 ± 0.16	36.2 ± 2.3	11.5 ± 1
175	120	-9.21 ± 0.14	35.8 ± 2.1	21.5 ± 2
175	160	-6.71 ± 0.15	31.1 ± 2.2	31.0 ± 2
175	160	-6.52 ± 0.13	33.0 ± 1.8	22.5 ± 1
175	160	-6.45 ± 0.14	33.6 ± 1.2	25.5 ± 1
175	200	-5.85 ± 0.15	28.4 ± 1.6	22.0 ± 2
200	120	-4.54 ± 0.14	28.7 ± 2.1	3.5 ± 1
200	160	-4.37 ± 0.13	25.7 ± 1.2	2.0 ± 1
200	200	-4.29 ± 0.14	24.4 ± 2.0	3.5 ± 1
Without treatment		-9.90 ± 0.17	35.2 ± 2.2	6.5 ± 2

Table 8

Correlation coefficients corresponding to each model coefficient of gelatinization transition enthalpy, crystallinity degree, and resistant starch content for fluidized bed heated samples

Polynomial term	Gelatinization transition enthalpy	Crystallinity degree	Resistant starch content
T^a	5×10^4	1.14×10^2	2.4×10^3
M^b	1.08×10^2	7.04×10^2	6.09×10^2
$T \times T$	8.30×10^2	0.2991	0.7352
$T \times M$	0.7223	0.2201	2.96×10^2
$M \times M$	1.93×10^2	0.9231	0.3388
Lack of fit	1.66×10^2	0.3434	20.194
R^c (%)	92.76	92.72	90.61

^{a,b,c} Refer to Table 2.

structure have to account for the high consistencies of the cooked dispersion showed by FBH samples.

Table 8 shows the ANOVA results corresponding to ΔH and CR, for FBH samples. T and M affect both responses significantly, and the lack of fit is also significant for ΔH . Only two EH samples, which correspond to low moisture level (120 g/kg wb), showed both small gelatinization transition and low crystallinity degree values, being 0.90 and 0.85 J/g for enthalpy and 20.3 and 19.5% for crystallinity degree corresponding to 150 °C and 175 °C respectively. These values are small if compared to those of the untreated and FBH samples. This indicates that some starch granules have retained their crystalline structure after the extrusion at these particular extrusion conditions. Other works have shown (González et al., 2000) that, at very low moisture levels, an incomplete fluid transformation can occur and so some incomplete crystallite fusion after the extrusion is found, even when the extrusion temperature is high enough for the fusion of the native starch crystalline structure. These results agree with those discussed before, because these two extruded samples also showed a small amylographic peak and also presented the lowest WA and initial consistency values.

3.10. Resistant starch content

Only the results corresponding to FBH are reported (Table 7), because no significant differences were found for RSC among the extruded samples. Table 8 shows the ANOVA results and the significant effects of T and M . A similar trend like that found for the crystallinity degree and for ΔH is observed. According to López et al. (1994), the increase in RSC could be due to interactions among molecules within the starch granules during the heat treatment.

4. Conclusions

Taking the results obtained in this work into account we can make the following remarks: most of the changes caused by both processes can be explained on the basis of changes on the crystalline structure and the degree of the granule integrity damage.

EH causes high degree of granule disruption and almost a complete loss of crystallinity (except for the two samples extruded at 120 g/kg wb moisture). These effects are explained considering the values of the following properties: very high solubility, low W , intermediate level of initial consistency, absence of amylographic peak, low retrogradation consistency and low values of both elastic modulus (G'_h and G'_c).

On the other hand, FBH causes some loss of crystallinity but preserves the granule integrity. These effects are explained considering the values of the following properties: low S , higher W and lower initial consistency if compared to the extruded samples; high peak and retrogradation consistencies. The fact that these last two properties are even higher than those of the untreated samples it has to be explained on the basis of some structural changes and new interactions between starch and others components, occurring during FBH; which would explain not only the high consistencies of the cooked suspensions but the high elastic modulus also.

The increase in RSC could be due to some degrees of the molecular rearrangements caused by FBH. However, the increases in both peak and RC consistencies and also in the elastic modulus, (higher than those of the untreated samples), could be explained considering that new interactions between protein and starch at the surface of starchy particles occur during FBH. These interactions could lead to the formation of complexes which, during the swelling of the starch while cooking, cause an increase in hydrodynamic size of the cooked particles if compared to those of the untreated sample.

The crystalline structure disappears in EH samples while it remains in FBH samples, but crystallinity decreases as treatment temperature increases. The loss of crystalline structure in EH treatments justifies the differences between the two heating methods tested. According to González et al. (1986, 1987), EH thermal treatment is associated to a profound disruption of the starch structure, which avoids starch–protein complexes influence on rheological properties or RSC.

According to the findings above discussed, the starch-rich fraction obtained by differential milling of the amaranth grain can be considered as an interesting raw material for the production of precooked flours having a wide range of hydration properties by applying either extrusion or FBH processes, depending on which characteristic is desired. High degree of cooking, with high solubility and low consistency of suspensions either cold or hot can be obtained by EH at high *T* and low *M*. On the other hand, by FBH treatments at high *T* and low *M*, low solubility and high consistency of hot suspensions can be obtained. If a lower hot suspension consistency but still with low solubility is desired, a FBH with higher *M* must be applied.

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References

- American Association of Cereal Chemists. (1994). *Approved methods of AACC*. St. Paul, MN: The Association.
- Asp, N. (1994). Nutritional classification of food carbohydrates. *American Journal of Clinical Nutrition*, 45, 588–595.
- Baldwin, M. (2001). Starch granule-associated proteins and polypeptides a review. *Starch/Starke*, 53, 475–503.
- Betschart, A. A., Irving, D. W., Shepard, A. D., & Saunders, R. (1981). *Amaranth cruentus*: Milling characteristics, distributions of nutrients within seed components and effects of temperature on nutritional quality. *Journal of Food Science*, 46, 1181–1184.
- Bressani, R., Kalinowsky, L. S., Ortiz, M. A., & Elias, L. G. (1987). Nutritional evaluation of roasted, flaked and popped *Amaranth candatus*. *Archivos Latinoamericanos de Nutrición*, 37, 525–531.
- Colonna, P., Tayeb, J., & Mercier, C. (1989). Extrusion cooking of starch and starchy products. In C. Mercier, P. Linko, & M. Harper (Eds.), *Extrusion cooking* (pp. 321–341). St. Paul, MN, USA: American Association of Cereal Chemists.
- Goñi, I., Garcia-Dig, L., Mañas, E., & Saura-Calixto, F. (1996). Analysis of resistant starch: A method for foods and food products. *Food Chemistry*, 56, 445–449.
- González, R. J., De Greef, D. M., Torres, R. L., & Gordo, N. A. (1987). Efectos de algunas variables de extrusión sobre la harina de maíz. *Archivos Latinoamericanos de Nutrición*, 37, 578–591.
- González, R. J., Torres, R. L., & Añón, M. C. (2000). Comparison of rice and corn cooking characteristics before and after extrusion. *Polish Journal of Food and Nutrition Sciences*, 9/50(1), 29–34.
- González, R. J., Torres, R. L., & De Greef, D. M. (2002b). Extrusión-Cocción de Cereales. *Boletim da Sociedade Brasileira do Ciencia e Tecnologia do Alimentos, Campinas, SP, Brasil*, 36(2), 104–115.
- González, R. J., Torres, R. L., De Greef, D. M., & Gordo, N. A. (1986). Evaluación de almidón de maíz precocido por extrusión-cocción. *Revista de Agroquímica y Tecnología de Alimentos*, 26(4), 552–564.
- González, R. J., Torres, R. L., De Greef, D. M., Tosi, E., & Ré, E. (2002a). Effects of popping and extrusion processes on amaranth hydration properties. *Brazilian Journal of Chemical Engineering*, 19(4), 391–395.
- Holm, J., Björck, I., & Eliasson, A. C. (1988). Effects of thermal processing of wheat on starch. I. Physico-chemical and functional properties. *Journal of Cereal Science*, 8, 249–260.
- Irving, D. W., Betschart, A., & Saunders, R. (1981). Morphological studies on *Amaranthus cruentus*. *Journal of Food Science*, 46, 1170–1174.
- Jenkins, D. J. A., Vuksan, V., Kendall, C. W. C., Würsch, P., Jeffcoat, R., Waring, S., et al. (1998). Physiological effects of resistant starches on fecal bulk, short chain fatty acids, blood lipids and glycemic index. *Journal of the American College of Nutrition*, 17(6), 609–616.
- Koeppel, S. J., Harris, P. L., Hanna, M. A., Rupnow, J. H., Walker, C. E., & Cuppet, S. L. (1987). Physical properties and some nutritional characteristic and extrusion product with defatted amaranth seeds and defatted maize gluten meal (80:20 ratio). *Cereal Chemistry*, 64, 332–336.
- Kokini, J. L., Chang, C. N., & Lai, L. S. (1992). The role of rheological properties on extrudate expansion. In J. Kokini, Ch. T. Ho, & M. Karwe (Eds.), *Food extrusion science and technology* (pp. 631–652). New York: Marcel Dekker.
- Lehman, J. W. (1996). Case history of Amaranth grains as an alternative crop. *Cereal Foods World*, 41(5), 399–411.
- López, G., Ros, M., Periago, C., & Rincón, F. (1994). Métodos de determinación de la fibra dietética. Aspectos críticos. *Revista Española de Ciencia y Tecnología de Alimentos*, 33, 241–254.
- Mason, W. R., & Hosney, R. C. (1986). Factors affecting the viscosity of extruded cooked wheat starch. *Cereal Chemistry*, 63, 436–441.
- Mendoza, C., & Bressani, R. (1987). Nutritional and functional characteristic of extrusion cooked amaranth flour. *Cereal Chemistry*, 64, 218–223.
- Mercier, C., & Feillet, P. (1975). Modification of carbohydrate components by extrusion-cooking of cereal products. *Cereal Chemistry*, 52, 283–295.
- Sanders, R. M., & Becker, R. (1984). Amaranth: A potential food and feed resource. *Advances in cereal science and technology*, VI.
- Teutonico, R., & Knorr, D. (1985). Amaranth: Composition, properties and applications of a rediscovered food crop. *Food Technology*, 39, 49–52.
- Torgensen, H., & Toledo, R. T. (1977). Physical properties of protein preparations related to their functional characteristics in comminuted meat systems. *Journal of Food Sciences*, 42, 286–289.
- Tosi, E., Ré, E., Cazzoli, A., & Masciarelli, R. (1982). Essicamiento del grano sul letto fluidizado. *Técnica Molitoria*, 1, 3–16.
- Tosi, E., Ré, E., Ciappini, M. C., & Masciarelli, R. (1996). Aplicación de la técnica de lecho fluidizado a la producción de rosetas de amaranto. *Alimentaria*, 269, 45–47.
- Tosi, E., Ré, E., Lucero, H., & Masciarelli, R. (2000). Amaranth (*Amaranthus* spp.) grain conditioning to obtain hyperproteic flour by differential milling. *Food Science and Technology International*, 5, 60–63.