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Amaranth starch-rich fraction properties modified by high-temperature heating

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Abstract

The effect of high-temperature fluidized-bed heating on some properties of an amaranth high-starch fraction obtained from *Amaranthus cruentus* grains was evaluated. A two-factor at three levels factorial experimental design (3^2) was adopted, one factor being the heating temperature (190, 200 and 210 °C) and the other, the moisture content of the high-starch fraction (12%, 16% and 20% wet basis). The effects on the responses water solubility, swelling power, amylographic and dynamic responses, crystallinity degree and gelatinization enthalpy were established by using response surface methodology. A partial loss of starch crystalline structure was observed but most of their granular integrity was preserved. As temperature and moisture increased, loss of crystalline structure and degree of gelatinization also increased. The obtained amaranth high-starch flours were of a solid character at low temperature, with high consistency when cooked and low water solubility, which make them suitable for industrial applications.

Keywords: Amaranth; *Amaranthus cruentus*; Starch; Rheology; Crystallinity; Swelling power

1. Introduction

Development of products that fit with the desired properties in food formulations such as modified starches, are required by the food industry. In search for new raw materials, amaranth (*Amaranthus* spp.), which has been cultivated in America and Africa for centuries (Bressani, Kalinowski, Ortiz, & Elias, 1987), had great importance in pre-Colombian American diets and is now being re-discovered. The amaranth grain is nearly spherical, about 1 mm in diameter, with remarkable nutritional properties. It contains approximately 63% starch, with waxy characteristics (Lorenz, 1981; Yañez, Messinger, Walker, & Rupnow, 1986) and 15% proteins, with significant content of sulphur amino acids and lysine (Becker et al., 1981; Betschart, Irving, Shepherd, & Saunders, 1981; Lehman, 1996; Saunders & Becker, 1984; Teutonico & Knorr, 1985). Although it is a dicotyledonous plant, some authors consider it a pseudocereal (Breene, 1991) as a consequence of its properties and characteristics.

Due to the particular amaranth grain structure and morphology (Irving, Betschart, & Saunders, 1981), it is possible to separate its anatomic parts and thus to obtain

Abbreviations: AHSF, amaranth high-starch fraction; ANOVA, analysis of variance; FBH, fluidized-bed heating; CYTED, Ciencia y Tecnología para el Desarrollo; DSC, differential scanning calorimetry; XRD, X-ray diffraction.

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Nomenclature

CD	crystallinity degree (%)	SP	swelling power (%)
ΔH	gelatinization enthalpy (J/g)	IC	initial consistency (Brabender Unit)
$T_{G'\text{inc}}$	temperature where the storage moduli (G'_h) showed a sharp increase (°C)	PC	peak consistency (Brabender Unit)
		RC	retrogradation consistency (Brabender Unit)
G'_h	maximum storage moduli (G'_h) on heating (Pa)	T	temperature (°C)
G'_c	maximum storage moduli (G'_c) on cooling (Pa)	t	time (s)
S	water solubility (%)	M	moisture (% wb)

fractions with different compositions. A differential dry milling process, which is able to separate the different amaranth grain parts, was developed by Tosi, Ré, Lucero, and Masciarelli (2000). Differential milling, operated in a continuous stream, produces two milling fractions: a high-protein fraction, containing more than 40% protein and the amaranth high-starch fraction (AHSF), containing about 79% starch, which is constituted by the entire amaranth grain endosperm or the degermed and dehulled grain.

During starch dry cooking, the major change which occurs is the disruption of the crystalline regions followed by the loss of granule integrity. The degree of these structural changes depends on the processing variable values. The loss of crystalline structure is evidenced by 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. This last change can be detected by measuring solubility of the treated material in water (González, Torres, De Greef, & Gordo, 1986; Mercier & Feillet, 1975).

Fluidized bed heating using hot air, due to its valuable characteristics treatment homogeny, both high mass and heat transference coefficients, and easy temperature control of the treated solid, is a suitable technique for high-temperature short-time food processing. This technique has been used for grain drying, enzyme inactivation and starch-structure modification (Osella, Gordo, Tosi, & Ré, 1997; Tosi & Ré, 1999; Tosi, Ré, Cazolli, & Tapiz, 1999; Tosi, Ré, Tapiz, & Lucero, 1999; Tosi, Tamburelli, & Cantador, 1990; Tosi, Tamburelli, & Prado, 1990) and for producing pregelatinized flours (Koeppe et al., 1987; Mendoza & Bressani, 1987; Tosi, Ré, Masciarelli, & Ciappini, 1996).

Taking into account that AHSF, obtained by differential milling, can be considered a good raw material to obtain amaranth high-starch flours with singular functional properties, and that there is a lack of bibliography about high-temperature treatments on starch at low moisture content, the aim of this work was to evaluate the modification of properties of low moisture AHSF by high-temperature short-time fluidized-bed heating (FBH).

2. Materials and methods

2.1. Amaranth high-starch fraction (AHSF)

Amaranthus cruentus grains were obtained from farms in Río Cuarto, Argentina. They were treated by differential milling to obtain AHSF according to Tosi et al. (2000). AHSF proximate composition (dry basis), determined according to AACC (1994) and AOAC (1995) methods was 6.7% protein ($N\% \times 6.25$) (AACC 46-11), 1.7% ash (AACC 08-01), 4.3% ethereous extract (AOAC 920.85) and 87.3% carbohydrates (as difference), with 79% starch (AACC 76-11).

2.2. Experiment design

Due to the explorative nature of the present work, a two-factor at three levels factorial experimental design (3^2), with a triplicate central point (11 experiments) was adopted. The fluidizing air temperature (T) and the moisture (M) content of AHSF were selected as factors, which values were 190, 200 and 210 °C and 12%, 16% and 20% wb, respectively. The following properties were evaluated as responses: solubility in water; swelling power; initial, peak and retrogradation consistencies; the storage moduli reached both at the end of the heating period and at the end of the cooling period; the temperature at which the storage modulus showed a sharp increase; the enthalpy of gelatinization transition and the crystallinity degree. The target was to set in which way responses were modified by heating temperature and AHSF moisture, without the intention to elucidate completely the mechanisms that justify such changes.

2.3. Fluidized-bed heating treatment

Before heating treatments, AHSF moisture was raised from its initial storage value (approx. 11.5%) to the desired tested values (12%, 16%, 20%) by rewetting, adding a quantity of water determined by calculations, and leaving for 48 h homogenization. FBH was carried out on AHSF rewetted samples in a pilot-scale fluidized-bed equipment (Tosi, Ré, Cazzoli, & Catalano, 1982; Tosi et al., 1996). Heating time was kept constant and equal

to 18 s, which was the maximum attainable one. Once that time was exceeded, under the given experimental conditions, a sudden expansion (or "pop" up) of the heated grains occurred, resulting in a huge decrease of their density. Consequently, grains were dragged out of the fluidized bed by pneumatic transport, thus interrupting the heating treatment. After FBH treatment, all AHSF samples were cooled to ambient temperature (20–25 °C). Then, they were moisture-stabilized by leaving them in a constant relative humidity atmosphere until their final moisture content of $11.0 \pm 0.2\%$ wb. After that, the treated samples were milled to a 200 mesh granulometry, obtaining the AHSF flour and kept until analysed. Untreated or control samples were moisture-stabilized, milled and kept just like the treated ones.

2.4. Gelatinization temperature and gelatinization enthalpy

Gelatinization temperature and gelatinization enthalpy were evaluated by differential scanning calorimetry (DSC) in a Thermal Analysis System (Mettler Toledo DSC821, Schwerzenbach, Switzerland). The samples (13–20 mg, wet weight and 80:20 water:sample ratio) were placed in the DSC hermetic aluminum pans. Afterwards, they were run from 25 to 110 °C at a rate of 10 °C/min. The equipment was calibrated with indium and an empty double pan was used as reference.

2.5. Crystallinity degree

Starch crystallinity degree (CD) was evaluated by X-ray diffraction analysis (XRD). It was performed in a powder diffractometer Shimadzu DX-1; with KαCu radiation, at 30 kV, 40 mA and 0.5°/min run velocity from 5° to 30° (2θ).

2.6. Dynamic rheological properties: storage modulus reached at the end of the heating period, storage modulus reached at the end of the cooling period and the temperature at which the storage modulus showed a sharp increase

Dynamic rheological properties were determined with a Paar Physica Controlled Stress Rheometer MCR 300 (Gaz, Austria), equipped with parallel plate geometry. The measurements were performed in the linear region at 0.01% strain and 1 Hz frequency. The temperature of the bottom plate was controlled with a Peltier System Viscotherm VT2, Paar Physica (Gaz, Austria), and liquid paraffin was applied to the sample exposed surfaces to prevent evaporation. Sample suspensions (20% wt) were heated from 20 to 90 °C at a rate of 10 °C/min and then kept at 90 °C for 10 min, time enough to allow the storage modulus (G') equilibration, then cooled to 20 °C at 10 °C/min and held for 15 min at this temperature. The storage modulus reached at the end of the heating period (G'_h), the storage modulus reached at the end of the cooling period (G'_c) and the temperature ($T_{G'inc}$) at which the storage modulus (G'_h) showed a sharp increase were evaluated from the dynamic measurements.

2.7. Hydration properties: water solubility and swelling power

Water solubility and swelling power (both at 30 and 90 °C) were determined according to González et al. (1986), González, De Greef, Torres, and Gordo (1987) González, Torres, and Añón (2000). Water solubility (S) was expressed as grams of soluble solids per 100 g of AHSF flour (db). Swelling power (SP) was expressed as grams of moist hydrated residual solids (or gel) per 100 g flour (db). Both parameters were obtained by dispersing 1 g AHSF flour in 50 ml water in a centrifuging tube, keeping in a shaking water bath at 30 or 90 °C for 30 min, and centrifuging at 2000g. Soluble solids were obtained by weighing the separated supernatant dried at 105 °C. The remaining moist hydrated residual solids were used for swelling power determination.

2.8. Amylographic consistencies: initial, peak and retrogradation consistencies

Amylograms were obtained using 0.086 g solid/g suspension, in a VISCO/amylo/GRAPH (Brabender Instruments Inc., South Hackensack, NJ, USA), using the 250 g cm head. Initial consistency (IC), was determined at 150 rpm, while the other characteristics, peak consistency (PC) and retrogradation consistency at 30 °C (RC) were determined at 75 rpm. The three consistencies were expressed in Brabender Units (BU).

2.9. Statistics

The Statgraphic 3.0 (Statistical Graphics Corp., Rockville, MD, USA) software was used to obtain the response surfaces and the ANOVA. The effects of the variables or factors T and M, in their linear, quadratic $T \times T$, $M \times M$, and interaction $T \times M$ form on the responses, were evaluated by a second grade polynomial model (Eq. (1))

$$Y = b_0 + b_1 \times T + b_2 \times M + b_3 \times T^2 + b_4 \times M^2 + b_5 \times T \times M \quad (1)$$

where Y and b_i were the modelized response and the regression coefficients given by the model, respectively. The statistical significance or p values corresponding to each polynomial term of the regression models for each heating process were evaluated. Independent variables which were found significant at $p < 0.05$ in the full model were retained in the reduced models. Data analysis was carried out by using the response surface graphics but they were not included in this paper. Reported values are the means ± standard deviation from three replications.

3. Results and discussion

3.1. Crystallinity degree (CD)

Data in Table 1 indicate that the CD of starch granules of treated AHSF decreased to a maximum of 37% if compared to the untreated sample. Thus, FBH moderately modifies the crystalline structure, although CD remains quite high even after the 210 °C treatments. The ANOVA shows that only the linear terms T and M were significant on CD of treated AHSF samples (Table 2). The high R^2 value (93.36%) and the non-significant "lack of fit" were the evidence of the model applicability. The most important variable influencing CD was T. The negative values of regression coefficients indicate that CD decreased by increasing T and M.

3.2. Gelatinization enthalpy (ΔH)

The peak temperatures from DSC thermograms did not vary significantly (75–77 °C) between the FBH-treated and untreated AHSF (data not shown). Similar values have previously been reported for *Amaranthus* ssp. (Keetels, van Vliet, & Walstra, 1996). FBH treatments cause very small gelatinization, which is attributable to the low water content and short treatment time. Sakonidou, Karapantsios, and Raphaelides (2003), comparing gelatinization by conventional and microwave heating, found that due to the short time it takes to reach the desired temperature, microwave heating does not allow a complete gelatinization even if the amount of water was adequate. The ANOVA for the endothermic enthalpy transition (or gelatinization enthalpy) shows (Table 2) that the only non-significant term was M^2. In spite of the significant "lack of fit", the high R^2 (96.17%) supports the validity of the regression model. T and M linear terms were important in such order for determining the gelatinization enthalpy, and negative values T and M indicate that gelatinization enthalpy decreased by increasing T and M. The interaction term was significant but, because of its low value, it had little effect on the enthalpy.

3.3. Dynamic rheological properties: storage modulus reached at the end of the heating period, storage modulus reached at the end of the cooling period and the temperature at which the storage modulus showed a sharp increase

Storage modulus (G') and loss modulus (G'') were recorded during a heating and cooling cycle to reflect the structure development during the cooking of AHSF FBH-treated samples. Fig. 1 shows a typical G' and G'' evolution curve as regards heating time. Temperature evolution is also depicted in Fig. 1. In order to understand the rheological changes during gelatinization of starch, gel can be considered as a composite material with the starch granules as the filler in a polysaccharide matrix. For all treatments, AHSF dispersions at 20% wt exhibited a visco-

Table 1
Storage modulus at the end of the heating period (G'_h), storage modulus at the end of the cooling period (G'_c), temperature at which the storage modulus showed a sharp increase ($T_{G'inc}$), crystallinity degree (CD) and gelatinization enthalpy (ΔH) of fluidized-bed heated (FBH) amaranth high-starch fraction (AHSF)

Nominal FBH temperature	Nominal AHSF moisture content	Storage moduli[a]		Temperature G' increases[a]	Crystallinity degree[a]	Gelatinization enthalpy[a]
T[b] (°C)	M[c] (% wb)	G'_h[d] (Pa)	G'_c[e] (Pa)	$T_{G'inc}$[f] (°C)	CD (%)	ΔH (J/g)
190	12	701.9 ± 10.2	942.3 ± 11.5	53.7 ± 2.3	32.1 ± 2.1	8.69 ± 1.3
190	16	446.2 ± 9.8	602.7 ± 10.8	63.3 ± 4.1	30.5 ± 1.9	6.37 ± 1.2
190	20	346.9 ± 11.3	517.6 ± 9.5	61.8 ± 4.2	27.5 ± 1.5	5.60 ± 0.9
200	12	577.8 ± 10.5	716.4 ± 8.2	54.7 ± 3.5	28.7 ± 2.5	4.83 ± 0.8
200	16	347.2 ± 8.3	475.8 ± 9.6	61.1 ± 3.9	24.5 ± 2.4	4.54 ± 1.0
200	16	359.0 ± 9.9	486.8 ± 9.1	62.6 ± 4.5	27.1 ± 0.9	4.74 ± 0.8
200	16	355.7 ± 7.9	514.8 ± 8.2	61.8 ± 5.0	25.6 ± 1.6	4.43 ± 0.7
200	20	280.5 ± 8.6	427.9 ± 10.1	63.3 ± 4.8	24.4 ± 1.8	4.05 ± 1.1
210	12	436.6 ± 8.9	578.3 ± 11.1	60.4 ± 5.1	26.4 ± 2.0	4.29 ± 0.8
210	16	320.9 ± 10.3	497.1 ± 9.2	61.9 ± 4.5	22.2 ± 2.5	3.58 ± 0.6
210	20	262.9 ± 9.5	447.4 ± 7.3	64.8 ± 3.9	22.6 ± 1.7	3.54 ± 0.9
Untreated sample[a]		476.8 ± 10.1	743.2 ± 11.2	66.2 ± 3.5	35.2 ± 1.8	9.90 ± 1.2

[a] Reported values are the means ± SD ($n = 3$).
[b] Temperature actual values were $T \pm 1.0$.
[c] Moisture actual values were $M \pm 1.5$.
[d] G'_h: maximum storage modulus at heating.
[e] G'_c: maximum storage modulus at cooling.
[f] $T_{G'inc}$: temperature at which the storage modulus (G'_h) showed a sharp increase.

Table 2
Coefficients of Eq. (1) to model the responses, estimated by multiple regression analysis for storage modulus reached at the end of the heating period (G'_h), storage modulus reached at the end of the cooling period (G'_c), temperature at which the storage modulus showed a sharp increase ($T_{G'inc}$), crystallinity degree (CD) and gelatinization enthalpy (ΔH) of fluidized-bed heated (FBH) amaranth high-starch fraction (AHSF)

Factors (Eq. (1))	Storage moduli		Temperature G' increases	Crystallinity degree	Gelatinization enthalpy
	G'_h [a]	G'_c [b]	$T_{G'inc}$ [c]	CD	ΔH
Constant	14411.4	31188.8	296.75	369.3	395.04
T	−98.77*	−250.88*	−3.42*	−2.827*	−3.45*
M	−388.61*	−553.17*	10.74***	−3.145**	−3.58*
$T \times T$	0.182***	0.531*	0.01***	0.006***	0.007*
$T \times M$	1.133*	1.836*	−0.02***	0.005***	0.015*
$M \times M$	4.986*	4.711*	−0.16***	0.050***	0.015***
Lack of fit	0.072***	0.593***	0.095***	0.679***	0.087**
R^2	99.12	97.74	86.89	93.36	96.17

[a] G'_h: maximum storage modulus at heating.
[b] G'_c: maximum storage modulus at cooling.
[c] $T_{G'inc}$: temperature at which the storage modulus (G'_h) showed a sharp increase.
* Significant ($p < 0.01$).
** Significant ($p < 0.05$).
*** Not significant.

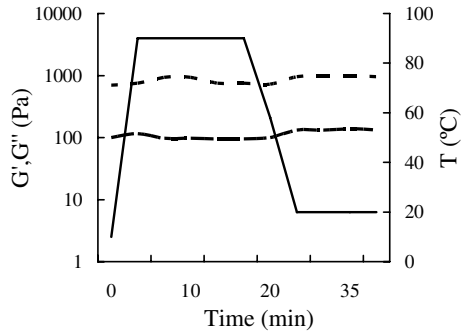

Fig. 1. Storage (G') and loss (G'') moduli and temperature (T) as regard of time. (...) Storage modulus; (---) loss modulus; (—) temperature.

elastic character before heating and, both G' and G'' developed similarly during heating. The temperature at which the storage modulus showed a sharp increase ($T_{G'inc}$) was considered as the temperature the structure formation started. This temperature was in the range 53.7–64.8 °C for the treated samples (Table 1). These values were lower than those observed for the untreated sample (66.2 °C). The initial increase of the storage moduli can be ascribed to the swelling of starch granules that starts to fill the whole sample volume (Keetels et al., 1996). This initial increase in G' coincides with the amylographic pasting temperatures (50– 66.5 °C) and occurs before the crystallite melting, as observed by DSC. In fact, the onset temperatures for DSC measurements were between 66 and 69 °C. Nevertheless, it is clear that $T_{G'inc}$ is related to the hydration and swelling process of the amorphous regions of starch granules and that this starting temperature depends on the changes on granule structure promoted by FBH. Even though a small gelatinization due to FBH processing was attained, as it was shown by the CD modification, the starch granules would increase in size so that the treated AHSF would get a tightly packed system at a temperature lower than the non-processed AHSF. Eliasson (1986), also reported that the initial increase in G' and G'' was caused by the starch granules swelling progressively and finally becoming close packed. G' values increased during heating and during holding at 90 °C leveled off. The temperature range where maximum G' values were attained during the heating period was 70–75 °C which coincides with the peak temperatures for DSC gelatinization endotherms (74.5–77.7 °C) and also with the temperatures corresponding to amylographic peaks (72.5–83 °C). This indicates that when the gel structure of the AHSF is fully developed, the melting of crystallites is almost accomplished.

Cooling to 20 °C caused a small increase in the stiffness of the AHSF (Fig. 1), thus the gel structure was mainly developed during the cooking period. The short-time increase of storage modulus during cooling has been ascribed to gelation of solubilized amylose in the continuous phase (Biliaderis & Zawistowski, 1990; Miles, Morris, Orford, & Ring, 1985). The small increase of stiffness on cooling if compared to wheat or potato starch (Keetels et al., 1996) may be attributed to the low amylose content of amaranth starch (Yañez et al., 1986). Lii, Shao, and Tseng (1995) showed a similar behaviour for waxy starch rice. In addition, the high concentration of the systems (20%) would prevent the leaching out of amylose from starch granules.

Table 1 shows that the elastic moduli attained on heating (G'_h) and after cooling (G'_c) were generally lower in the FBH-processed samples, except in those processed at the lowest temperature and moisture (190–200 °C and 12% moisture). Table 2 shows the ANOVA results of the dynamic rheological measurements. The temperature at which both the storage modulus showed a sharp increase ($T_{G'inc}$) was significantly affected by M. The higher the M, the higher the $T_{G'inc}$. It was observed that M and T also significantly affected both moduli (G'_h and G'_c). The negative

values of the linear terms indicated that the higher the M and T of the FBH treatment, the lower the solid character of the AHSF after cooking. Errors in $T_{G'\text{inc}}$ and the storage moduli determination were less than 14% and 5%, respectively.

3.4. Solubility in water

Table 3 shows the solubility in water (S) at 30 and 90 °C ($S30$, $S90$). $S30$ was marginally affected by FBH, showed a low R^2 value (69%) (Table 4), and none of the factors was significant at the 95% confidence level. $S90$ decreased about 50% with regard to untreated AHSF. A low R^2 value (64.83%) and a significant "lack of fit" for $S90$ were obtained.

3.5. Swelling power

Table 3 shows the swelling power (SP) at 30 and 90 °C (SP30 and SP90). SP30 increased 9.6% in compared the untreated AHSF value (2.83%). SP90 was decreased about 60–75% by FBH with regard the untreated AHSF (Table 3). The high R^2 (88.76%) and the non-significant "lack of fit" were evidences of the applicability of the model within the range of variables tested. The most important linear variable influencing SP90 was M. The positive value of the linear regression coefficient for M indicates that SP90 increased by increasing M. The interaction term was significant but showed a small value. The response surface analysis of SP30 shows that the highest SP was obtained at the highest M and T conditions.

3.6. Amylographic consistencies: initial, peak and retrogradation consistencies (IC, PC and RC)

For the three consistencies, the most important linear variable was moisture (Table 4); the other terms being less important. Initial consistency (IC) was increased by processing the AHSF at the highest M and T conditions (Table 3). Nevertheless, the peak and retrogradation consistencies in these conditions were the lowest. The peak and retrogradation consistencies of AHSF were increased or decreased, depending on the treatment conditions. According to these results on the hydration properties and the amylographic consistencies, it seems that FBH treatment does not produce a high degree of disruption on starch granules. This is based on the fact that $S30$ values are in the same order than that of untreated samples. Low $S30$ values indicate that most of the granular structure was preserved after FBH treatment, because water solubility is related to the degree of rupture of the granular structure (González et al., 2000). However, higher values of SP30 are related to a partial destruction of crystalline structure and concomitantly with gelatinization increase, which allows more water to be retained in the solids after centrifugation.

Table 3
Water solubility at 30 and 90 °C ($S30$, $S90$), swelling power at 30 and 90 °C (SP30, SP90), initial (IC), peak (PC) and retrogradation (RC) amylographic consistencies of amaranth starch-rich fraction of fluidized-bed heated (FBH) amaranth high-starch fraction (AHSF)

Nominal FBH temperature T^c (°C)	Nominal AHSF moisture content M^d (% wb)	Water solubility[a] at		Swelling power[a] at		Amylographic consistencies[b]		
		30 °C, $S30$ (%)	90 °C, $S90$ (%)	30 °C, SP30 (%)	90 °C, SP90 (%)	Initial, IC (BU)	Peak, PC (BU)	Retrogradation, RC (BU)
190	12	7.5 ± 0.8	19.2 ± 1.2	3.9 ± 0.5	21.5 ± 1.3	60	3560	2520
190	16	8.2 ± 0.9	20.5 ± 1.8	5.8 ± 0.6	22.1 ± 1.5	200	3040	2330
190	20	8.8 ± 0.8	21.9 ± 2.0	6.5 ± 0.4	22.8 ± 1.0	350	1980	1860
200	12	7.6 ± 0.5	17.2 ± 2.1	4.8 ± 0.2	20.2 ± 1.3	80	3640	2540
200	16	8.0 ± 0.7	22.2 ± 1.5	6.5 ± 0.3	22.0 ± 1.8	340	2820	2170
200	16	8.4 ± 0.6	21.7 ± 1.4	7.1 ± 1.0	22.6 ± 1.2	320	2800	2160
200	16	9.2 ± 0.8	22.1 ± 1.8	8.0 ± 0.8	22.3 ± 1.5	360	2640	2100
200	20	9.9 ± 0.9	22.0 ± 2.0	9.1 ± 0.5	22.3 ± 1.3	600	1750	1780
210	12	8.0 ± 1.0	19.4 ± 1.9	6.4 ± 0.3	20.6 ± 2.0	130	3380	2450
210	16	9.9 ± 0.9	20.5 ± 1.6	8.1 ± 0.5	22.4 ± 1.8	380	2400	2070
210	20	9.6 ± 1.1	23.5 ± 2.0	9.6 ± 0.9	25.7 ± 1.7	700	1220	1370
Untreated sample[a]		8.4 ± 0.6	40.9 ± 2.7	2.8 ± 0.8	32.2 ± 1.5	70	2072	1890

BU: Brabender Unit.
[a] Reported values are the means ± SD ($n = 3$).
[b] Reported values are single ones (each set corresponding to the same T was verified by linear correlation).
[c] Temperature actual values were $T \pm 1.0$.
[d] Moisture actual values were $M \pm 1.8$.

Table 4
Coefficients of Eq. (1) to modelize the responses, estimated by multiple regression analysis for water solubility at 30 and 90 °C (*S*30, *S*90), swelling power at 30 and 90 °C (SP30, SP90), initial (IC), peak (PC) and retrogradation (RC) amylographic consistencies of amaranth starch-rich fraction of fluidized-bed heated (FBH) amaranth high-starch fraction (AHSF)

Factors	Water solubility at		Swelling power at		Amylographic consistencies		
Eq. (1)	30 °C (*S*30)	90 °C (*S*90)	30 °C (SP30)	90 °C (SP90)	Initial (IC)	Peak (PC)	Retrogradation (RC)
Constant	−134.85	213.73	−268.93	361.805	−12605.3	−41800.0	−15379.5
T	1.415***	−1.622***	2.846*	−3.155*	139.89*	431.67*	152.54*
M	−1.029***	−3.977**	−3.750***	−3.865***	−313.55*	740.42*	562.94*
$T\times T$	−0.003***	0.003***	0.008***	0.007***	−0.395***	−1.0***	−0.310***
$T\times M$	0.002***	0.026***	0.029***	0.024**	1.75*	−3.625**	−2.625**
$M\times M$	0.025***	−0.029***	−0.054***	−0.017***	0.658***	−7.813***	−4.441***
Lack of fit	0.308***	0.001*	0.210***	0.118***	0.281***	0.641***	0.170***
R^2	69.14	64.83	84.10	88.76	98.999	99.33	98.02

* Significant ($p < 0.01$).
** Significant ($p < 0.05$).
*** Not significant.

Comparing *S*30 and SP30 results as regards *S*90 and SP90, both former responses were affected in the same way; values were high compared to with those attained at a lower temperature, but smaller than the correspondent to the control samples. FBH treatment at high temperatures may modify starch by cooking, making starch partially inaccessible to water causing incomplete hydration and consequently giving comparatively lower solubilization or swelling values. Another explanation may be the interaction of starch with lipids or proteins from the endosperm matrix (Baldwin, 2001), forming hydrophobic complexes (Tolstogusov, 1997) during dry heating, thus decreasing *S* and SP values of treated samples if compared to *S* and SP values of the untreated AHSF.

4. Conclusions

Results show that a partial loss of the crystalline starch structure occurred, but most of the granular integrity preservation of AHSF was produced by FBH. The loss of crystalline structure and degree of gelatinization increased by increasing *T* and *M*. Nevertheless, quite a high-starch crystallinity was retained even after 210 °C treatment. The response surface analysis shows that at the lowest combined *T* and *M* treatment conditions (i.e., 190 °C and 12% moisture), the lowest loss of starch crystalline structure and CD was produced, and a modified amaranth high-starch flour of a solid character at low temperature (i.e., 54 °C) with high consistency when cooked must be obtained. According to these findings, the AHSF obtained by differential milling of the amaranth grain can be considered as an interesting raw material for production of precooked amaranth high-starch flours having a wide range of hydration properties by applying high-temperature short-time FBH processes to low moisture AHSF. Using these 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. It must be noted that such changes may be obtained by a single, short-time and dry processing step. Some modified starch must be obtained by a wet enzymatic processing, requiring subsequent drying stages which can modify the properties of the desired product.

Due the limited scope of this work no complete understanding can be reached about the mechanisms that justify the results so obtained. More extensive studies are needed to explain the effects of high-temperature treatments on dry starch, and on the modifications that take place on responses.

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